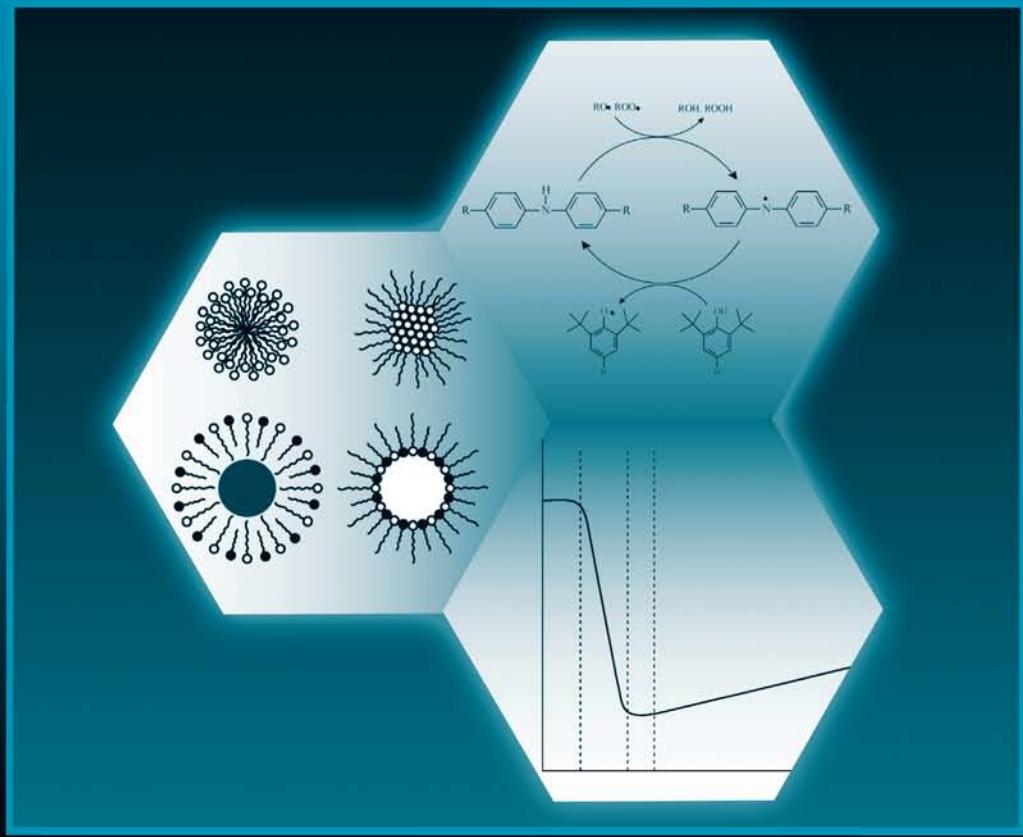


Lubricant Additives

Chemistry and Applications

Second Edition



Edited by
Leslie R. Rudnick

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Chemistry and Applications

Second Edition

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Preface

Lubricant additives continue to be developed to provide improved properties and performance to modern lubricants.

Environmental issues and applications that require lubricants to operate under severe conditions will cause an increase in the use of synthetics. Owing to performance and maintenance reasons, many applications that have historically relied on petroleum-derived lubricants are shifting to synthetic lubricant-based products. Cost issues, on the contrary, tend to shift the market toward group II and III base oils where hydrocarbons can be used. Shifts to renewable and biodegradable fluids are also needed, and this will require a greater need for new effective additives to meet the challenges of formulating for various applications.

There are several indications that the lubricant additive industry will grow and change.

Legislation is driving changes to fuel composition and lubricant components, and therefore, future lubricant developments will be constrained compared to what has been done in the past. Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in the European Union (EU) is placing constraints on the incentive to develop new molecules that will serve as additives. The cost of introduction of new proprietary materials will be the burden of the company that develops the new material. For many common additives that are produced by several manufacturers, they will share costs to generate any needed data on the toxicology or biodegradability of the materials.

Continued progress toward new engine oil requirements will require oils to provide improved fuel economy and to have additive chemistry that does not degrade emission system components. This will require a new test to evaluate the volatility of phosphorus in engine oils and to improve the oil properties in terms of protecting the engine. Future developments and requirements will undoubtedly require new, more severe testing protocols.

The market for lubricant additives is expected to grow. China and India, for example, represent highly populated markets that are expected to see growth in infrastructure, and therefore a growth in industrial equipment and number of vehicles. Many U.S. and EU companies continue to develop a presence in Pacific and Southeast Asia through either new manufacturing in that region or sales and distribution offices.

More advanced technologies will require application of new types of lubricants, containing new additive chemistries required for exploration of space and oceans. Since these remote locations and extremes of environment require low maintenance, they will place new demands on lubricant properties and performance.

This book would not have developed the way it has without the invaluable help and encouragement of many of my colleagues. I want to thank all of the authors of the chapters contained herein for responding to the deadlines. There is always a balance between job responsibilities and publishing projects like this one. My heartfelt thanks to each of you. It is your contributions that have created this resource for our industry.

I especially want to thank Barbara Glunn, at Taylor & Francis Group, with whom I have worked earlier on *Synthetics, Mineral Oils and Bio-Based Lubricants*, for her support to this project from its early stages through its completion. I also want to thank Kari Budyk, project coordinator, who has been invaluable in every way in the progress of this project and has been a tremendous asset to me as an editor and helpful to the many contributors of this book. I also want to thank Jennifer Derima, Jennifer Smith, and the team at Macmillan Publishing Solutions for their efforts, patience, and understanding during the time I have been working on this book.

I also thank Paula, Eric, and Rachel for all of their support during this project.

Les Rudnick

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Part 1

Deposit Control Additives

1 Antioxidants

Jun Dong and Cyril A. Migdal

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1.1 INTRODUCTION

Well before the mechanism of hydrocarbon oxidation was thoroughly investigated, researchers had come to understand that some oils provided greater resistance to oxidation than others. The difference was eventually identified as naturally occurring antioxidants, which varied depending on crude source or refining techniques. Some of these natural antioxidants were found to contain sulfur- or nitrogen-bearing functional groups. Therefore, it is not surprising that, certain additives that are used to impart special properties to the oil, such as sulfur-bearing chemicals, were found to provide additional antioxidant stability. The discovery of sulfurized additives providing oxidation stability was followed by the identification of similar properties with phenols, which led to the development of sulfurized phenols. Next, certain amines and metal salts of phosphorus- or sulfur-containing acids were identified as imparting oxidation stability. By now numerous antioxidants for lubricating oils have been patented and described in the literature. Today, nearly all lubricants contain at least one antioxidant for stabilization and other performance-enhancing purposes. Since oxidation has been identified as the primary cause of oil degradation, it is the most important aspect for lubricants that the oxidation stability be maximized.

Oxidation produces harmful species, which eventually compromises the designated functionalities of a lubricant, shortens its service life, and to a more extreme extent, damages the machinery it lubricates. The oxidation is initiated upon exposure of hydrocarbons to oxygen and heat and can be greatly accelerated by transitional metals such as copper, iron, nickel, and so on. when present. The internal combustion engine is an excellent chemical reactor for catalyzing the process of oxidation with heat and engine metal parts acting as effective oxidation catalysts. Thus, in-service engine oils are probably more susceptible to oxidation than most other lubricant applications. For the prevention of lubricant oxidation, antioxidants are the key additive that protects the lubricant from oxidative degradation, allowing the fluid to meet the demanding requirements for use in engines and industrial applications.

Several effective antioxidant classes have been developed over the years and have seen use in engine oils, automatic transmission fluids, gear oils, turbine oils, compressor oils, greases, hydraulic fluids, and metal working fluids. The main classes include oil-soluble organic and organometallic antioxidants of the following types:

1. Sulfur compounds
2. Sulfur–nitrogen compounds
3. Phosphorus compounds
4. Sulfur–phosphorus compounds
5. Aromatic amine compounds
6. Hindered phenolic (HP) compounds
7. Organo–copper compounds

8. Boron compounds
9. Other organometallic compounds

1.2 SULFUR COMPOUNDS

The initial concepts of using antioxidants to inhibit oil oxidation date back to the 1800s. One of the earliest inventions described in the literature [1] is the heating of a mineral oil with elemental sulfur to produce a nonoxidizing oil. However, the major drawback to this approach is the high corrosivity of the sulfurized oil toward copper. Aliphatic sulfide with a combined antioxidant and corrosion inhibition characteristics was developed by sulfurizing sperm oil [2]. Additives with similar functionalities could also be obtained from sulfurizing terpenes and polybutene [3–5]. Paraffin wax has also been employed to prepare sulfur compounds [6–9]. Theoretical structures of several sulfur compounds are illustrated in Figure 1.1. Actual compounds can be chemically complex in nature.

Aromatic sulfides represent another class of sulfur additives used as oxidation and corrosion inhibitors. Examples of simple sulfides are dibenzyl sulfide and dixylyl disulfide. More complex compounds of a similar type are the alkyl phenol sulfides [10–15]. Alkyl phenols, such as mono- or di-butyl, -amyl, or -octyl phenol, have been reacted with sulfur mono- or dichloride to form either mono- or disulfides. As shown in Figure 1.1, the aromatic sulfides such as benzyl sulfide have the sulfur attached to carbon atoms in the alkyl side groups, whereas the alkyl phenol sulfides have the sulfur attached to carbon atoms in the aromatic rings. In general, the alkyl phenol sulfide chemistry appears to have superior antioxidant properties in many types of lubricants. Mono- and dialkyl-diphenyl sulfides obtained by reacting diphenyl sulfide with C₁₀–C₁₈ alpha-olefins in the presence of aluminum chloride have been demonstrated to be powerful antioxidants for high-temperature lubricants especially those utilizing synthetic base stocks such as hydrogenated poly-alpha-olefins, diesters, and polyol esters [15]. The hydroxyl groups of the alkyl phenol sulfides may also be treated

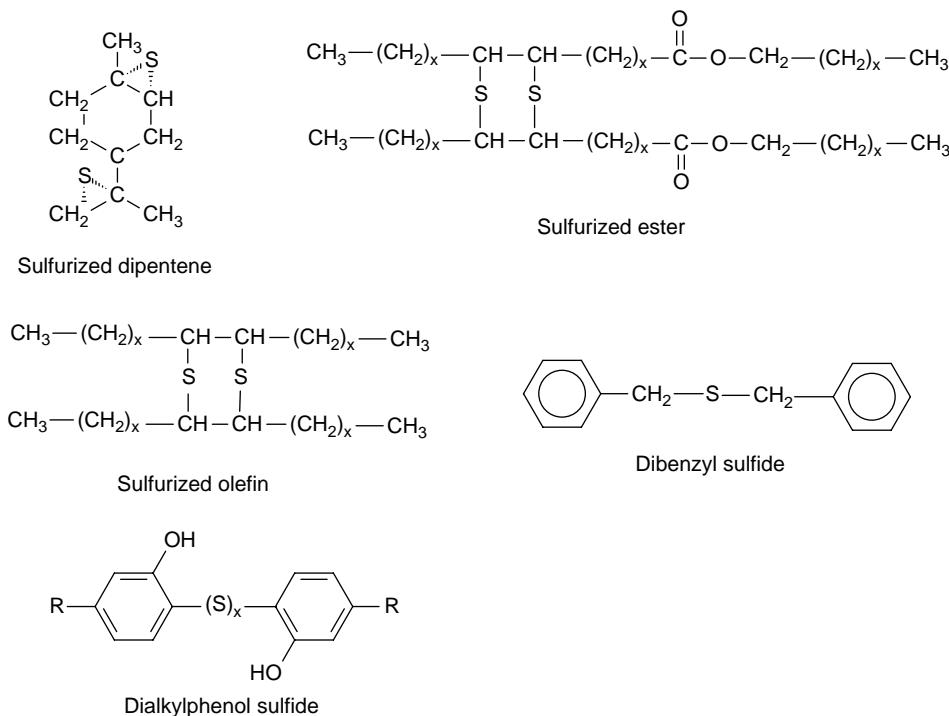


FIGURE 1.1 Examples of sulfur-bearing antioxidants.

with metals to form oil-soluble metal phenates. These metal phenates play the dual role of detergent and antioxidant.

Multifunctional antioxidant and extreme pressure (EP) additives with heterocyclic structures were prepared by sulfurizing norbornene, 5-vinylnorbornene dicyclopentadiene, or methyl cyclopentadiene dimer [16]. Heterocyclic compounds such as *n*-alkyl 2-thiazoline disulfide in combination with zinc dialkyldithiophosphate (ZDDP) exhibited excellent antioxidant performance in laboratory engine tests [17]. Heterocyclic sulfur- and oxygen-containing compositions derived from mercaptobenzothiazole and beta-thiodialkanol have been found to be excellent antioxidants in automatic transmission fluids [18]. Novel antioxidant and antiwear additives based on dihydrobenzothiophenes have been prepared through condensation of low-cost arylthiols and carbonyl compounds in a one-step high-yield process [19].

1.3 SULFUR–NITROGEN COMPOUNDS

The dithiocarbamates were first introduced in the early 1940s as fungicides and pesticides [20]. Their potential use as antioxidants for lubricants was not realized until the mid-1960s [21], and since then, there have been continuous interests in this type of chemistry for lubricant applications [22]. Today, dithiocarbamates represent a main class of sulfur–nitrogen-bearing compounds being used as antioxidants, antiwear, and anticorrosion additives for lubricants.

Depending on the type of adduct to the dithiocarbamate core, ashless and metal-containing dithiocarbamate derivatives can be formed. Typical examples of ashless materials are methylene bis(dialkyldithiocarbamate) and dithiocarbamate esters with general structures being illustrated in Figure 1.2. Both are synergistic with alkylated diphenylamine (ADPA) and organomolybdenum compounds in high-temperature deposit control [23]. In particular, methylene bis(dialkyldithiocarbamate) in combination with primary antioxidants such as arylamines or HPs and triazole derivatives is known to provide synergistic action in stabilizing mineral oils and synthetic lubricating oils [24–26]. This material has been used to improve antioxidation characteristics of internal combustion engine oils containing low levels (<0.1 wt%) of phosphorus [27]. In another effort to reduce phosphorus content in aviation gas turbine lubricants, methylene-bridged bis(dialkyl) or bis(alkylaryldithiocarbamate) was used as high-temperature antioxidant and antiwear agent to replace tricresyl phosphates that are of a concern to produce neurotoxic ortho-cresol isomers in trimethylolpropane triester base oil under high-temperature service conditions [28].

It has been known that metal dithiocarbamates such as zinc, copper, lead, antimony, bismuth, and molybdenum dithiocarbamates (MoDTCs) possess desirable lubricating characteristics including antiwear and antioxidant properties. The associated metal ions affect the antioxidantity of the additives. Within the group, MoDTCs are of greater interest particularly for engine crankcase lubricants. Certain molybdenum additives possess good oxidation resistance and acceptable corrosion characteristics, when prepared by reacting water, an acidic molybdenum compound, a basic nitrogen complex, and a sulfur source [29,30]. Oil-soluble trinuclear MoDTCs prepared by reacting

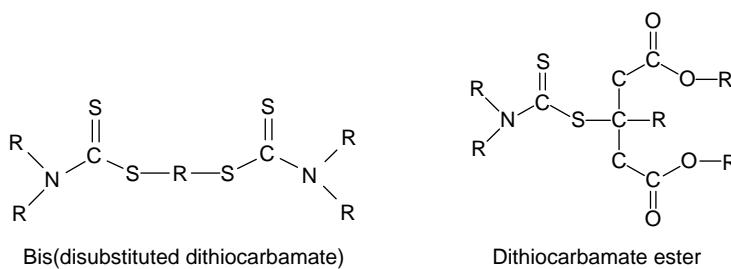


FIGURE 1.2 Ashless dithiocarbamates for lubricants.

ammonium polythiomolybdate with appropriate tetralkylthiuram disulfides were found to be superior to dinuclear molybdenum compounds in terms of providing lubricants antioxidant, antiwear, and friction-reducing properties [31].

When combined with an appropriate aromatic amine, MoDTCs can exhibit synergistic antioxidant effects in oxidation tests [32]. As a result, molybdenum dialkyldithiocarbamates (C_{7-24}) and ADPAs are claimed broadly for lubricating oils [33]. More restrictive are claims for molybdenum dialkyldithiocarbamates (C_{8-23} and C_{3-18}) and ADPAs in lubricating oils that contain <3 wt% of aromatic content and <50 ppm of sulfur and nitrogen [34]. Molybdenum dialkyldithiocarbamates and HP antioxidants are jointly claimed for lubricating oils that contain 45 wt% or more one or two ring naphthenes and <50 ppm sulfur and nitrogen [35]. MoDTC was used to top-treat engine oils formulated with group I base stocks (>300 ppm S) and an additive package designed for group II base stocks. The oils passed the sequence IIIF oxidation test, in which the oils would otherwise fail without the molybdenum top-treatment [36]. Further demonstrated is a combination of ADPAs, sulfurized olefin, or HP and oil-soluble molybdenum compounds including MoDTC. The mixture is highly effective in stabilizing lubricants, especially those formulated with highly saturated, low-sulfur base oils [37].

Thiadiazole derivatives, particularly the monomers and dimers, represent another class of sulfur- and nitrogen-bearing multifunctional additives with antioxidant potency. For example, the monomeric 2-alkylesterthio-5-mercaptop-1,3,4-thiadiazole has been reported to increase oxidative stability of engine oils under thin-film oxidation conditions by using thin-film oxygen uptake test (TFOUT) [38]. Lithium 12-hydroxystearate grease containing 2,5-dithiobis(1,3,4-thiadiazole-2-thiol), a dimer, exhibited superior oxidative stability in the American Society for Testing and Materials (ASTM) D 942 pressure bomb oxidation test [39]. When used in conjunction with ADPA and organomolybdenum compound, the thiadiazole derivative improved the thermal-oxidation engine oil simulation test (TEOST) deposition (ASTM D 7097) characteristic of an engine oil from the control oil containing sulfurized isobutylene instead [40]. In addition to providing antioxidant benefit, the thiadiazole derivatives have been widely used as ashless antiwear and EP additives. Some of them can also provide corrosion inhibition and metal deactivation properties to nonferrous metals such as copper.

Phenothiazines are also well-known sulfur- and nitrogen-bearing antioxidants and have been used to stabilize aviation fluids. Recent advances have lead to *N*-substituted thio alkyl phenothiazines, having improved antioxidant activities and oil solubility [41] as well as *N*-aminopropylphenothiazine that can be used for further derivatization of the *N*-amino group [42]. For example, alkyl phenothiazines together with aromatic amines can be attached to olefin copolymers to result in a multifunctional antioxidant, antiwear agent, and Viscosity index (VI) improver for lubricants [43].

Diamine sulfides, including diamine polysulfides, can also provide effective oxidation control when used in conjunction with oil-soluble copper. In demonstration, dimorpholine disulfide and di(dimethyl morpholine) disulfide were compared to primary alkyl ZDDP and found to be superior in controlling oil viscosity increase of engine crankcase lubricants at elevated temperatures [44].

1.4 PHOSPHORUS COMPOUNDS

The good performance of phosphorus as an oxidation inhibitor in oils was identified early on in lubrication science. The use of elemental phosphorus to reduce sludge formation in oils has been described [45]. However, elemental phosphorus, like elemental sulfur, may have corrosive side effects to many nonferrous metals and alloys, so it is rarely incorporated in oils in this form, rather oil-soluble organic compounds of phosphorus are preferred. Naturally occurring phosphorus compounds such as lecithin have been utilized as antioxidants and many patents have been issued on these materials for single use or in combination with other additives [46–49]. Lecithin is a phosphatide that has been produced commercially as a by-product from the processing of crude soybean oil.

The antioxidant property of synthetic neutral and acid phosphite esters has been known for sometime. Alkyl and aryl phosphites such as tributyl phosphite and triphenyl phosphite are efficient

TABLE 1.1
Applications of Organophosphites as Antioxidants for Lubricants

Applications	Phosphites	Supplementary Antioxidants	References
Compressor oils	Trinonylphenyl phosphite, tributyl phosphite, tridecylphosphite, triphenylphosphite, trioctylphosphite, dilaurylphosphite	Secondary aminic and hindered phenolic	55
Automotive and industrial lubricants	Triaryl phosphites, trialkyl phosphites, alkyl aryl phosphites, acid dialkyl phosphites	Secondary aminic and hindered phenolic	56
Automotive and industrial lubricants	Triphenyl phosphite, diisodecyl pentaerythritol diphosphite, tri-isodecyl phosphite, dilauryl phosphite	Secondary aminic and hindered phenolic	57
Hydraulic fluids, steam turbine oils, compressor oils, and heat-transfer oil	Steric hindered tributyl phosphite, bis(butylphenyl pentaerythritol) diphosphite	(3,5-Di- <i>t</i> -butyl)4-hydroxybenzyl isocyanurate	52
Steam turbine oils, gas turbine oils	Triphenyl phosphite, trialkyl-substituted phenyl phosphite	Alkylated diphenylamine, phenyl-naphthylamine	58
Hydraulic fluids, Automatic transmission fluids	Trialkyl phosphites	Secondary aminic and hindered phenolic including bis-phenol	59

antioxidants in some petroleum base oils, and many patents have been issued on such compositions [50,51]. Table 1.1 summarizes the patenting activities of the past three decades on the stabilization of various lubricants with organophosphites. For optimum antioxidant performance, phosphites are customarily blended with aminic or HP antioxidants that can lead to synergistic effect. For better hydrolytic stability, tri-substituted phosphites with sterically hindered structures such as tris-(2,4-di-*tert*-butylphenyl) phosphite and those based on pentaerythritol as described in the U.S. Patent 5,124,057 [52] are preferred. The aluminum, calcium, or barium salts of alkyl phosphoric acids are another type of phosphorus compound that displays antioxidant properties [53,54].

1.5 SULFUR-PHOSPHORUS COMPOUNDS

The identification of sulfur and phosphorus compounds as powerful antioxidants for protection of hydrocarbons has led to the development of oil-soluble antioxidants, having both elements in one molecule. Numerous patents have been issued on such compositions, and a considerable number have been used commercially [60–67]. In fact, antioxidants containing both sulfur and phosphorus are usually more effective and efficient in a wider variety of base stocks than those containing only phosphorus or sulfur. Many commercial oils have employed one kind or other of these sulfur–phosphorus-type additives.

One widely used class of sulfur–phosphorus additive is the metal dialkyldithiophosphates, which are typically prepared by the reaction of phosphorus pentasulfide with alcohols to form dithio-phosphoric acids, followed by neutralization of the acids with an appropriate metal compound. Many types of alcohols such as the aliphatic, cyclic [62], and phenolic derivatives have been used, and those of relatively high molecular weight (such as lauryl, octyl, cyclohexyl, methyl cyclohexyl alcohols, and amyl [65] or butyl phenols) are preferred to give sufficient thermal stability to the final products while rendering sufficient solubility in oils. For the second-step reaction, zinc,

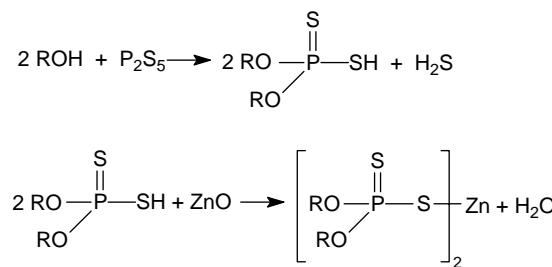


FIGURE 1.3 Synthesis of ZDDP.

barium, molybdenum, or calcium oxides are usually chosen. For more than 60 years, zinc salts of dialkylthiophosphoric acids (ZDDP) have been one of the most cost-effective antioxidants and therefore have been included as a key component in many oxidation inhibitor packages for engine oils and transmission fluids. In addition, ZDDPs show good antiwear properties, especially in the valve train area owing to the formation of sulfide and phosphate films through corrosive reactions on metal surfaces. These films can also provide protection against corrosive attack from the organic acids formed during the oxidation process. The salts of C₄/C₅ dialkyldithiophosphoric acid are the most common, but a broad range of other alkyl and aryl derivatives have been developed to meet special needs, for instance, protection at higher temperatures. The reaction scheme of making ZDDP is shown in Figure 1.3.

A number of patents describe modifications to the first step of the reactions shown in Figure 1.3; by conducting preliminary condensation reaction of phosphorus pentasulfide with unsaturated organic compounds such as terpenes, polybutenes, wax olefins, fatty acids, fatty esters, sperm oil, and so on to form high-molecular-weight intermediate products [68–89]. During these reactions, hydrogen sulfide is liberated, and the intermediates are usually acidic. The mechanism of the P₂S₅ reaction with olefins in these cases may be one of substitution (replacement of reactive hydrogen atoms) as well as of addition. In preparing the final additives, these acidic intermediates were neutralized by the treatment with alkaline earth oxides or hydroxides to form metal salts. The calcium, barium, or potassium salts are the most preferred products. Some additives may also display detergency characteristics. The concept of conducting preliminary condensation reactions provides a facile route to the synthesis of a wide variety of products from the reaction of phosphorus pentasulfide and an unsaturated organic moiety. Several of these, particularly the terpene and polybutene reaction products, have been used extensively in commercial applications.

To reduce the staining effect of ZDDP on metal parts (especially copper), addition of alkyl or aryl phosphites during the synthesis has been attempted [90]. For example, triphenyl phosphite is added to the dialkyldithiophosphoric acid and heated at 110°C for an hour before the addition of zinc oxide. In another patent, a novel dithiophosphate with improved oxidation stability is described [91]. An acid is reacted with a glycol, to give a monoester having a hydroxyl group, which is then reacted with P₂S₅ to give the dialkyl dithiophosphoric acid. Zinc oxide is subsequently added to give the novel dithiophosphates. To improve solubility, the salts can be made of lower dialkyl dithiophosphates by utilizing both primary and secondary alcohols, including butyl alcohols in the process [92]. Mixed metal salts of dialkyl dithiophosphoric acids and carboxylic acids are claimed to have higher thermal stability [93].

Many descriptions have recently appeared of organomolybdenum phosphorodithioate complexes that impart excellent oxidation stability to lubricants. In certain circumstances, oil-soluble molybdenum compounds are preferred additives owing to their multifunctional characteristics such as antiwear, EP, antioxidant, antipitting, and antifriction properties. For instance, several molybdenum dialkylphosphorodithioate complexes with varying alkyl chain length of amyl, octyl, 2-ethylhexyl, and isodecyl were reported to exhibit appreciable antioxidation, antiwear,

and antifriction properties [94]. Novel trinuclear molybdenum dialkyldithiophosphates prepared by reacting an ammonium polythiomolybdate and an appropriate bis(alkyldithiophosphoric) acid possess excellent antioxidant as well as antiwear and friction-reducing properties [31]. Some molybdenum compounds have been used commercially in engine oils and metal working fluids as well as in various industrial and automotive lubricating oils, greases, and specialties [95]. The combination of ZDDP with a molybdenum-containing adduct, prepared by reacting a phosphosulfurized polyisobutylene or alpha olefin with a molybdenum salt, has been described [96]. In this case, the molybdenum adduct alone gave poor performance in oxidation tests, but the mixture with ZDDP provided good oxidation stability. Novel organomolybdenum complexes prepared with vegetable oil have been identified as synergist with ADPAs and ZDDPs in lubricating oils [97].

Owing to increasing concerns on the use of metal dithiophosphates that are related to toxicity, waste disposal, filter clogging, pollution, etc., there have been extensive research activities on the use of ashless technologies for both industrial and automotive applications. A number of ashless compounds based on derivatives of dialkylphosphorodithioic acids had been reported as multifunctional additives. Upon reacting diisoamylphosphorodithioic acid with various primary and secondary amines, eight alkylamino phosphorodithioates with varying chain length from C₅ to C₁₈ were obtained and found to possess excellent antiwear and antioxidant properties as compared to ZDDP [98]. Alkylamino phosphorodithioates obtained from reacting heptylated or octylated or nonylated phosphorodithioic acids with ethylene diamine, morpholine, or *tert*-alkyl (C₁₂–C₁₄) amines have been demonstrated to impart similar antioxidant and antiwear efficacy and superior hydrolytic stability over ZDDP [99]. Phosphorodithioate ester derivatives containing a HP moiety are also known to have antioxidant potency. This type of chemistry can be obtained by reacting metal salts of phosphorodithioic acids with HP halides [100] or with HP aldehydes [101]. Substituting the phenol aldehydes with hindered cyclic aldehydes, in which the carbon atom attached to the carbonyl carbon contains no hydrogen atoms, may also result in products having excellent antioxidant and thermal stability characteristics [102].

1.6 AMINE AND PHENOL DERIVATIVES

Oil-soluble organic amines and phenol derivatives such as pyrogallol, gallic acid, dibutylresorcinol, hydroquinone, diphenylamine, phenyl-alpha-naphthylamine, and beta-naphthol are early examples of antioxidants used in turbine oils and lubricating greases [103,104]. In engine oils, these types of compounds showed only limited effectiveness. Other amines and phenol derivatives such as tetramethyldiaminodiphenylmethane and alizarin were used to some degree, rarely alone, but more often in combination with other types of antioxidants. For example, a mixture of a complex amine with a phosphorus pentasulfidepolybutene reaction product has been reported [105]. Another reported mixture is a complex phenol derivative such as alizarin in combination with an alkyl phenol sulfide and a detergent additive [106]. As technology advances, numerous amine and phenol antioxidants have been invented, and many of them have become the most widely used antioxidants in the lubricant industry.

1.6.1 AMINE DERIVATIVES

ADPAs are one of the most important classes of amine antioxidants being used today. Owing to their higher reactivity over the unsubstituted diphenylamine, ADPAs have been workhorse antioxidants for engine oils and various industrial lubricants for more than two decades. Figures 1.3 and 1.4 illustrate the typical synthesis routes of some commonly used ADPAs. The reactions start with benzene, which is first converted into nitrobenzene [107], followed by a high-temperature reduction to aniline [108]. Under very high-temperature (400–500°C) and high-pressure (50–150 psi) conditions, aniline can undergo a catalytic vapor-phase conversion to form diphenylamine [109].

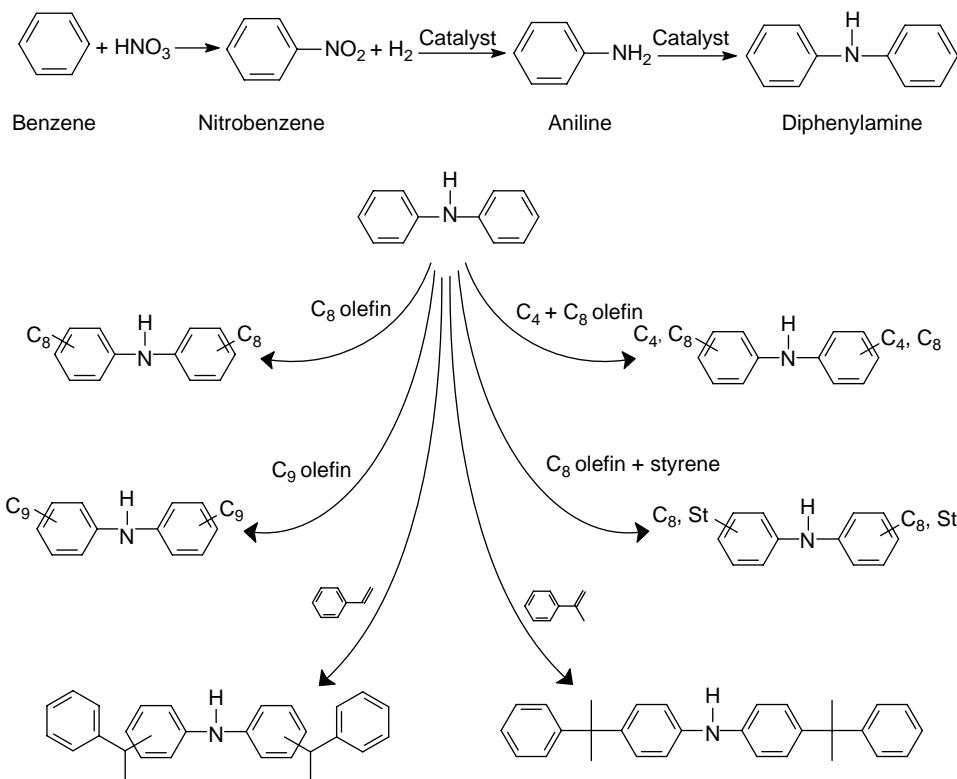


FIGURE 1.4 Synthesis routes of ADPA antioxidants.

To make ADPAs, diphenylamine is reacted with an appropriate alkylating agent such as alcohol, alkyl halide, aliphatic carbonyl compound, or an olefin. The olefins are preferred for economic reason. The most commonly used are isobutylene (C₄), diisobutylene (C₈), nonenes (C₉), styrene, and propylene tetramer (C₁₂). Depending on the acidic catalyst, olefin, and other reaction conditions, for instance, the temperature, the degree of alkylation will vary from mono- to di-alkylation.

Mono-ADPA is generally more effective than the corresponding disubstituted on a weight basis because additional alkylation substantially reduces the number of moles of diphenylamine per weight unit. However, in practice, obtaining monosubstituted diphenylamine in relatively pure format is difficult because as soon as the diphenylamine is monoalkylated, it quickly proceeds to dialkylation. Attempt in the preparation of high content of mono-ADPAs has led to the use of novel clay catalyst with greater selectivity in alkylation reactions and C₆–C₁₈ linear olefins to produce high levels (at least 50 wt%) of mono-ADPAs with lower levels of dialkyl diphenylamines and undesirable unsubstituted diphenylamine [110]. Alkyl groups of six or more carbon of mono-ADPA tend to render the material lower yellow color and higher resistance to discoloration [111].

It was found that monosubstituted diphenylamines more readily oligomerize under various conditions to produce higher-molecular weight, linear oligomers. Oligomers with 2–10 degrees of polymerization are desirable antioxidants especially for high-temperature applications. Disubstituted and polysubstituted diphenylamines, however, are more restricted from forming oligomers higher than dimers. Oligomeric versions of monosubstituted diphenylamine prepared from reacting diphenylamine with C₄–C₁₆ olefins have been described for use in ester lubricants [112]. The products are claimed to be more effective than simple diphenylamines for extremely high-temperature applications. Homo-oligomers of alkylated (C₄–C₈) diphenylamines, styrenated diphenylamines,

or cross-oligomers of the ADPAs with substituted *N*-phenyl- $\alpha(\beta)$ -naphthylamine (PNA) are claimed to possess superior antioxidant efficacy in synthetic ester lubricants for high-temperature applications [113]. Oligomeric products derived from thermal and chemical condensation of ADPA and alkylated PNA in the presence of aldehyde can provide high performance and nonsludging attributes, as evident in the rotating pressure vessel oxidation test (RPVOT, ASTM D 2272) and the ASTM D 4310 sludging tendency test designed for turbine oils [114].

There appears to be a great number of patenting activities on the process of using isobutylene derivatives as alkylating agents. Under certain mole ratio range, diphenylamine can be reacted with diisobutylene at a temperature of 160°C or higher to facilitate chain scission of diisobutylene [115]. In the presence of an acid clay catalyst, the resulting product has <25% of 4,4'-dioctyl diphenylamine, which yields a liquid at room temperatures. In another process that involves two-step reactions [116], a light-colored, liquid product is obtained by first reacting diphenylamine with diisobutene, followed by reaction with a second olefin, preferably isobutene. Specific mole ratio, reaction temperature, and reaction duration are critical to obtain the desired ADPAs. To obtain higher levels (>50 wt%) of monosubstituted diphenylamine content in the final product, diisobutylene is allowed to react at a lower temperature range of 105–157°C in the presence of a clay catalyst. By carefully controlling mole ratio of the reactants together with reaction duration, the process, as disclosed, selectively results in a higher proportion of mono-ADPA and a lower proportion of unsubstituted diphenylamine and disubstituted or polysubstituted diphenylamines [90,117]. U.S. Patent 6,355,839 [118] discloses a one-step process using highly reactive polyisobutylene oligomers having an average molecular weight of ~160 to 280 and at least 25% of 2-methylvinylidene isomers as the alkylating agents to make ADPAs and other types of alkylated diarylamine. The resulting products are liquid at ambient temperatures.

Several antioxidant patents based on alkylation of benzotriazole compounds have been issued. One particular benefit of using this class of antioxidant over the ADPAs is their additional activity in the reduction of copper corrosion. Examples are *N*-*t*-alkylated benzotriazoles obtained by reacting a benzotriazole with an olefin such as diisobutylene [119], and the reaction products of a benzotriazole with an alkyl vinyl ether or a vinyl ester of a carboxylic acid such as vinyl acetate [120]. Antioxidant and antiwear properties were reported for benzotriazole adducts of an amine phosphate [121] or an organophosphorodithioate [122]. The former type also exhibited rust prevention characteristics in the ASTM D 665 corrosion test.

Aromatic diamines are a broad group of aminic antioxidants suitable for lubricants. 3,5-diethyltoluenediamines with the amino moieties being located on the 2,4 and 2,6 positions relative to the methyl group have been claimed to be effective in the prevention of oil viscosity increase and acid buildup [123]. The additives are relatively noncorrosive to copper and lead bearings and are compatible with seals at high temperatures and pressures. Substituted benzylamines or substituted 1-amino-1,2,3,4-tetrahydronaphthalene is particularly useful for synthetic lubricants such as polyalphaolefins (PAOs) or polyol esters. Oils bearing these additives demonstrate very low metal corrosion, low viscosity increase, and low sludge buildup [124]. *N,N'*-diphenyl-*p*-phenylenediamines in which the phenyl groups may be substituted with methyl, ethyl, or methoxy have been claimed as effective antioxidants [125]. A broader range of substituted *p*-phenylenediamines has been claimed for crankcase lubricating oils for use in environments where iron-catalyzed oxidation reactions can take place [126]. 2,3-Dihydroperimidines that are prepared from the condensation of 1,8-diaminonaphthalenes with ketones or aldehydes show good oxidation inhibition in the RPVOT (ASTM D 2272). Synergistic behavior of the amines was also observed when an appropriate phenolic antioxidant is present [127]. Oils containing *N,N'*-disubstituted-2,4-diaminodiphenyl ethers and imines of the same ethers have shown low viscosity increase, low acid buildup, and reduced metal corrosion in bench tests [128,129]. The reaction product of a hydrocarbyl succinic anhydride and 5-amino-triazole demonstrated antioxidant efficacy in a railway diesel oil composition [130].

1.6.2 PHENOL DERIVATIVES

Phenols, especially the sterically hindered phenols are another class of antioxidants being extensively used in industrial and automotive lubricating oils and greases. Based on the chemical structure, phenols may be customarily categorized into simple phenols such as 2,6-di-*tert*-4-methylphenol (also known as BHT) and complex phenols that are typically in polymeric forms having molecular weights of 1000 or higher. The structures, important physical properties, and typical applications of some commonly used HPs are given in Table 1.2.

Similar to the alkyl phenol sulfides discussed earlier, the combinations of HPs and sulfur chemistry have been widely reported. For example, the reaction products of simple phenols such as the 2,6-di-*tert*-butylphenol listed in Table 1.2 with selected thioalkenes have shown effectiveness in the prevention of acid buildup and oil viscosity increase, without causing lead corrosion [131]. Another patent describes a process for preparing hydrocarbylthio-HPs by reacting substituted phenols with hydrocarbyl disulfides using an aluminum phenoxide catalyst [132]. Using a 4,4'-methylene bis(2,6-di-*tert*-butylphenol) as reference, the thiophenols were found to be superior in bulk oil oxidation tests and bench corrosion test on bearings. High oligomeric phenolic antioxidants in the form of hindered and sulfur bridged have been developed [133]. These compounds have lower volatility, better thermal stability, and improved seal compatibility and corrosion properties. In general, sulfur-bridged HPs are more effective than the conventional phenolics under high-temperature oxidation conditions and are considered particularly suitable for the lubricants formulated with highly refined base stocks [134]. Figure 1.5 shows structures of some commercial sulfur-bridged HPs that have found use in various lubricant formulations. Thioalkene-bridged hemi-HPs prepared from catalytic reaction of HP with thioalkene have also been reported to be active in the stabilization of mineral oils and synthetic oils [135].

1.6.3 AMINE AND PHENOL-BEARING COMPOUNDS

Given the high popularity and effectiveness of amine and phenol derivatives as lubricant antioxidants, the combination of amine and phenolic moieties in one molecule represents a logic approach to enhance performance. In a prior art [136], fusing amine with a long carbon chain 3,5-di-*tert*-butyl-4-hydroxyphenalkyl group that separates the phenol group from the amino nitrogen leads to novel products with lower volatility, better thermal stability, and higher solubility in oils. Nelson and Rudnick [137] reacted an ethoxyxylated alkyl phenol with an alkyl arylamine in the presence of an aldehyde. The resulting product had improved antioxidant potency owing to a synergistic action between the phenolic moiety and the amine, and also showed enhanced solubility in oils owing to the presence of alkylated aromatic moiety in the molecule. Phenolic imidazolines have been prepared from polyaminophenols and carbonyl compounds [138]. In addition to providing antioxidant activity, the products also have corrosion inhibition and metal deactivation properties owing to the cyclic imidazoline moiety.

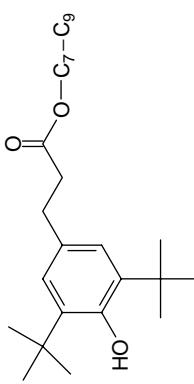
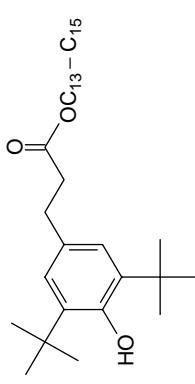
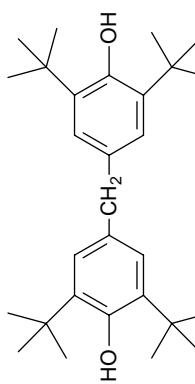
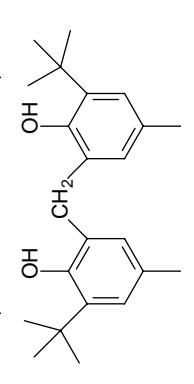
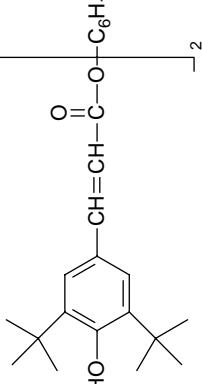
Multifunctional additives containing sulfur, nitrogen, and phenolic moieties in one molecule have been reported. In this instance, mercaptobenzothiazoles or thiadiazoles are Mannich reacted with HP antioxidants to yield oil-soluble compounds with antioxidant and antiwear properties [139]. More complex product having similar functionalities was obtained by reacting a sulfur-containing HP ester with an ADPA [140].

1.6.4 MULTIFUNCTIONAL AMINE AND PHENOL DERIVATIVES

The industry-wide trend in the reduction of phosphorus and sulfur, in particular, ZDDP in finished lubricants has led to increasing activities in the development of novel multifunctional additives that have combined properties of antioxidant, antiwear, and to some extent dispersancy, while having low-to no-sulfur and phosphorus contents. It has been shown that products obtained from

TABLE 1.2
Structure, Physical Properties, and Typical Applications of Commercial Hindered Phenols for Lubricants

Phenols	Structure	Melting Point (°C)	Solubility (in mineral oils)	Applications
2,6-Di- <i>tert</i> -butyl-4-phenol		36–37	>5	Industrial oils, power transmission fluids, greases, fuels
2,6-Di- <i>tert</i> -butyl-4-methylphenol (BHT)		69	>5	Industrial oils, power transmission fluids, food grade lubricants, greases
(3,5-Di- <i>tert</i> -butyl-4-hydroxyhydrocinnamate)methane		110–125	0.1–0.5	Industrial oils, food grade lubricants, greases
Octadecyl 3-(3',5'-di- <i>tert</i> -butyl-4'-hydroxyphenyl)propionate		50–55	>5	Industrial oils, eco-friendly oils

	3,5-Di- <i>tert</i> -butyl-4-hydroxyhydrocinnamic acid, C ₇ -C ₉ alkyl ester	Liquid at 25°C	>5	Engine oils, power transmission fluids, industrial oils
	3,5-Di- <i>tert</i> -butyl-4-hydroxy-3-methylhexanoic acid, C ₁₃ -C ₁₅ alkyl ester	Liquid at 25°C	>5	Engine oils, power transmission fluids, industrial oils
	4,4'-Methylene bis(2,6-di- <i>tert</i> -butylphenol)	NA	154	Engine oils, industrial oils, food grade lubricants, greases
	2,2'-Methylene bis(4-methyl-6- <i>tert</i> -butylphenol)	128	2-5	Engine oils, industrial oils, greases
	2-Propenoic acid, 3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1,6-hexanediyil ester	105	<1	Industrial oils, greases, food grade lubricants

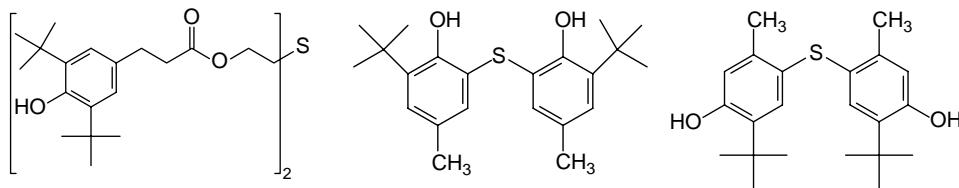


FIGURE 1.5 Examples of commercial sulfur-bridged phenolic antioxidants.

reacting alkyl or alkenyl succinic acid anhydride with an appropriate amine may impart such multifunctionalities. Product made by reacting a polyalkenylsuccinic acid or anhydride first with an aromatic secondary amine, then with an alkanol amine, was found to provide appreciable antioxidant, dispersancy, and anticorrosion effects to engine oils as tested in a Caterpillar engine test [141]. A more recent U.S. Patent literature [142] discloses materials made from the reaction of alkyl or alkenyl succinic acid derivative with a diamino naphthyl compound for use as antioxidant, antiwear, and soot dispersing agents for lubricating oils. By fusing a HP moiety to an alkenyl succinimide domain, a novel dispersant having antioxidant property was obtained [143]. The product improved the performance of engine oils in the sequence VG, an industry recognized sludge test to evaluate the ability of a lubricant in preventing the formation of sludge and varnish deposits in a fired engine. U.S. Patent 5,075,383 [144] describes novel antioxidant-dispersant additives obtained by reacting amino-aromatic polyamine compound, including aromatic secondary amines, with ethylene-propylene copolymer grafted with maleic anhydride. Engine oils containing the additives displayed improved performance characteristics in laboratory oxidation and sludge dispersancy tests, as well as in the sequence VE and the MWM-B engine tests.

1.7 COPPER ANTIOXIDANTS

The ability of copper compounds to function as oxidation inhibitors has been of interest to the lubricant industry for years. Copper is usually considered to be an oxidation promoter, and its presence is of a concern in lubricants such as power transmission oils, where fluid contact with copper-containing bearings and sintered bronze clutch plates takes place [145]. It has been suggested that copper corrosion products, originating from surface attack of copper metal, are generally catalysts that accelerate the rate of oxidation [146], whereas oil-soluble copper salts are antioxidants [147]. To maximize the full antioxidant strength of a copper compound, the initial concentration needs to be maintained at an optimum range, normally from 100 to 200 ppm [145,147]. Below this range, the antioxidant effect of the copper compounds will not be fully realized, whereas above the range, interference with antiwear additives may occur, leading to pronounced increase in wear on high-stress contact points [148].

Examples of oil-soluble copper antioxidants developed in early years were a group of copper-sulfur complexes, obtained by sulfurizing certain types of unsaturated hydrocarbons in the presence of copper [149–151]. A more recent patent describes lubricant compositions that are stabilized with a zinc hydrocarbyl dithiophosphate (ZDDP) and 60–200 ppm of copper derived from oil-soluble copper compounds such as copper dihydrocarbyldithiophosphate or copper dithiocarbamates [148]. Oxidation data are given for fully formulated engine oils containing the ZDDP and various supplemental antioxidants including amines, phenolics, a second ZDDP, and copper salts. Only the blends with copper salts passed the oxidation test. With the other additives, the viscosity increase was excessive. Organo-copper compounds including copper naphthenates, oleates, stearates, and polyisobutylene succinic anhydrides have been reported to be synergistic with multiring aromatic compounds in controlling high-temperature deposit formation in synthetic base stocks [147].

More complex compounds obtained from further reactions of copper salts have also been reported to be effective antioxidants in various lubrication applications. For example, copper carboxylate or copper thiocyanate was reacted with a mono-oxazoline, bis-oxazoline, or lactone oxazoline dispersant to form coordination complexes, wherein the nitrogen contained in the oxazoline moiety is the ligand that complexes with copper. The resulting products exhibit improved varnish control and oxidation inhibition capabilities [152]. Reaction products of a copper salt (acetate, carbonate, or hydroxide) with a substituted succinic anhydride derivative containing at least one free carboxylic acid group are effective high-temperature antioxidants and friction modifiers. When incorporated in an engine oil formulation, the oil passed rust, oxidation, and bearing corrosion engine tests [153]. In another patent [154], a HP carboxylic acid was used as the coupling reagent. The resulting copper compounds are reported to be effective in the controls of high-temperature sludge formation and oil viscosity increase when used alone or in synergistic mixtures with a conventional aminic or phenolic antioxidant.

1.8 BORON ANTIOXIDANTS

The search for more eco-friendly additives to replace ZDDP has led to renewed interest in boron esters owing to their ability to improve antioxidation, antiwear, and antifriction properties of lubricants when used alone or in combination with other additives. The complex tribological behavior of boron compounds in formulated lubricants depends on their particular chemical structures and the interactions between boron and other active elements such as sulfur, phosphorus, nitrogen, or their combinations when present [155,156].

A number of boron–oxygen-bearing compounds have been reported to be effective oxidation inhibitors in terms of prevention of oil viscosity increase and acid formation at elevated temperature (163°C) [157–161]. Representatives are boron epoxides (especially 1,2-epoxyhexadecane) [157], borated single and mixed alkanediols [158], mixed hydroquinone-hydroxyester borates [159], phenol esters of hindered phenyl borates [160], and reaction products of boric acid with the condensates of phenols with aromatic or aliphatic aldehydes [161].

Borate esters with nitrogen are known for their antioxidant activity and improved antiwear properties probably due to the formation of additional boron nitride film on rubbing surface [162]. Borated adducts of alkyl diamines with long-chain hydrocarbylene alkoxides and low-molecular-weight carboxylic acids have been reported to have antifriction properties and high inhibition ability especially at elevated temperatures [163]. Appreciable oxidation inhibition effect has also been reported for borate esters of hydrocarbyl imidazolines [164], borates of mixed ethyoxyamines and ethoxyamides [165], and borates of etherdiamines [166].

Synergistic antioxidant effect of borate esters with ADPAs or with zinc dithiophosphates has been established. When tested at 180°C in a PAO using a pressurized differential scanning calorimetry (PDSC), strong synergistic antioxidant action was observed between borate esters and a diethyl diphenylamine at a 1:1 (w/w) blending ratio [167]. Similar effect was observed in the mixtures of borate esters and a ZDDP [155]. The synergism with ZDDP is of practical importance as it allows reduced phosphorus level in a finished lubricant without sacrifice of oxidative stability. The catalytic effect of boron in enhancing antioxidant performance has led to the development of phenolic-phosphorodithioate borates, obtained from coborating HP and alkyl phosphorodithioate-derived alcohol. The borates were found to possess exceptional antioxidant and antiwear properties. Both the HP moiety and the phosphorodithioate alcohol moiety were believed to provide the basis for the synergy each of which are subsequently enhanced by the integral boron coupling moiety [168].

Despite many tribological and antioxidation benefits that borate esters can offer, large use of the chemistry for lubricant applications has not taken place. One serious drawback with most borate esters has been their high susceptibility to hydrolysis, a process that liberates oil-insoluble and

abrasive boric acid. Following attempts have been made to address the issue with varying degrees of success:

1. Incorporation of HP moiety to sterically inhibit the boron–oxygen bonds from hydrolytic attack. Commonly used HPs are 2,6-dialkyl phenols [169], 2,2'-thiobis(alkylphenols) and thiobis(alkylnaphthols) [170].
2. Incorporation of amines that have nonbonding pairs of electrons. The amines coordinate with the electron-deficient boron atom, thus preventing hydrolysis. U.S. Patents 4,975,211 [171] and 5,061,390 [172] disclose the stabilization of borated alkyl catechol against hydrolysis by complexing with diethylamine. Significant improvement in hydrolytic stability was reported for borate esters incorporated with a *N,N'*-dialkylamino-ethyl moiety [156]. It was hypothesized that the formation of a stable five-member ring structure in molecules involving coordination of nitrogen with boron substantially inhibited the hydrolytic attack from water.
3. Use of certain hydrocarbon diols or tertiary amine diols to react with boric acid to form stable five-member ring structures [173].

1.9 MISCELLANEOUS ORGANOMETALLIC ANTIOXIDANTS

More recently, a number of oil-soluble organometallic compounds, for example, organic acid salts, amine salts, oxygenates, phenates and sulfonates of titanium, zirconium, and manganese have been claimed to be effective stabilizers for lubricants [174,175]. Some of the compounds are essentially devoid of sulfur and phosphorus, therefore, suitable for modern automotive engine oils where lower contents of the two elements are desired. In one example [174], lubricating oils having 25 to ~100 ppm of titanium derived from titanium (IV) isopropoxide exhibited excellent oxidative stability in the high-temperature (280°C) Komatsu hot tube test and ASTM D 6618 test evaluate engine oils for ring sticking, ring and cylinder wear, and the accumulation of piston deposits in a four-stroke cycle diesel engine. In another example [175], titanium (IV) isopropoxide was used to react with neodecanoic acid, glycerol mono-oleate, or polyisobutylene bis-succinimide to form respective titanated compounds. These compounds, when top-treated in a SAE 5W30 engine oil to result in 50 to ~800 ppm of titanium in oil, improved the deposit control capability of the oil as tested by using the TEOST (ASTM D 7097). Similar antioxidant effect was observed for neodecanoates of zirconium and manganese in the same oil.

Oil-soluble or dispersible tungsten compounds, more specifically, amine tungstates and tungsten dithiocarbamates, have been attempted as antioxidants for lubricants and found to be synergistic with secondary diarylamine and alkylated phenothiazines. The mixtures, when added to an engine crankcase lubricant to result in ~20 to 1000 ppm of tungsten, were highly effective in controlling oil oxidation and deposit formation [176].

Sulfur-free molybdenum salts such as molybdenum carboxylates have been attempted as antioxidants and found to be synergistic with ADPAs in lubricating oils [177,178]. The synergistic mixtures improved oxidation stability of crankcase lubricants while providing additional friction modification characteristics.

1.10 MECHANISMS OF HYDROCARBON OXIDATION AND ANTIOXIDANT ACTION

It is now understood that oxidation of hydrocarbon-based lubricants undergoes autoxidation, a process that leads to the formation of acids and oil thickening. To a more severe extent, oil-insoluble sludge and varnish may be formed, causing poor lubrication, reduced fuel economy, and increased wear.

Antioxidants are essential additives incorporated in lubricant formulations to delay the onset of autoxidation and minimize its impact. The mechanisms of lubricant degradation and its stabilization by antioxidants are discussed in the following sections.

1.10.1 AUTOXIDATION OF LUBRICATING OIL

The well-documented autoxidation mechanism involves a free-radical chain reaction [179–181]. It consists of four distinct reaction steps: chain initiation, propagation, branching, and termination.

1.10.1.1 Initiation



The initiation step is characterized as the formation of free alkyl radicals ($R \cdot$) from the breakdown of hydrocarbon bonds by hydrogen abstraction and dissociation of carbon–carbon bonds. These reactions take place when hydrocarbons are exposed to oxygen and energy in the form of heat, UV light, or mechanical shear stress [182]. The ease of homolytic cleavage of an R–H bond follows this order, as determined by the C–H bond strength and the stability of the resulting radical [183]: phenyl < primary < secondary < tertiary < allylic < benzylic. Thus, hydrocarbons containing tertiary hydrogen or hydrogen in an alpha position to a carbon–carbon double bond or aromatic ring are most susceptible to oxidation. The reaction rate of chain initiation is generally slow under ambient conditions but can be greatly accelerated with temperature and the presence of catalytic transitioning metal ions (copper, iron, nickel, vanadium, manganese, cobalt, etc.).

1.10.1.2 Chain Propagation



The first propagation step involves an alkyl radical reacting irreversibly with oxygen to form an alkyl peroxy radical ($ROO \cdot$). This reaction is extremely fast, and the specific rate is dependent on the radical's substituents [179]. Once formed, the peroxy radical can randomly abstract hydrogen from another hydrocarbon molecule to form hydroperoxide ($ROOH$) and a new alkyl radical ($R \cdot$). Based on this mechanism, each time a free alkyl radial is formed, a large number of hydrocarbon molecules may be oxidized to hydroperoxides.

1.10.1.3 Chain Branching

1.10.1.3.1 Radical Formation



1.10.1.3.2 Aldehyde or Ketone Formation



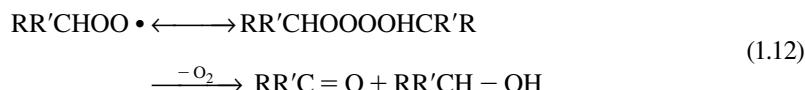
The chain-branched steps begin with the cleavage of hydroperoxide into an alkoxy radical ($\text{RO}\cdot$) and a hydroxyl radical ($\text{HO}\cdot$). This reaction has high activation energy and is only significant at temperatures $>150^\circ\text{C}$. Catalytic metal ions accelerate the process. The resulting radicals will undergo a number of possible reactions: (a) the alkoxyl radical abstracts hydrogen from a hydrocarbon to form a molecule of alcohol and a new alkyl radical according to reaction 1.6, (b) the hydroxyl radical follows the pathway of reaction 1.7 to abstract hydrogen from a hydrocarbon molecule to form water and a new alkyl radical, (c) a secondary alkoxyl radical ($\text{RR}'\text{HCO}\cdot$) may decompose through reaction pathway 1.8 to form an aldehyde, and (d) a tertiary alkoxyl radical ($\text{RR}'\text{R}''\text{CO}\cdot$) may decompose to form a ketone (reaction 1.9).

The chain-branched reaction is a very important step to the subsequent oxidation state of the oil as not only will a large number of alkyl radicals be formed that expedites the oxidation process, but also the lower-molecular-weight aldehydes and ketones generated will immediately affect the physical properties of the lubricant by decreasing oil viscosity and increasing oil volatility and polarity. Under high-temperature oxidation conditions, the aldehydes and ketones can undergo further reactions to form acids and high-molecular-weight species that thicken the oil and contribute to the formation of sludge and varnish deposits. Detailed mechanisms will be discussed in Section 1.10.3.

1.10.1.4 Chain Termination



As oxidation proceeds, oil viscosity will increase due to the formation of high-molecular-weight hydrocarbons. When oil viscosity has reached a level that diffusion of oxygen in oil is significantly limited, chain termination reactions will dominate. As indicated by reactions 1.10 and 1.11, two alkyl radicals can combine to form a hydrocarbon molecule. Alternatively, an alkyl radical can combine with an alkyl peroxy radical to form a peroxide. This peroxide, however, is not stable and can easily breakdown to generate more alkyl peroxy radicals. During the chain-termination processes, formation of carbonyl compounds and alcohols may also take place on the peroxy radicals that contain an extractable α -hydrogen atom:



1.10.2 METAL-CATALYZED LUBRICANT DEGRADATION

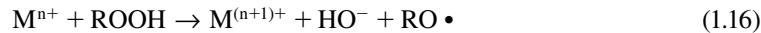
Metal ions are able to catalyze the initiation step as well as the hydroperoxide decomposition in the chain-branched step [184] through a redox mechanism illustrated in the following section. The required activation energy is lowered for this mechanism, and thus, the initiation and propagation steps can commence at much lower temperatures.

1.10.2.1 Metal Catalysis

1.10.2.1.1 Initiation Step



1.10.2.1.2 Propagation Step



1.10.3 HIGH-TEMPERATURE LUBRICANT DEGRADATION

The preceding discussion provides the basis for the autoxidation stage of lubricant degradation under both low and high-temperature conditions. The end result of low-temperature oxidation is the formation of peroxides, alcohols, aldehydes, ketones, and water [185,186]. Under high-temperature oxidation conditions ($>120^\circ\text{C}$), breakdown of peroxides including hydroperoxides becomes predominant, and the resulting carbonyl compounds (e.g., reactions 1.8 and 1.9) will first be oxidized to carboxylic acids as shown in Figure 1.6. As an immediate result, the oil acidity will increase. As oxidation proceeds, acid or base-catalyzed Aldol reactions take place. The reaction mechanism is illustrated in Figure 1.7 [187]. Initially, α,β -unsaturated aldehydes or ketones are formed, and further reaction of these species leads to high-molecular-weight products. These products contribute to oil viscosity increase and eventually can combine with each other to form oil-insoluble polymeric products that manifest as sludge in a bulk oil oxidation environment or as varnish deposits on hot metal surface. Oil viscosity increase and deposit formation have been identified to be the principal oil-related factors to engine damages [188].

1.10.4 EFFECT OF BASE STOCK COMPOSITION ON OXIDATIVE STABILITY

Mineral base stocks used to formulate lubricants are hydrocarbons that are originated from crude oils and essentially contain mixtures of *n*-paraffins along with isoparaffins, cycloparaffins (also called naphthenes), and aromatics having about 15 or more carbon atoms [189]. In addition, small amounts of sulfur-, nitrogen-, and oxygen-containing species may be present depending on the refinery techniques employed. In the American Petroleum Institute (API) base oil classification system, mineral oils largely fall into the groups I, II, III, and V, with some distinctions shown in Table 1.3 in terms of saturates, sulfur contents, and viscosity index. Group I base oils still dominate the base oil market, accounting for more than 50% of global capacity. Groups II and III base stocks

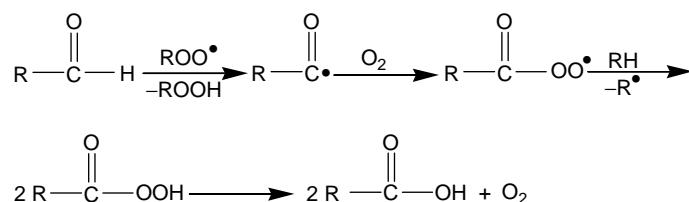


FIGURE 1.6 High-temperature ($>120^\circ\text{C}$) lubricant degradation leading to the formation of carboxylic acids.

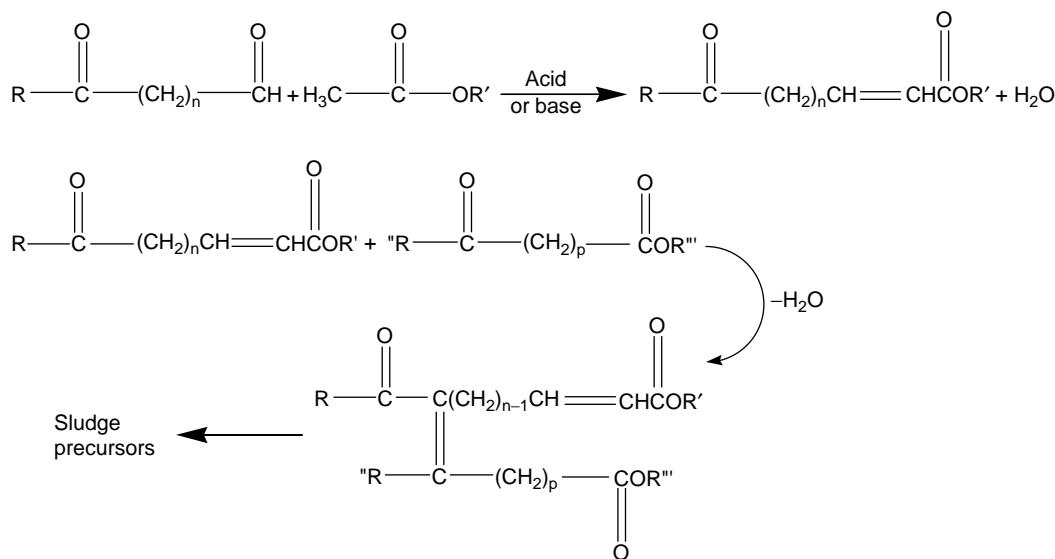


FIGURE 1.7 High-temperature ($>120^{\circ}\text{C}$) lubricant degradation leading to the formation of high-molecular-weight hydrocarbons.

TABLE 1.3
API Base Oil Categories

API Category	Percent Saturates	Percent Sulfur	Viscosity Index
Group I	≤ 90	≥ 0.03	≥ 80 and ≤ 120
Group II	≥ 90	≤ 0.03	≥ 80 and ≤ 120
Group III	≥ 90	≤ 0.03	≥ 120
Group IV	PAOs		
Group V	Includes all other base oils not included in the first four groups		

are on the horizon, and their use is expected to grow in large scale in the coming future, especially after the completion of nearly a dozen new group II/III oil refinery plants worldwide [190].

It has been widely recognized that base oil composition, for example, linear and branched hydrocarbons, saturates, unsaturates, monoaromatics, polycyclic aromatic hydrocarbons, together with traces of nitrogen-, sulfur-, and oxygen-containing heterocycles, etc., plays an important role in the oxidative stability of the oil. There have been quite extensive research activities attempting to establish correlations between base stock composition and oxidative stability [191–195]. However, owing to the large variations in the origin of the oil samples, the test methods, test conditions, and the performance criteria employed, the conclusions are not always consistent and in some cases contradictory to each other. In general, it has been agreed that saturated hydrocarbons are more stable than the unsaturated toward oxidation. Of the different saturated hydrocarbons found in mineral oils, paraffins are more stable than cycloparaffins. Aromatic compounds, due to their complex and large variation in the chemical makeup, play a more profound role. Monocyclic aromatics are relatively stable and resistant to oxidation, whereas bi and polycyclic aromatics are unstable and susceptible to oxidation [196]. Alkylated aromatics oxidize more readily due to

the presence of highly reactive benzylic hydrogen atoms. Kramer et al. [193] demonstrated that the oxidative rate of a hydrocracked 500N base oil doubled when the aromatic content increased from 1 to 8.5 wt%. Naturally occurring sulfur compounds are known antioxidants for the inhibition of the early stage of oil oxidation. Laboratory experiments have shown that mineral oils containing as little as 0.03% of sulfur had good resistance to oxidation at 165°C over sulfur-free white oils and PAOs [145]. In hydrocracked oils that are essentially low in aromatics, better oxidative stability was found with elevated sulfur concentration (>80 ppm) versus a level at 20 ppm or lower [192]. It has been proposed that sulfur compounds act as antioxidants by generating strong acids that catalyze the decomposition of peroxides through a nonradical route or by promoting the acid-catalyzed rearrangement of arylalkyl hydroperoxides to form phenols that are antioxidants [145,179]. Contrary to sulfur, nitrogen-bearing compounds, especially the heterocyclic components (also called “basic nitrogen”), accelerate oil oxidation even at relatively low concentrations [197]. In highly refined groups II and III base stocks that are essentially devoid of heteroatom-containing molecules, aromatic and sulfur contents are considered as the main factors which influence the base oil oxidative stability [192,193]. It has been shown that oxidative stability of a given base stock can be enhanced when the combinations and concentrations of base stock sulfur and aromatics are optimized [194].

1.10.5 OXIDATION INHIBITION

The proceeding mechanistic discussion makes clear several possible counter measures to control lubricant oxidation. Blocking the energy source is one path. However, this is only effective for lubricants used in low shear and temperature situations. A more practical approach for most lubricant applications is the trapping of catalytic impurities and the destruction of alkyl radicals, alkyl peroxy radicals, and hydroperoxides. This can be achieved through the use of a metal deactivator and an appropriate antioxidant with radical scavenging or peroxide decomposing functionality, respectively.

The radical scavengers are known as primary antioxidants. They function by donating hydrogen atoms to terminate alkoxy and alkyl peroxy radicals, thus interrupting the radical chain mechanism of the auto-oxidation process. The basis for a compound to become a successful antioxidant is that peroxy and alkoxyl radicals abstract hydrogen from the compound much more readily than they do from hydrocarbons [198]. After hydrogen abstraction, the antioxidant becomes a stable radical, the alkyl radical becomes a hydrocarbon, and the alkyl peroxy radical becomes an alkyl hydroperoxide. HPs and aromatic amines are two main classes of primary antioxidants for lubricants.

The peroxide decomposers are also called secondary antioxidants [180]. They function by reducing alkyl hydroperoxides in the radical chain to nonradical, less-reactive alcohols. Organosulfur and organophosphorus compounds and those containing both elements, such as ZDDPs, are well-known secondary antioxidants.

Since transitional metals are present in most lubrication system, metal deactivators are usually added to lubricants to suppress the catalytic activities of the metals. Based on the functioning mechanisms, metal deactivators for petroleum products can be classified into two major types: chelators [180] and surface passivators [199]. The surface passivators act by attaching to metal surface to form a protective layer, thereby preventing metal–hydrocarbon interaction. They can also minimize corrosive attack of metal surface by physically restricting access of the corrosive species to the metal surface. The chelators, however, function in bulk of the lubricant by trapping metal ions to form an inactive or much less-active complex. With either mechanism, metal deactivators can effectively slow the oxidation process catalyzed by those transitional metals, which in turn lends metal deactivators an antioxidant effect. Table 1.4 lists examples of metal deactivators that are commonly found in lubricant formulations.

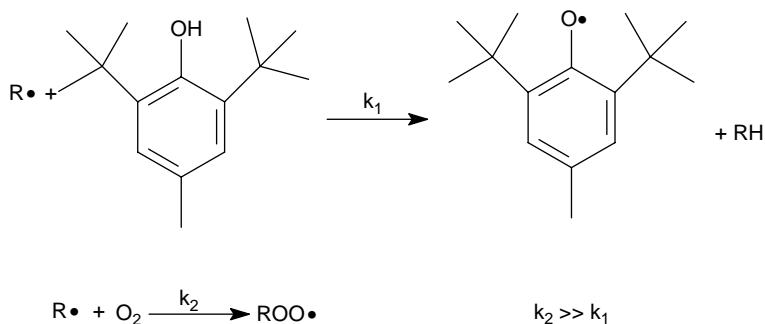
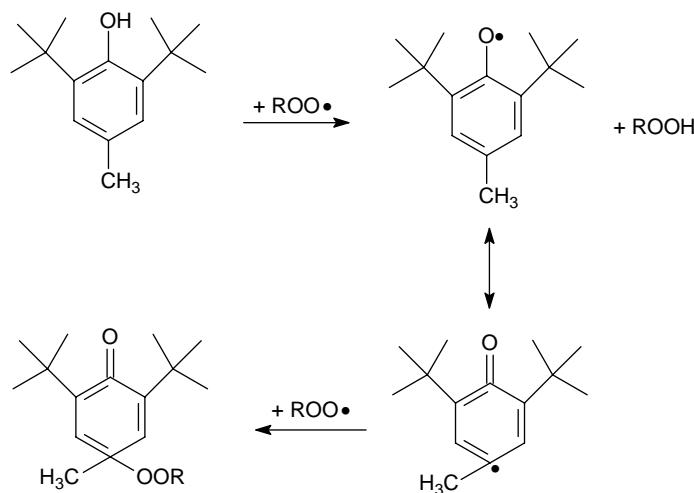
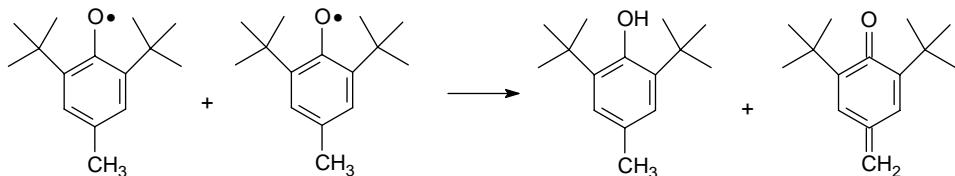
TABLE 1.4
Metal Deactivators for Lubricants

Surface Passivators	Basic Structure
Triazole derivative	
Benzotriazole	
2-Mercaptobenzothiazole	
Tolyltriazole derivative	
Chelators	
<i>N,N'</i> -disalicylidene-1,2-diaminopropane	

1.10.6 MECHANISMS OF PRIMARY ANTIOXIDANTS

1.10.6.1 Hindered Phenolics

A representative example of HP antioxidant is 3,5-di-*t*-butyl-4-hydroxytoluene (2,6-di-*t*-butyl-4-methylphenol), also known as BHT. Figure 1.8 compares the reaction of an alkyl radical with BHT versus oxygen. The reaction rate constant (k_2) of alkyl radical with oxygen to form alkyl peroxy radicals is much greater than that (k_1) of alkyl radical with BHT [179]. Hence with an ample supply of oxygen, the probability of BHT to react with alkyl radicals is low. As oxidation proceeds with more alkyl radicals being converted to alkyl peroxy radicals, BHT starts to react by donating a hydrogen atom to the peroxy radical as shown in Figure 1.9. In this reaction, the peroxy radical is reduced to hydroperoxide, whereas the BHT is converted into a phenoxy radical that is stabilized through steric hindrance and resonance structures. The steric hindrance provided by the two butyl moieties on the ortho positions effectively prevent the phenoxy radical from attacking other hydrocarbons. The cyclohexadienone radical resonance structure can further combine with a second alkyl peroxy radical to form the alkyl peroxide, which is stable at temperatures $<120^\circ\text{C}$ [200]. Without resonance transformation, an alternative reaction pathway for phenoxy radicals is to combine with

**FIGURE 1.8** Reactivity of BHT with alkyl radical.**FIGURE 1.9** Hydrogen donation and peroxy radical trapping mechanisms of BHT.**FIGURE 1.10** Termination reaction of phenoxy radicals.

each other into a chain termination step. As depicted in Figure 1.10, a hydrogen atom is donated from one phenoxy radical to the other, thus regenerating one BHT molecule and one methylene cyclohexadienone.

Under higher-temperature oxidation conditions, the cyclohexadienone alkyl peroxide previously formed is no longer stable. As illustrated in Figure 1.11, it will decompose to form an alkoxy radical, an alkyl radical, and a 2,6-di-*t*-butyl-1,4-benzoquinone. As can be expected, the generation of new radicals will deteriorate the overall effectiveness of the BHT under high-temperature oxidation conditions.

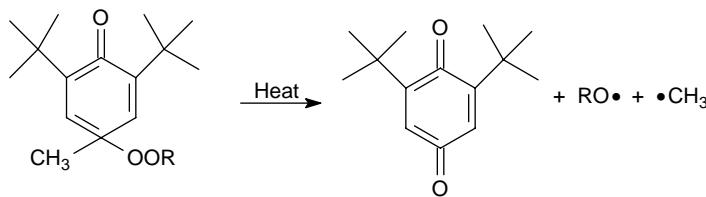


FIGURE 1.11 Decomposition of cyclohexadienone alkyl peroxide at higher temperatures.

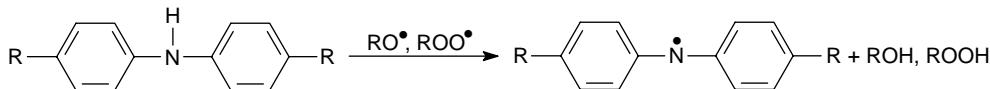


FIGURE 1.12 ADPA as a hydrogen donor.

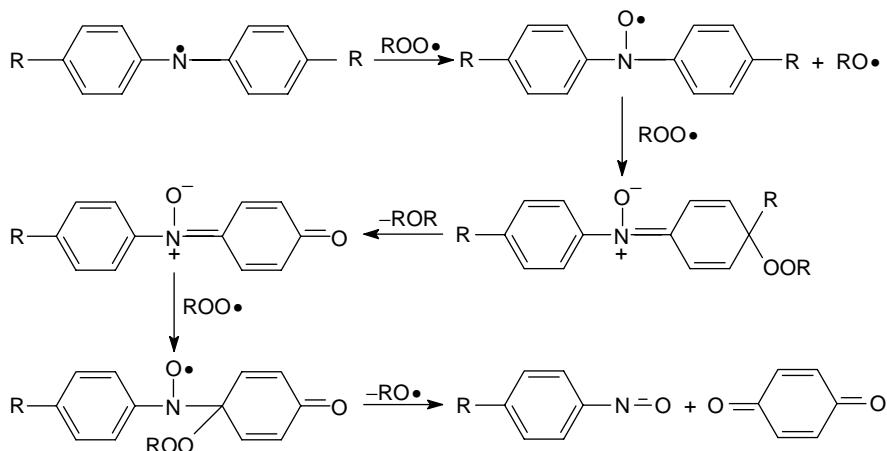


FIGURE 1.13 Low-temperature function mechanism of ADPA.

1.10.6.2 Aromatic Amines

A particularly effective class of aromatic amines useful as primary antioxidants is the ADPAs. The reaction of the antioxidants begins with hydrogen atom abstraction by alkyl peroxy radical and alkoxy radical, the mechanism of which is illustrated in Figure 1.12. Owing to the rapid reaction of alkoxy radicals with oxygen, the resulting alkyl peroxy radical is present at higher concentration, and its reaction with ADPA predominates. The aminyl radical formed can undergo a number of possible reaction pathways depending on temperature, degree of oxidation (relative concentration of peroxy radicals versus alkyl radicals), and the chemical nature of the ADPA [201]. Figure 1.13 shows the low-temperature (<120°C) oxidation inhibition mechanism [179,202], starting with aminyl radical attacking a second alkyl peroxy radical to form a nitroxyl radical and alkoxy radical. The nitroxyl radical is stabilized through three possible resonance structures [182,202], as illustrated in Figure 1.14. Next, a third alkyl peroxy radical reacts with the nitroxyl radical to form a nitroxyl–peroxide complex, which can further eliminate an ether molecule, forming a nitroxyl cyclohexadienone. Following reactions involve a fourth alkyl peroxy radical being added to the nitroxyl cyclohexadienone to form nitroxyl cyclohexadienone peroxide, followed by a dissociation reaction to form 1,4-benzoquinone and an alkylated nitrosobenzene. Therefore, on

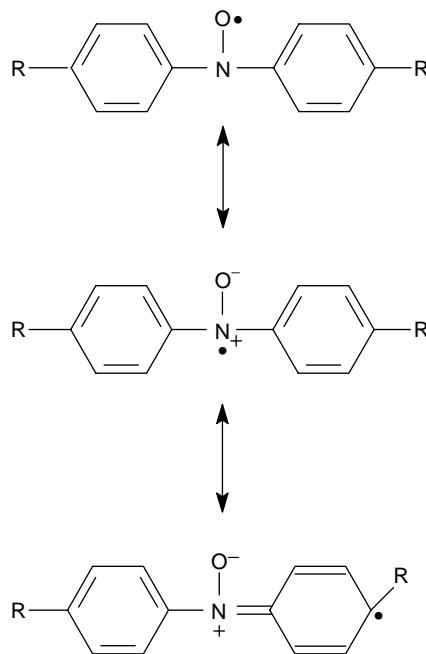


FIGURE 1.14 Resonance structures of nitroxyl radical.

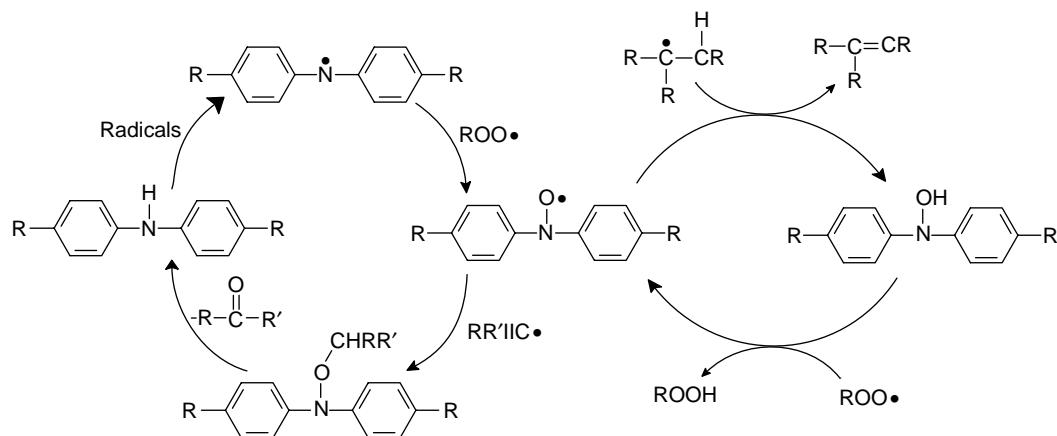


FIGURE 1.15 High-temperature ($>120^{\circ}\text{C}$) function mechanism of ADPAs.

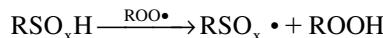
an equal mole basis, in theory, ADPAs can quench twice as many alkyl peroxy radicals as a mono HP under low-temperature conditions. At high temperatures ($>120^{\circ}\text{C}$), the nitroxyl radical intermediate can undergo one of two possible reaction pathways by either reacting with a secondary or a tertiary alkyl radical to form an *N*-*sec*-alkoxy diphenylamine [179,186,203] or an *N*-hydroxyl diphenylamine intermediate, respectively. These mechanisms are illustrated in Figure 1.15. In the former case, the resulting alkoxy amine intermediate can thermally rearrange to form a ketone and regenerate the starting ADPA. In the latter case, nitroxyl radical is regenerated upon reaction of the hydroxyl diphenylamine intermediate with an alkyl peroxy radical. Thus, at high temperatures, one molecule of ADPA can catalytically scavenge a large number of radicals before the nitroxyl

radical is destroyed. It has been reported that such regeneration process can provide ADPAs with a stoichiometric efficiency of more than 12 radicals per molecule [186].

1.10.7 MECHANISMS OF SECONDARY ANTIOXIDANTS

1.10.7.1 Organosulfur Compounds

Organosulfur compounds function as hydroperoxide decomposers through the formation of oxidation and decomposition products. The mechanism is illustrated in Figure 1.16 for an alkyl sulfide. The antioxidant action starts with the reduction of an alkyl hydroperoxides to a less reactive alcohol, with the sulfide being oxidized to a sulfoxide intermediate. A preferred mechanism for the subsequent reaction of sulfoxide intermediate is the intramolecular beta-hydrogen elimination, leading to the formation of a sulfenic acid (RSO_xH), which can further react with hydroperoxides to form sulfur-oxy acids. At elevated temperatures, sulfinic acid (RSO_2H) may decompose to form sulfur dioxide (SO_2), which is a particularly powerful Lewis acid for hydroperoxide decomposition through the formations of active sulfur trioxide and sulfuric acid. Previous work has shown that one equivalent of SO_2 was able to catalytically decompose up to 20,000 equivalents of cumene hydroperoxide [204]. Further enhancing the antioxidantancy of sulfur compounds is that, under certain conditions, the intermediate sulfur-oxy acids (RSO_xH) can scavenge alkyl peroxy radicals, thus giving the sulfur compound primary antioxidant characteristics:



1.10.7.2 Organophosphorus Compounds

Phosphites are a main class of organophosphorus compounds being used as secondary antioxidants. Phosphites decompose hydroperoxides and peroxy radicals following the reaction

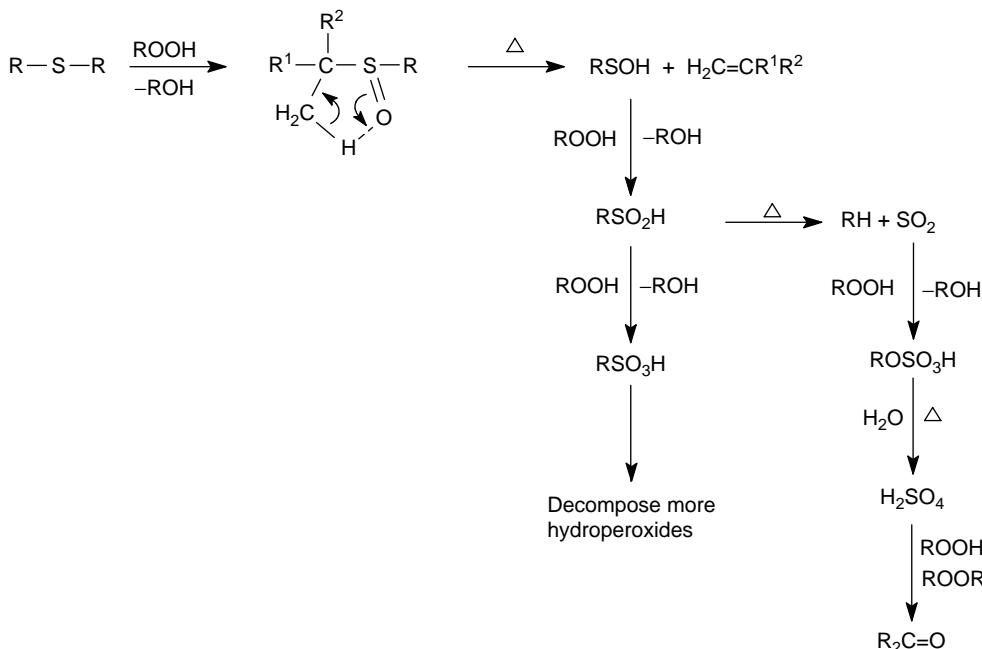


FIGURE 1.16 Antioxidation mechanism of alkyl sulfide.

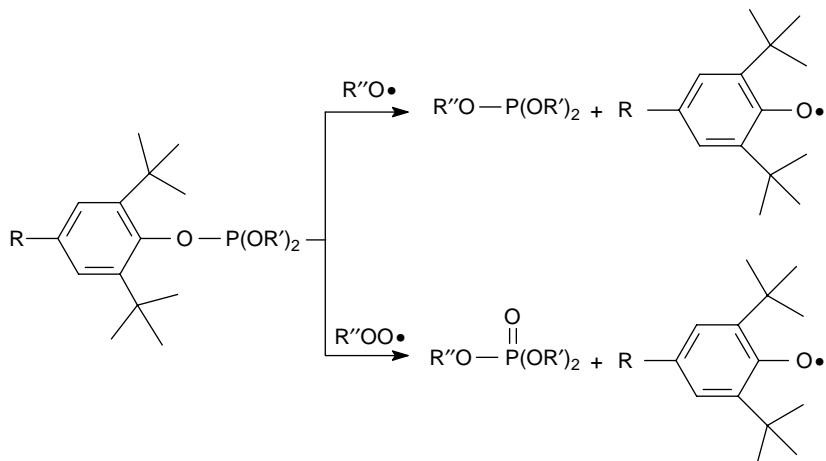
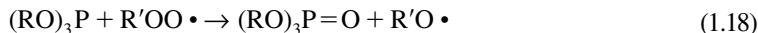
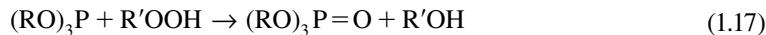


FIGURE 1.17 Alkoxy and peroxy scavenging mechanisms of phenyl phosphite.

mechanisms. In these reactions, phosphite is oxidized to corresponding phosphate, with the hydroperoxide and the peroxy radical being reduced to less-reactive alcohol and alkoxy radical, respectively.



Phosphites with certain substituted phenoxy groups may also behave as peroxy and alkoxy radical scavengers as shown in Figure 1.17. The resulting phenoxy radicals can further eliminate peroxy radicals upon resonance transformation to cyclohexadienone radical as discussed earlier. Owing to the steric hindrance provided by the alkyl groups on the ortho-positions, these phosphites tend to be more stable against hydrolysis and are preferred for use in moist lubrication environment.

1.10.8 ANTIOXIDANT SYNERGISM*

Antioxidant synergism describes the effect or response of a combined use of two or more antioxidants being greater than that of any individual antioxidant. Synergistic antioxidant systems offer practical solutions to problems where using a single antioxidant is inadequate to provide satisfactory results, or where the treatment level has to be limited due to economic or environmental reasons. Three types of synergy have been proposed for lubricant antioxidants [205]: (a) homosynergism, (b) heterosynergism, and (c) autosynergism.

Homosynergism occurs when two antioxidants acting by the same mechanism interact, generally in a single-electron-transfer cascade. A classic example is an ADPA in combination with a HP antioxidant. ADPA is initially more reactive than HP in scavenging alkyl peroxy radicals. As illustrated in Figure 1.18, the amine is first converted to an aminyl radical, which is relatively less stable and will accept a hydrogen atom from the HP to regenerate the alkylated amine [179,182]. In consequence, the HP is converted to a phenoxy radical. The driving force for this regeneration cycle to occur is the higher reactivity of the ADPA compared to the HP and the greater stability of the phenoxy radical relative to the aminyl radical [201]. After the HP is consumed, the aromatic amine antioxidant begins to deplete. By regenerating the more reactive amine, the overall effectiveness of the system is enhanced, and the useful antioxidant lifetime is extended.

* With permission from Dong, J. and C.A. Migdal, Synergistic Antioxidant Systems for Lubricants. 12th Asia Fuels and Lubes Conference Proceedings, Hong Kong, 2006.

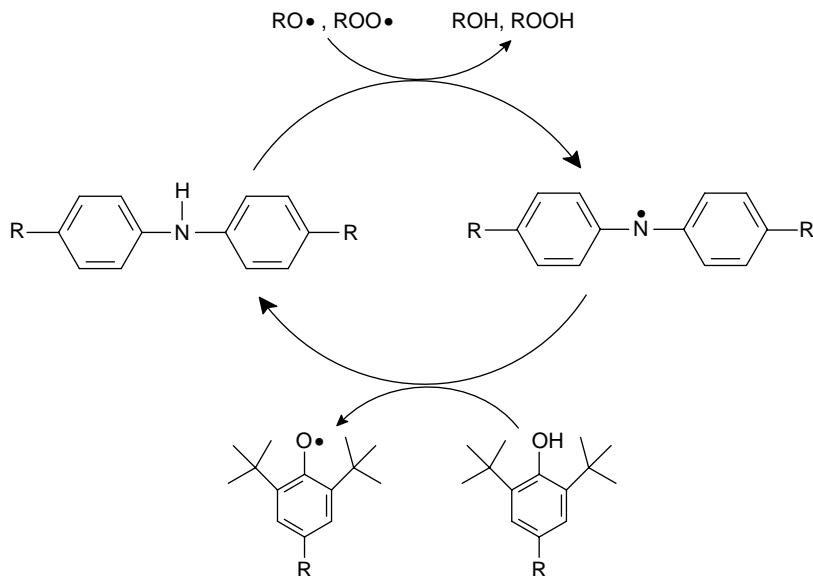


FIGURE 1.18 Mechanism of synergism between ADPA and hindered phenol.

Heterosynergism occurs when antioxidants act by a different mechanism and hence complement each other. This type of synergy usually takes place when a primary antioxidant and a secondary antioxidant are present in one lubricant system. The primary antioxidant scavenges radicals, whereas the secondary antioxidant decomposes hydroperoxides by reducing them to more stable alcohols. Through these reactions, chain propagation and branching reactions are significantly slowed or inhibited. A representative example of a heterosynergism is an amine antioxidant in combination with a ZDDP.

Autosynergism is a third type of synergistic response that results from two different antioxidant functions in the same molecule. Usually, antioxidants having functional groups that provide radical scavenging and hydroperoxide decomposing functions exhibit autosynergy. Examples of this type of antioxidants are sulfurized phenols and phenothiazines.

1.11 OXIDATION BENCH TESTS

Oxidative degradation of lubricants can be classified into two main reactions: bulk oil oxidation and thin-film oxidation. Bulk oil oxidation usually takes place in a larger oil body at a slower rate. The exposure to air (oxygen) is regulated by the surface contact kinetics, and the gas diffusion is limited. The oxidation leads to increases in oil acidity, oil thickening, and, to a more severe extent, oil-insoluble polymers that may manifest as sludge when mixed with unburned/oxidized fuel components, water, and other solids. Thin-film oxidation describes a more rapid reaction in which a small amount of oil, usually in the form of a thin-film coating on metal surface, is exposed to elevated temperatures and air (oxygen). Under these conditions, hydrocarbons decompose much more quickly and the polar oil oxidation products formed at the oil–metal interface can rapidly build up on the metal surface, leading to the formation of lacquer or deposits.

Over the years, many oxidation bench tests have been developed and proven to be valuable tools for lubricant formulators, particularly in the screening of new antioxidants and the development of new formulations. Most bench tests attempt to simulate the operating conditions of more expensive engine and field tests, when taking into consideration the oxidation mechanisms described earlier. In addition, a third mechanism based on oxygen uptake in a closed system has been employed in some bench tests, such as the RPVOT [206].

Owing to the limitation of laboratory setup, a single bench test cannot address all oxidation aspects of a real world scenario. The large variation in test conditions, particularly test temperature, use of catalyst, performance parameter, oxidation mechanism, and targeted oxidation stage, etc., makes it rather difficult or even impractical to correlate one test with another. It is therefore a common practice to run multiple tests at a time when characterizing a lubricant formulation and its additives. This section selectively reviews oxidation bench tests more closely related to the characterization of antioxidants. These tests have been standardized by some of the international standardization organizations such as ASTM and the Co-ordinating European Council (CEC), etc., and are more widely used in the industry. It is important to note that there are a number of custom-tailored test methods designed for specific needs that have been proven to be advantageous in certain circumstances. The value of these tests should not be underestimated.

1.11.1 THIN-FILM OXIDATION TEST

1.11.1.1 Pressurized Differential Scanning Calorimetry

Differential scanning calorimetry (DSC), including PDSC, is an emerging thermal technique for rapid and accurate determination of thermal-oxidative stability of base oils and performance of antioxidants. PDSC has been a more sought after technique for two main reasons. First, high pressure elevates boiling points, thus effectively reducing experimental errors caused by volatilization losses of additives and light fractions of base oil; second, it increases the saturation of the reacting gases in sample, allowing the use of lower test temperature or shorter test time at the same temperature [207].

PDSC experiments can be run in an isothermal mode to measure oxidation induction time (OIT) corresponding to the onset of oil oxidation or in a programmed temperature mode to measure the onset temperature of oxidation. The temperature technique has been utilized to study deposit-forming tendency of five engine oils, and the results obtained were consistent with their engine test ranking [208]. The OIT technique, however, is more commonly used for its simplicity and speed. Its early use can be traced back to the 1980s when Hsu et al. [209] tested a number of engine oils and found the induction periods of the samples to be indicative of the sequence IIID viscosity break points. Soluble metals consisting of lead, iron, copper, manganese, and tin together with a synthetic oxidized fuel were included as catalysts to promote oil oxidation.

The CEC L-85 and the ASTM D 6186 [210,211] are two standard methods that are based on OIT technique. Key test conditions of the methods are listed in Table 1.5. The CEC L-85 test method was originally developed for European Association des Constructeurs Europeens de l'Automobile (ACEA) E5 specification for heavy-duty diesel oils and has been incorporated in the current E7 specification. The test is capable of differentiating between different quality base oils, additives, indicating antioxidant synergies and correlating with some bulk oil oxidation tests [212]. With appropriate modifications to the standard methods, PDSC has been successfully utilized in the characterization of various lubricants in addition to automotive engine oils. These include, but not limited to, base oils [213,214], greases [215], turbine oils [214], gear oils [216], synthetic ester lubricants [217], and biodegradable oils [218,219]. Using PDSC to study the kinetics of base oil oxidation [220] and antioxidant structure–performance relationship [221] has also been reported.

1.11.1.2 Thermal-Oxidation Engine Oil Simulation Test (ASTM D 6335; D 7097)

The TEOST was originally developed to assess the high-temperature deposit-forming characteristic of API SF quality engine oils under turbocharger operating conditions [222]. The original test conditions were specified as the 33C protocol and subsequently standardized in the ASTM D 6335 method [223]. In this test, oil containing ferric naphthenate is in contact with nitrous oxide and moist air and is cyclically pumped to flow past a tared depositor rod. The rod is resistively heated through 12 temperature cycles, each going from 200 to 480°C for 9.5 min. After the heating cycle

TABLE 1.5
Conditions of Oxidation Test Methods

Test	Test Designation	Oxidation Regime	Temperature (°C)	Gas	Gas Flow or Initial Pressure	Catalyst	Sample Size	EOT	Parameter Measured
PDSC	D 6186	Thin film	130, 155, 180, 210	O ₂	500 psi, 100 mL/m	None	3.0 mg	Occurrence of oxidation exotherm	OIT
PDSC	CEC L-85	Thin film	210	Air	100 psi, no flow	None	3.0 mg	120 min maximum cycles	OIT
TEOST 33C	D 6335	Bulk	100, 200–480	N ₂ O, moist air	3.6 mL/min	Fe naphthenate	116 mL	12 Programmed cycles	Deposits
TEOST MHT	D 7097	Thin film	285	Dry air	10mL/m	Oil-soluble Fe, Pb, Sn	8.4 g	24 h	Deposits, volatile OIT
TFOUT	D 4742	O ₂ uptake, thin film	160	O ₂	90 psig	Fuel, naphthenates of Fe, Pb, Cu, Mg, and Sn, H ₂ O	1.5 g	Sharp pressure drop	TAN, sludge, metal weight loss
TOST	D 943, D 4310	Bulk	95	O ₂	3.0 L/h	Fe, Cu, H ₂ O	300 mL	ΔTAN = 2.0 1000 h	Viscosity, carbon residue
IP48	IP48	Bulk	200	Air	1.5 L/h	None	40 mL	6 h × 2	Volatile acids, oil acidity, sludge
IP 280/CIGRE	IP 280	Bulk	120	O ₂	1 L/h	Cu, Fe naphthenates	25 g	164 h	OIT
RPVOT	D 2272	O ₂ uptake	160	O ₂	90 psig	Cu, H ₂ O	50 mL	ΔP = 25 psi	OIT

is complete, deposit formed on the depositor rod is determined by differential weighting. The 33C protocol was found capable of discriminating engine oils with known ability in resisting deposit formation in critical areas of engines [222].

The successful use of high-temperature deposition test to characterize engine oils has led to the development of a TEOST mid-high temperature (MHT) protocol, a simplified procedure for the assessment of oil deposition tendency in the piston ring belt and under-crown areas of fired engines [224]. Thin-film oxidation condition was thought to be predominant in these areas, and accordingly, the depositor assembly was revised to allow the oil flows down the rod in a slow and even manner to obtain a desired thin film. To better reflect the thermal-oxidative conditions of the engine zone of interest, a continuous depositor temperature of 285°C together with modified catalyst package and dry air is employed. The test runs for 24 h, and afterward, the amount of deposits formed on the tared depositor is gravimetrically determined [225]. Since introduction, the TEOST MHT has been incorporated in the International Lubricant Standardization and Approval Committee (ILSAC) gas fuel (GF)-3 and GF-4 engine oil specifications with an upper limit of 45 and 35 mg, respectively. Aside from being a thermal-oxidation test, TEOST can also be used to characterize neutral and overbased detergents of automotive engine oils [226].

1.11.1.3 Thin-Film Oxidation Uptake Test (ASTM D 4742)

The TFOUT method was originally developed under the U.S. Congress mandate to monitor batch-to-batch variations in the oxidative stability of re-refined lubricating base stocks [227]. The test stresses a small amount of oil to 160°C in a high-pressure reactor pressurized with oxygen along with a metal catalyst package, a fuel catalyst, and water to partially simulate the high-temperature oxidation conditions in automotive combustion engines [228]. Better oxidative stability of oil corresponds to a longer time it takes to observe a sharp drop in oxygen pressure. TFOOUT can be carried out in a RPVOT apparatus upon proper modification to the sampling accessories. Based on the results obtained from testing a limited number of reference engine oils, qualitative correlation between TFOOUT and the sequence IID engine dynamometer test has been established [229]. Since being adopted as an ASTM standard method, there has been a wider utilization of the TFOOUT to screen lubricants, base stocks, and additive components before sequence III engine testing [227].

1.11.2 BULK OIL OXIDATION TEST

1.11.2.1 Turbine Oil Stability Test (ASTM D 943, D 4310)

The turbine oil stability test (TOST) has been widely used in the industry to assess the oxidative stability of inhibited steam turbine oils under long-term service conditions. It can be used on other types of industrial lubricants such as hydraulic fluids and circulating oils and in particular on those that are prone to water contamination in service. The test runs at relatively low temperature (95°C) to represent the thermal-oxidative conditions of real steam turbine applications. Two versions of the TOST, namely, ASTM D 943 and D 4310 [230,231], have been developed. Both the methods share some common test conditions including test apparatus, catalysts, sample size, temperature profile, and gas, with minor differences in the test duration and target oxidation parameters to be monitored. The ASTM D 943 measures oxidation lifetime, which is the number of hours required for the test oil to reach an acid number of 2.0 mgKOH/g or above. The ASTM D4310 determines the sludging and corrosion tendencies of the test oil by gravimetrically measuring oil-insoluble products after 1000 h of thermal and oxidative stresses. The total amount of copper in oil, water, and sludge phases is also determined.

A modified TOST method that operates at higher temperature (120°C) and in the absence of water has been proposed [232]. The procedure requires RPVOT as a monitoring tool and is specifically suitable for the determination of sludging tendencies of long-life steam and gas turbine oils formulated with the more stable groups II and III base stocks and high-performance aminic

antioxidants. The “dry” TOST method is a potential alternative to the original methods that have found to be less discriminatory on such high-performance turbine oils.

1.11.2.2 IP 48 Method

The Institute of Petroleum (IP) 48 is a high-temperature bulk oil oxidation test originally designed for the characterization of base oils [233]. The test stresses a 40 ml of oil sample in a glass tube at 200°C, along with air bubbling at 15 L/h, for two 6 h periods with a 15–30 h standby period in between. Oil viscosity increase and the formation of carbon residue are determined after the oxidation. The test is considered unsuitable for additive-type oils (other than those containing ashless additives) or those which form solid products or evaporate more than 10% by volume during the test. However, successful assessment of engine oils using a modified IP 48 method with four 6 h cycles has been reported [233,234].

1.11.2.3 IP 280/CIGRE

The IP 280, also known as the CIGRE test, was designed to assess the oxidative stability of inhibited mineral turbine oils, targeting formations of volatile acid products (through water absorption), sludge, and increase of oil acidity [235]. The IP 280 and the TOST D 943 are similar to each other in terms of the oxidation regime employed. However, their test conditions are different, and it is a common practice to conduct both tests because in some internal turbine oil specifications, the limits for both the tests are stipulated. The IP 280 test was found to be more suitable for discriminating performance of additive packages, whereas the D943 is more suitable for comparative evaluation of base oils derived from different crude source and processing techniques [236].

1.11.3 OXYGEN UPDATE TEST

1.11.3.1 Rotating Pressure Vessel Oxidation Test (ASTM D 2272)

The RPVOT, originally known as the rotating bomb oxidation test (RBOT), was designed to monitor the oxidative stability of new and in-service turbine oils having the same composition. It can also be used to characterize other types of industrial lubricants, for example, hydraulic fluids and circulating oils. The test utilizes a steel pressure vessel where sample oil is initially pressurized to 90 psi with oxygen and thermally stressed to 150°C in the presence of water and copper coil catalyst until a pressure drop of 25 psi is observed [237]. The test temperature was chosen to promote measurable oil breakdown in a relatively short time. However, such temperature causes a lack of representation to most steam turbines that operate below 100°C and to the combustion turbines that operate at much higher temperatures [238]. Owing to its sensitivity to specific additive chemistries, RPVOT finds limited use in comparing differently formulated oils. In addition, the test is more suitable for the determination of remaining useful life of in-service turbine oils rather than the qualification of new oils. Attempting to correlate RPVOT to the lengthy TOST D 943 on steam turbine oils has been successful, suggesting that the results from RPVOT may be used to estimate the relative lifetime of turbine oils in the TOST D943 [239].

1.12 EXPERIMENTAL OBSERVATIONS

The following two experiments demonstrate (a) performance behaviors of aminic antioxidant versus HP that is in agreement with the mechanisms discussed earlier, and (b) how proper selection and combinations of antioxidants can lead to synergy that further enhances performance.

In the first experiment, two turbine oils, each formulated with a base oil selected from an API group I or group IV base stock, a standard additive package of metal deactivator and corrosion inhibitor, and 0.8 wt% of antioxidants of interest were tested by using the TOST D 943 lifetime method. The aminic antioxidant was an ADPA containing a mixture of butylated and octylated diphenylamines. The HP was a C₇–C₉ branched alkyl ester of 3,5-di-*tert*-butyl-4-hydroxyhydrocinnamic acid. As can be seen from Figure 1.19, in either oil, the HP significantly outperformed the ADPA by

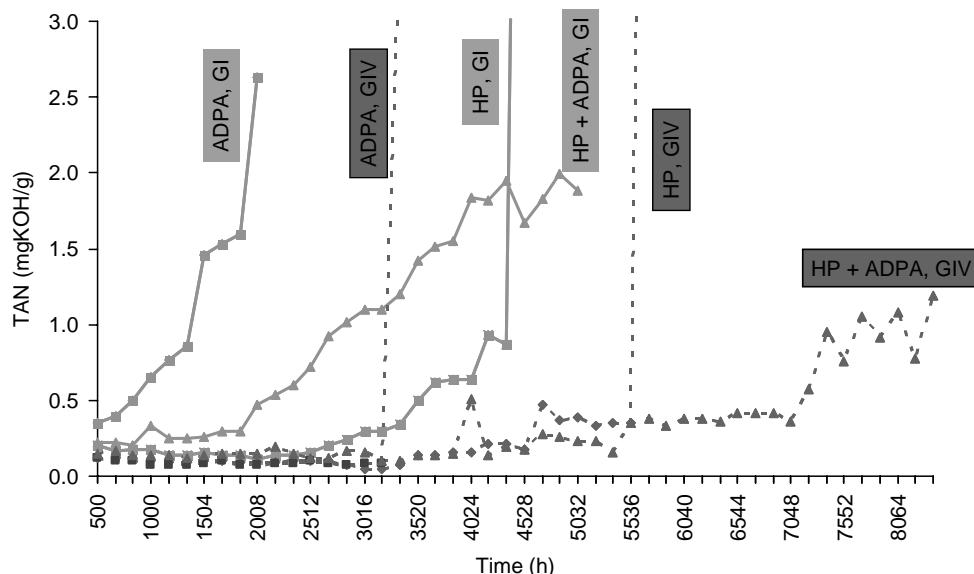


FIGURE 1.19 TOST results of turbine oils containing group I or IV base oil and 0.8 wt% of antioxidant.

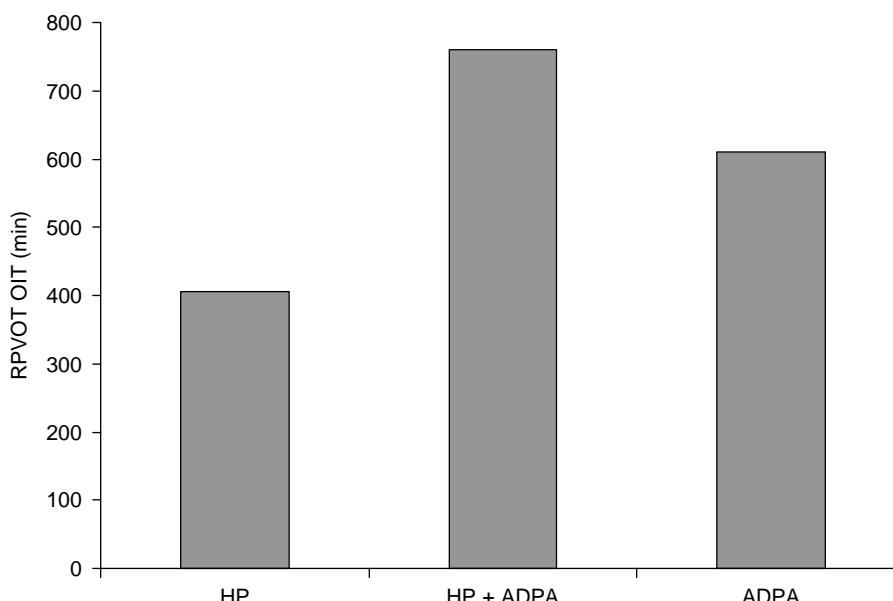


FIGURE 1.20 RPVOT results of turbine oil containing a group I base oil and 0.5 wt% of antioxidant.

providing longer protection time against oxidation. Mixtures of the ADPA and the HP at 0.4 wt% each in the oils provided even stronger protection, leading to an extended lifetime of ~5000 h for the group I turbine oil and well over 8000 h for the group IV turbine oil. Thus, under the low-temperature test conditions, the HP was superior to the ADPA. Proper mixing of the two additives produced synergy, in this case a homosynergism that led to the maximum protection.

In the second experiment, a turbine oil formulated with an API group I base stock, a metal deactivator, a corrosion inhibitor, and a 0.5 wt% of the same antioxidants as before was tested by using the RPVOT (ASTM D 2272). The results are graphically presented in Figure 1.20. At the higher

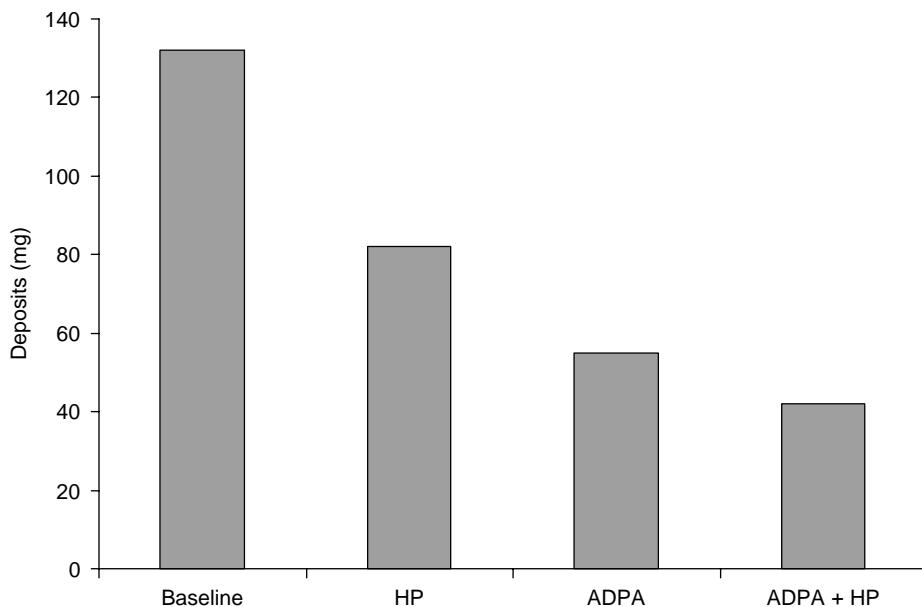


FIGURE 1.21 TEOST results of a prototype PCMO containing a group II base stock and a total of 1.0 wt% of antioxidant.

test temperature (150°C), the OIT of the blend containing ADPA was ~ 600 min, while the ADPA was depleted. The HP protected the oil for ~ 300 min, indicating that the HP is only half as effective as the ADPA under the same test conditions. A mixture of ADPA and HP with 0.25 wt% of each additive present provided a protection for over 700 min. Therefore, in contrast to the TOST results, under high-temperature conditions, the ADPA was superior to the HP. Similar to what was observed in the TOST, a synergistic mixture of the two additives provided the maximum protection.

The superiority of ADPA over HP and the benefit of antioxidant synergy for maximum oxidation protection have been further demonstrated in a GF-4 prototype passenger car motor oil (PCMO). The oil contained an API group II base oil, a low level (0.05 wt%) of phosphorus derived from ZDDP, and a number of other additives (detergents, dispersant, viscosity index improvers, pour point depressant, etc.) that are commonly found in engine oil formulations. The ADPA, HP, and their mixture were tested at 1.0 wt% in the oil on a TEOST MHT apparatus, using the ASTM D 7097 standard procedure. The results are presented in Figure 1.21. The baseline blend, which contained all other additives except the antioxidant, produced a fairly high level (130 mg) of deposits. With the addition of the HP, the deposit was substantially reduced to ~ 80 mg, with the ADPA, down to ~ 55 mg. By properly mixing the two antioxidants while keeping the total level constantly at 1.0 wt%, the deposit was further reduced to ~ 40 mg. The TEOST results confirm the superior performance of ADPA and further demonstrate the benefit of antioxidant synergy for high-temperature oxidation conditions.

The antioxidant mechanisms discussed earlier well explain the experimental results and can serve as a foundation to guide lubricant formulators in the selection of correct antioxidant(s) for a particular end use. To obtain a successful formulation, other factors such as cost performance, volatility, color, solubility, odor, physical form, toxicity, and compatibility with other additives also need be taken into consideration. From a performance standpoint, HPs are excellent primary antioxidants for their stoichiometric reactions with free radicals under lower-temperature conditions. In contrast, ADPAs are excellent primary antioxidants for high-temperature conditions owing to their catalytic radical scavenging actions. The homosynergism facilitated between the

ADPA and the HP is powerful in the inhibition of different stages of oil oxidation as demonstrated. It is, however, important to note that the generation and the magnitude of an antioxidant synergy are dependent on the formulation, base oil, and test method used. The ADPA/HP synergy appears robust as it was successfully reproduced in two oil formulations and tests that vastly differ from each other in terms of base oil makeup, additive type and complexity, test conditions, and oxidation regimes. In fact, this type of synergy has been used in a wide range of lubricants. In a more recent development, a methylene-bridged HP was utilized and found to be synergistic with ADPA in low-phosphorus engine oils [240]. Several instances of other types of synergy have been demonstrated and discussed in greater depth elsewhere. These include, but are not limited to, synergy between sulfur-bearing HP and ADPA antioxidants for hydro-treated base stocks [134,241], synergy between aminic antioxidants [242], and synergy between primary antioxidants and organophosphites [57].

1.13 ANTIOXIDANT PERFORMANCE WITH BASE STOCK SELECTION

Driven by escalating environmental and performance requirements, the lubricant industry is rapidly changing for the better with the advances of additive and base oil technologies. One notable change from a formulation point of view is that the conventional solvent-extracted base oils (group I) are gradually being replaced by high-quality, high-performance groups II and III base stocks made from hydrotreated (hydrocracked), hydrotreating, and hydrocatalytic dewaxing processes. These processes provide oils with low sulfur, high degree of saturation, and viscosity index (Table 1.3). Lubricants formulated with these base stocks generally have improved performance characteristics such as superior oxidative stability, lower volatility, improved low-temperature properties, longer drain intervals, and improved fuel economy. Because of these benefits, the API group III base oils are becoming a serious challenge to synthetic PAOs for top-tier oil formulations.

Many efforts have been made to understand the relationship between the base oil composition and the response to added antioxidants. Such knowledge is extremely important for lubricant formulators when it comes to the selection of an appropriate antioxidant system for a given oil. Figure 1.22 shows the RPVOT test results of four base oils with and without the presence of an antioxidant. Each oil

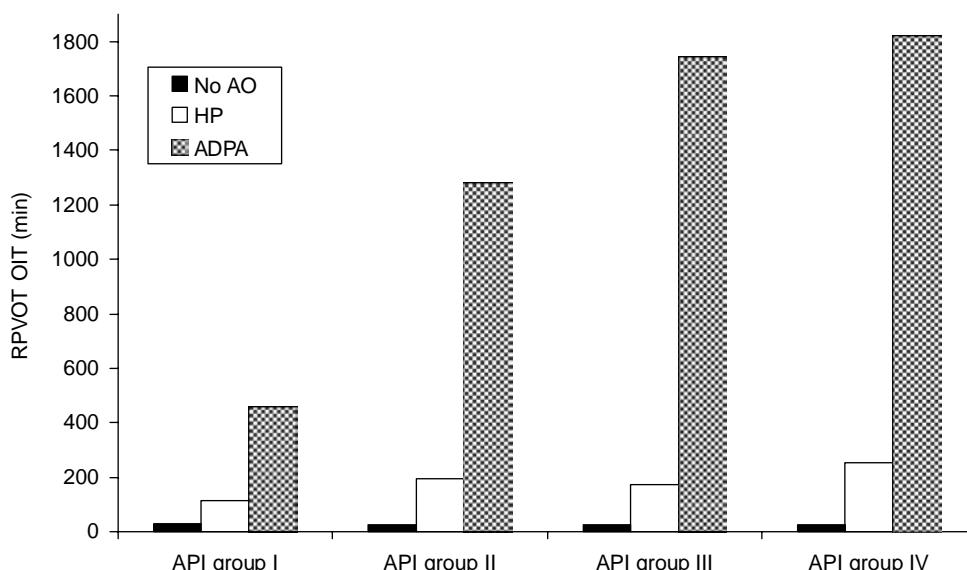


FIGURE 1.22 RPVOT results of HP and ADPA in API groups I–IV base oils.

represents an API group from I to IV. The HP and the ADPA are the same as before. Clearly, without the protection of antioxidant, all oils performed equally poor. A 0.5 wt% of the HP antioxidant gave modest levels of protection that marginally increase from API group I to IV. When the base oils were treated with the same level of the ADPA, a drastic performance boost is seen across the board. The performance responses of the highly refined groups II, III, and the group IV to the added ADPA appear to be particularly strong.

The superior antioxidant response of the groups II and III base oils over the conventional group I base oils may be attributed to the removal of aromatic hydrocarbons and polar constituents and the large presence of saturated hydrocarbons in the oils [243,244]. One school of thought hypothesized that oxygen-, sulfur-, and nitrogen-containing polar species may exist in the form of micellar aggregations in base oil. When an antioxidant is added, some of the natural polar molecules may interact physically and chemically with the additives, leading to a reduction in additive effectiveness in some circumstances. In those highly refined base oils where the natural compounds are essentially low or absent, the added antioxidant is able to exert its maximum effectiveness [245].

ZDDP, another important class of antioxidant/antiwear agent, has been studied by others, and the results indicated that its antioxidant performance is dependent on the base oil aromatics, alkyl-substituted aromatics, average chain length of hydrocarbons, and the relative presence of normal paraffins and isoparaffins [196]. In group I base oils, ZDDP gave good responses to highly saturated hydrocarbons characterized with normal paraffins having shorter chain length. Isoparaffins were found to decrease the antioxidant activity of ZDDP due to the steric hindrance of the side chains, which restricts the additive molecules from interacting with the hydrocarbons. In oils with higher monoaromatic hydrocarbons, ZDDP tends to perform better, which was believed to be related to improved solvency.

1.14 FUTURE REQUIREMENTS

The need for antioxidants in future lubricants will continue and the demands for both quality and quantity will likely to increase to meet new environment and performance requirements. Although such trend is inevitably to take place in the entire lubricant industry, three specific areas may see more rapid and dynamic advancements: (a) modern engine oils, (b) biodegradable lubricants, and (c) engine oils that operate on biofuels.

New engine designs and engine oil formulations are being frequently rolled out. The primary driving force is environmental in nature: the requirements for less oil consumption, better fuel economy, extended drain intervals, and lower emissions (particulates, hydrocarbons, CO, and NO_x). To meet these requirements, new automotive engines are designed lighter and smaller but are required to operate under more severe conditions for higher output and speeds, which lead to higher engine and oil temperatures. It has been well established that every 10°C of temperature increase will approximately double the rate of oil oxidation. Therefore, to maintain satisfactory service lifetime in a more severe service environment, increasing the level of antioxidant and using those suitable for high-temperature conditions, such as aminic antioxidants, are expected. Modern catalytic converters are highly effective in reducing the emissions. However, they are vulnerable to the deterioration effects of sulfur, phosphorus, and ash derived from engine oils and fuels. Accordingly, initiatives have been made to reduce the ZDDP content in engine oils. The current ILSAC GF-4 specification has limited the sulfur and phosphorus levels to a maximum of 0.7 and 0.08 wt%, respectively, and these numbers are likely to be even lower for future engine oils. With the ZDDP being reduced, it is expected that the uses of ashless, primary antioxidants as well as secondary antioxidants (as a substitute for ZDDP) will increase.

To meet the increasing performance requirements set for modern engine oils, high-quality groups II and III base stocks are emerging to replace the conventional solvent-refined group I oils. The hydrotreating and isodewaxing processes that are used to make these oils significantly lower the unsaturated hydrocarbons and polyaromatics, which contribute to poor oxidative stability.

However, the naturally occurring sulfur species that can function as antioxidants have also been largely removed. Previous discussion has clearly demonstrated that the superior oxidative stability of these oils can only be realized when an appropriate synthetic antioxidant is used. Therefore, as lubricant formulators increase the use of hydrotreated and synthetic base stocks, the requirements for antioxidants in lubricants are expected to rise.

The environmental and toxicity issues of petroleum-based oils as well as their rising cost related to a global shortage have led to renewed interest in the use of vegetable oils, such as soybean oil, canola oil, sunflower oil, and coconut oil as lubricants and industrial fluids. The industry has already seen vegetable oils being utilized to make environmentally friendly automotive engine oils, two-cycle engine oils, hydraulic fluids, total loss lubricants, and marine lubricants. Vegetable oils generally possess some excellent lubrication properties, for example, good inherent lubricity, low volatility, high viscosity index, excellent solvency for lubricant additives, and easy miscibility with other fluids. However, vegetable oils are known for their poor oxidative stability as compared to mineral oils. Research has found that typical soybean oil formed polymers at a rate an order of magnitude faster than mineral oils [246]. To overcome this drawback, it is expected that vegetable oil-based lubricants will need more antioxidants to meet the performance requirements set for mineral oil-based lubricants. Owing to the unique hydrocarbon composition of vegetable oils, antioxidant response in these new fluids will be different from mineral oils. Recent work [218] has indicated that ADPAs that have proven track of high-temperature performance in mineral base oils are not as effective in stabilizing soybean oil at elevated temperatures (e.g., 170°C). In addition, environmentally friendly lubricants need to use additives that satisfy biodegradation and bioaccumulation standards. Antioxidants suitable for mineral oils may become problematic for use in vegetable oil-based lubricants. As such, the development of new classes of biodegradable antioxidants may be needed.

The increasing use of biofuels such as biodiesel methyl esters derived from oil seeds, animal fats, and reclaimed cooking oils, represents a new challenge to the stabilization of engine oils that operate on such fuels. Recent work [247] has discovered that biodiesels of various vegetable sources (canola, soybean, palm oils, coconut, etc.) promote the oxidation of in-service engine oils even at a low dilution level, primarily shortening inhibited period, and leading to rapid oil viscosity increase. Further aggravating the situation is the high and narrow boiling points of biodiesels, which make them more persistent than mineral diesels after entering the crankcase. For an engine oil to perform satisfactorily with these new fuels, antioxidant level has to be maintained at an effective level to counteract the strong degradation impact from the biofuels.

Overall, future lubricants will favor antioxidants having high-performance, cost-effective, ashless, multifunctional, and environmentally-friendly attributes. The ultimate driving force is environmental in nature while taking into account the emerging base oil technologies and performance specifications.

1.15 COMMERCIAL ANTIOXIDANTS

Product	Company	Chemistry
Ethanox® 310	Albemarle	Tetrakis(methylene (3,5-di- <i>t</i> -butyl-4-hydroxyhydrocinnamate)methane
Ethanox 323	Albemarle	Nonylphenol disulfur oligomer
Ethanox 376	Albemarle	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C ₁₈ alkyl ester
Ethanox 4701	Albemarle	2,6-Di- <i>t</i> -butyl phenol
Ethanox 4702	Albemarle	4,4'-Methylene bis(2,6-di- <i>t</i> -butyl phenol)
Ethanox 4703	Albemarle	2,6-Di- <i>t</i> -butyl-alpha-dimethylamino- <i>p</i> -cresol
Ethanox 4716	Albemarle	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C ₇ –C ₉ alkyl ester
Ethanox 4733	Albemarle	Mixture of mono-, di-, and tri- <i>t</i> -butyl phenols
Ethanox 4735	Albemarle	Mixture of <i>t</i> -butyl phenols
Ethanox 4755	Albemarle	Boron containing derivatives of Ethanox 4702
Ethanox 4872J	Albemarle	Multiring <i>t</i> -butyl phenol, 53% active

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Product	Company	Chemistry
Ethanox 4827J	Albemarle	Multiring <i>t</i> -butyl phenol, 30% active
Ethanox 4777	Albemarle	Alkylated diphenylamine
Additin® 7010	Rhein Chemie	Oligomerized 1,2-dihydro-4-trimethylquinoline
Additin 7130	Rhein Chemie	Phenyl-alpha-naphthylamine
Additin 7110	Rhein Chemie	2,6-Di- <i>t</i> -butyl- <i>p</i> -cresol
Additin 7120	Rhein Chemie	2,6-Di- <i>t</i> -butyl phenol
Additin 7115	Rhein Chemie	Phenol derivative sterically hindered
Additin 7135	Rhein Chemie	Styrenated diphenylamine
Naugalube® 15	Chemtura	2,2'-Thiodiethylene bis(3,5-di- <i>t</i> -butyl-4-hydroxyphenyl)propionate
Naugalube 16	Chemtura	4,4'-Thiobis(2- <i>t</i> -butyl-5-methyl phenol)
Naugalube 18	Chemtura	2,2-Thiobis(4-methyl-6- <i>t</i> -butyl phenol)
Naugalube 22	Chemtura	Mixture of <i>t</i> -butyl phenol
Naugalube 32	Chemtura	Tetrakismethylene (3,5-di- <i>t</i> -butyl-4-hydroxyhydrocinnamate)methane
Naugalube 37	Chemtura	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C ₁₈ alkyl ester
Naugalube 38	Chemtura	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C ₁₃₋₁₅ alkyl ester
Naugalube 531	Chemtura	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C _{7-C₉} alkyl ester
Naugalube 438	Chemtura	Diocyl diphenylamine
Naugalube 438L	Chemtura	Dinonyl diphenylamine
Naugalube 635	Chemtura	Styrenated diphenylamine
Naugalube 640	Chemtura	Butylated-, octylated-diphenylamine
Naugalube 680	Chemtura	Octylated-, styrenated-diphenylamine
Naugalube AMS	Chemtura	Alpha-methystyrenated DPA
Naugard® PANA	Chemtura	Phenyl-alpha-naphthylamine
Naugalube APAN	Chemtura	Alkylated PANA
Naugalube TMQ	Chemtura	Oligomerized 1,2-dihydro-4-trimethylquinoline
Naugalube 403	Chemtura	N,N'-di-sec-butyl- <i>p</i> -phenylenediamine
Naugalube TPP	Chemtura	Triphenyl phosphite
Irganox® L 01	Ciba	Diocyl diphenylamine
Irganox L 06	Ciba	Octylated PANA
Irganox L 57	Ciba	Butylated, octylated diphenylamine
Irganox L 67	Ciba	Dinonyl diphenylamine
Irganox L 101	Ciba	Tetrakismethylene (3,5-di- <i>t</i> -butyl-4-hydroxyhydrocinnamate)methane
Irganox L 107	Ciba	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C ₁₈ alkyl ester
Irganox L 109	Ciba	Hindered bis-phenol
Irganox L 115	Ciba	2,2'-Thiodiethylene bis(3,5-di- <i>t</i> -butyl-4-hydroxyphenyl)propionate
Irganox L 118	Ciba	High MW liquid hindered phenolic with thioether
Irganox L 135	Ciba	3,5-Di- <i>t</i> -butyl-4-hydroxy-hydrocinnamic acid, C _{7-C₉} alkyl ester
Irganox E 201	Ciba	Liquid di-alpha-tocopherol (vitamin E)
Irgaphos® 168	Ciba	Tri-(<i>d</i> - <i>t</i> -butylphenyl) phosphite
Vanlube® AZ	RT Vanderbilt	Zinc diamyldithiocarbamate in oil
Vanlube EZ	RT Vanderbilt	Zinc diamyldithiocarbamate and diamyl ammonium Diamyldithiocarbamate
Vanlube NA	RT Vanderbilt	Nonylated, ethylated diphenylamine
Vanlube PCX	RT Vanderbilt	2,6-Di- <i>t</i> -butyl- <i>p</i> -cresol
Vanlube RD	RT Vanderbilt	Oligomerized 1,2-dihydro-4-trimethylquinoline
Vanlube SL	RT Vanderbilt	Octylated, styrenated diphenylamine
Vanlube SS	RT Vanderbilt	Octylated diphenylamine

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Product	Company	Chemistry
Vanlube 81	RT Vanderbilt	Diethyl diphenylamine
Vanlube 7723	RT Vanderbilt	Methylene bis(dibutylthiocarbamate)
Vanlube 869	RT Vanderbilt	Zinc dithiocarbamate/sulfurized olefin blend
Vanlube 8610	RT Vanderbilt	Antimony dithiocarbamate/sulfurized olefin blend
Vanlube 887	RT Vanderbilt	Toltriazole compound in oil
Vanlube 887E	RT Vanderbilt	Toltriazole compound in ester
Vanlube 9317	RT Vanderbilt	Organic amine in synthetic ester
Vanlube 961	RT Vanderbilt	Butylated, octylated diphenylamine
Vanlube 996E	RT Vanderbilt	Methylene bis(di-butyl-dithiocarbamate) and toltriazole derivative

1.16 COMMERCIAL METAL DEACTIVATORS

Product	Company	Chemistry
Ethanox® 4705	Albemarle	<i>N,N</i> -disalicylidene-1,2-diaminopropane
Irgamet® 30	Ciba	Triazole derivative
Irgamet 39	Ciba	Toltriazole derivative
Irgamet 42	Ciba	Water-soluble toltriazole derivative
Irgamet BTZ	Ciba	Benzotriazole
Irgamet TTZ	Ciba	Toltrizole
Cuvan® 303	RT Vanderbilt	<i>N,N</i> -bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine
Cuvan 484	RT Vanderbilt	2,5-Dimercapto-1,3,4-thiadiazole derivative
Cuvan 826	RT Vanderbilt	2,5-Dimercapto-1,3,4-thiadiazole derivative
NACAP®	RT Vanderbilt	Sodium 2-mercaptopbenzothiazole, 50% active
ROKON®	RT Vanderbilt	2-Mercaptobenzothiazole
Vanchem® NATD	RT Vanderbilt	Disodium, 2,5-dimercaptothiadiazole, 30% active
Vanlube 601	RT Vanderbilt	Heterocyclic sulfur–nitrogen compound
Vanlube 601E	RT Vanderbilt	Heterocyclic sulfur–nitrogen compound
Vanlube 704	RT Vanderbilt	Proprietary blend

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2 Zinc Dithiophosphates

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CONTENTS

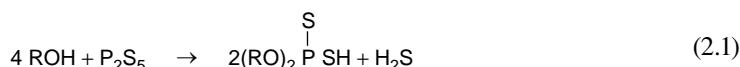
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2.1 INTRODUCTION

Zinc dialkyldithiophosphates (ZDDPs) have been used for more than 50 years in the lubricant industry as low-cost, multifunctional additives in engine oils, transmission fluids, hydraulic fluids, gear oils, greases, and other lubricant applications. The power of this particular compound is in its ability to simultaneously function as an excellent antiwear agent, a mild extreme-pressure (EP) agent, and an effective oxidation and corrosion inhibitor, all at a very low cost in comparison with the alternate chemistries available in the market. This is why it is still manufactured on a large scale by companies such as the ExxonMobil Corporation, Chevron Corporation, Ethyl Corporation, Lubrizol Corporation, and others. To date, as much as 300 million lb of ZDDP is still manufactured annually in the industrialized West.

2.2 SYNTHESIS AND MANUFACTURE

ZDDP was first patented on December 5, 1944, by Herbert C. Freuler of the Union Oil Company of California in Los Angeles [1]. The multifunctionality of ZDDP was immediately noticed as Freuler indicated a noticeable increase in both the oxidation and the corrosion resistance of the lubricants tested with the novel compound at a 0.1–1.0% treatment level. The initial synthesis Freuler carried out involved the reaction of 4 mol of the intermediate dialkyldithiophosphate acid and 1 mol of hydrogen sulfide



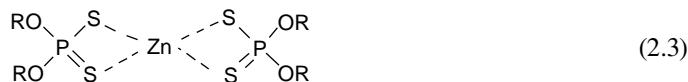
followed by neutralization of the acid with 1 mol of zinc oxide



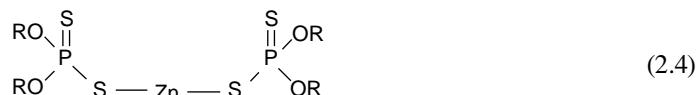
This synthetic route is still used today in the manufacturing of ZDDP. The P_2S_5 , a flammable solid produced from the high-temperature reaction between elemental sulfur and phosphorus, is provided to the ZDDP manufacturer in sealed aluminum bins containing 500–7200 lb P_2S_5 . The P_2S_5 is hoppered into the reactor containing alcohol under a blanket of nitrogen. This is due to the ignitability of both the alcohol and the P_2S_5 when exposed to air. The hydrogen sulfide by-product, a highly toxic gas, is either converted to sodium sulfide solution in a caustic scrubber or thermally oxidized to sulfur dioxide. The heat of reaction and rate of hydrogen sulfide evolution are controlled by the addition rate of the P_2S_3 as well as the flow rate of the cooling water. The acid is then neutralized by zinc oxide; the reaction temperature is controlled by the addition rate of reaction depending on whether it is an acid to oxide or oxide to acid, addition scheme. Enough zinc oxide is used to neutralize the acid to a pH range, which will give a product suitably stable to thermal degradation and hydrogen sulfide evolution. The water formed from the reaction and the residual alcohol is vacuum-distilled. Any unreacted zinc oxide is then filtered, requiring a filtration system capable of removing particles as small as 0.1–0.8 μm . A larger molar excess of zinc oxide is often necessary to obtain the pH required for stability. The various manufacturers have done much work to reduce the amount of zinc oxide used to obtain product stability (such as the addition of low-molecular-weight alcohols or carboxylic acids to lower the amount of residual sediment in the product before filtration) [2]. The filtered liquid product, with or without additional petroleum oil, is then provided to the customer in drums or in bulk.

2.3 CHEMICAL AND PHYSICAL NATURE

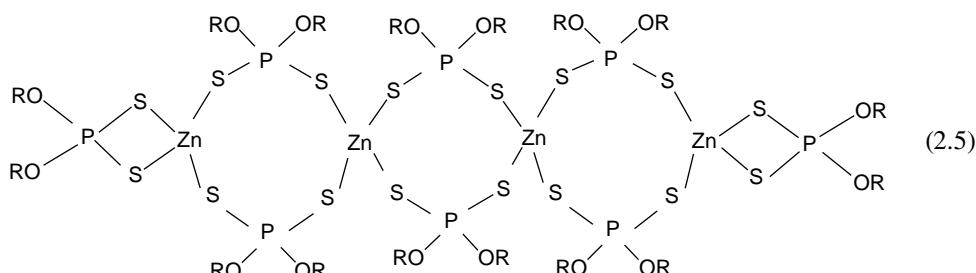
ZDDP is an organometallic compound having four sulfur atoms coordinated to the zinc atom, which is in a tetrahedral, sp^3 hybridized state. A Raman spectrum of ZDDP shows a strong P=S symmetric stretching band near 540 cm^{-1} and the absence of a strong Raman band near 660 cm^{-1} , indicating a symmetrical sulfur–zinc coordination arrangement as in the following structure



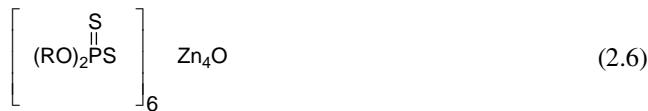
versus structure 2.4



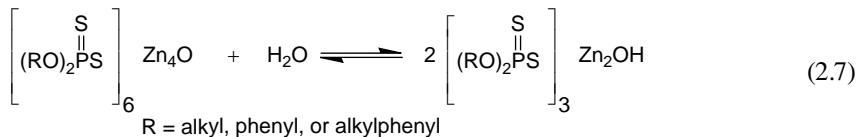
often given in the literature. The strong IR band at 600 cm^{-1} pointing to P=S stretching would be more consistent with PS_2 antisymmetrical stretching in light of the Raman spectrum [3]. The neutral ZDDP molecules as represented in structure 3.1 actually exist as monomer, dimer, trimer, or oligomer depending on the state of the ZDDP, crystalline or liquid, the concentration of ZDDP in solvent, and the presence of additional compounds. The proposed structure for a tetramer in the case of a neutral zinc diisobutylthiophosphate in hexane as determined by dynamic light scattering is shown in the following structure [4]:



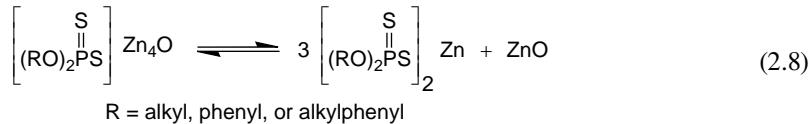
Under overbased condition, when the ratio of dialkyldithiophosphate acid to zinc oxide is less than 2:1, a basic zinc salt



will be synthesized along with the neutral salt. The basic salt is a tetrahedron of zinc atoms surrounding a central oxygen atom with $(\text{RO})_2\text{PS}_2$ ligands along each edge of the tetrahedron. Crystallographic analysis of pure basic zinc salts has established the near equivalency of P–S–Zn bonds. Raman spectra have also shown symmetrical P–S stretching, supporting a symmetrical sulfur–zinc coordination arrangement for the basic ZDDPs [3]. In the presence of water, as one would encounter during commercial ZDDP manufacture, the basic zinc salt will be in equilibrium with the basic zinc double salt as seen in the following reaction:



The stoichiometric excess of zinc oxide used in commercial ZDDP manufacture gives rise to a mixture of basic zinc salt (or zinc double salt) and neutral salt, the ratio depending on the amount of excess zinc oxide used and the molecular weight of the alkyl groups involved, where short alkyl groups tend to promote the formation



but performance differences seen between the two salts with respect to wear would imply that a more complex situation may exist [5]. As reported in the literature, basic ZDDP salts spontaneously decompose in solution into neutral complexes and zinc oxide when the temperature is increased [6].

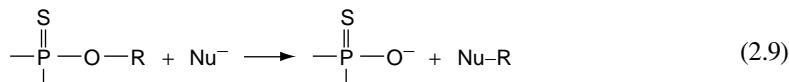
Pure ZDDPs, with alkyl groups of four carbons or less, are solid at ambient temperatures (with the exception of *sec*-butyl, which is a semisolid at room temperature) and tend to have limited or no solubility in petroleum base stocks. ZDDPs with aryl or alkyl groups with more than five carbons are liquid at ambient temperature. To utilize the less-expensive and more readily available low-molecular-weight alcohols and yet to produce oil-soluble products, commercial manufacturers use mixtures of high- (i.e., more than four carbons) and low-molecular-weight alcohols to obtain a statistical distribution of products favoring lesser amounts of pure low-molecular-weight ZDDPs. Other methods have also been developed to increase the amount of lower-molecular-weight alcohols in ZDDPs. These include the addition of ammonium carboxylates to inhibit precipitation [7] and the use of alkyl succinimides as solubilizing-complexing agents [8].

2.4 THERMAL AND HYDROLYTIC STABILITY

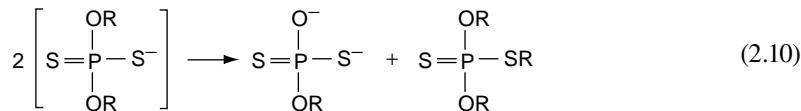
The study of the thermal degradation of ZDDP is important in that much of the tribological characteristics of ZDDP can be explained by the effects of its decomposition products. The thermal decomposition of ZDDP in mineral oil has been found to be extremely complex. ZDDP in oil, upon heating to degradation, will give off volatile compounds such as olefin, alkyl disulfide,

and alkyl mercaptan. A white precipitate will also form, which has been determined to be a low-sulfur-containing zinc pyrophosphate. The oil phase will contain varying amounts of *S,S,S*-trialkyltetraethylphosphosphate, *O,S,S*-trialkyltrithiophosphate, and *O,O,S*-trialkyldithiophosphate depending on the alkyl chain and the extent of degradation. The decomposition products of ZDDPs made from secondary alkyl alcohols, straight-chain primary alkyl alcohols, and branched primary alkyl alcohols appear similar in content but differ in proportions. This implies a similar mechanism for both primary and secondary ZDDP decomposition.

O-alkyl thiophosphate esters are powerful alkylating agents. The P–O–R group is susceptible to nucleophilic attack, thus producing an alkylated nucleophile and thiophosphate anion. The incoming nucleophile initiates the reaction by an attack on the alpha carbon. This shows a kinetic dependence on alkyl structure



Steric hindrance to the approach of the nucleophile will play a large rate-controlling factor here. The only nucleophile initially present is the dithiophosphate itself. The decomposition is initiated by one dithiophosphate anion attacking another, possibly on the same zinc atom:



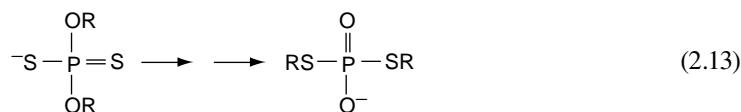
The resulting di-anion then attacks the triester, producing *O,S*-dialkyldithiophosphate anion



resulting in the migration of an alkyl group from oxygen to sulfur. This anion then, in a route analogous to the dialkyldithiophosphate anion, reacts with itself in a nucleophilic attack to effect another alkyl transfer from oxygen to sulfur producing *O,S,S*-trialkyldithiophosphate



The net effect of the above reactions is a double alkyl migration from oxygen to sulfur

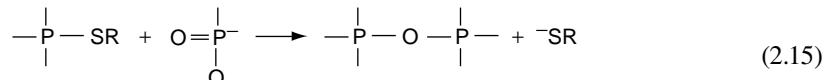


The major gases associated with ZDDP decomposition are dialkylsulfide (RSR), alkyl mercaptan (RSH), and olefin. The relative amounts of each of these gases depend on whether the alkyl group in the ZDDP is primary, branched primary, or secondary [9]. In the presence of mercaptide anion (RS^-)

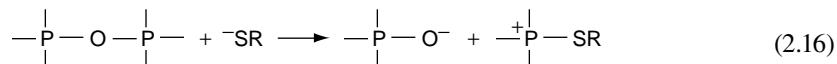
from the intermediate zinc mercaptide ($\text{Zn}[\text{RS}_2]$), O,S,S -trialkyldithiophosphate will react with mercaptide to produce alkyl mercaptan and results in the following structure:



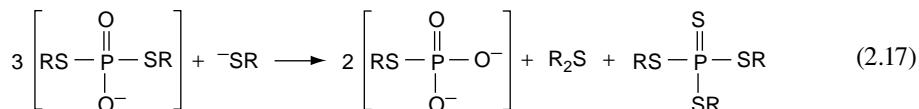
The nucleophilic phosphoryl oxygen ($\text{P}=\text{O}$) will then attack another phosphorus atom to produce a $\text{P}-\text{O}-\text{P}$ bond as in the following reaction:



A mercaptide anion subsequently cleaves the $\text{P}-\text{O}-\text{P}$ bond at the original $\text{P}-\text{O}$ site, giving rise to a net exchange of one atom of oxygen for one atom of sulfur between the two phosphorus atoms:



This gives rise to a net reaction for conversion of Structure 2.14 to S,S,S -trialkyltetrathiophosphate, dialkylsulfide and S -alkylthiophosphate di-anion as shown in the following reaction:



The dialkylsulfide and S,S,S -trialkyltetrathiophosphate decomposition products are soluble in oil.

The S -alkylthiophosphate decomposition product can also react with itself by way of a phosphoryl nucleophilic attack and elimination of mercaptide anion as in Reaction 2.15. This process will continue until a zinc pyro- and polypyrophosphate molecule with low sulfur content is formed. The chain will continue to extend until the product precipitates out of solution.

The decomposition of primary alkyl ZDDPs can be accurately described as discussed earlier. ZDDPs made from branched primary alcohols will decompose in a similar fashion, although at a much slower rate. This can be explained by the fact that the alpha carbon of the branched primary alkyl group, being more sterically hindered than the unbranched primary alkyl group, will be less susceptible to nucleophilic attack, as described in Reaction 2.9. The increased steric hindrance from beta carbon branching will also decrease the amount of successful mercaptide anion attack on the branched alkyl $\text{P}-\text{O}-\text{R}$ bond, resulting in less dialkylsulfide formation and a higher yield of mercaptan, an olefin by-product (through a competing protonation or elimination reaction with mercaptide anion). Lengthening the alkyl chain will have a much less pronounced effect on thermal stability than branching at the beta carbon due to the greater steric hindrance derived from the latter.

The decomposition of secondary alkyl ZDDPs, although similar to primary decomposition, shows that olefin formation is much more pronounced. The increase in elimination over nucleophilic substitution in secondary ZDDPs over primary ZDDPs is easily explained by the fact that elimination is accelerated by increasing the alkyl substitution around the double bond formed. Thus, secondary alkyl groups will favor a thermal decomposition into olefins and phosphate acids at the expense of the sulfur–oxygen interchange noted earlier. In a similar but much more pronounced way, tertiary ZDDP decomposition will be dominated by facile production of olefin through elimination. This occurs at even moderate temperatures, making their use in commercial applications prohibitive.

Aryl ZDDPs, due to the stability of the aromatic ring, are not susceptible to nucleophilic attack. Thus, the initial thermal decomposition reaction described in Reaction 2.9 cannot occur. Also the formation of olefin from an acid-catalyzed elimination reaction cannot occur. Aryl ZDDPs are, therefore, very thermally stable.

A rating of various ZDDPs in terms of thermal stability would, therefore, be aryl > branched primary alkyl > primary alkyl > secondary > tertiary. The varying amounts of decomposition products that depend on the heat history and the alkyl or aryl chain involved will directly control the amount of EP and wear protection the ZDDP will provide in a given circumstance [10].

Hydrolysis of ZDDP begins with cleavage of the carbon–oxygen bond of the thiophosphate ester, with the hydroxide anion displacing the thiophosphate-anion-leaving group. The stability of the intermediate alkyl cation determines the ease with which this cleavage takes place. The secondary alkyl cation is more stable and more easily formed than the primary alkyl cation; therefore, hydrolysis of secondary ZDDP occurs more easily than hydrolysis of primary ZDDP. For the case of an aryl ZDDP, the carbon–oxygen bond cannot be broken, and the site of hydrolytic attack is the phosphorus–oxygen bond with the displacement of phenoxide anion with hydroxide anion. The order of hydrolytic stability is, therefore, primary > secondary > aryl.

2.5 OXIDATION INHIBITION

Base oils used in lubricants degrade by an autocatalytic reaction known as *auto-oxidation*. The initial stages of oxidation are characterized by a slow, metal-catalyzed reaction with oxygen to form an alkyl-free radical and a hydroperoxy-free radical as seen in the following reaction:



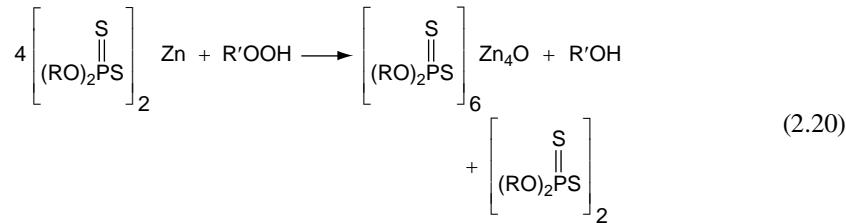
This reaction is propagated by the reaction of the alkyl-free radical with oxygen to form an alkylperoxy radical. This radical further reacts with the base oil hydrocarbon to form alkyl hydroperoxide and another alkyl radical as seen in the following reaction:



This initial sequence is followed by chain branching and termination reactions forming high-molecular-weight oxidation products [11].

The antioxidant functionality of ZDDP is ascribed to its affinity for peroxy radicals and hydroperoxides in a complex pattern of interaction.

The initial oxidation step of ZDDP by hydroperoxide is the rapid reaction involving the oxidative formation of the basic ZDDP salt as seen in the following reaction:

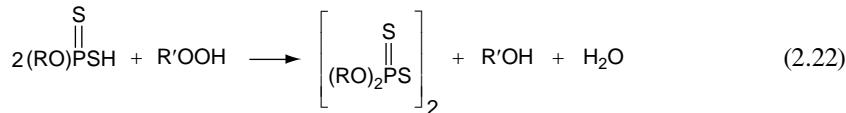


In this reaction, 1 mol of alkyl hydroperoxide converts 4 mol of neutral ZDDP to 1 mol of basic ZDDP and 2 mol of the dialkyldithiophosphoryl radical (which subsequently reacts to produce the disulfide) [12]. The rate of hydroperoxide decomposition slows during an induction period during which the basic zinc thermally breaks down into the neutral ZDDP and zinc oxide [6]. This is followed by the neutral ZDDP further reacting with hydroperoxide to produce more dialkyldithiophosphoryl disulfide and more basic ZDDP. When the concentration of the basic ZDDP becomes low enough,

a final rapid neutral salt-induced decomposition of the hydroperoxide will occur in which the dialkyldithiophosphoryl radical will not react with itself to form the disulfide but will react with hydroperoxide to form the dialkyldithiophosphoric acid as seen in the following reaction [13]:

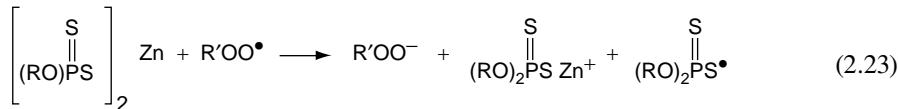


The dialkyldithiophosphoric acid then rapidly reacts with alkyl hydroperoxide, producing oxidation products that are inactive in oxidation chain reactions. The simplest reaction scheme for the reduction of the hydroperoxide is seen in the following reaction:



Oxidation products include the disulfide mentioned earlier, the analogous mono- and trisulfides, and compounds of the form $(RO)_n(RS)_{3-n}$ P=S and $(RO)_n(RS)_{3-n}$ P=O [3]. These products show little activity as either oxidation inhibitors or antiwear agents.

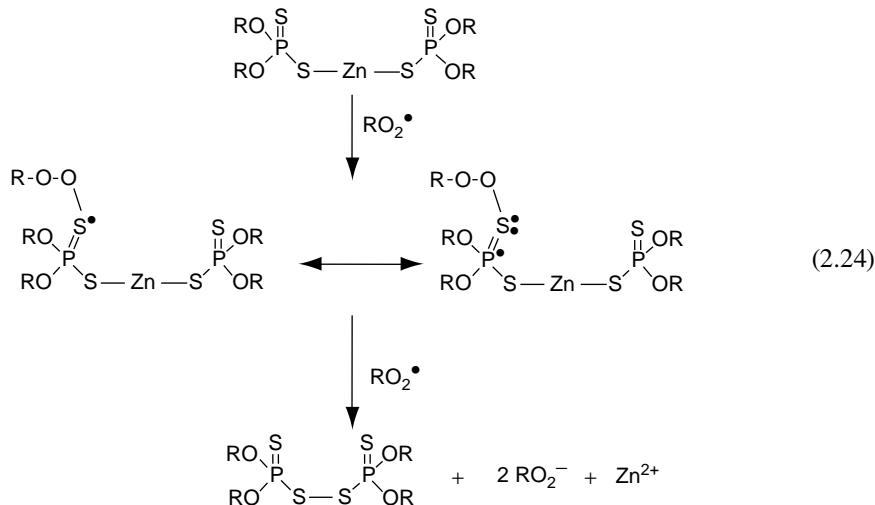
The literature also reveals an ionic process that will produce more dialkyl-dithiophosphoric acid as seen in the following reaction:



followed by Reaction 2.21 [14].

At low concentrations of ZDDP, hydrolysis of the ZDDP to the zinc basic double salt and dialkyldithiophosphoric acid becomes viable. At temperatures $>125^{\circ}\text{C}$, the dialkyldithiophosphoryl disulfide decomposes into the dialkyldithiophosphoryl radicals, which further react with hydroperoxide to produce more dialkyldithiophosphoric acid [6]. Thus, many pathways are available to form the active dialkyldithiophosphoric acid.

The neutral ZDDP also reacts with alkyl peroxy radicals. This is an electron-transfer mechanism that involves the stabilization of a peroxy intermediate. An attack by a second peroxy radical leads to the intramolecular dimerization of the resulting dithiophosphate radical forming the inactive dialkyldithiophosphoryl disulfide as seen in the following reaction:



The zinc metal atom provides an easy route for heterolysis of the radical intermediate; thus, the disulfide, by itself, has little antioxidant functionality [15]. ZDDP acts as an oxidation inhibitor not only by trapping the alkyl radicals, thus slowing the chain reaction mechanism, but also by destroying alkyl hyperoxides and inhibiting the formulation of alkyl radicals. Empirical determination of the relative antioxidant capability of the three main classes of ZDDP shows secondary ZDDP > primary > aryl ZDDP. The relative performance of each ZDDP type may correlate with the stabilization of the dialkyl(aryl)dithiophosphoryl radical and its subsequent reactivity with alkyl hydroperoxide to produce the catalyzing acid.

Commercial ZDPs are a mixture of both neutral and basic salts. It has recently been determined that neutral and basic ZDDPs give essentially equivalent performance with respect to antioxidant behavior. This can be explained by the equilibrium shown in Reaction 2.8. At elevated temperatures, as would occur in an oxidation test, the basic ZDDP is converted into the neutral ZDDP. As the temperature is lowered, the equilibrium shifts back toward the formation of the basic ZDDP, indicating that the concentration of basic ZDDP as a function of temperature. The solvent used and the presence of other additives also play a role in this equilibrium. Thus, the exact composition of neutral versus basic salts at any time in an actual formulation is a complex function of many variables.

2.6 ANTIWEAR AND EXTREME-PRESSURE FILM FORMATION

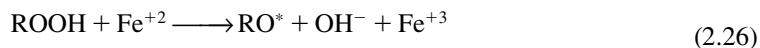
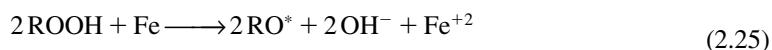
ZDDPs operate mainly as antiwear agents but exhibit mild EP characteristics. As an antiwear agent, ZDDP operates under mixed lubrication conditions with a thin oil film separating the metal parts. Surface asperities, however, intermittently penetrate the liquid film, giving rise to metal-on-metal contact. The ZDDP reacts with these asperities to reduce the contact. Likewise, when the load is high enough to collapse the oil film, the ZDDP reacts with the entire metal surface to prevent welding and to reduce wear. A great deal of study has been done to determine the nature of this protective film and the mechanism of deposition, where the thermal degradation products of the ZDDP are the active antiwear agents.

The antiwear film thickness and composition are directly related to temperature and the extent of surface rubbing. Initially, ZDDP is reversibly absorbed onto the metal surface at low temperatures. As the temperature increases, catalytic decomposition of ZDDP to dialkyldithiophosphoryl disulfide occurs, with the disulfide absorbed onto the metal surface. From here, the thermal degradation products (as described in Section 2.3) are formed with increasing temperature and pressure until a film is formed on the surface [16]. The thickness and composition of this film have been studied using many different analytical techniques, but no analysis gives a concise description of the film size and composition for the various kinds of metal-to-metal contact found in industrial and automotive lubrication regimes. In general, the antiwear/EP ZDDP film can be said to be composed of various layers of ZDDP degradation products. Some of these degradation products are reacted with the metal making up the lubricated surface. The composition of the layers is temperature-dependent.

The first process that takes place is the reaction of sulfur (from the ZDDP thermal degradation products) with the exposed metal leading to the formation of a thin iron sulfide layer [17]. Next, phosphate reacts to produce an amorphous layer of short-chain ortho- and metaphosphates with minor sulfur incorporation. The phosphate chains become longer toward the surface, with the minimum chain length approaching 20 phosphate units. Some studies have indicated that this region is best described as a phosphate “glass” region in which zinc and iron cations act to stabilize the glass structure. At the outermost region of the antiwear film, the phosphate chains contain more and more organic ligands, eventually giving way to a region composed of organic ZDDP decomposition products and undegraded ZDDP itself. The thickness of the film has been analyzed to be as small as 20 nm using ultra thin film interferometry and as large as 1 μm using electrical capacitance [18–21].

Recent work has concluded that, although the rate of film formation is directly proportional to temperature, a stronger correlation exists between film formation and the extent of metal-to-metal rubbing as quantified by the actual distance that the metal slides during a given test period. The film reaches a maximum thickness at which point a steady state between formation and removal exists, the rate of formation being more temperature-dependent than the rate of removal. It was also found that the ZDDP reaction film has a “solid-like” nature (as opposed to be a highly viscous liquid) due to the lack of reduction of film thickness observed with time on a static test ball [22].

Another mechanism of wear found to be inhibited by ZDDP is wear produced from the reaction of alkyl hydroperoxides with metal surfaces. It was found that the wear rate of automobile engine cam lobes is directly proportional to alkyl hydroperoxide concentration. The mechanism proposes the direct attack of hydroperoxide (generally through fuel combustion and oil oxidation) on fresh metal, causing the oxidation of an iron atom from a neutral charge state to Fe^{+3} by reaction with 3 mol of alkyl hydroperoxide as described in the following reactions:



The ZDDP and its thermal degradation products neutralize the effect of the hydroperoxides by the mechanism described in Reactions 2.20 through 2.23 in Section 2.5. It was also shown that peroxy and alkoxy radicals were far less aggressive toward metal surfaces than hydroperoxides, indicating that free-radical scavengers such as hindered phenols would be ineffective in controlling this kind of engine wear. This may explain why the antiwear performance of ZDDP is directly related to its antioxidant performance in the order of secondary ZDDP > primary ZDDP > aryl ZDDP rather than correlating with the order of thermal stability (aryl > primary > secondary) [23].

A recent study has been conducted to investigate the difference in wear performance between neutral and basic ZDDPs in the sequence VE engine test. The neutral ZDDP performed better in value train wear protection than the basic ZDDP. The basic salt actually failed the sequence VE engine test, indicating that using commercial ZDDPs with lower basic salt content may be preferred when limited to 0.1% maximum phosphorus content (as mandated by the International Lubricant Standardization and Approval Committee [ILSAC] GF-3 motor oil specification). It was suggested that the increased wear protection by neutral ZDDP could be explained by the superior adsorption of the oligomeric structure of the neutral salt, leading to the formation of longer polyphosphate chains relative to the basic salt [5].

2.7 APPLICATIONS

ZDDPs are used in engine oils as antiwear and antioxidant agents. Primary and secondary ZDDPs are both used in engine oil formulations, but it has been determined that secondary ZDDPs perform better in cam lobe wear protection than primary ZDDPs. Secondary ZDDPs are generally used when increased EP activity is required (i.e., during run-in to protect heavily loaded contacts such as valve trains). ZDDPs are generally used in combination with detergents and dispersants (alkaline earth sulfonate or phenate salts, polyalkenyl succine amides or Mannich-type dispersants), viscosity index improvers, additional organic antioxidants (hindered phenols, alkyl diphenyl amines), and pour point depressants. A typical lubricant additive package for engine oils can run in high at 25% in treatment level. The ILSAC has designated its GF-3 engine oil specification to include a maximum limit of 0.1% phosphorus to minimize the engine oil’s negative impact on the emissions catalyst. For the GF-4 specification, the limit in phosphorus was reduced even further. As a result

of the minimum phosphorus requirement, the treatment level for ZDDP in organic oils is limited to ~0.5 to 1.5%, depending on the alkyl chain length used.

The new challenge to motor oil formulators is in passing the required ILSAC tests while keeping the ZDDP level low. Yamaguchi et al. have shown that the antioxidant effect of ZDDP is significantly enhanced in API group II base stocks with as much as 50% increase noted for a basic ZDDP. An increase in antioxidant was also noted when using ZDDPs in polyol ester [24]. Several studies have also shown that ZDDP oxidation by-products are effective antiwear agents. The use of these base-stock effects to extend the oxidation life of the ZDDP may be a suitable method for the formulator to reduce the level of ZDDP needed to accommodate the GF-3 limits.

The synergistic effect between organic molybdenum compounds and ZDDP in wear reduction is currently being studied as a means of lowering phosphorus content in engine oils. In U.S. patent 5,736,491, molybdenum carboxylate is used with ZDDP to give a synergistic reduction in friction coefficient by as much as 30%, thus allowing a reduction in the total phosphorus content and an improvement in fuel economy [25]. The patent literature has cited other organic molybdenum compounds such as molybdenum dithiocarbamates (MoDTC) and dialkyldithiophosphates (MoDTP) as being useful, synergistic secondary antiwear agents [26].

ZDDPs are also used in hydraulic fluids as antiwear agents and antioxidants. The treatment level for ZDDP in hydraulic fluids is lower than that used for engine oils, typically running between 0.2 and 0.7% by weight. They are used in combustion with detergents, dispersants, additional organic antioxidants, viscosity index improvers, pour point depressants, corrosion inhibitors, defoamers, and demulsifiers for a total treatment level of between 0.5 and 1.25% [27]. Primary ZDDPs are preferred over secondary ZDDPs due to their better thermal and hydrolytic stability. One problem faced by hydraulic fluid formulators is the need for a fluid that will service both high-pressure rotary vane pumps and axial piston pumps, preferably out of the same sump. High-pressure vane pumps require a hydraulic fluid with antiwear properties and oxidative stability commonly achieved through the use of ZDDPs. High-pressure piston pumps need only rust and oxidation protection and do not require ZDDPs. ZDDPs can cause catastrophic failure to axial piston systems by adversely affecting the sliding steel–copper alloy interfaces. The patent literature has several examples of formulators trying to overcome this problem with the use of additional wear-moderating chemistries such as sulfurized olefins, polyol esters or borates of them, fatty acid imidazolines, aliphatic amines, and polyamines. Another problem faced by hydraulic fluid formulators is the interaction of ZDDPs with overbased alkaline earth detergent salts (as well as the interaction of carboxylic acid and alkenyl succinic anhydride rust preventatives with these detergents) in the presence of water to give filter-clogging by-products. Formulators have tried to overcome this problem of poor “wet” filterability by using nonreactive rust inhibitors (i.e., alkenyl succinimides) and improving the hydrolytic stability of ZDDP antiwear agent [28].

ZDDPs are used in EP applications such as gear oils, greases, and metalworking fluids. Secondary ZDDPs are preferred due to their thermal instability resulting in quick film formation under high loads. In automotive gear oils, ZDDPs are used at 1.5–4% in combination with EP agents (such as sulfurized olefins), corrosion inhibitors, foam inhibitors, demulsifiers, and detergents. Total multifunctional additive package treatment levels for automotive gear lubricant additives are from 5 to 12% by weight. Industrial gear oil formulators have generally gone to ashless systems using sulfur–phosphorus-based EP antiwear chemistries at total additive package treatment levels of 1.5–3%. In general, the recent focus in gear oil technology improvement has centered on increased thermal stability and EP properties.

ZDDPs are used in greases in chemical systems that closely resemble gear oil formulations. Many gear oil lubricant additives are used in EP greases. In general, the ZDDP treatment level for greases is in the same range as that used for gear oils. ZDDP, usually secondary or a mixture of secondary and primary, is used in combination with sulfurized olefins, corrosion inhibitors, ashless antioxidants, and additional friction modifiers. A recent advancement in grease technology is the use of ZDDP/sulfurized olefin synergy to replace antimony and lead in high-EP grease

formulations. This has generally been limited to the European market, having been pioneered in Germany.

ZDDPs, in combination with sulfurized olefins, are also used to replace chlorinated paraffins in medium- to heavy-duty metalworking fluids. This is due to the possible carcinogenicity of the low-molecular-weight analogs of chlorinated paraffin. European formulators, and to a certain extent Japanese formulators, use ZDDPs in this way. The use of ZDDPs in metalworking fluids in the United States is limited due to environmental concerns. The U.S. Environmental Protection Agency classifies them as marine pollutants.

In conclusion, after 50 years, ZDDPs still enjoy a wide variety of uses in the lubrication industry, with production volumes remaining at high levels. The majority of ZDDP production is used in automobile engine oil. The impact of the GF-2 and GF-3 phosphorus-level specification of 0.1%, however, was reduction of ZDDP production in the past 10 years. The Ford Motor Company is currently evaluating engine oils with 0–0.6% phosphorus levels in fleet tests in preparation for the looming GF-4 standard in 2004, which will require engine oils to have minimal impact on emission system deterioration. This could further negatively impact ZDDP production. The need to understand clearly how ZDDPs function in terms of wear and oxidation protection is reinforced by the need to develop satisfactory phosphorus-free alternatives to ZDDP. The development of such chemistries, within the economic and functional limits that ZDDPs impose, will be a daunting task for future researchers. Until that time, the elimination of ZDDPs from various industrial lubricants will mandate either higher costs or less performance.

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3 Ashless Phosphorus-Containing Lubricating Oil Additives

W. David Phillips

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3.1 INTRODUCTION AND SCOPE

In any discussion of phosphorus-containing lubricating oil additives, the products that probably come most rapidly to mind are the zinc dialkyldithiophosphates (ZDDPs)—multifunctional additives that have been widely used in both automotive and industrial oils for many years. However, a wide variety of ashless phosphorus-containing additives are used in the lubricating oil industry. As with the metal-containing dithiophosphates, they have been in use over a long period and, despite considerable research into alternative chemistries, the basic structures introduced in the 1930s are still used today. In contrast, the technology of most other additive types and that of the base stocks themselves have steadily developed over this time.

Many different types of phosphorus-containing molecules have been examined as additives for lubricating oils, with most attention given to their potential as antiwear (AW) and extreme-pressure (EP) additives. Consequently, the patent literature contains a host of references to different structures displaying this characteristic. However, regardless of composition, all the additives used in this application serve the same and specific function of bringing phosphorus into contact with the metal surface, where it can be adsorbed and, under certain conditions, react. The resulting surface film improves the lubrication properties of both mineral and synthetic oils.

This chapter discusses the use of chemicals that contain only phosphorus to improve the performance characteristics of oils, specifically neutral and acid phosphates, phosphites and phosphonates, and the amine salts of the acids (see Figures 3.1 and 3.2 for an outline of the main classes and their structures). These are the principal types of phosphorus compounds in current commercial use, but other types have also been examined and claimed in the patent literature, for example, phosphoramides. There are also ashless compounds in which sulfur or chlorine has been incorporated

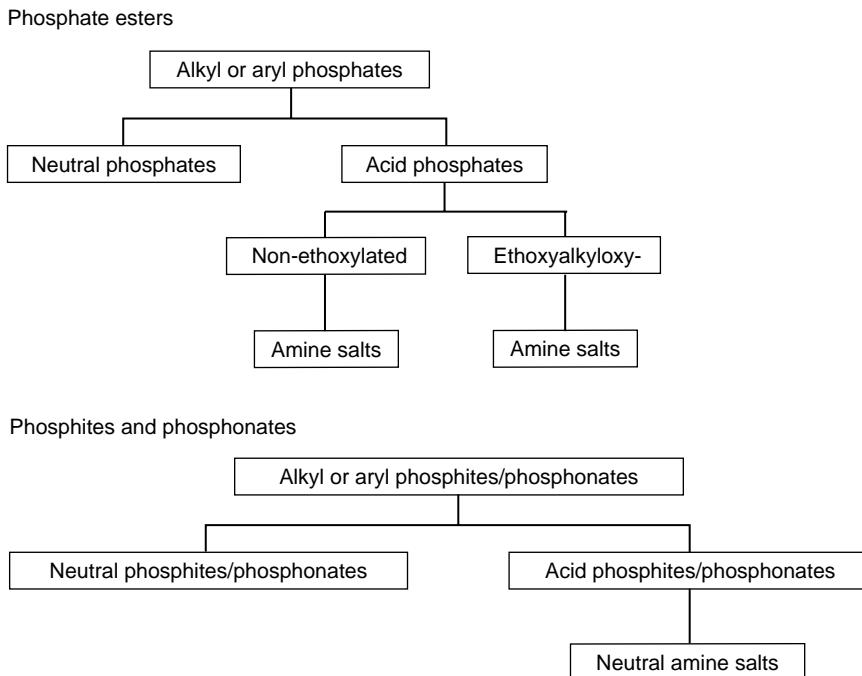


FIGURE 3.1 The main classes of phosphorus-containing additives for lubricating oils.

into the molecule as, for example, in thiophosphates and chlorinated phosphates. These are, however, outside the scope of this discussion, but the performance of mixtures of compounds separately containing phosphorus and sulfur or chlorine will be mentioned.

In addition to examining the impact of ashless phosphorus compounds on lubrication performance, this chapter also looks at their performance as antioxidants, rust inhibitors, and metal passivators. Additionally, their polar nature makes them good solvents and assists the solution of other additives in nonpolar base stocks. The versatility displayed by phosphorus-containing additives is such that usage of these products continues to grow nearly half a century after their introduction, and they find application in the latest technological developments.

3.2 HISTORICAL BACKGROUND

Until the 1920s, additive-free mineral oils met the majority of industry's lubrication requirements. In the applications where their performance was unsatisfactory, an increase in viscosity or the sulfur content of the oils then available usually provided adequate lubrication. For very severe applications, the oil would be blended with animal or vegetable oils—for example, tallow or rapeseed oils were used for steam engine cylinder lubrication. Fish oils were used in the early locomotive axle boxes, while castor oil reduced friction in worm gear drives and flowers of sulfur were added to cutting oils. However, when hypoid gears were introduced, they quickly revealed the limited lubrication of oils then available. This resulted in the development of additives such as sulfurized lard oil and lead naphthenate. These were followed by sulfurized sperm oil, an additive that eventually became widely used in both industrial and automotive applications.

The earliest type of an organic phosphorus chemical to find use as a lubricating oil additive is thought to have been a neutral triaryl phosphate, specifically tricresyl phosphate (TCP). This material was originally synthesized in about 1854 [1] although trialkyl phosphates were synthesized slightly earlier, in about 1849 [2]. Commercial production of TCP began in about 1919, when

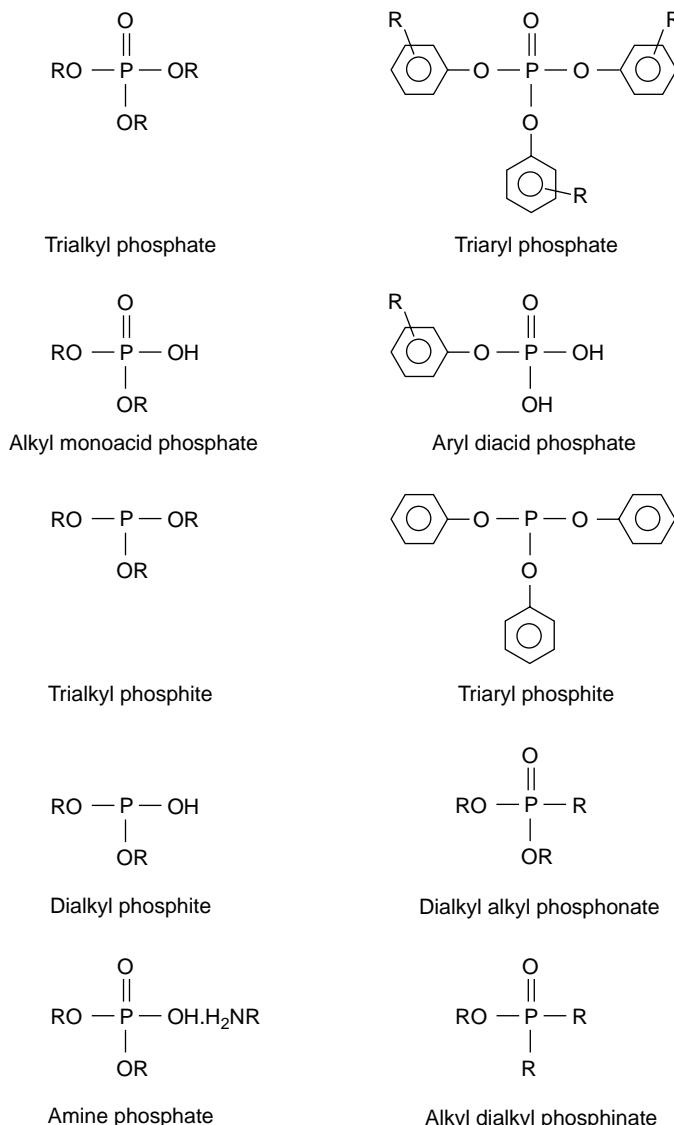


FIGURE 3.2 The structures of some common phosphorus-containing lubricating oil additives.

this product was introduced as a plasticizer for cellulose nitrate, but it was not until the 1930s that patents began to appear claiming improved lubrication when TCP was blended with mineral oil. In 1936, this use was claimed in gear oils [3], but a detailed investigation into their behavior as AW additives was not published until 1940 [4,5], by which time TCP was already said to be in widespread use. During World War II, extensive research into phosphorus-containing additives took place in Germany [6,7]. This research was facilitated by the recent availability of test equipment for assessing wear and load-carrying behavior, for example, the four-ball machine [8]. The results of the research concluded that for high load-carrying (later known as EP) performance, the molecule must contain the following:

- A phosphorus atom
- Another active group, for example, Cl^- or OH^- (for attachment to the metal surface)
- At least one aryl or alkyl group (phosphoric acid was not thought to be active)

Subsequent to these studies, the market adopted chlorine-containing phosphates such as tris-(2-chloroethyl) phosphate, but they were later replaced in most applications by other EP additives as chlorine tended to produce corrosion.

The 1940s and 1950s saw significant development activity in the oil industry involving TCP, and patents appeared claiming the use of this AW/EP additive in general industrial oils [9], rolling oils [10], cutting oils [11], greases [12], rock drill lubricants [13], and aviation gas turbine lubricants [14,15]. Some military specifications, for example, on hydraulic oils (NATO codes H515/520/576), were published, which initially called for the use of this additive. However, in the late 1960s, the difficulty of obtaining good-quality feedstocks for the manufacture of *natural* phosphates based on cresol and xylene, together with the concern regarding the neurotoxicity of TCP [16,17], led to the reformulation of many products with the less toxic *synthetic* triaryl phosphates based on alkylated phenols. TCP is still used today in aviation applications, but the quality of the phosphate in terms of its purity and freedom from the *o*-cresol isomers that were mainly responsible for the neurotoxicity behavior, has significantly improved in the past 10–20 years.

In addition to its use as an oil additive, TCP was also used for a period in the 1960s as an ignition control additive for motor gasoline to avoid preignition arising from the deposition of lead salts. These were formed by the interaction of the lead tetraethyl antiknock additive and the alkyl halide scavenger [18–21]. Alkyl phosphates were claimed for this application in 1970 [22].

As a result of their polar nature, neutral triaryl phosphates have also been claimed as corrosion inhibitors for hydrocarbons [23,24], but they are unlikely to be promoted for this application today in view of the availability of more active species, such as the acid phosphates.

The use of trialkyl phosphates as AW and EP additives has been much less extensively evaluated. Although a flurry of patent activity took place in the late 1920s and 1930s covering methods for their manufacture [25–34], there was little interest in their use as lubricating oil additives for further 20 years. This was probably a result of the focus, in the interim period, on chlorinated derivatives. It was not until the late 1950s that tributyl phosphate (TBP) was disclosed in blends with isopropyl oleate [35] for use in gear oils and claimed in blends with chlorinated aromatics. In 1967, a patent appeared claiming the use of alkyl phosphates or the amine salts of alkyl acid phosphates in a water-based lubricating composition [36].

In addition to alkyl phosphates, various other types of phosphorus-containing compounds have been evaluated as AW/EP additives. Patents on acid phosphates claiming their use as EP additives for oil appeared in 1935 and 1936 [37–39], whereas the first publication with detailed information on the use of ethoxylated alkyl or aryl phosphate oil additives (in metalworking applications) appeared in 1964 [40]. Patents on the use of these products in mineral oils [41] and in synthetic esters [42] appeared later. Alkoxylated acid phosphates were also found to have good rust inhibition properties [43], a feature that was additionally observed for the alkyl (or aryl) acid phosphates [44,45].

Neutral amine salts of alkyl acid phosphates were claimed in 1964 [43] and, in 1969, in admixture with neutral phosphates [46]. These are, however, just a few examples of the patent estate covering these product groups.

The other main phosphorus-containing products to be discussed are the phosphites. The basic chemistry of alkyl and aryl phosphites, like that of the phosphate esters, was also uncovered in the nineteenth century. In a similar fashion, their utilization as oil additives was not exploited until much later. Patents appeared in 1940 on the use of mixed aryl phosphites as oil antioxidants [47] and on their activity as AW/EP additives at least as early as 1943 [48].

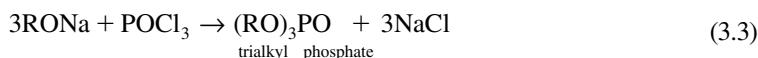
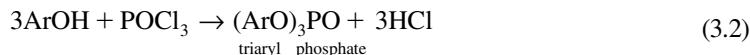
Isomeric with the acid phosphites are phosphonates (Figure 3.2). Dialkyl alkyl phosphonates were claimed as lubricants in 1952 and 1953 [49,50] but not until about 1971 as friction modifiers and EP additives [51,52].

The preceding summary focused on the use of phosphorus compounds alone. In reality, they are widely used in admixtures with sulfur-containing materials to provide good lubrication over a wider range of performance requirements. Examples of some of the combinations patented are given in Appendix A.

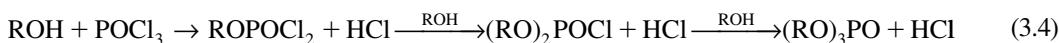
3.3 MANUFACTURE OF PHOSPHORUS-CONTAINING LUBRICATING OIL ADDITIVES

3.3.1 NEUTRAL ALKYL AND ARYL PHOSPHATE ESTERS

Although phosphate esters can be regarded as *salts* of orthophosphoric acid, they are currently not produced from this raw material because the yields are relatively low (~70% for triaryl phosphates). Instead, phosphorus oxychloride (POCl_3) is reacted with either an alcohol (ROH), a phenol (ArOH), or an alkoxide (RONa) as indicated in the following reactions:

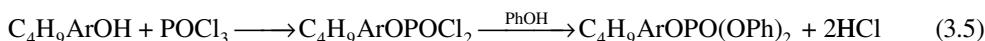


Reactions 3.1 through 3.3 pass through intermediate steps as shown in the following reaction:

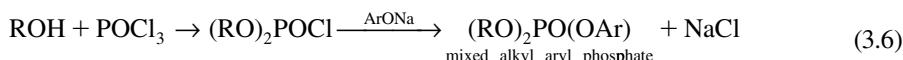


The intermediate products are called *phosphorochloridates*, and, if desired, it is possible to obtain a mixture rich in a particular intermediate by changing the ratio of reactants.

In 2001, a two-stage process for the production of a tertiarybutylphenyl phosphate with low levels of triphenyl phosphate (TPP) was described [53]. In this process, the POCl_3 is first reacted with sufficient tertiarybutylphenol ($\text{C}_4\text{H}_9\text{ArOH}$) to produce mainly the diprophorochloridate. Phenol is then added to the reaction mixture to produce predominantly the mono-tertiarybutylphenyl diphenyl phosphate (reaction 3.5). This product was said to give unusually low air entrainment values and was therefore mainly of interest as a hydraulic fluid base stock.



The production of mixed products can be achieved by using different alcohols or by an alcohol and alkoxide (reaction 3.6). These materials are not in significant use as AW/EP additives.



Trialkyl (or alkoxyalkyl) phosphates can be produced by either reaction 3.1 or 3.3, although in reaction 3.1, unless catalyzed, a considerably excess alcohol is required to drive the reaction to completion. The hydrogen chloride (HCl) by-product is removed as rapidly as possible—usually by vacuum or water washing while the reaction temperature is controlled to minimize the thermal degradation of the phosphate. In the alkoxide route (reaction 3.3), the chlorine precipitates as sodium chloride (NaCl), somewhat simplifying the purification treatment. After a water wash to remove the NaCl , purification consists of a distillation step to remove excess alcohol, an alkaline wash, and a final

distillation to remove water [54]. With the alkoxide method, any residual chloride can be removed by water washing followed by a final distillation under vacuum.

Despite early research into the alkyl phosphates, a rigorous investigation into the preparation of the lower alkyl derivatives and their properties did not take place until 1930 [55]. In contrast to the large range of aryl phosphates available, the range of neutral alkyl phosphates is currently limited to tri-*n*-butyl phosphate and tri-*iso*-butyl phosphate, trioctyl phosphate, and tributoxyethyl phosphate. Other ether phosphates [56] have been claimed in the past but, as far as is known, are not currently manufactured.

Although the neutral trialkyl phosphates have been available for sometime, they have not been widely used as additives for mineral oil. Those products in commercial production are used principally as components of aircraft hydraulic fluids, in turbine oils, rolling oils, or as solvents in industrial processes. However, interest in these materials as AW additives for applications where the release of phenols from the degradation of the phosphate is to be avoided currently exists. They also offer advantages as alternatives to the acid phosphates, alkoxylated acid phosphates, and their salts in metalworking applications, where there are concerns over instability in hard water and foam production in use (Canter, N., Private Communication, August 2001).

Triaryl phosphates, which are the most widely used of all ashless phosphorus-based AW additives, are currently manufactured almost exclusively by reaction 3.2. Phosphorus oxychloride is added to the reaction mass containing excess of phenol in the presence of a small amount of catalyst, typically aluminum chloride or magnesium chloride, before heating slowly. The hydrogen chloride is removed as it is formed under vacuum, followed by absorption in water. On completion of the reaction, the product is distilled to remove most of the excess phenol(s), the catalyst residue, and traces of polyphosphates. Finally, the product may be steam-stripped to remove volatiles including residual phenol(s) and is dried under vacuum.

The raw material for the manufacture of triaryl phosphates was originally obtained from the destructive distillation of coal. This process yields coal tar, which is a complex mixture of phenol and alkyl phenols including cresols (methylphenols) and xylenols (dimethylphenols). Distillation of this mixture (sometimes known as cresylic acids) produces feedstocks rich in cresols and xylenols, which are then converted into the neutral phosphate. An early patent on the production of triaryl phosphates from tar acids was issued in 1932 [26].

Unfortunately, in the 1960s, as the number of coal tar distillers declined due to the move from coal to natural gas as a fuel, it became progressively more difficult to obtain cresols and xylenols from this source. As a consequence, the phosphate manufacturers turned their attention to the use of phenol, which was alkylated with propylene or butylene. The resultant mixtures of alkylated phenols were then converted into phosphates [57,58]. To distinguish phosphates from these two sources of raw materials, the cresol and xylenol-based products became known as natural phosphates and the phosphates from alkylated phenols as synthetic phosphates. This distinction is no longer valid today as synthetic cresol and xylenol are now available and used in phosphate manufacture. However, the nomenclature remains a simple way of distinguishing between the cresol/xylene-based products and the newer products based on phenol. As the physical and chemical properties of each product type are slightly different, customer selection may depend on the application. For example, if the requirement is for a product that requires good oxidation stability, then the choice would be a tertiarybutylphenyl phosphate (TBPP), but a xylyl phosphate would be selected if the product required the best hydrolytic stability.

3.3.1.1 Natural Phosphates

The main products available in this category are TCP and trixylyl phosphate (TXP) (Figure 3.3). These products, based on cresols and xylenols, are complex mixtures of isomeric materials [59]. However, the variation in phosphate isomer distribution, which arises from changes to the feedstock

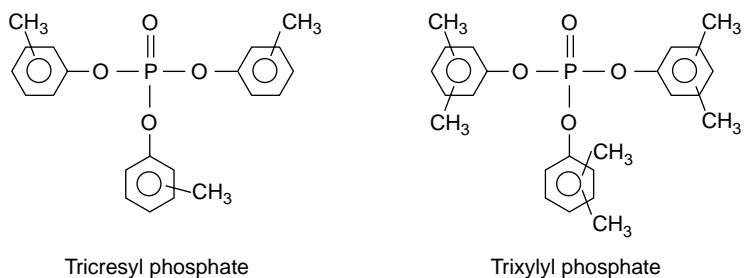


FIGURE 3.3 The structures of tricresyl and trixylyl phosphate.

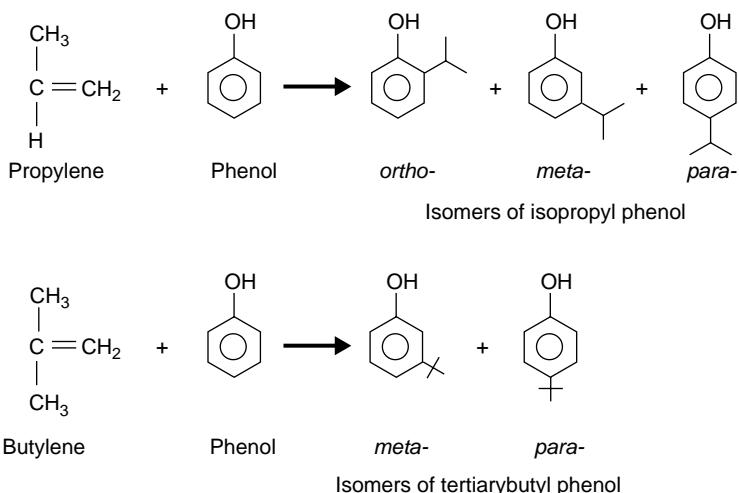


FIGURE 3.4 Process for the production of feedstocks used in the manufacture of synthetic phosphates.

composition, has little impact on AW properties. Of greater importance are the actual phosphorus content and the level of impurities present, particularly those that are acidic.

In the past, the tri-*o*-cresyl phosphate content was a source of much concern in view of the high neurotoxicity of the material (see Section 3.19). However, the feedstock that is most widely used today in the production of TCP, is predominantly a mixture of *m*- and *p*-cresol, and *o*-cresol levels are extremely low.

3.3.1.2 Synthetic Phosphates from Isopropylphenols

In this case, phenol is alkylated with propylene to produce a mixture of isomers of isopropylated phenol (Figure 3.4). Depending on the reaction conditions and the degree of alkylation, it is possible to produce a range of isopropylphenyl phosphates (IPPPs) with viscosities varying from ISO VG 22 to VG 100. In seeking an alternative product to TCP (an ISO 32 viscosity-grade fluid), the products with the closest phosphorus contents and viscosities (IPPP/22 and IPPP/32) are most widely used.

3.3.1.3 Synthetic Phosphates from Tertiarybutylphenols

In a similar fashion to the manufacture of isopropylphenyl phosphates, it is possible to produce a range of phosphates from butylated phenols prepared by the reaction of isobutylene with phenol (Figure 3.4). The tertiarybutyl substituent is larger in size than the isopropyl substituent, and this

TABLE 3.1
Phosphorus Contents and Viscosity Levels for Neutral Trialkyl and Triaryl Phosphate AW Additives

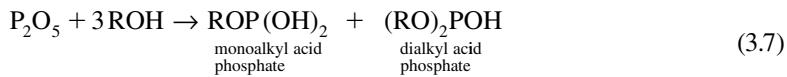
Phosphate Ester	Phosphorus Content (%)	Typical Viscosity at 40°C (cSt)
TiBP	11.7	2.9
TOP	7.8	7.9
TBEP	7.1	6.7
TCP	8.3	25
TXP	7.8	43
IPPP/22	8.3	22
IPPP/32	8.0	32
TBPP/22	8.5	24
TBPP/32	8.1	33
TBPP/100	7.1	95

reduces the overall level of alkylation in the molecule necessary to achieve the same viscosity, resulting in the presence of more unsubstituted phenyl groups. Again, the TBPPs from this range, which are used as AW additives in mineral oil, are those closest in phosphorus content and viscosity to TCP, that is, TBPP/22 and TBPP/32 (Table 3.1).

3.3.2 ACID PHOSPHATE ESTERS

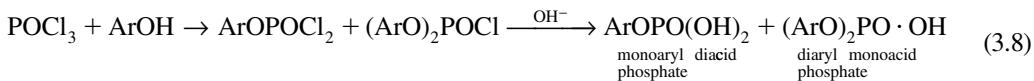
3.3.2.1 Alkyl and Aryl Acid Phosphates (Non-ethoxylated)

The manufacture of acid phosphates, particularly alkyl acid phosphates, is also based on technology that has its roots in the nineteenth century but was commercialized only during the past 50 years. The process involves the reaction of phosphorus pentoxide with an alcohol in the absence of water (reaction 3.7).



The ratio of monophosphate to diphosphate is usually 40–50% monophosphate and 50–60% diphosphate, with very small amounts of phosphoric acid ($\leq 1\%$). Small amounts of neutral ester may also be produced. Products commercially available are made from C₅, C₇–C₉ alcohols, mixtures of C₁₀–C₁₂ and alcohols, and C₁₈ alcohols.

Monoaryl and diaryl acid phosphates (also known as monoaryl and diaryl hydrogen phosphates) are by-products in the manufacture of triaryl phosphates and may be produced by stopping the reaction before completion and hydrolyzing the intermediate phosphorochloridates (reaction 3.8).

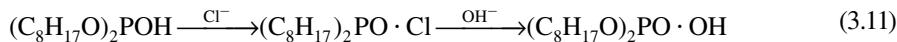


Di(alkyl)aryl monoacid phosphates, soluble in mineral oil, are reported to be produced by reacting phosphorus oxychloride with an alkylated phenol in the presence of base (reaction 3.9) or by the reaction of monoarylphosphorodichloridate with an alkylated phenol (reaction 3.10). The reactions

are carried out at temperatures of about 60–90°C using lower than equivalent quantities of phenol. The former process gives predominantly the monoacid phosphate with a small amount of neutral phosphate ester. The latter produces a somewhat greater amount of neutral mixed phosphate ester but mainly the mixed monoacid phosphate [60]. Examples of commercially available lubricating oil additives of this chemistry are amylphenyl- and octylphenyl acid phosphates.



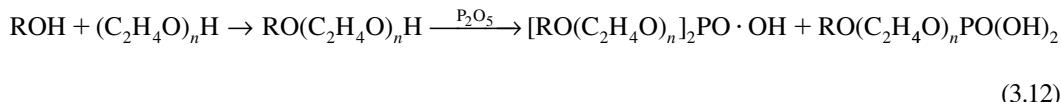
Other processes reported for the production of mixtures of mono-2-ethylhexyl and di-2-ethylhexyl acid phosphates include the chlorination of bis-(2-ethylhexyl) phosphonate followed by hydrolysis (reaction 3.11) or the hydrolysis of the tris-(2-ethylhexyl) phosphate.



The alkyl acid phosphates are quite widely used as AW/EP additives in metalworking lubricant applications and as corrosion inhibitors for circulatory oils.

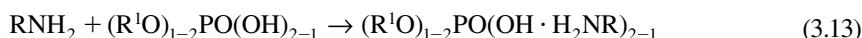
3.3.2.2 Alkyl- and Alkylarylpolyethoxylated Acid Phosphates

A range of polyethoxylated acid phosphate esters was introduced for metalworking lubricant applications in the early 1960s. These products, which consisted of both the free acids and their barium salts, were manufactured by reacting an ethoxylated alcohol with phosphorus pentoxide (reaction 3.12). The properties of the resulting acid phosphate mix can vary significantly depending on the chain length of the alcohol and the number of units of ethoxylation. For example, products that are only soluble in either oil or water can be produced as well as compounds that are soluble (or dispersible) in both media.



3.3.3 AMINE SALTS OF ACID PHOSPHATES AND OF POLYETHYLENEOXIDE ACID PHOSPHATES

Although the acidic products are very active AW/EP additives, their acidity can lead to precipitation problems in hard water and potential interaction with other additives. To minimize such adverse effects, the acids are sometimes used as their neutral amine (or metal) salts. The salts are produced by reacting an equivalent weight of the base with that of the acid (reaction 3.13). The choice of base will depend on whether oil or water solubility is required. The use of short-chain amines will normally result in water-soluble additives, whereas using, for example, tertiaryalkyl primary amines with a chain length of C_{11–14} will tend to produce oil-soluble derivatives. The chain length of the acid phosphate also influences the solubility. The selection of the appropriate mixture of amine and phosphate for a given application is largely a compromise because the most active mixtures may also produce disadvantageous side effects, for example, on foaming and air release properties. The fact that a neutral salt is used also does not prevent the product from titrating as an acid and from forming a different salt in the presence of the stronger base.



where R is an alkyl group, typically C₈–C₂₂. It is also possible to use secondary and tertiary amines, R₂NH and R₃N in the production of these salts.

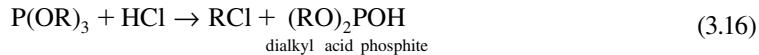
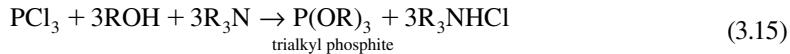
3.3.4 NEUTRAL PHOSPHITE ESTERS

As with phosphate esters, it is possible to produce both neutral and acid phosphite esters. The neutral triaryl phosphites are produced by reacting phosphorus trichloride with a phenol or substituted phenol (reaction 3.14).

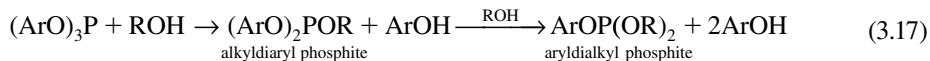


This is also a stepwise process occurring through the production of the monoaryl and diaryl hydrogen phosphite intermediates.

The production of neutral trialkyl phosphites using PCl₃ requires the addition of a tertiary amine base to neutralize the acid formed (reaction 3.15). Unless the HCl is removed quickly, it can cause the process to reverse with the production of an alkyl halide and the dialkyl acid phosphite (reaction 3.16).



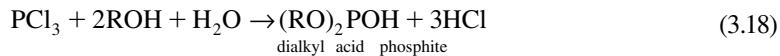
The use of mixtures of different alcohols or different phenols can result in the production of mixed alkyl or aryl phosphites. Mixed alkylaryl phosphites can be produced by reacting triaryl phosphite with alcohols to give a mixture of aryldialkyl- and alkyl diaryl phosphites (reaction 3.17). A commercial example of such a product promoted as an oil additive is decyldiphenyl phosphite.



Because of their widespread use in the plastics industry as stabilizers for polyvinylchloride, etc., many different neutral phosphites are commercially available. These range from C₂ to C₁₈ alkyl (normally saturated) and from C_{1–9} alkaryl. In lubricant applications, the most common products are those with alkyl chains of C₈–C₁₈ and C₁₀–C₁₅ alkaryl, for example, trioctyl phosphite and tris-(2,4-ditertiarybutylphenyl) phosphite. The last type is increasingly important in view of its better hydrolytic stability.

3.3.5 ALKYL AND ARYL ACID PHOSPHITES

Alkyl and aryl acid phosphites are manufactured by reacting together phosphorus trichloride, an alcohol (or phenol), and water (reaction 3.18):



Mixtures of alcohols, as indicated earlier, may also be used to produce di-mixedalkyl phosphites. The commercially available dialkyl acid phosphites vary from C₁ to C₁₈ with use as oil additives falling mainly in the range of C₈–C₁₈.

Little mention is made in the literature of the use of aryl acid phosphites, and there is no known oil industry using ethoxylated neutral or acid phosphites. Phosphites are, however, generally unsuitable for applications where water contamination is likely in view of their hydrolytic instability, and ethoxylation, certainly in respect of water-soluble products, would not offer any obvious advantage.

3.3.6 DIALKYL ALKYL PHOSPHONATES

Although these products are isomeric with the dialkyl phosphites (Figure 3.2), they are a distinct class of materials with different properties. They are claimed as friction modifiers as well as AW/EP additives and are prepared by the Arbusov rearrangement in which a trialkyl phosphite is heated with an alkyl halide, for example, an iodide (reaction 3.19):



Commercially available materials range from the dimethyl methyl derivative to products based on dodecyl phosphite, although the higher-molecular-weight products are likely to be of greatest interest for oil applications. Polyethyleneoxy phosphonates, produced by the reaction of diphosphites with epoxides, have been claimed as friction modifiers [61], whereas diaryl hydrogen phosphonates, such as diphenyl phosphonate, are produced by hydrolysis of the corresponding phosphite with water.

3.4 THE FUNCTION OF LUBRICITY ADDITIVES

The earliest additives used for improving lubrication performance were known as oiliness additives and film strength additives. While these descriptions are no longer used, others are now employed. The current terminology together with typical examples of the chemistries employed is shown in Table 3.2.

TABLE 3.2

Different types of additives used to improve lubrication performance

Additive Description	Performance	Mechanism	Typical Chemistries
Friction modifier	Reduces friction under near-boundary lubrication conditions	Physical adsorption of polar materials on metal surfaces	Long-chain fatty acids and esters, sulfurized fatty acids, molybdenum compounds, long-chain phosphites, and phosphonates
Antiwear additive (usually with mild EP properties)	Reduces wear at low to medium loads	Reacts chemically with the metal surface to form a layer (normally a metal soap) that reduces frictional wear at low-medium temperature and loads	Neutral organic phosphates and phosphites, zinc di-alkyldithiophosphates
Extreme-pressure additive, also known as: -film strength additive, -load-carrying additive -antscuffing additive	Increases the load at which scuffing, scoring, or seizure occurs	Reacts chemically with the metal surface to form a layer, e.g. as a metal halide or sulfide which reduces frictional wear at high temperatures/loads	Sulfurized or chlorinated hydrocarbons, acidic phosphorus-containing materials, and mixtures thereof; some metal soaps, e.g. of lead, antimony, and molybdenum

TABLE 3.3
A General Classification of Chemicals as Friction Modifiers, AW, and EP Additives

Additive	Friction Modifier	AW Additive	EP Additive
Natural oils and fats	1	4	5
Long-chain fatty acids, amines, and alcohols	1	4	5
Organo-molybdenum compounds	1	2	4
Synthetic esters	2	3	4
Organo-sulfur compounds	2	2	3
ZDDP	3	1	3
Phosphorus compounds	3	1	3
Sulfur compounds	4	3	1
Chlorine compounds	5	4	1

Note: The lower the number, the better the rating.

Table 3.3 [62] offers a generalized classification of the different chemical types of additives used to improve lubrication performance, but, depending on the structure of the additive, some variation in the performance can be expected. In reality, the distinction between AW and EP additives is not clear-cut. AW additives may have mild EP properties, whereas EP additives can have moderate AW performance, and both produce coatings on the metal surface. In fact, EP additives have been described as additives that reduce or prevent severe wear [63]. However, as seen from the Table 3.3, EP additives are unlikely to function satisfactorily as friction modifiers, and vice versa.

3.4.1 THE BASIC MECHANISM OF LUBRICATION AND WEAR AND THE INFLUENCE OF ADDITIVES

An understanding of the basic mechanism of lubrication is useful to appreciate the way in which additives behave and their relative performance. The following is therefore a somewhat simplified explanation of a complex process.

Lubrication can be described as the ability of oil (or another liquid) to minimize the wear and scuffing of surfaces in relative motion. It is a function of the properties of the lubricant (e.g., viscosity), the applied load, the relative movement of the surfaces (e.g., sliding speeds), temperature, surface roughness, and the nature of the surface film (hardness and reactivity, etc.).

All surfaces are rough. Even those that appear smooth to the naked eye, when examined microscopically, consist of a series of peaks and troughs. The simplest situation arises when the lubricating film is thick enough to completely separate the two surfaces so that metal-to-metal contact does not occur (Figure 3.5). Such a situation could arise at low loads or with highly viscous liquids, and the lubricating characteristics depend on the properties of the lubricant as the load is fully supported by the lubricant. This condition is known as *hydrodynamic* or *full-film lubrication*.

As the load increases, the lubricating film becomes thinner and eventually reaches a condition where the thickness is similar to the combined height of the asperities on the mating surfaces. At this stage, metal contact commences, and as the asperities collide, they are thought to weld momentarily (causing friction) before shearing with loss of metal (wear) (Figure 3.5). The wear particles then abrade the surface and adversely affect friction, with the resulting damage depending on the hardness of the particle and the surface it contacts. This condition is known as *mixed-film lubrication* as it is a mixture of full-film lubrication and *boundary lubrication* with the trend toward the latter with increasing load.

As the film thins still further, the load is increasingly supported by the metal surface and friction rises rapidly. When eventually a film that is only a few molecules thick separates the surfaces,

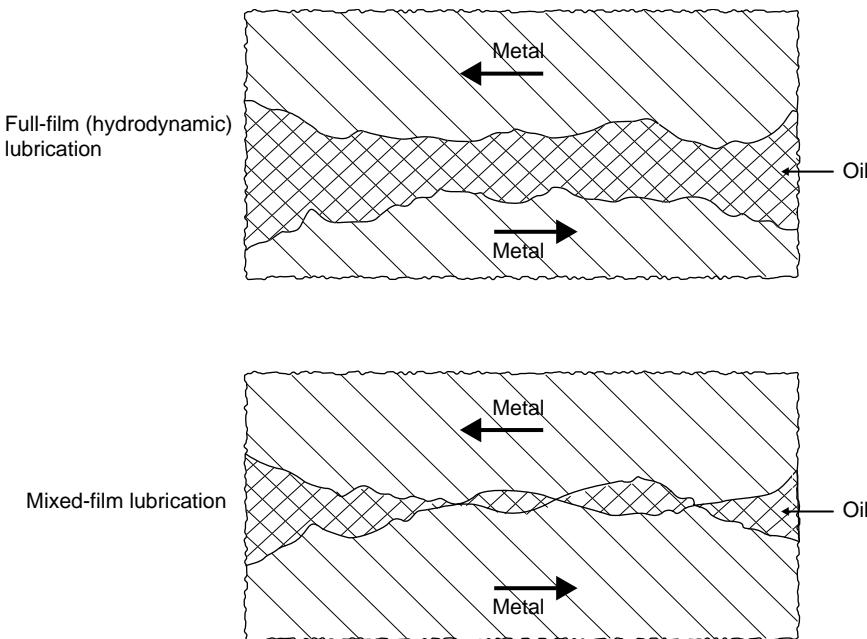


FIGURE 3.5 A diagrammatic representation of full-film (hydrodynamic) and mixed-film lubrication.

the roughness, composition, and melting point of the surfaces strongly influence the resulting friction. At this stage, viscosity plays little or no part in the frictional behavior. This stage is known as boundary lubrication and is characterized by high frictional values that now change little with further increases in load or sliding speed. The wear process that takes place under boundary conditions is perhaps the most complicated of those involved in lubrication in that it involves four different types of wear: corrosive, fatigue, ploughing, and adhesive.

Corrosive wear occurs when the metal surfaces react with their environment to form a boundary film, whereas fatigue wear is the process of the fracture of asperities from repeated high stress. Micropitting is an example of this form of wear, which is the subject of considerable investigation today. Micropitting is the result of plastic deformation of the surface that eventually causes the fracture of the asperity, leaving a small *pit* in the surface. Ploughing wear arises when a sharp particle is forced along the surface, leaving a groove behind, whereas adhesive wear is the tendency of very clean surfaces to adhere to each other. However, this action requires the generation of fresh surfaces during the wear process, perhaps by plastic deformation. It is now thought that this mechanism is much less prevalent than was earlier believed [64].

The relationship between friction, viscosity, load, and sliding speeds can be represented graphically for a bearing by what is known as a *Stribeck curve*. This is shown in Figure 3.6 [65], where the frictional coefficient is plotted against the dimensionless expression ZN/P , where Z represents the fluid viscosity, N the sliding speed, and P the load. Friction is reduced as the value of ZN/P is lowered until a minimum is reached. For a bearing, this minimum value is ~ 0.002 for an ideal hydrodynamic condition. At this point, metal contact begins, and friction rises and continues to do so with increasing contact. In the mixed friction zone, the friction value lies in the region of $0.02\text{--}0.10$. Eventually, when the film is very thin, friction becomes independent of viscosity, speed, and load and can reach a value of 0.25 .

By experiment it was established that

- Continually increasing the load reduced the ZN/P value, assuming that speed and the viscosity remained constant. The same results can be obtained by reducing either the speed or viscosity, or both, provided the unit load remains constant or is increased.

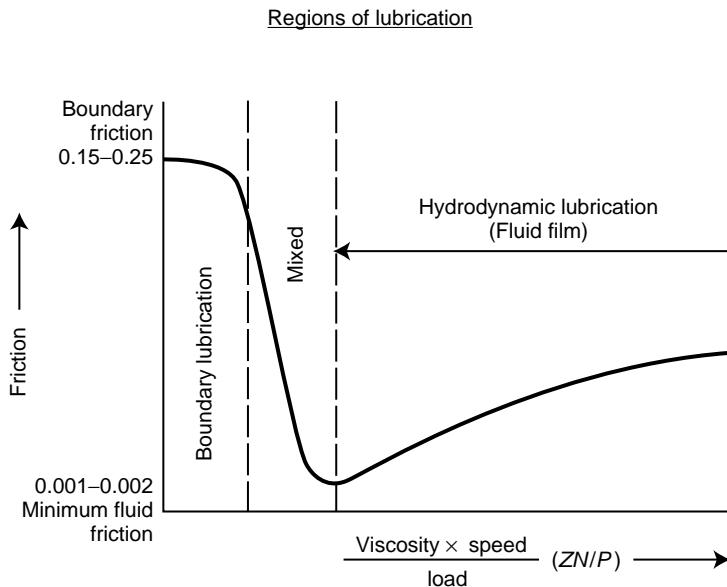


FIGURE 3.6 Relationship between coefficient of friction and ZN/P .

- Friction varied directly with viscosity; it was proportional to velocity at lower speeds but varied inversely with velocity at higher speeds [65].

As the surfaces move closer together, the lubricant is squeezed out from between them. Some additives, when adsorbed onto the surface, display a molecular orientation perpendicular to the surface that reduces the level of contact and hence lowers the friction. Such products are known as *friction modifiers*. Those additives effective in reducing wear and (usually) friction in the mixed friction zone are called *antiwear additives*, whereas products effective in reducing wear (and increasing seizure loads) in the boundary lubrication process are known as *extreme-pressure additives*. However, due to the importance of temperature in the lubrication process, it has been pointed out in the past that the latter should, perhaps, be better described as *extreme-temperature additives*.

The temperature at which an additive reacts physically or chemically with the metal or metal oxide surface significantly affects its activity. Each AW/EP additive type has a range of temperature over which it is active (Figure 3.7) [66]. The lowest temperature in the range would normally be the temperature at which physical adsorption takes place. This can occur at ambient or at higher temperatures depending on the polarity of the additive and the impact on surface energy. The greater the reduction in surface energy, the stronger will be the absorption of the surface film and the greater will be the likelihood that the additive remains in place for a chemical reaction with the surface. Additives that are only weakly bound to the surface may desorb as the temperature rises and cease to function further in the wear-reducing process.

As the temperature increases so does the surface reactivity. Fatty acids and esters react at fairly low temperatures to produce metal soaps followed by chlorine-containing compounds (to form chlorides), phosphorus (as phosphates, polyphosphates, and/or phosphides), and, finally, sulfur, which reacts at very high temperatures to form metal sulfides [66].

Chlorine-based additives can be film-forming even at ambient temperatures, but as the temperature rises they become aggressive and, with the release of HCl, can cause significant corrosion. Although the $FeCl_2$ film has a fairly well-defined melting point at $670^\circ C$, the optimum operating temperature is much lower. Klamann [67] indicates that the efficiency of metal chlorides starts to

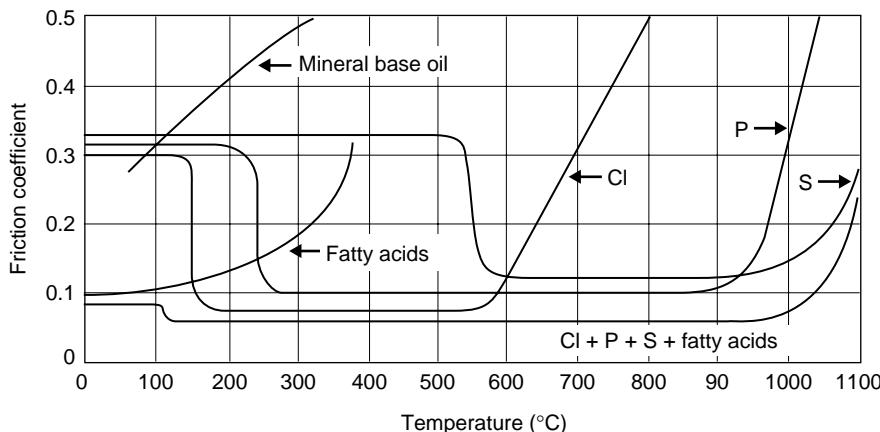


FIGURE 3.7 Effect of temperature on EP additive activity. (From Mandakovic, R., *J. Syn. Lubr.*, 16(1), 13–26, 1999. With permission.)

TABLE 3.4
Corrosion Films Formed on Sliding Iron Surfaces

Lubricant Type	Nature	Friction Coefficient (Dry)	Melting Point (°C)
Dry or hydrocarbon	Fe	1.0	1535
	FeO	0.3	1420
	Fe ₃ O ₄	0.5	1538
	Fe ₂ O ₃	0.6	1565
Chlorine	FeCl ₂	0.1	670
Sulfur	FeS	0.5	1193

Source: Fundamentals of Wear, *Lubrication*, 12(6), 61–72, 1957. Permission from Chevron.

drop above 300°C and that the friction coefficient at 400°C is already a multiple of the optimum value. However, the dry friction coefficient of the chloride film is substantially lower than that for iron sulfide (Table 3.4) [68]. The relatively low friction associated with this film is probably one reason why chlorinated products are so effective as EP additives. Phosphorus, by comparison, does not react until at higher temperatures and then at slower rates. However, the upper temperature limit of ~550°C in an air environment is thought to be a result of the oxidation of the carbon in the film rather than the degradation of a metal soap (Forster, N.H., Private Communication, July 2007).

The soaps, phosphates/phosphides, chlorides, and sulfides formed on the metal surface were originally considered to produce a lower melting and less-shear stable film than that of the metal/metal oxide. This film would cause a smoothing of the metal surface that was then able to support a higher unit loading. This is now thought to be an oversimplified explanation as research has found the EP films to be considerably different to those postulated and without the expected lower shear stability [69]. What it certainly does not consider are additional “subprocesses” of removal of the film by mechanical wear and its possible regeneration *in situ* by further action of the AW/EP additive (Figure 3.8).

Since surface temperature is largely dependent on load, additives that might be effective at high loads may be completely ineffective at low loads (and vice versa). Under such circumstances, therefore, significant wear could occur before the load-carrying properties of the EP additive come into play. To minimize this effect, additives are often used in combination, resulting in extending the temperature (and load) range over which they are active.

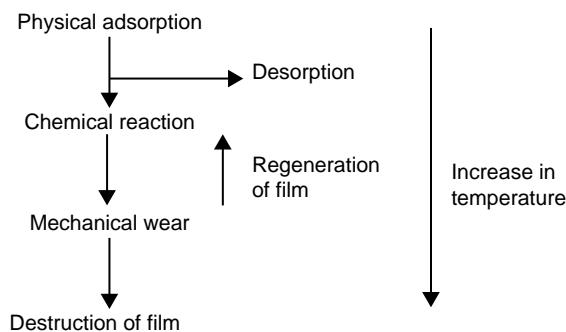


FIGURE 3.8 Basic processes involved in the mechanism of action of lubricity additives.

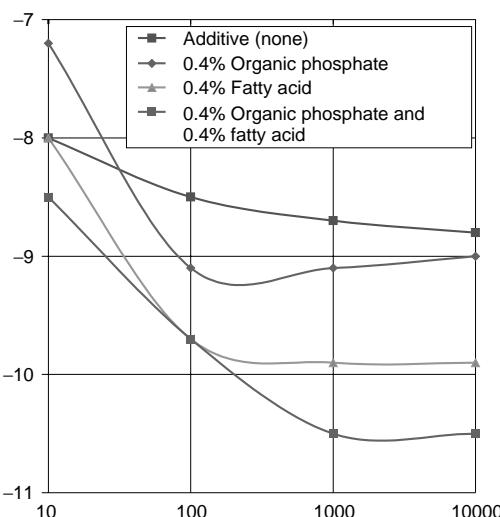


FIGURE 3.9 Effect of fatty acid and phosphate ester on wear rate. (Fundamentals of Wear, *Lubrication*, 12(6), 61–72, 1957. Permission from Chevron.)

Although single AW/EP additives can be used to meet application and specification requirements, combinations of additives can produce both synergistic and antagonistic effects. The use of mixtures of phosphorus- and chlorine- or sulfur-containing compounds, to extend the temperature range over which a lubricating film is available, has already been mentioned. Another example of synergy was reported by Beeck et al. [5], who described the effect of combinations of TCP and long-chain fatty acids. It was suggested that the use of such mixtures in some way improved the *packing* of the film on the surface and therefore helped to reduce metal contact. Figure 3.9 [68] in fact shows that combinations of phosphate and fatty acid can result in lower wear rates than either component. Such synergy is useful in that it reduces additive costs and the possibility that the additives might have an adverse effect on product stability, etc. An example of additive antagonism is given in Section 3.12.

3.5 INVESTIGATIONS INTO THE MECHANISM AND ACTIVITY OF PHOSPHORUS-CONTAINING ADDITIVES

Many papers have been written about the way in which TCP and other phosphorus-containing compounds work as AW/EP additives. As might be expected, researchers have had differences

of opinion. These have probably arisen as a result of the different test conditions found in the wide variety of test equipment developed for measuring wear. For example, different test specimen geometries, surface finish, sliding speeds, and the use of additives with different levels of purity have meant that the data have not been strictly comparable.

After a brief review of the early development of AW/EP additives, a number of papers exploring the mechanism of action of different phosphorus-based additives are summarized in this section. It is not inclusive, and the results of many other workers could have been mentioned. An additional selection of papers on the topic is therefore given in Appendix B. Some papers evaluate several classes of product (e.g., phosphates, phosphites, phosphonates, etc.); these may be located in sections other than that on neutral phosphates if information on these other structures is limited.

3.5.1 EARLY INVESTIGATIONS INTO ANTIWEAR AND EXTREME ADDITIVES

Some of the earliest experiments into the effects of different lubricants on friction were carried out by Hardy in 1919 [70], who noted the superior performance of castor oil and oleic acid. He found that good lubricating properties were closely related to the ability of substances to lower surface energy. A series of papers from Hardy and Doubleday followed in 1922–1923 examining the activity of lubricants under boundary conditions.

In 1920, Wells and Southcombe [71] discovered that the addition of a small amount of a long-chain fatty acid significantly reduced the static coefficient of friction of mineral oil. Bragg postulated in 1925 [72] that long-chain molecules with a polar terminal group were attached to the surface by adsorption of the polar group and that the long hydrocarbon chains were orientated perpendicular to the surface. He also suggested that the formation of films on both the moving surfaces assisted lubrication by sliding over one another, with their long chains being “flattened” as the distance between the surfaces was reduced. However, in 1936, Clark and Sterrett [73] showed that the lubricating film could be up to 200 molecules in thickness but that only the first layer would have the strength to withstand the shearing stresses produced under sliding conditions. They also found that certain ring structures (e.g., trichlorophenol) that were active as “film strength” additives also showed molecular orientation, in this case, parallel to the metal surface, and attributed the good load-carrying performance to the ability of the layers to slide over one another. Orientation was not the only factor involved, as compounds with a similar orientation could show a wide difference in performance.

The mechanism and influence of additives on boundary lubrication were first investigated and reported by Beeck et al. [4]. They found that friction was reasonably constant with sliding velocity up to a critical velocity, beyond which there was a significant reduction. Additives were found to reduce the friction at low speeds relative to the base oil alone and also had a significant, but variable, effect on the reduction at different critical velocities. Low critical velocities were found for compounds that were strongly adsorbed and that showed orientation of the surface film. It was recognized that the adsorbed layer is thinner than the roughness of even the best machined surfaces and that high temperatures (or loads) at points of contact would cause decomposition of the molecules with the formation of a high-melting corrosion product and an increase in friction. If the surfaces were *highly polished*, then sliding could take place without destruction of the surface film. It was concluded that most of the friction-reducing compounds, principally, the long-chain fatty acids, were not able to produce a highly polished surface and therefore were not effective AW additives.

3.5.2 NEUTRAL ALKYL AND ARYL PHOSPHATES

3.5.2.1 Historical Background

One additive examined by Beeck et al. [5] that was able to reduce both friction and wear was TCP, a product that was, at that time, beginning to find widespread commercial use as an AW additive. The authors proposed that TCP acted by a *corrosive* action, preferentially reacting with the high

spot on the surface, where the surface temperatures are highest (from metal contact). It was thought that in the reaction, the phosphate ester formed a lower melting phosphide (or possibly an iron/iron phosphide eutectic) that flowed over the surface and caused a smoothing or chemical polishing effect. They also observed that there appeared to be an optimum level of addition of the TCP (1.5%), a conclusion later confirmed by other workers in the field.

Beeck et al. claimed in these papers that their research had produced a better understanding of the AW mechanism and enabled more precise distinctions to be drawn between the different types of additives; more specifically, that

A wear prevention agent reduces pressure and temperature through better distribution of the load over the apparent surface. If the resulting minimum pressure is still too high for the maintenance of a stable film, metal to metal contact will take place in spite of the high polish. Since in this case the surface of actual contact is relatively very large, seizure and breakdown will follow very rapidly ...

The intervention of the war years encouraged German researchers to prepare and evaluate a number of phosphorus compounds as EP/AW additives, principally phosphinic acid derivatives and also acid phosphates [6,7], while other workers [74] continued to investigate the behavior of TCP. The performance of the latter in white oil was examined, and it was suggested that the additive reacted with steel to form a thin, solid, nonconducting film that prevented seizure by shearing in preference to metal-to-metal contacts. The improved behavior of blends of TCP with fatty acids was explained as being due to the improved adsorption of the fatty acid onto the surface of the chemically formed film.

In 1950, an extensive evaluation of different neutral alkyl and aryl phosphates and phosphites, in some cases containing chlorine and sulfur, was undertaken [75]. The results of this investigation showed that the action of sulfur and chlorine on the surface is to form a sulfide and a chloride film, respectively. In the presence of phosphorus, mixed films of phosphide/sulfide or phosphide/chloride were formed. The presence of phosphide was established chemically by the liberation of phosphine in the presence of hydrochloric acid.

Although the concept of phosphide film formation was challenged at this time [76,77], it remained as the generally held theory until the mid-1960s when several papers appeared with contradictory data. Godfrey [78] pointed out that the experiments that had indicated the presence of phosphide had all been static, high-temperature investigations, and none had identified phosphide on a sliding surface lubricated with TCP. He experimented with the lubrication of steel-on-steel surfaces by TCP followed by an examination of the metal surface. This revealed the presence of white crystalline material, which was shown by electron diffraction measurements to be predominantly a mixture of ferric phosphate, FePO_4 , and its dihydrate, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Phosphides, if present, were in extremely small quantities. Furthermore, a paste made from the dihydrate showed similar frictional characteristics to TCP, whereas a paste from iron phosphide showed no significant reduction in friction. Tests also suggested the importance of air to the performance of TCP as tests carried out under nitrogen revealed substantially increased wear. *Pure* TCP was evaluated and, unlike *commercial* material, showed no significant friction-reducing properties.

The presence and role of *impurities* in the activity of commercial TCP was the subject of investigations using radioactive P^{32} [79]. Results suggested that the phosphorus-containing polar impurities—not the neutral TCP—were adsorbed onto the metal surface. The P^{32} found in the wear scar appeared to be chemically bound—not physically adsorbed, but the latter process seemed to be the way that the phosphorus was initially made available on the surface. The authors indicated that the impurities resembled acid phosphates (rather than phosphoric acid, which Godfrey had assumed) and carried out wear tests comparing the neutral ester with both an acid phosphate (dilauryl acid phosphate) and hydrolyzed TCP. They found that lower concentrations of these compounds generally gave equivalent performance to the neutral ester. Of interest was the observation that, although TCP showed no wear minimum in the reported tests (cf. the results given by

TABLE 3.5
Effects of Various Additives on the Adsorption of P³²

Additive Concentration (wt%)	Activity (Counts/min)
0.5% TCP alone	280
+2% Barium sulfonate A	0
+2% Barium sulfonate B	80
+0.1% Rust inhibitor	16
+0.5% Diisopropyl acid phosphite	25
+0.1% Dilauryl acid phosphate	24
+5.5% Acryloid dispersant	82
+7.9% Polymeric thickener	78
+0.7% Sulfur-chlorine EP additive	120
+0.5% Thiophosphate	150
+0.5% 2,2'-Methylene-bis(2-methyl, 4-tertiarybutyl phenol)	250
+0.5% Sulfurized terpene	290

Source: Klaus, E.E., Bieber, H.E., *ASLE Preprint 64-LC-2*, 1964.
With permission.

Beeck et al. [5]), the data on acid phosphate, acid phosphite, and phosphoric acid did display such minima.

The work using radioactive P³² also allowed a study of the competition between TCP and different types of additives for the metal surface. This was determined by measuring the residual surface radioactivity after wear tests. Table 3.5 shows the effect of various types of additives on the adsorption of P³² from TCP. The lower the number of counts, the greater the interaction between the additive and TCP.

Radiochemical analysis was also the technique used to investigate the deposition of phosphorus on steel surfaces in engine tests [80]. In this study, the effect of different types of aryl phosphates (TPP, TCP, and TXP) on case-hardened tappets was examined. The results suggested that the efficacy of these additives is correlated directly with their hydrolytic stability, that is, their ability to produce acid phosphates as degradation products. This was confirmed by tests on a series of other phosphates (largely alkyl diaryl phosphates), which showed good correlation between antiscuffing performance and hydrolytic stability (Table 3.6). Examination of the tappet surface revealed the presence of aryl acid phosphates on the surface and the absence of phosphides. Adsorption studies of the neutral aryl and acid phosphates on steel surfaces indicated that, although the film of neutral ester could be more easily removed, the adsorption of the acid phosphate was irreversible, suggesting salt formation. These studies led the authors to conclude that the mechanism involved initial adsorption of the phosphate on the metal surface followed by hydrolytic decomposition to give an acid phosphate. This reacted with the surface to give iron organophosphates, which then decomposed further to give iron phosphates.

The importance of impurities in determining the level of activity of TCP was confirmed in yet another paper [81]. The composition of impurities in commercial grades of TCP was determined using thin-layer chromatography and analysis by neutron activation. Acidic impurities, probably the monocresyl and dicesyl acid phosphate (and also small amounts [$2 \times 10^{-4}\%$] of phosphoric acid), were found at 0.1–0.2%, that is, at levels that had previously been shown to produce a significant reduction in wear when added to mineral oil. Other impurities ranged from 0.2 to 0.8%. This latter category was assumed to contain chlorophosphates based on the amount of chloride ion produced.

TABLE 3.6
**Correlation between the Antiscuffing Performance and Ease of Hydrolysis
 (Acid Formation) of Organic Phosphates**

Additive (0.08% wt Added P)	Relative Ease of Hydrolysis ^a	Time to Scuffing (min) ^b at a Spring Load	
		305 lb	340 lb
Benzylidiphenyl phosphate	100	>30	9
Allyldiphenyl phosphate	100	>30	Not tested
Ethyldiphenyl phosphate	80	28	Not tested
Octyldiphenyl phosphate	50	15	6
Triphenyl phosphate	50	15	5
Tritolyl phosphate	30	8	Not tested
2-Ethylhexylidiphenyl phosphate	5	2–3	Not tested
None	—	2–3	Not tested

Note: Camshaft, Ford Consul (cams phosphated); Tappet, Ford Consul (non-phosphated); Camshaft speed, 1500 rpm (equivalent engine speed 3000 rpm); Base oil, SAE 10W/30 oil without EP additive.

^a Because of the wide range of hydrolytic stability of these compounds, it was not possible to compare the stabilities of all these compounds in the same acid medium. Consequently, an arbitrary scale was drawn up with benzylidiphenyl phosphate assigned a value of 100.

^b Mean of several tests.

Source: Barcroft, F.T., Daniel, S.G., *ASME J. Basic Eng.*, 64-Lub-22, 1964. With permission.

The authors commented that the TCP used for the investigation was the best grade available, but even this material contained up to 25% polar impurities. It was thought typical of the TCP used in the wear studies to date and reported in the literature.

Wear tests on TCP, acid phosphates, and phosphites in a super-refined mineral oil and a synthetic ester (di-3-methylbutyl adipate) indicated that relatively small amounts (0.01%) of additive can produce a significant wear reduction in mineral oils and that the acidic materials were more active. However, in the polar base stock, where there is competition for the surface, the amount of TCP required to provide a similar reduction in wear is substantially greater. The effectiveness of the alkyl acid phosphates is not significantly reduced in the synthetic ester, suggesting that their polarity (and hence adsorption) is greater than that of the neutral phosphate, the synthetic ester, and its impurities (Table 3.7). The authors concluded that the activity of TCP was due to the acidic impurities and that the neutral ester acted as a reservoir for the formation of these impurities during the life of the lubricant.

Until about 1969, the theory regarding the production of a phosphate film on the steel surface seemed to be widely accepted. Reports then appeared suggested that the situation was more complicated. One paper [82] examined and compared the corrosivity toward steel, the load-carrying capacity, and the AW performance of several phosphorus compounds. Using the hot-wire technique at 500°C [83] followed by an x-ray analysis of the surface films that were produced, the reactivity (or corrosivity) was studied. Perhaps, not surprisingly, the neutral phosphate and phosphite evaluated showed relatively little reactivity with the steel, whereas the acid phosphate and phosphite produced substantially more corrosion. The anomaly was the behavior of a neutral alkyl trithiophosphate, which showed a very high reactivity but low load-carrying ability, suggesting a different mode of breakdown. Analysis of the films formed confirmed the major presence of basic iron phosphate (or principally iron sulfide in the case of the thiophosphate), but small amounts of iron phosphide were

TABLE 3.7
Effect of Concentration on the AW Properties of Phosphorus-Containing Additives in a Synthetic Ester

Additive	Concentration (wt%)	Average Wear Scar Diameter (mm)		
		1 kg	10 kg	40 kg
None	—	0.39	0.71	0.91
TCP	1.0	0.38	0.71	0.97
	3.0	0.40	0.64	0.97
	0.5	0.23	0.25	0.78
Hydrolyzed TCP	0.1	0.57	0.74	—
	1.0	0.17	0.25	0.46
Dilauryl acid phosphate	0.01	0.21	0.41	0.84
	0.05	0.19	0.28	0.43
	1.0	0.17	0.28	0.42
Diisopropyl acid phosphite	0.02	—	0.72	—
	0.05	0.16	0.25	—
	0.15	—	0.33	—
Phosphoric acid	0.001	0.41	0.69	0.90
	0.01	0.16	0.37	0.50
	1.0	0.38	0.60	0.78

Note: ASTM D 4172. Four-ball wear test conditions: test time, 1 h; test temperature, 167°C; test speed, 620 rpm.

Source: Bieber, H.E., Klaus, E.E., Tewkesbury, E.J., *ASLE Preprint 67-LC-9*, 1967. With permission.

also found in all the x-ray analyses of the degradation products. Evaluation of the load-carrying capacity of the additives was found to vary directly with corrosivity except for the alkyl trithiophosphate. The authors surmised from this that the load-carrying capacity of phosphorus-containing additives was not only due to the reactivity of the films but also due to the properties of the film that was formed. The relationship between wear and reactivity also varied directly for several compounds, but in the case of the neutral phosphite and the alkyl trithiophosphate, there was no correlation. This was attributed to the different composition of the film in these cases. In fact, the authors proposed that the main reaction product of the phosphite could be iron phosphide. They suggested that the load-carrying capacity of the films formed by EP additives fell in the following order:



whereas the order of AW properties was



The first of these sequences is, of course, different to the order in EP activity predicted from the stability of the films formed on the metal surface and from the general perception that phosphorus is less active than either chlorine or sulfur. Similarly, for AW performance, phosphorus is normally regarded as more active than sulfur.

A paper by Goldblatt and Appeldoorn [84] cast doubt on the theory that the activity of TCP was due to the generation of acidic impurities. In this study, the activity of TCP in different atmospheres and in different hydrocarbon base stocks was examined. The resulting data showed that TCP

was much more effective in a low viscosity white (paraffinic) oil than in an aromatic base stock. Aromatics are good AW agents and compete with the TCP for the surface. Under these conditions, either the iron phosphate reaction products are less stable or perhaps a thinner and less complete layer is produced and is worn away, leading to an increase in corrosive wear. Surprisingly, the AW performance of the mixed aliphatic/aromatic base stock was better than either of the components and was not improved by addition of TCP.

The behavior of TCP in different atmospheres focused on the effect of moisture in a wet-air atmosphere and also under dry argon, that is, in the absence of oxygen and moisture. No significant differences were found in the results indicated previously for the different hydrocarbon base stocks. However, in a further series of tests comparing the behavior under both wet and dry air and wet and dry argon in an ISO 32 grade white oil, TCP was shown to have a slight AW effect. The exception was in wet air, when it increased wear but also generally showed higher scuffing loads than when used in dry argon. In a naphthenic oil of similar viscosity, the use of wet air (or wet argon) again resulted in increased wear and exhibited higher scuffing loads. This behavior was also observed with other phosphates and phosphites. The authors suggested that in dry air the TCP film forms very rapidly and metallic contact quickly falls. In dry argon the same thing happens, only at a slower rate. In wet air the film is not as strong, and metallic contract remains high, whereas in the case of wet argon, it does not form at all. "Thus the formation of a protective film is enhanced by oxygen but hindered by the presence of moisture." The observation [78] that air was necessary for the action of TCP did not consider that moisture was present in the air and could have been responsible for the improvement in wear performance.

The previous theory indicating it was necessary for the TCP to hydrolyze to form acid phosphates before it became active was also challenged. Wear tests on standard and very low acid TCP in dry argon showed no significant difference in activity. It was concluded that TCP was reacting directly with the surface without first hydrolyzing to acid phosphate and without being preferentially adsorbed at the metal surface.

In 1972, Forbes et al. [85] summarized the current thinking on the action of TCP, which indicated that TCP was an effective AW additive at high concentrations independent of the base oil, but at low concentrations was adversely affected by the presence of aromatics. The acidic degradation products have similar properties but show better performance at low concentrations. It was felt that TCP adsorbed onto the metal surface decomposed to give acid phosphates that reacted with the surface to give metal organophosphates.

The results of further investigations into the effects of oxygen and temperature on the frictional performance of TCP on M-50 steel were published in 1983 [86]. The critical temperature at which friction is reduced as surface temperature rises was measured under different conditions and was found to be 265°C in dry air (<100 ppm water) when full-flow lubrication is used; 225°C under conditions of limited lubrication and 215°C under nitrogen, also with limited lubrication. Analysis of the surface indicated that TCP had reacted chemically at these temperatures, causing a substantial increase in the amount of phosphate deposited (phosphide was not observed). Oxygen was said to be necessary for this reaction, but the suggestion that prior hydrolysis of the phosphate was required could not be substantiated.

The debate regarding the formation of iron phosphate or phosphide as reaction products in the wear mechanism rumbled on into the late 1970s and early 1980s. In 1978, Yamamoto and Hirano [87] carried out scuffing tests on several aryl and alkyl phosphates. The aryl phosphates showed better scuffing resistance, and it was suggested that the alkyl phosphates reacted with the steel surface, forming a film of iron phosphate under mild lubricating conditions, but that the aryl phosphates reacted only slightly until conditions became more severe with the formation of iron phosphide. The implication was that the phosphide (formed as a result of a reaction between the phosphate and the metal surface) acted as a good EP additive but that the iron phosphate had only AW activity. Surface roughness measurements showed a polishing action for the aryl phosphates (particularly for TCP) but not, under these conditions, for the alkyl phosphates.

The concept of corrosive wear and of phosphates as chemical polishing agents as expressed by Beek et al. [5] was examined by Furey in 1963 [88]. In his work, surfaces of different roughness were prepared and friction measurements were made when in contact with a solvent refined oil under different applied loads. In tests on an additive-free oil (unfortunately, no information was available on the sulfur or aromatic content), it was found that friction, in addition to being load-dependent, was low for highly polished surfaces and rose with increasing roughness up to a roughness of $\sim 10 \mu\text{in}$. At about this roughness, the percentage metal contact was also found to be at its maximum but decreased thereafter. The explanation given for this was that with increasing roughness, the distances between the peaks and troughs increase but the peaks become flatter. The flatter the peak, the better the load-carrying capacity, whereas the deeper troughs allow for a greater reserve of oil available locally for lubrication and cooling. When several AW/EP additives were evaluated in the oil, it was found that, although there was a reduction in surface roughness, it was less than that found by the oil alone. Furthermore, at low loads, TCP was able to reduce metal contact significantly but had no effect on surface roughness. At moderate to high loads, although the metal contact was reduced, the surface roughness was increased. The author concluded that TCP was not acting through a polishing action.

In 1981, Gauthier et al. [89] looked again at the wear process and film formation. They categorized the process into three wear phases: an initial, very rapid phase followed by a medium wear rate, and finally a slow wear phase. In the rapid wear phase, a brown film was formed that, on analysis, was found to be a mixture of ferrous oxide and phosphate. A blue film, which is formed as the wear rate slows (and the surface becomes smoother), contained no iron and was described as a polymeric acid phosphate. (No mention was made of the “white crystalline film” Godfrey reported.)

When both films were removed and the roughness of the underlying surface was measured, it was found that the surface below the brown film was very smooth. The surface under the blue film was much rougher and $\sim 1000 \text{ \AA}$ thicker. The authors suggested that the smooth surface was the result of polishing arising from corrosive wear. They concluded that in the first phase of wear, a corrosive wear process is involved because of the presence of ferrous phosphate on the surface. When a “critical value” for the surface coverage by the phosphate was achieved, the organic phosphoric acids produced by the decomposition of TCP polymerized to form a polyphosphate. As a result, in the last two wear phases, “the wear of metal is almost completely replaced by the wear of the additive.” In this way, the disparate observations of TCP behavior (polishing versus increased surface roughness) could be related and combined.

The presence of polyphosphate was also noted by Placek and Shankwalkar [90] when investigating the films produced on bearing surfaces by pretreatment with phosphate esters. Tests were carried out on 100% phosphates and also on their 10% solutions in mineral oil, the latter condition because the combination had been reported to provide better wear protection than the individual components alone, apparently by the formation of a “friction polymer” [91,92]. Phosphates chosen for the work included both aryl and alkyl types. Analyses of the films formed by immersion in the phosphates at 250°C revealed the presence of a high level of carbon together with iron phosphate/polyphosphate and a small amount of phosphide. At 300°C , the hydrocarbon had all but disappeared and no phosphide was detected. The films formed by the mineral oil solutions were mainly hydrocarbon-based, but the film formed by the alkyl phosphate was unique in that it contained needlelike fibers. The effect of pretreatment on wear found under four-ball test conditions is indicated in Table 3.8. The bearings treated with the mineral oil solutions displayed at least as good wear reduction as those treated with the 100% phosphate.

3.5.2.2 Recent Technical Developments

In 1996, Yansheng et al. [93] reported on the effect of TCP on the wear performance of sulfurized, oxy-nitrided, and nitrided surfaces. A synergistic effect on nitrided and oxy-nitrided surfaces was found, resulting in significant increases in load-bearing capacity while reducing friction and wear, but no improvement was seen on sulfurized surfaces.

A recent application in this brief survey relates to the use of aryl phosphates as vapor-phase lubricants. Although not strictly an additive application, this development has been the focus of

TABLE 3.8
Friction and Wear Reduction from Bearing Surface Pretreatment by Phosphate Esters

Bearing Preparation	Average Scar Diameter (mm)	Improvement (%)	Maximum Torque (gf m)	Improvement (%)
Untreated reference	1.00	—	46.1	—
TCP	0.72	28	18.4	60
IPPP	0.75	25	18.4	60
TOF	0.81	19	18.4	60
10% TCP in mineral oil	0.72	28	18.4	60
10% IPPP in mineral oil	0.72	28	15.0	68
10% TOF in mineral oil	0.64	36	19.6	58

Note: ASTM D 4172–88. Four-ball wear test conditions: test time, 60 min; test temperature, 75°C; test load, 40 kgf; test speed, 600 rpm. IPPP = isopropylphenyl phosphate; TCP = tricresyl phosphate; TOF = tris (2-ethylhexyl) phosphate. All wear tests performed in 100 solvent neutral paraffinic mineral oil.

Source: Placek, D.G., Shankwalkar, S.G., *WEAR*, 173(1-2), 1994. Permission from Elsevier.

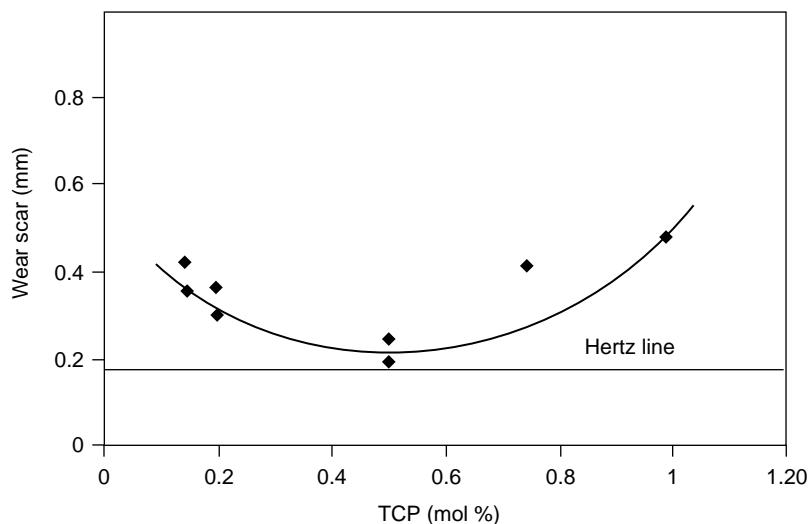


FIGURE 3.10 Four-ball wear values at 370°C with vapor lubrication as a function of tricresyl phosphate (TCP) vapor concentration. (From Klaus, E.E., Jeng, G.S., Duda, J.L., *Lubr. Eng.* 45(11), 717–723, 1989. With permission.)

most recent analytical studies into the mode of action of these additives; therefore, the conclusions represent the current thinking. Aryl phosphates were chosen for this application because of their oxidation stability and good boundary lubrication performance at high temperatures. The initial studies took place with TCP [94] and involved examination of the films formed on tool steel balls and on iron, stainless steel, copper, nickel, tungsten, and quartz wire specimens. (TCP vapor had previously been shown to form tenacious films on graphite, tungsten, and aluminum at temperatures above its thermal decomposition point [95].) Wear tests on tool steel with vapor at 370°C showed low levels of wear even at 0.1 mol% concentration (Figure 3.10). An optimum concentration was reached at ~0.5 mol%. Reaction with the metals indicated above is displayed in Figure 3.11, which shows that deposition on iron and copper is relatively fast but slow for quartz, nickel, and tungsten.

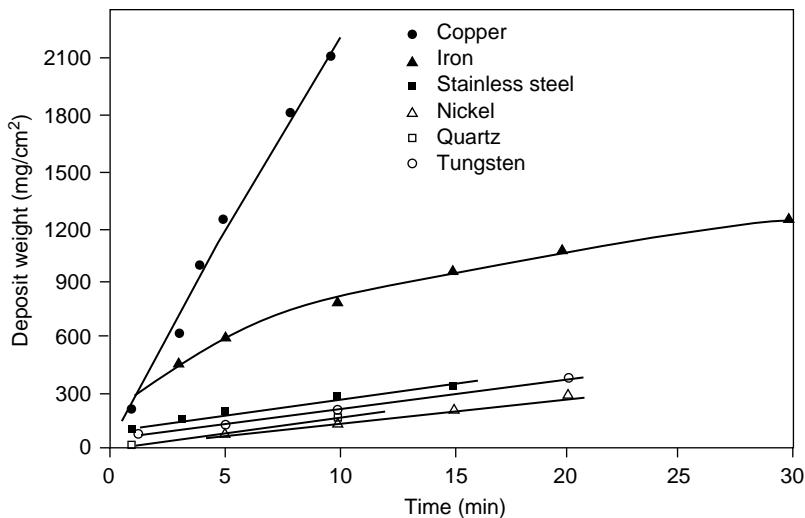


FIGURE 3.11 Deposition on various substrates with 1.55% TCP in a nitrogen stream at 700°C. (From Klaus, E.E., Jeng, G.S., Duda, J.L., *Lubr. Eng.*, 45(11), 717–723, 1989. With permission.)

Rates of formation are, of course, temperature-dependent, but films are produced up to at least 800°C. Increases in temperature and TCP concentration caused an increase in deposit formation.

The use of TCP vapor to lubricate high-speed bearings made from M50 steel at 350°C was examined by Graham et al. in 1992 [96] with excellent results. In fact, the wear area was smoother than the unused surface. Surprisingly, similar results were found when lubricating silicon nitride surface without prior activation. Here, the results were clouded by the transfer of copper to the test specimens, and it was thought that activation could have occurred by reaction of TCP with copper components of the vapor delivery system, which was then deposited onto the ceramic surface. Analysis of the film formed by TCP on a ceramic surface was also investigated by Hanyaloglu and Graham [97]. In this case, the ceramic was activated by a film (~20 atoms thick) of iron oxide. The presence of TCP at 0.5% in nitrogen or air at 500°C gave a friction coefficient of 0.07 and produced a polymer containing mainly carbon, oxygen, and a small amount of phosphorus with a molecular weight range of 6,000–60,000 g/mol.

A combination of vapor and mist lubrication has also been evaluated in the lubrication of gas turbine bearings [98]. The data indicated that organophosphates worked well with ferrous metal due to the rapid formation of a predominantly iron phosphate film. This was followed by the development of a pyrophosphate-based film over the iron phosphate. As long as iron was present, the organophosphates worked well, but continued production of the phosphate/pyrophosphate film reduced access to iron and eventually led to surface failure. Morales and Handschuh [99] reported a solution to this problem in which the phosphate contained a small quantity of ferric acetylacetone. Evaluation of this solution in comparison with the pure phosphate showed that the iron salt enabled a phosphate film to be successfully deposited onto an aluminum surface, which the pure phosphate is unable to do. (Neutral phosphates are known not to wet the surface of aluminum.) Vapor/mist lubrication of a gearbox using pure phosphate was compared with the performance of the phosphate containing the iron salt; a significant improvement in scuffing performance was noted. This was enhanced when the mist was directed onto the gear teeth immediately before contact. Evaluation of the surface film on the gear teeth revealed no phosphorus when the pure phosphate was tested but showed the presence of “fair amounts” of both iron and phosphorus when using the soluble iron salt.

A recent study of the mechanism of film formation by aryl phosphates [100] involved examining the reaction of phosphates with metal in the form of foil or powder and also with various metal oxides in different oxidation states. The tests were carried out in both oxygen-rich and oxygen-depleted environments and they revealed that the reactivity of both the commercial grade of TCP

and the pure isomers increased with steel and other metals with increasing oxidation state of the metal/oxide. In comparison with little or no degradation in the absence of metal/metal oxides, limited degradation took place in the presence of metal, but almost complete breakdown of the phosphate occurred (at the same temperature—in the range 440–475°C) in the presence of Fe_2O_3 and Fe_3O_4 . The isomeric forms of TCP also displayed different levels of reactivity with tris-*ortho*-cresyl phosphate (TOCP), more active than the meta and para isomers. The authors indicated that these relativities are consistent with the oxide's free energy of formation; those oxides with the highest free energy of formation show the lowest level of activity, and vice versa. Different types of steel surface also displayed different levels of reactivity, with 316C stainless steel being the least active.

Surface analysis of the steel specimens used indicated that, depending on whether the metal surface was oxygen-rich or poor, different mechanisms of degradation predominate. When excess oxygen was present, the film produced was a polyphosphate with good lubricating properties, whereas a surface with only a thin oxide coating produced iron phosphate, which has poor lubrication properties. No phosphide was found in the surface coating, but an iron/amorphous carbon layer, possibly rich in fused aromatics, arising from the degradation of the aromatic part of the phosphate was found when using the TBPP, but not when TCP was examined. Since these aromatics have a planar structure, they may assist with lubrication by allowing the surface to move more easily over one another. However, it is likely that the end result is a composite of the behavior of the polyphosphate and the carbonaceous film, if formed. Indeed the author suggests that the polyphosphate may be acting as a “binder” for the carbon, and it is the latter that is providing the lubrication. The proposed mechanism for the formation of the polyphosphate film was thought to involve the cleavage of the C–O bond on one of the pendant groups as the phosphate attaches itself to the surface (presumably through the $-\text{P}=\text{O}$ function), eliminating a cresyl radical. This is followed by the elimination of another cresyl radical as the second C–O bond breaks, and an Fe–O bond is formed. In this way a “lattice of cross-linked PO_3 is formed with the Fe surface.” Wear of the film is not a problem as it appears to be self-healing due to diffusion of Fe ions through the polyphosphate layer to the surface where reaction with phosphate continues. There was no suggestion that hydrolysis of the phosphate is involved.

3.5.2.3 Recent Commercial Developments

Although the majority of phosphates used as AW/EP additives are relatively low-viscosity products, interest has been expressed in materials of high molecular weight for aerospace applications, where low volatility is important; for example, high-temperature lubricants for aero-derivative gas turbines and greases for space vehicles. Three products have become commercially available and have been evaluated: an ISO 100 tertiarybutylphenyl phosphate with low TPP content, resorcinol tetraphenyl bisphosphate (Figure 3.12), and isopropylidene di-*p*-phenylenetetraphenyl bisphosphate (Figure 3.12). The hydrolytic stability of the resorcinol diphenyl phosphate is relatively poor, but this would not be of major concern for aerospace applications, for example, in greases. However, this material has been claimed as an AW additive for fuels and lubricants [101], whereas the TBPP has been incorporated into an aerospace grease formulation [102].

As part of an assessment of the high-molecular-weight additives for use in high-temperature aviation gas turbine oils, they were compared under coking, four-ball wear, and oxidation test conditions. The results are given in Table 3.9. Although the AW performance of the butylphenyl phosphate is not as good as that of TCP, the reduced impact on deposit formation and magnesium corrosion performance has made it the most promising candidate.

Although much of the recent focus of activity has been on aryl phosphates, there have also been developments with alkyl phosphates. TBP, for example, is now used as an EP additive for EP steam and gas turbine oils used when the turbine is driving a reduction gear (Ertelt, R. Private Communication, September 2001). About 1.5% of the additive is used to increase the FZG gear test performance (DIN 51354) from a load stage failure of about 6–8 to 10–11. Again, the neutral nature of the molecule is of advantage in minimizing interaction with other components of the formulation.

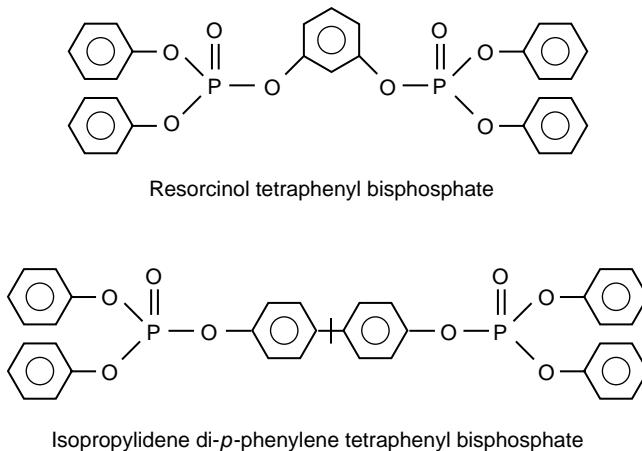


FIGURE 3.12 Structures of high-molecular-weight phosphate esters.

TABLE 3.9

The Effect of High-Molecular-Weight AW Additives on the Coking, Wear and Magnesium Corrosivity of Ester-Based Gas Turbine Oil Formulations

AW Additive	Deposit Formation ^a (mg)	Wear ^b (mm)	Magnesium Corrosivity ^c
Blank—no additive	89	0.655	High
TCP	98	0.40	High
Tris-C ₉ –C ₁₀ alkylphenyl phosphorodithioate	103	0.505	Pass
TBPP	94	0.54	Pass
Resorcinol tetraphenyl phosphate	Not determined	0.425	Fail

Note: Additives used at 1% addition in the ester base.

^a Fluid held at 300°C for 3 h; method described in paper by Gschwender et al., *Lubrication Engineering*, pp. 20–25, May 2000.

^b ASTM D 4172-88. Four-ball wear test for 1 h at 40 kg, 600 rpm, and 75°C.

^c 20 mL sample held for 48 h at 232°C with 1 l/h, air flow.

Source: Gschwender, L., Private Communication, August 2001. With permission.

An additional application where interest has been expressed in alkyl phosphates is metalworking. Owing to a desire on environmental grounds to move away from chlorine, mixtures of neutral phosphates and sulfur-containing additives have been promoted as alternatives [103–106]. As concerns exist about the possible release of phenolic materials into the environment, the alkyl phosphates are, perhaps, best suited for this application and are able to provide similar or better performance to the chlorparaffins when used together with sulfur carriers. Table 3.10 summarizes the drill life and other AW/EP performance in a neat oil for both neutral isopropylphenyl phosphate and neutral alkyl phosphate in combination with a sulfurized olefin when compared with a chlorparaffin.

In an extension to this work, drill life test data were obtained on tri-isobutyl and tributoxyethyl phosphate in comparison with a commercially available acid phosphate (oleyl acid phosphate). Each phosphate was evaluated at the same phosphorus level in the presence of a sulfur carrier (a 4:1 mixture of a sulfurized fatty acid ester with 26% total sulfur and a dialkyl polysulfide with 40% total sulfur content), and all additives were dissolved in a neat paraffinic mineral oil of

TABLE 3.10
A Comparison of the AW/EP Performance of a Chlorparaffin and an Alkyl or Aryl Phosphate/Active Sulfur Combination in a Simple Oil-Based Cutting Fluid Formulation

Formulation and Test Data	A	B	C	D
ISO 22 paraffinic oil	92	95.7	96.9	—
Tri-isopropylphenyl phosphate	—	—	—	1.0
Trialkyl phosphate	—	—	0.6	—
Active sulfur compound (40% S)	—	4.3	2.5	2.5
Chlorinated paraffin (40% Cl)	8	—	—	—
Four-ball wear test (ASTM D 4172)-mm	0.65	—	—	0.43
Four-ball EP properties (ASTM D 2783)				
Weld load (kgf)	400	—	—	620
Seizure load (kgf)	80	—	—	80
Load wear index	51	—	—	104
Pin and V-block wear (ASTM D 3233)				
Failure load (lb)	>3100	—	—	2726
Drill Life test				
Holes drilled to failure (EN24T mild steel at 1200 rpm/0.13 mm/min feed rate)	140	100	280	200

TABLE 3.11
Results of Drill Life Tests on Alkyl and Alkoxyalkyl Phosphates in the Presence of Sulfur Carriers

Formulation (w/w) and Test Data	A	B	C	D
Sulfur carrier	5.2	5.2	5.2	5.2
Tri-isobutyl phosphate	—	4.17	—	—
Tributoxyethyl phosphate	—	—	6.4	—
Oleyl acid phosphate	—	—		10.0
Neat oil	94.8	90.63	88.4	84.8
Holes drilled to failure	84	432	>500	18

ISO VG 22. The test was carried out on an automatic drilling machine, drilling holes of 18 mm depth in a 40 mm thick disk of stainless steel type 304 with a feed rate of 0.13 mm/rev and at 1200 rpm. The test was concluded when either the drill broke or showed excessive wear. The results in Table 3.11 [107] show a significant improvement for the butoxyethyl phosphate over the isobutyl phosphate, whereas the oleyl acid phosphate showed little activity. The reason for the poor behavior of the acid phosphate is not known.

Also, in the field of metalworking, phosphates have been claimed as components of hot forging compositions [108,109].

3.5.3 ALKYL AND ARYL ACID PHOSPHATES

3.5.3.1 Non-ethoxylated

Although the range in commercial use is limited, acid phosphates are important components of metalworking oils—frequently in combination with chlorparaffins. However, because of

environmental concerns associated with the use of chlorinated hydrocarbons, their possible replacement by mixtures of phosphorus and sulfur compounds has been investigated [66].

Mixtures of monophosphoric and diphosphoric acid esters were compared with a dithiophosphate acid amide in macroemulsions using a variety of EP tests. Performance in drilling and tapping tests (which are regarded as the conditions most closely simulating cutting performance) indicated that the dithiophosphate amide gave the best performance, whereas the monoacid and diacid phosphates produced levels of performance similar to or better than that of the chlorparaffin alone.

Traditionally, the acid phosphates in commercial use have high acid numbers (200–300 mg KOH/g). As a consequence, in addition to their use as AW/EP additives, they are used as corrosion inhibitors [110], and certain structures are promoted as copper passivators [110]. A recent development has been the availability of aryl phosphate-based products that have a relatively low level of acidity (typically 10–15 mg KOH/g) while offering a combination of good AW/EP performance with rust prevention and oxidation inhibition. The multifunctionality of this product type offers opportunities for the simplification of additive packages and use in a wide range of hydraulic and circulatory oils, metalworking, and gear applications, whereas the lower level of acidity reduces the potential for additive interaction and the promotion of foaming, etc.

Increased activity in alkyl acid phosphates has been reported in the patent literature. This arises from the use of long-chain alcohols (C_{16} – C_{18}) to produce an acid phosphate ester mix with a high monoacid content (preferably greater than 80:20% monoacid–diacid ratio) [111]. With this acid distribution, it has been possible to achieve lower wear than for the conventional ethoxylated alkyl phosphates with a monoacid to diacid ratio of 60:40%.

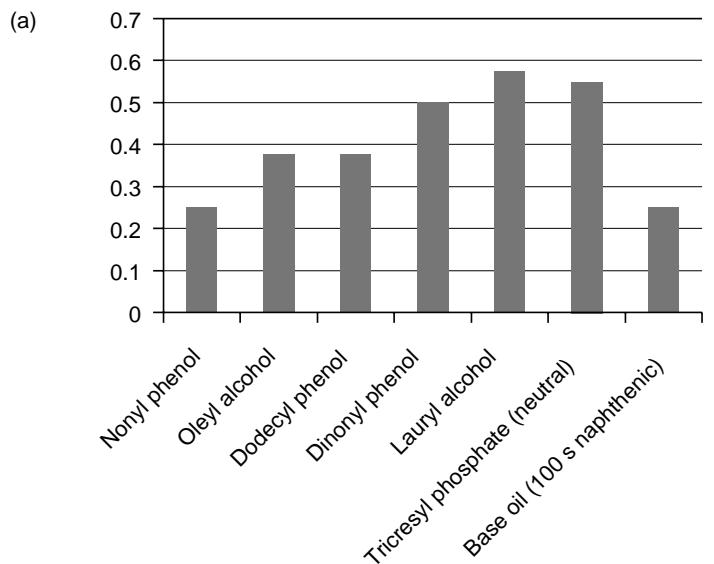
3.5.3.2 Alkyl and Alkarylpolyethyleneoxy Acid Phosphates

Polyethyleneoxy acid phosphates are a potentially very large class of compounds. Not only are variations possible in the type of alcohol or phenol chosen but also in the type of alkoxylation (although ethylene oxide [EO] is invariably used) and the EO content. Products of this process were originally claimed to be more active than the non-ethoxylated variety, but the latest advances in the latter types [111] suggest this may no longer be the case.

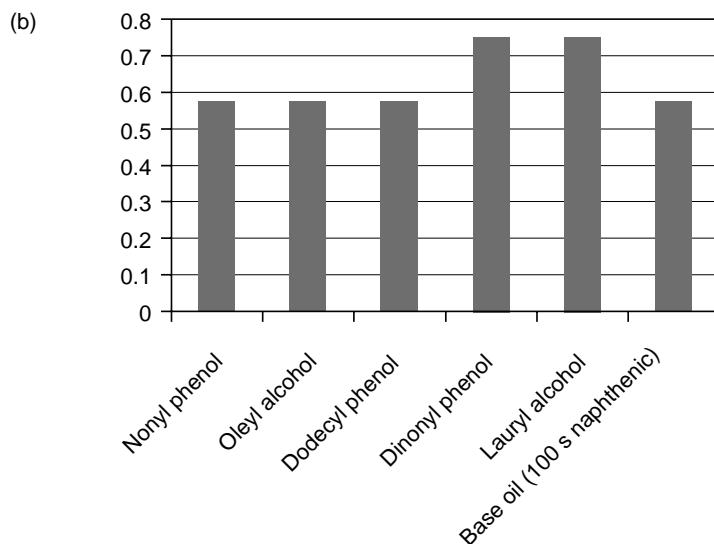
Depending on the choice of raw materials, the finished product may be oil- or water-soluble or water-dispersible. Alkyl and (alk)arylpolyethyleneoxy acid phosphate esters acids containing <55% EO were found to be oil-soluble; products with an EO content of more than 60% were water-soluble as the free acids and their amine salts, whereas products with 40–60% of EO were both oil- and water-soluble or water-dispersible [40]. The free acids are used in oil applications, whereas amine (usually triethanolamine) or metal salts of the acids are used in aqueous applications. The alcohols and phenols initially selected for evaluation were lauryl and oleyl alcohols and nonyl, dinonyl, and dodecyl phenol. Other raw materials used today include C_8 – C_{10} alcohols, 2-ethyl hexanol, tridecanol, cetyl-oleyl mixed alcohols, and phenol. The products are nonionic surfactants with excellent wetting and emulsification properties, and certain types do not support bacterial growth. They are also good corrosion inhibitors—an important factor for their use in metalworking applications. The higher EO-content products tend to produce a heavy and stable foam, and materials containing ~45% EO are therefore preferred for metalworking applications [40].

The effect of the alcohol or phenol and the impact of EO content on the wear behavior in a naphthenic oil can be seen in Figures 3.13 and 3.14, respectively [112].

The performance of the product based on oleyl alcohol is interesting in that it does not appear to change with EO content, yet is simultaneously capable of producing materials that vary from oil- to water-soluble. However, the four-ball or pin and v-block tests, although widely used as screening tests for the metal-working application, are not considered to be capable of predicting the performance under cutting conditions. This is confirmed in the paper given in 1995 by Werner et al. [113], which compares the performance of different ethoxylated acid phosphates under various test



Test conditions: 40 kg, 100 rpm, 60 min, 121°C
 Four-ball wear scar diameter (mm)



Test conditions: 100 kg, 100 rpm, 60 min, 121°C
 Four-ball wear scar diameter (mm)

FIGURE 3.13 Effect of hydrophobe on wear properties—four-ball wear scar diameter. Acid phosphate esters based on nonionics containing 23–25% ethylene oxide.

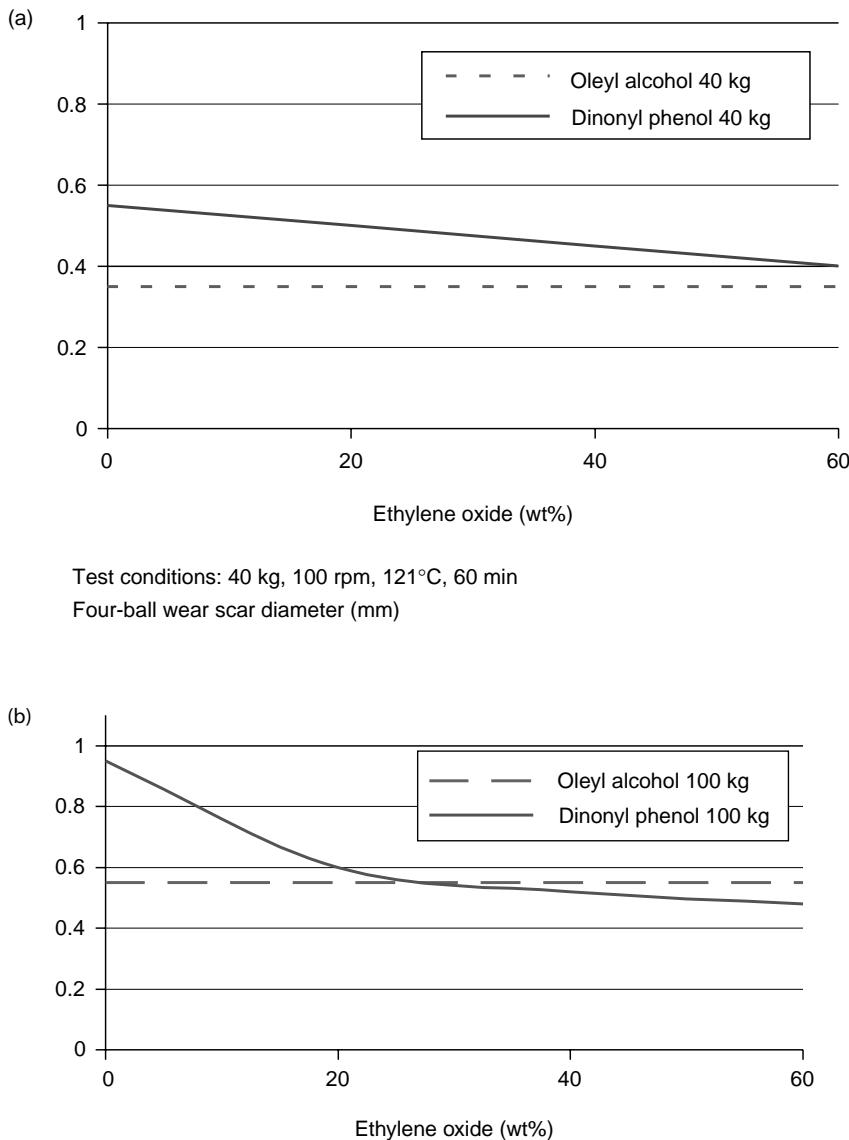


FIGURE 3.14 Effect of ethylene oxide content on wear properties 1% of additive in 100 SUS (100°F) naphthenic base oil.

conditions. Of greater relevance than conventional four-ball or pin and v-block tests are actual cutting or tapping torque tests. The results given in Table 3.12 show that (1) products with a hydrophilic-lipophilic balance (HLB) value of 11–12 give the best results and (2) in general, the further the value deviates from this, the worse the results become. Unfortunately, no studies appear to have

TABLE 3.12
Phosphate Ester Surfactant Ranking on Steel in a Water-Based System as a Function of Structure

Alcohol	Phosphate EO Units	Pin-on-Vee Block	Rankings of Sample		Overall Rating	HLB Number
			Four-Ball Wear	Tapping Torque		
C9–16	5.5	4	1	4	9	1
C18	4	6	4	2	12	2
Nonylphenol	4	10	2	1	13	3
C13	10	2	9	5	16	4
C12	6	1	12	7	20	5
C8–10	6	8	7	6	21	6
C12	12	5	8	12	25	7
C13	6	9	6	10	25	8
C12	9	7	5	14	26	9
Nonylphenol	6	14	3	9	26	10
Phenol	6	12	13	3	28	11
Dinonylphenol	5	3	14	11	28	12
Nonylphenol	9.5	11	11	8	30	13
C13	4	13	10	15	38	14
butanediol	6	15	15	13	43	15
						—

been made on the nature of surface film deposited on the metal, but the adsorption mechanism indicated previously is probably still valid.

3.5.3.3 Amine Salts of Acid Phosphates

One amine phosphate that appeared in the patent literature as early as 1934 as a corrosion inhibitor for aqueous systems (and is still occasionally used) is triethanolamine phosphate [114]. Formed by the neutralization of phosphoric acid with triethanolamine, this product was widely used as a corrosion inhibitor for automotive antifreeze formulations for many years [115].

In 1970, Forbes and Silver [116] reported on their work investigating the effect of chemical structure on the load-carrying properties of different phosphorus compounds. In this case, the structures under review were di-*n*-butylphosphoramidates, amine salts of di-*n*-butyl phosphate, and derivatives of dialkylphosphinic and alkylphosphonic acids. The results indicated that the phosphoramidates were more effective load-carrying additives than the neutral phosphates, TBP and TCP, but less active than the amine salts of di-*n*-butyl phosphate. The evaluation of the series of dialkylphosphinic and alkylphosphonic acid esters indicated that the AW performance related directly to the strength of the acid from which they had been produced (Figure 3.15), suggesting that adsorption through the polarity of the ester group was an important step in the process.

In addition to the work carried out in hydrocarbon base stocks, some testing was also performed in a synthetic ester. This fluid enabled a comparison to be made of tetra-alkylammonium salts of dibutylphosphate (otherwise insoluble in mineral oil), which displayed the best AW/EP properties of all the amine phosphates tested (Table 3.13). The authors suggested that this was probably due to the stability of the ions.

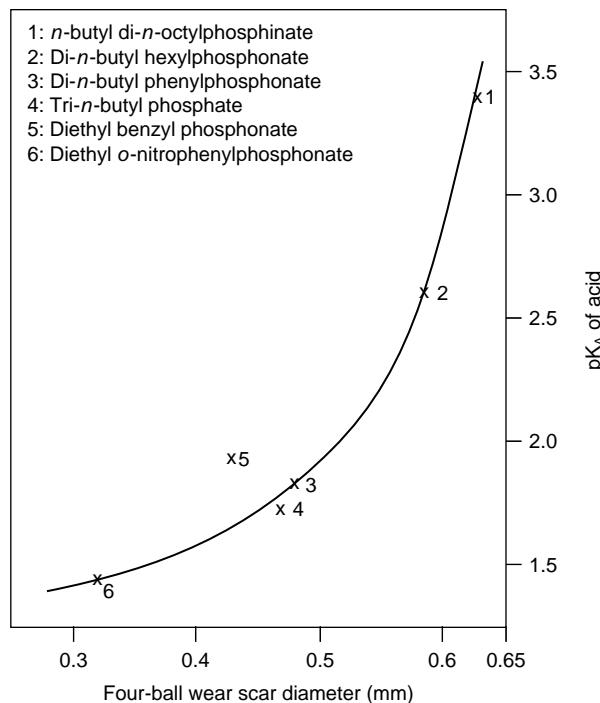


FIGURE 3.15 Effect of acid strength on AW performance. (From Forbes, E.S., Silver, H.B., *J. Inst. Pet.* 56(548), 90–98, 1970. With permission.)

TABLE 3.13

Four-Ball Test Results of Various Amine Dibutyl Phosphates in Diisooctyl Sebacate

$(\text{BuO})_2 \text{PO}_2 \text{NR}^1 \text{R}^2 \text{R}^3 \text{R}^4$	EP Test			AW Test		
	MHL (kg)	WL (kg)	ISL (kg)	30 min	WSD (mm) after 45 min	60 min
$n\text{C}_4\text{H}_9\text{NH}_2$	40.5	130	125	0.38	0.38	0.36
$n\text{C}_6\text{H}_{11}\text{NH}_2$	40.0	130	115	0.37	0.38	0.39
PhNH ₂	43.6	140	120	0.37	0.38	0.39
$[n\text{C}_4\text{H}_9]_2\text{NH}$	34.8	140	100	0.26	0.27	0.33
$[n\text{C}_4\text{H}_9]_3\text{NH}$	37.8	150	110	0.37	0.38	0.42
$[n\text{C}_4\text{H}_9]_4\text{N}$	54.4	150	150	0.25	0.25	0.26
$[\text{CH}_3]_2 [n\text{C}_8\text{H}_{17}]_2\text{N}$	56.1	165	165	0.30	0.35	0.40
None	18.6	120	55	0.57	0.61	0.64
TCP	19.8	110	60	0.31	0.33	0.35

Note: % additive = 4 milliatoms of P/100 g of fluid. (MHL, Mean Hertz Load; WL, Weld Load; ISL, Incipient Seizure Load; WSD, Wear Scar Diameter.)

Source: Forbes, E.S., Silver, H.B., *J. Inst. Pet.*, 56(548), 90–98, 1970. With permission.

A further study of the mechanism of amine phosphates by Forbes and Upsdell appeared in 1973 [117]. Adsorption/reaction studies of dibutyl and di-2-ethylhexyl phosphates with either *n*-octylamine or cyclohexylamine and iron powder showed that both the amine and the acid phosphate were adsorbed onto the metal surface and that the rate and extent of their adsorption/desorption varied with chemical structure. The higher the solubility of the iron–phosphate complex formed,

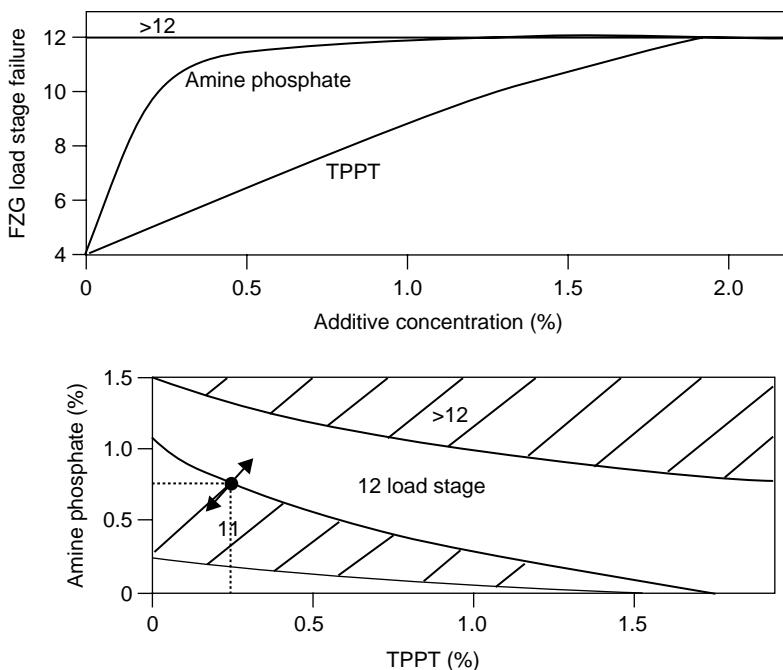


FIGURE 3.16 FZG performance of an amine phosphate and TPPT separately and in mixtures in an ISO VG 32 polyalphaolefin. (From Kristen, U., *Additive für Schmierstoffe*, Expert Verlag, Renningen-Malmshaim, German, 1994. With permission.)

the greater was the likelihood of desorption. Furthermore, good AW performance depended on high phosphate and amine adsorption and retention of the phosphate moiety on the surface.

The conversion of a dialkyl acid phosphite to an amine phosphate and the use of the mixed product as a multifunctional AW/EP additive, antioxidant, and corrosion inhibitor with improved metal passivation properties were claimed in 1997 [118].

An amine salt and TCP were studied as AW agents for different synthetic esters by Weller and Perez [119] and compared with a sulfurized hydrocarbon. The neutral ester (TCP) generally showed an increasing amount of wear up to 1% addition before reducing at higher levels. The amine salt, however, rapidly reduced wear to very low levels. Friction coefficients were also consistently lower with the amine salt.

Kristen [120] reported the effect of additive interaction between amine phosphates and a phosphorothionate. The additives were evaluated under FZG gear test conditions (DIN 51354). The results showed that the additives respond differently in nonpolar and polar base stocks, specifically a polyalphaolefin and a synthetic ester (Figures 3.16 and 3.17). In the synthetic hydrocarbon base, a level of 0.75% amine phosphate and 0.25% phosphorothionate (or perhaps 0.5% of each) provided a borderline FZG 12 load stage pass/fail. In comparison, 0.75% of amine phosphate ester and 1% of phosphorothionate were required to achieve the same level of performance in the ester. Monitoring the response of additive combinations reveals not only the most cost-effective mixtures but also any antagonisms between additives, as were found here in the ester base at higher additive levels. Such information is invaluable to formulators when trying to meet specification requirements and ensuring that the performance level is consistently above the minimum limit.

Amine salts, for example, triethanolamine salts of alkyl and arylpolyethoxylated acid phosphates, are widely used in metalworking applications. Some of these products are not only commercially available but are also produced *in situ* when the pH of the product is adjusted by the addition of base to ensure the product is alkaline in use. This is to avoid corrosion and minimize skin irritation.

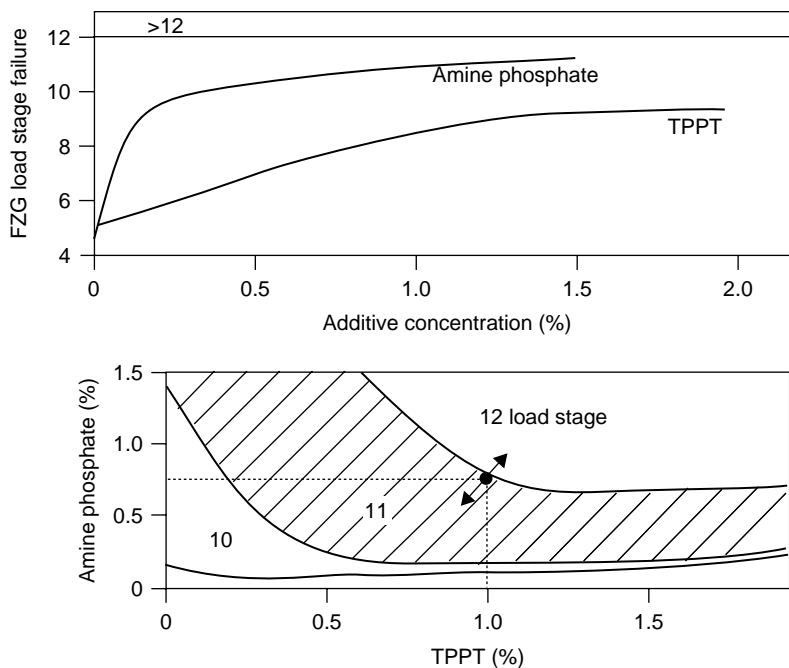


FIGURE 3.17 FZG performance of an amine phosphate and TPPT separately and in mixtures in an ISO VG 22 pentaerythritol ester. (From Kristen, U., *Additive für Schmierstoffe*, Expert Verlag, 1994. With permission.)

3.5.4 NEUTRAL ALKYL AND ARYL PHOSPHITES

3.5.4.1 Use as Antiwear/Extreme-Pressure Additives

The earliest known reference to the evaluation of phosphites as AW/EP additive is in a 1950 paper by Davey [75]. As a result of these investigations, which also included a comparison with phosphates and the effect of incorporating chlorine into the phosphate/phosphite molecule, it was found that

- Phosphites have superior EP properties to the phosphates, and long alkyl chains are more effective than aryl groups.
- Evaluation of TBP and TXP revealed similar optimum concentrations of between 1 and 2% as were found in the previous study with TCP [5].
- Polar compounds such as acids or esters improve the lubricating (AW) properties of phosphites and phosphates by being strongly adsorbed on to the surface.
- The incorporation of chlorine or sulfur into the molecule (or the addition of small amounts of free sulfur) improves the EP properties. Chlorine is more effective when part of an alkyl residue, and when sulfur is added to a P/Cl compound (e.g., a chlorinated phosphite), the EP properties are further improved.

Following the study by Davey, a number of patents appeared claiming the use of phosphites in lubricant applications [121–124], but it was not until 1960 that a further detailed study of the behavior of phosphites, this time by Sanin et al. [125], was published. The study emphasized the correlation between structure and activity, and the short-chain derivatives were found to be the most active.

In 1993, Ohmuri and Kawamura [126] carried out fundamental studies into the mechanism of action of phosphite EP additives. They found that initial adsorption rates of phosphorus-containing

esters depended largely on the existence of $-\text{OH}$ and $-\text{P}=\text{O}$ bonds in the structure. The extent of adsorption was influenced by the hydrolytic stability of the esters, and this process was found to occur through reaction with water adsorbed onto the iron surface. Adsorption of the phosphites varied depending on the degree of esterification; triesters were adsorbed after being decomposed hydrolytically to monoesters, whereas diesters were adsorbed without hydrolysis. Phosphite esters eventually hydrolyzed to *inorganic acid* regardless of the degree of esterification, followed by its adsorption and conversion to the iron salt. It was suggested the adsorbing and hydrolyzing properties of the esters depended on the arrangement of the molecules physisorbed onto the surface.

Evaluation of a range of alkyl phosphites as EP additives in gear oils was reported by Riga and Rock Pistillo [127]. The most effective products were those with short chains, particularly dibutyl phosphite, which resulted in a wear layer of $>1000\text{ \AA}$ and the formation of both iron phosphate and phosphide. Other phosphites formed only traces of phosphide, and as the chain length increased, the resulting film became thinner and contained less phosphorus, possibly due to steric hindrance. Long-chain (C_{12}) alkyl phosphites have also been claimed as AW additives for aluminum rolling oil [128] and, in fact, are still used in metalworking applications.

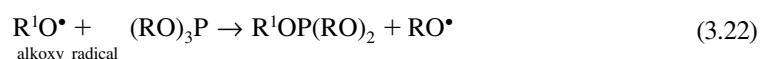
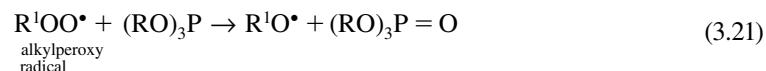
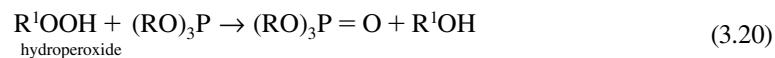
In view of the work carried out on the use of phosphates as vapor-phase lubricants, an investigation into the effect of phosphites on the frictional properties of ceramic-on-ceramic and ceramic-on-metal surfaces was carried out in 1997 [129]. The phosphites (and other additives evaluated) had no effect on ceramic-on-ceramic friction; in fact, short-chain phosphites significantly increased friction. When several types of metal were slid against oxide ceramics, the alkyl phosphites were found to lower the friction for each metal except copper. Apparently, the reaction products between copper and the phosphite had adhesive properties and increased friction.

The decomposition of trimethylphosphite on a nickel surface was also studied to obtain insight into the initial steps in the decomposition of phosphates when used as vapor-phase lubricants [130]. The main breakdown path is the cleavage of the $-\text{P}-\text{O}-$ bond to yield the methoxy species, which then degrades to CO and H_2 or reacts with the nickel surface. Following heating to 700°K , the surface loses adsorbed species other than phosphorus, which is seen as a simple way for the controlled deposition of phosphorus onto a metal surface.

3.5.4.2 Use as Antioxidants for Lubricating Oils

In addition to their use as AW/EP additives, neutral (and acid) phosphite esters have long been used as antioxidants or stabilizer for hydrocarbons. They were originally introduced as stabilizers for rubber and thermoplastics. Trisnonylphenyl phosphite, for example, was first used to stabilize styrene-butadiene rubber in the early 1940s; this was shortly followed by patents claiming phosphites as antioxidants for lubricants [48,122,123,131,132].

Phosphites function as decomposers of hydroperoxide, peroxy, and alkoxy radicals (reactions 3.20 through 3.22) rather than eliminating the hydrocarbyl-free radicals formed in the chain initiation process. They also stabilize lubricants against photodegradation [133].



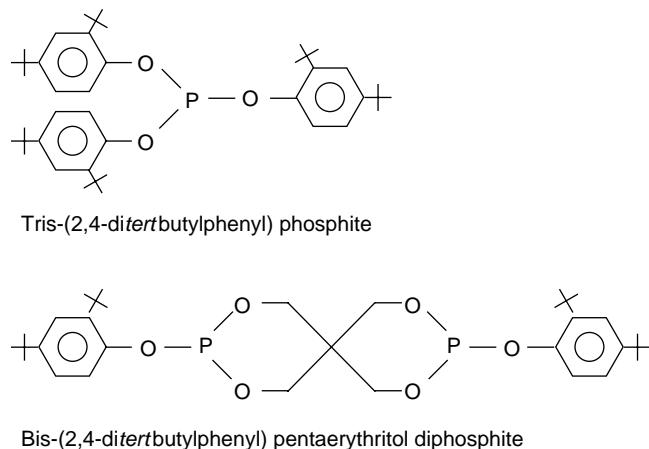


FIGURE 3.18 Structures of some commonly available hindered phosphites.

This behavior as *secondary* antioxidants by destroying the hydroperoxides, etc., formed in the chain propagation process results in their use in synergistic combination with those antioxidant types that are active as radical scavengers in the initiation process, for example, the hindered phenols and aromatic amines [134–138].

Phosphites are useful additives because of their multifunctionality. However, although they are still used as antioxidants in hydrocarbon oils, their relatively poor hydrolytic stability and the formation of acidic compounds that could affect the surface active properties of the oil have prompted the introduction of “hindered” phosphites with better hydrolytic stability: for example, tris-(2,4-ditertiarybutylphenyl) phosphite or tris-(3-hydroxy-4,6-ditertiarybutylphenyl) phosphite, and, where solubility permits, cyclic phosphites, for example, based on pentaerythritol such as bis-(2,4-ditertiarybutylphenyl) pentaerythritol diphosphite (Figure 3.18). These types are claimed as stabilizers or costabilizers for lubricating oils [139–142].

Table 3.14 [141] illustrates the significant improvement in oxidation stability shown by such blends.

In common with most other types of phosphorus-containing products, neutral (and acid) phosphites have also been claimed as corrosion inhibitors [143,144].

3.5.5 ALKYL AND ARYL ACID PHOSPHITES

As might be predicted from the behavior of the other types of phosphorus-containing additives, the acid phosphites have good AW/EP properties; the nonylphenyl acid phosphite is particularly effective [145,146]. When used in aviation gas turbine lubricants, the acid phosphites were sometimes formulated in combination with neutral phosphates (TCP); blends of the two products showed synergy even when the amount of the phosphite was very low [147]. The acid phosphites are also claimed to be corrosion inhibitors [144] and antioxidants [47,149,150].

The effects of structure on the AW and load-carrying properties of dialkyl phosphites was studied by Forbes and Battersby [151] in a liquid paraffin. AW performance was best with long-chain compounds (Figure 3.19), whereas the short-chain (highest phosphorus content) derivatives displayed the best load-carrying performance.

Scuffing behavior, however, appeared to reach a minimum at about a C₈ carbon chain length (Figure 3.20). This parallels the behavior of the neutral phosphites. Adsorption studies also showed that the phosphorus content of the solution was depleted in the same order of the load-carrying performance, namely, the most active products showed the highest loss from solution. The presence of water increased the uptake of phosphorus from solution. Comparison of the performance

TABLE 3.14
Antioxidant Synergism between Hindered Aryl Phosphites and a Hindered Phenol

Base Stock	Antioxidant	Oxidation Stability	
		% Viscosity Change	Total Acid Number Increase
1	Hindered phenol (0.5%)	357	11.5
	Hindered phosphite A (0.5%)	438	12.2
	Hindered phenol (0.1%) + phosphite A (0.4%)	8.7	0.01
	Hindered phenol (0.17%) + phosphite A (0.33%)	9.4	0.06
2	Hindered phenol (0.5%)	712	14.2
	Hindered phosphite B (0.5%)	452	10.6
	Hindered phenol (0.1%) + phosphite B (0.4%)	8.1	0.05
	Hindered phenol (0.17%) + phosphite B (0.33%)	8.7	0.03

Note: Hindered phenol is tetrakis-(methylene-3,5-ditert-butyl-4-hydroxy hydrocinnamate) methane; Phosphite A is tri-(2,4-ditert-butylphenyl) phosphite; Phosphite B is bis-(2,4-ditert-butylphenyl) pentaerythritol diphosphite. Test conditions: IP 48 (modified), 200°C for 24 h, air at 15 l/h in an ISO VG 32 mineral oil.

Source: U.S. Patent 4,652,385, Petro-Canada Inc., 1987.

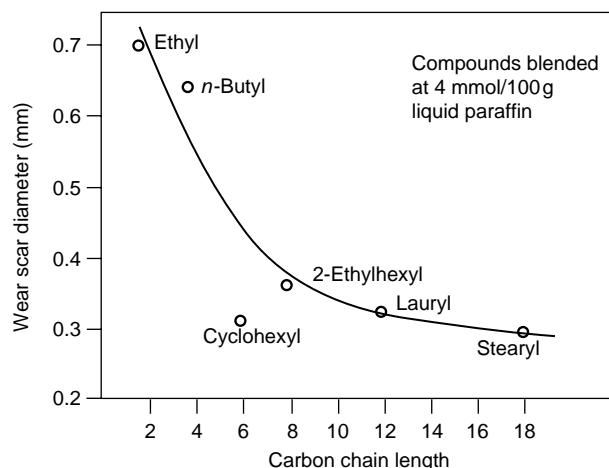
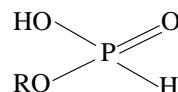


FIGURE 3.19 Effect of chain length on the four-ball AW performance of dialkyl phosphites. (From Forbes, E.S., Battersby, J., *ASLE Trans.*, 17(4), 263–270, 1974. With permission.)

of the phosphites against the corresponding acid phosphate revealed that the phosphites had better load-carrying but inferior AW behavior (see Table 3.15). The authors suggest that the activity of the phosphites is due to an initial hydrolysis to produce the following intermediate either in solution or on the metal surface:



This reacts with the iron surface to give an iron salt that was thought to be responsible for the AW properties of the product. Under much more extreme conditions as are found with scuffing,

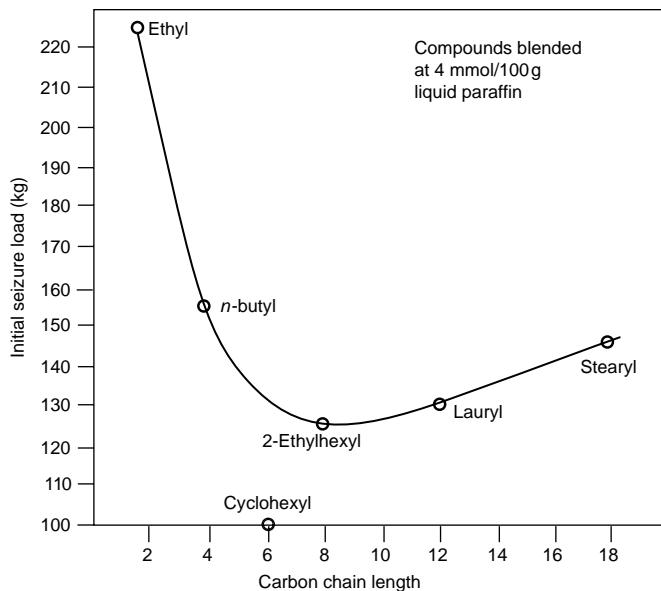


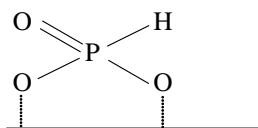
FIGURE 3.20 Effect of chain length on the initial seizure loads of dialkyl phosphites. (From Forbes, E.S., Battersby, J., *ASLE Trans.*, 17(4), 263–270, 1974. With permission.)

TABLE 3.15
Comparison of the Load-Carrying Properties of Dialkyl Phosphates
and Dialkyl Phosphites at 4 mmol/100 g Base Oil

	Initial Seizure Load (kg)	Wear Scar Diameter (60 min) mm
Diethyl phosphate	225	0.70
Diethyl phosphate	160	0.43
Dibutyl phosphate	155	0.64
Dibutyl phosphate	85	0.42
Di-2-ethylhexyl phosphite	125	0.36
Di-2-ethylhexyl phosphate	80	0.29
Dilauryl phosphate	130	0.32
Dilauryl phosphate	80	0.35

Source: Forbes, E.S., Battersby, J., *ASLE Trans.*, 17(4), 263–270, 1974. With permission.

the aforementioned salt was thought to decompose further to give the phosphorus-rich layer of the following type:



The authors postulated the load-carrying mechanism of phosphites given in Figure 3.21.

3.5.5.1 Amine Salts of Acid Phosphites

In 1975, Barber [152] investigated the four-ball test performance of several long-chain amine salts of short-chain acid phosphites, which were found to be very active. Unfortunately, he did not investigate

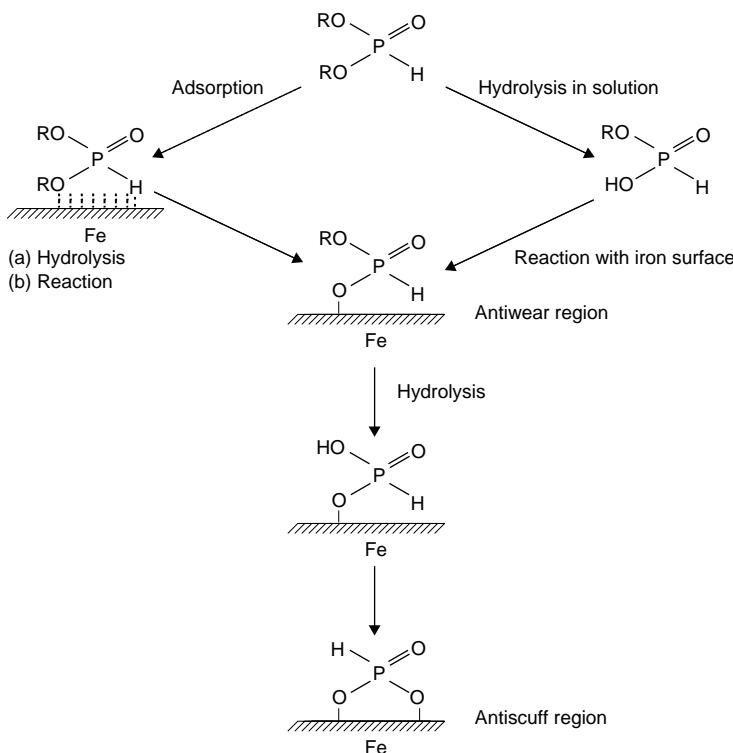


FIGURE 3.21 Mechanism of load-carrying action of dialkyl phosphites. (From Forbes, E.S., Battersby, J., *ASLE Trans.*, 17(4), 263–270, 1974. With permission.)

the effect of increasing the chain length of the phosphite while reducing the length of the amine. Most of the paper concerns the behavior of a wide range of phosphonate esters (see Section 3.16).

3.5.6 PHOSPHONATE AND PHOSPHINATE ESTERS

A large group of phosphonate esters was prepared by Barber in 1975 [152] and evaluated using the four-ball machine. Although short-chain esters were more effective in preventing scuffing, the most effective products were those containing chlorine. However, even at high levels of chlorine, the performance was still inferior to the amine phosphite reaction products reported earlier. In comparison with TCP, incipient seizure loads were generally higher, but the weld loads were broadly similar. Unfortunately, there were no direct comparative data under wear test conditions. A limited number of phosphinate esters were evaluated and found (also by four-ball tests) to give similar performance to the phosphonate esters.

The activity of a range of phosphonates was studied by Sanin et al. [153], who concluded that their effectiveness depended on their structure and the friction regime, but esters containing no chlorine had “no effect at either low or high load.” A further study, by the same authors, of the mechanism of activity of phosphonates again suggested the reaction of decomposition products with iron and the formation of a protective layer. Under severe conditions, this layer is removed, resulting in a sudden increase in friction followed by seizure or welding. Studies of the reaction of a dibutyltrichlorophosphonate ($\text{Cl}_3\text{CPO(OBu)}_2$) indicated that a reaction took place at 405–408K to give chlorobutane and an iron-containing polymer. At 413K, this polymer decomposed to give FeCl_3 , which gave additional protection.

Phosphonate (and pyrophosphonate) esters, as their metal or amine salts, have appeared in the patent literature over many years as AW/EP additives. Amine salts of dinonylphosphonate are, for example, claimed in aircraft gas turbine lubricants [154], and dimethyltetradecyl phosphonate has



where PIB = polyisobutylene

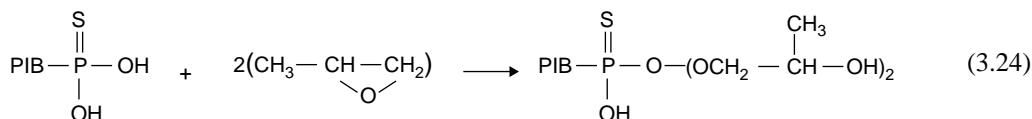


FIGURE 3.22 An example of the preparation of a phosphorus-based detergent. (From Colyer, C.C., Gergel, W.C., *Chemistry and Technology of Lubricants*, VCH Publishers, New York, 1992. With permission.)

been used in water-based formulations with good pump wear characteristics [155,156]. One of the most recent applications has been in refrigeration compressor oils (e.g., for automobiles) that are compatible with the more ecologically acceptable refrigerants. The reason for their selection in this application has probably been their good hydrolytic stability in view of the need for a long fluid life [157,158]. Other automotive industry applications for these products include use as friction modifiers, for example, in automatic transmission fluids [159], or possibly as detergents in engine oils [160–162] to keep insoluble combustion and oil oxidation products dispersed in the oil.

An alternative method for incorporating phosphorus into dispersant is exemplified in Ref. 160. This method involves reacting P_2S_5 with a sulfurized hydrocarbon, such as sulfurized polyisobutylene, at high temperatures to form a thiophosphorus acid (see reaction 3.23, Figure 3.22). This intermediate is then reacted with propylene oxide to form the hydroxypropyl esters of the phosphorus acid (see reaction 3.24, Figure 3.22).

Aminoethane phosphonate copolymers have also been claimed to provide dispersancy, corrosion protection, and pour point depression [163]. Among other applications mentioned in the literature for these products or their salts in lubricating oils are the extrusion, cold rolling, and cold forging of aluminum [164], offering improved rust inhibition [165] and antioxidant performance [166].

3.5.7 A SUMMARY OF THE PROPOSED MECHANISM FOR ANTIWEAR AND EXTREME-PRESSURE ACTIVITY OF PHOSPHORUS-BASED ADDITIVES

In attempting to produce an explanation for the activity of phosphorus-containing additives, it is not easy, as explained earlier, to compare the results of the preceding investigations because conditions vary from one investigation to another. No report evaluates all the different types of additives with the same (high) level of purity under identical test conditions. However, it is possible to draw together some of the more consistent “threads” running through the many papers. One parameter highlighted in past reports (and confirmed by recent observations) is that the presence of oxygen on the metal surface appears to be important for the activity of neutral aryl phosphates. This could perhaps be one of the major reasons why TCP is sometimes found to be inactive. The composition of the film formed on the surface is not yet completely defined, but current work points toward the formation of a self-regenerating polyphosphate layer in which amorphous carbon may be providing the lubrication benefits. The mechanism of formation of the polyphosphate layer and the role, for example, of moisture is not yet clear but appears to be a stepwise process as follows:

- The adsorption of the material onto the surface (occurring through the $-\text{P}=\text{O}$ and $-\text{P}-\text{OH}$ bonds in the molecule).
- Either the hydrolysis of a $-\text{P}-\text{OR}$ bond to form $-\text{P}-\text{OH}$ (probably arising from water on the surface but may also occur in solution) with the formation of acid phosphates/phosphites



FIGURE 3.23 An approximate ranking of the effect of structure on the AW, EP, and stability properties of the base stock.

or, in the case of neutral phosphates, the cleavage of the C–O bond to release an aryl radical and a residual --P--O^\bullet radical.

- Either reaction of the --P--OH or --P--(OH)_2 with the metal surface to form an iron salt, possibly followed by further hydrolysis to release the remaining hydrocarbon moieties and reaction of the new --P--OH groups with the surface to form polyphosphate, or the reaction of the residual --P--O^\bullet radical with the iron surface to form a succession of Fe--O--P-- bonds leading to the formation of polyphosphate.
- Products that contain --P--C bonds (e.g., the phosphonates and particularly the phosphinates) are less likely to operate by a mechanism involving hydrolysis, and the stability of the P–C bond might be expected to prevent or delay the formation of the phosphorus-rich surface layer with an adverse effect on EP properties. However, the same stability could result in better friction-modification properties. The fact that phosphinates and phosphonates are active as AW/EP additives suggests that the --P=O bond is also involved in the surface adsorption process, but that either the nature of the surface film may be different or a polyphosphate film is produced as a result of the scission of a --P--C bond.
- The formation of amine salts results in an increase in activity, possibly as a result of the stability of the ion and improved adsorption on the metal surface.

The mechanism of formation of phosphide, which is reported in many instances, has not yet been clarified but might possibly involve the amorphous carbon that then acts as a reducing agent on the phosphate/phosphite layer as it forms on the surface.

These conclusions lead, as a broad generalization, to the order in activity and impact on surface chemistry/stability as shown in Figure 3.23.

The preceding comments are, however, a simplification of the situation. Depending on the length of the alkyl or alkaryl chain, if the iron salts that are formed are soluble in the oil they may desorb from the surface, leading to poor AW/EP performance. Interaction with other surface-active materials will inevitably influence the performance of AW/EP additives, whereas depletion in use due to oxidation, etc., will also affect performance.

3.6 MARKET SIZE AND COMMERCIAL AVAILABILITY

Information on the market size for ashless phosphorus-containing AW/EP additives is limited. An approximate total market of ~10,000 tpa is broken down, as given in Table 3.16. The data exclude the use of phosphites as antioxidants in oil applications, which is separately estimated to be between 100 and 200 tpa.

The wide use of phosphorus-containing AW/EP additives is due, in addition to their good lubricity performance, to the following features of value to formulators:

- Ashless
- Low odor, color, and volatility
- Low acidity/noncorrosive (applies to the neutral esters only)

TABLE 3.16
A Breakdown of the Market for Ashless Phosphorus-Containing AW/EP Additives

Product	Market Size (t)
Alkyl phosphates	100
Aryl phosphates	6000
Acid phosphates, ethoxylated alkyl and aryl phosphates, and amine salts of acid phosphates	3000
Phosphites, acid phosphites, dialkyl alkyl phosphonates, and amine salts of acidic products	1000

TABLE 3.17
Typical Physical Properties of the Most Widely Used Grades of Phosphorus-Based AW Additives

Property	Unit	TiBP	TCP	IPP/32	TBPP/32
Viscosity at 40°C	cSt	2.9	25.0	32.3	33
Viscosity at 0°C	cSt	10.0	1000	990	1500
Specific gravity	20/20°C	0.965	1.140	1.153	1.170
Pour point	°C	<-90	-28	-27	-26
Acid number	mg KOH/g	0.06	0.05	0.05	0.06
Water content	%	0.01	0.06	0.05	0.05
Phosphorus level	%	11.7	8.3	8.0	8.1
Flash point	°C	155	240	245	255

- Low toxicity
- Biodegradable (many but not all products)
- Compatible with most other types of additives (particularly the neutral esters)
- Soluble in a wide range of base stocks, both mineral oil and synthetic, and able to assist the solvency of other additives

Although the physical properties of phosphorus-containing additives are not critical, the values for the most widely used types of phosphate ester AW additives are given in Table 3.17, with TiBP as an example of an alkyl phosphate, TCP as a natural phosphate, and ISO 32 grades of both types of synthetic ester.

The major suppliers of phosphorus-containing lubricant additives are listed in Table 3.18, and their current oil industry applications are summarized in Table 3.19. Undoubtedly, the most important applications for the neutral aryl phosphates are hydraulic, turbine, and general circulatory oils, whereas almost the entire market for the ethoxylated alkyl and aryl acid phosphates is to be found in metalworking. The acid phosphates, acid phosphites, and amine salts of these acidic materials are used in a mixture of metalworking, gear oils, hydraulic oils, etc., as indicated in Table 3.19.

The selection of an AW/EP additive depends on the specific requirements for the application; for example, whether both AW and EP performance is needed and what levels are required. When this has been ascertained, secondary considerations may be the level of stability required (oxidative or hydrolytic), potential interaction with other components of the formulation, and the effect on surface-active properties such as foaming. Table 3.20 attempts to identify the additives that should

TABLE 3.18 Principal Suppliers of Ashless Phosphorus-Containing Lubricating Oil Additives

TABLE 3.19**Principal Applications for Ashless Phosphorus-Containing AW/EP Additives**

Application	Triaryl Phosphate	Trialkyl Phosphate	Amine Phosphate	Acid Phosphates	Alkyl/Aryl Phosphites
<i>Automotive</i>					
ATF				✓	✓
Gear oil			✓		
Power steering	✓				
Shock absorber	✓				
Electric motor	✓				
<i>Industrial</i>					
Hydraulic oils	✓		✓		
Gear oil			✓	✓	✓
Turbine oils	✓	✓			
Compressor oils	✓				
Gas oil	✓		✓		
Universal tractor	✓				
Metalworking	✓	✓	✓	✓	✓
Grease	✓		✓	✓	
Way oils	✓				
Circulating oil	✓				
Vegetable oil		✓			
<i>Aircraft</i>					
Piston engine	✓				
Turbine engine	✓				
Grease	✓		✓	✓	

be given prime consideration when taking these secondary requirements into account. Products that demonstrate better AW than EP activity, and vice versa, are shown. However, the boundary between AW and EP performance is not clear-cut and much depends on the application requirements.

3.7 TOXICITY AND ECOTOXICITY

It was mentioned earlier in this chapter that concern had been expressed in the past regarding the toxicity of phosphorus-containing products, particularly TCP. Today, with increasing focus on the environmental behavior of chemicals, their ecotoxicity is also under scrutiny. As a result, detailed investigations into both the toxicity and the ecotoxicity have been carried out on alkyl and aryl phosphate esters. The results are summarized in recent publications [59,167], and most are available in the safety data sheets associated with different product types. The data demonstrate a relatively low (but variable) order of toxicity and ecotoxicity. No significant risks in handling are anticipated, provided the manufacturer's guidance, which is essentially the same as for mineral oils, is followed.

The concerns over TCP arose as a result of the *o*-cresol content in the feedstock as tri-*ortho*-cresyl phosphate (TOCP) was found to be a significant neurotoxin. Initially, the level of *o*-cresol in the feedstock was high (up to ~25%) and significant amounts of TOCP were present in the finished product. Although the initial focus was on TOCP, it was later acknowledged that any isomer containing the *o*-cresyl moiety was neurotoxic (e.g., mono-*o*-cresyldiphenyl phosphate was said to be 10 times more neurotoxic than TOCP [168]). For these reasons, the *o*-cresol content of the feedstock used in the manufacture of TCP has been progressively reduced over time. In recent years, production has moved to the use of 99% minimum *m*- and *p*-cresol. Levels of *o*-cresol in the feedstock are now frequently <0.05%, and the TOCP content can be as low as parts per billion. Mackerer et al. [169]

TABLE 3.20
Guidance on the Selection of AW and EP Additives

Required Characteristic	Good AW Performance	Good EP Performance	Combination of AW and EP Performance
Non-phenolic additive	Neutral alkyl phosphates; dialkyl alkyl phosphonates	Acid alkyl phosphates; acid alkyl phosphonates and their salts; neutral and acid alkyl phosphites	Mixtures of neutral and acid phosphates, etc.
Good hydrolytic stability	TXP, dialkyl alkyl phosphonates	Acid alkyl phosphonates and their salts	—
Good oxidation stability	Neutral tertbutylphenyl phosphates	Hindered aryl phosphites	—
Low foaming/air release	Neutral phosphates, dialkyl alkyl phosphonates	Neutral phosphites	—
Good toxicity performance	Neutral tertbutylphenyl phosphates	Acid IPPPs	—
Good ecotoxicity performance	Neutral IPPPs	—	—
Multifunctionality, for example, rust inhibition, antioxidant		Neutral and acid phosphites, acid phosphates	Acid IPPPs

estimate that the toxicity of the TCP now available commercially is ~400 times less than that of material available in the 1940s and 1950s, and a recent evaluation of the organophosphorus-induced delayed neurotoxicity (OPIDN) of a commercial aviation gas turbine oil containing TCP was negative [170]. However, in view of past concerns, the use of TCP is now largely restricted to aviation gas turbine oils. Most general industrial applications that require an aryl phosphate AW additive now use the isopropylphenyl or, to a lesser extent, the tertiarybutylphenyl variants. In standard tests, neither of these types display OPIDN from acute oral ingestion. There are, however, some differences in the toxicity and the ecotoxicity behavior between the different aryl phosphates. For example, the reproductive toxicity of the synthetic aryl phosphates, together with TXP, was recently studied in rats (according to Organisation for Economic Co-operation and Development [OECD] method 422). Both the isopropylphenyl phosphate and the TXP showed adverse effects at moderate to high dose levels, but these were reversible when exposure ceased. The TBPP (produced according to reaction 3.2) did not display any adverse effects.

Differences are also seen in ecotoxicity behavior. Owing to the high TPP content in the lower-viscosity grades of the synthetic phosphates (particularly ISO VG 22 and 32), these products have the worst ecotoxicity behavior. The tertiarybutylphenyl phosphates normally have a higher TPP content than the corresponding grade of IPPP and therefore, of the synthetic phosphates, possess relatively worse ecotoxicity. By comparison, the IPPPs generally show satisfactory behavior in these tests. One ISO VG 46 isopropylphenyl phosphate-based AW/EP additive has, for example, been approved by the German Environment Agency (Umweltbundesamt) for use in rapidly biodegradable hydraulic fluids, products that are eligible for the “Blue Angel” environmental award [171].

Another difference between the product types is displayed in biodegradability tests. The tests were carried out according to OECD method 301F (Manometric Respirometry). In this test, biodegradation is measured as the net oxygen uptake over that occurring in blank tests containing only

TABLE 3.21
OECD 301F Biodegradability Data on Different Types of Aryl Phosphates

Product (ISO VG 46 Base Stocks)	% Biodegradability After		
	10 Days	28 Days	68 Days
TXP	5	29	70
IPPP	18	47	65
TBPP	25	62	72

inoculated medium. The extent of biodegradation is calculated from the mass of test material added to the test vessels and its theoretical oxygen demand for complete biodegradation. The test was carried out in triplicate on the ISO VG 46 grades of different types of aryl phosphates manufactured according to reaction 3.2. The results are summarized in Table 3.21.

The results are initially in the order of their hydrolytic stability, but it is interesting that TXP, after a slow start, eventually reaches the same level as the synthetic fluids and might have exceeded them had the test been extended.

In view of these data, the tertiarybutylatedphenyl phosphate would be regarded as readily biodegradable (Pw1), whereas the TXP and IPPP would be classified as inherently biodegradable (Pw2).

Despite of relatively benign ecotoxicity of the *higher* viscosity grades of aryl phosphates, all these products are classified as marine pollutants because of the UN Marine Pollutant Classification. However, because they are used at low concentrations, they are unlikely to contribute significantly to the finished product's ecotoxicity.

The toxicity of other phosphorus-containing compounds is less well documented. Drake and Calamari [172] indicate that dialkyl alkyl phosphonates generally have a low level of acute toxicity, which decreases with increasing chain length, apparently a general observation for these classes of compounds. As with alkyl phosphates, certain short-chain products can be skin irritants. No clues were found to their environmental behavior, but in view of the absence of phenolics and improved hydrolytic stability, it might be surmised that fish toxicity could be good but biodegradability would be inferior to that of the phosphates. Neutral phosphites, particularly the alkyl phosphites, would be expected to have good toxicity and biodegradability behavior, but their ease of hydrolysis, which is the factor assisting the biodegradation, would probably result in poor aquatic toxicity. The future of the nonylphenyl phosphites is uncertain; the U.S. National Toxicology Program currently lists nonylphenol as an estrogen mimic and also as a thyroid disruptor. The acid phosphates, acid phosphites, and their salts, particularly amine salts, are likely to be classified as irritants and, due to their ease of hydrolysis, may again be toxic to aquatic organisms. In all cases, it is essential that reference be made to the health and safety information provided by the manufacturer.

3.8 THE FUTURE FOR ASHLESS PHOSPHORUS-BASED LUBRICATING OIL ADDITIVES

Although ashless phosphorus-containing additives are used in many industrial applications, there are certain market segments where they have not, to date, been successful. These are principally in automotive engine oils where the use of ZDDP dominates due to a combination of price and multifunctionality and in gear oils where sulfur continues to be the EP additive of choice. However, the use of chlorine as an EP additive, particularly in metalworking applications, is in decline for environmental reasons and is expected to be slowly substituted by P/S combinations. The use of sulfur alone in applications requiring high EP performance may also move to P/S mixtures to reduce the total sulfur level and the ability to more readily "tailor" the balance of AW and EP performance

to the application. The potential in other market segments including those traditionally using ZDDP is discussed in greater detail in the following:

3.9 LUBRICATING OIL FORMULATIONS (GENERAL)

The current trend toward the use of groups II and III mineral oil base stocks for general industrial applications, with improved antioxidant response but inferior lubricity as a result of the removal of aromatics and sulfur compounds, could encourage the wider use of phosphorus. The lack of competition for the surface, which has previously been shown for TCP in stocks containing naphthenics and aromatics, should result in the increased activity of phosphorus compounds. Their use may also be beneficial due to their ability to aid the dissolution of additives that might otherwise have limited solubility.

In Europe, legislation (Directive 2000/769/EC) implemented in 2004 requires a substantial reduction in sulfur dioxide (SO_2) emissions from the combustion of waste materials including waste oil. This may result in a move to lower sulfur levels in lubricating oils (including metalworking oils) and a possible replacement by phosphorus to restore the level of AW/EP performance.

3.10 HYDRAULIC OILS

In recent years, there has been a move toward the use of ashless hydraulic oils. This is mainly for two reasons. First, as a result of the sensitivity of ZDDPs toward moisture and the resulting deposition of zinc oxide/sulfide. This deposit can adversely affect the filterability of the oil and reduce oxidation stability. Second, there is increasing concern regarding the environmental behavior of heavy metals. Regulatory controls, however, are likely to extend further to cover metals such as zinc, as in the Great Lakes Initiative between the United States and Canada. As the zinc cannot be easily removed from waste at the effluent plant, there has been a focus on the reduction in use levels.

Concern has also been expressed in certain countries regarding the smell of sulfur arising from the degradation of the ZDDP when the hydraulic oil is used, for example, in elevators (Dixon, R., Shell Global Solutions, Private Communication, November 2007).

3.11 AUTOMOTIVE ENGINE OILS

Vehicle emissions legislation (e.g., in the United States, Europe, and Japan) now exists to control and substantially reduce the levels of particulates, hydrocarbons, carbon monoxide, and oxides of nitrogen in the engine exhaust. The engine manufacturers have met these requirements by a variety of design changes that impact the composition of oils and fuels in the following ways:

- The introduction of catalytic converters to oxidize the hydrocarbon and carbon monoxide components to carbon dioxide and water, and reduce the nitric oxide (NO) to nitrogen, has been very successful in reducing emissions. When they operate at their normal operating temperature and optimum level of efficiency, they are almost 100% efficient and most of the remaining emissions occur in the time before the catalyst reaches “light-off” temperature. Many studies into reducing this period to achieve yet lower emissions have been conducted. Although much success has been achieved, further progress may be hindered by the formation of a deactivating film on the catalyst surface by the phosphorus from the ZDDP antioxidant and AW/EP additive. As a consequence, there is pressure to reduce the phosphorus content of engine oils to minimize catalyst fouling. Currently, oil specifications such as ILSAC GF-4 and ACEA Cx limit the phosphorus content of both diesel and gasoline engine oils to 0.05–0.09% with the actual level being linked to the amount of catalyst used and the expected service interval. Further reductions below 0.05% are being considered, but there is a concern that such a low level could adversely affect the durability of certain engine parts, for example, the valve train and timing chain, as reducing the ZDDP content also reduces the wear protection. However, a recent study [173] suggests that

the behavior of phosphorus compounds in wear and catalyst tests varies according to the way in which phosphorus is incorporated into the molecule. Further work reports that it is possible to achieve improvements in catalyst protection (and fuel economy) by reducing the ZDDP content and then adding a metal-free phosphorus-containing AW additive [174].

- In an attempt to increase fuel economy, the so-called fuel-efficient lubricants are being developed. These are usually lower-viscosity products (since energy losses decrease with viscosity), sometimes complemented by the use of friction modifiers. However, low-viscosity oils may cause increased wear of some engine components, and the necessity for improving the wear protection is being studied. The ILSAC GF-5 specification, for example, will necessitate the use of some form of friction modifier to guarantee the required level of economy. Currently, molybdenum compounds or long-chain esters are under evaluation, but other approaches (e.g., the use of functionalized viscosity modifiers) are also being studied as the ability of these additives to deliver reduced friction over long periods is uncertain (Mainwaring, R., Shell Global Solutions, U.K.). ZDDP is linked to increased friction and therefore reduced ZDDP levels may also be required.
- To reduce the particulate (soot) levels in exhaust gas, the diesel engines in many passenger cars and trucks need to use particulate filters. These filters can also remove the ash-containing residue produced from metallic fuel and lubricant additives, and if they are not occasionally cleaned, they will block causing a deterioration in engine performance. The engine builders, however, are trying to preserve or even extend service intervals and consequently are interested in reducing the ash content of the oil. Although ZDDP is not the only source of metals in the oil, a reduction in zinc content will follow automatically from any reduction in the phosphorus content (as long as ZDDP remains in formulations) and will therefore help to reduce engine oil ash content (Mainwaring, R., Shell Global Solutions, U.K.).
- One of the techniques used to remove the soot from the particulate filters (and thereby maintain an acceptable engine back pressure) has been to oxidize the deposited carbonaceous material by nitrogen dioxide (NO_2). This is obtained from the exhaust gas by catalytically oxidizing the NO component. The oxidation of the soot to carbon dioxide effectively removes carbonaceous filter deposits, and the NO_2 is such a powerful oxidant that it enables the process to be carried out at a relatively low temperature ($\sim 250^\circ\text{C}$). Unfortunately, the catalyst used to oxidize the NO preferentially oxidizes any SO_2 in the exhaust, thereby reducing the efficiency of the NO conversion. Additionally, the sulfur trioxide (SO_3) formed passes through the trap in the gas phase and is converted there into sulfuric acid by the water in the exhaust. The sulfuric acid (monitored as “sulfates”) contributes, as droplets, to the overall level of particulate emissions and is clearly undesirable if the exhaust gas is inhaled. Any reduction in sulfur content by lowering ZDDP levels in engine oils also reduces the phosphorus content arising from this additive. Supplemental phosphorus may therefore be needed.
- Increased emphasis on fuel economy led some manufacturers to introduce direct injection stratified charge gasoline engines. Conventional catalysts cannot remove oxides of nitrogen (NO_x) in these “lean-burn” engines, and, as a result, NO_x storage catalysts have been developed in which the oxides are stored as nitrates by reaction with barium sulfate contained in the catalyst coating. When the barium-containing sites become saturated, the engine switches to stoichiometric or slightly rich operation at which temperature the nitrates break down and release the NO_x , thus promoting its reduction through the conventional route of reaction with hydrocarbons and carbon monoxide. Unfortunately, barium sites react preferentially with any sulfur oxides present, reducing their ability to “store” NO_x . As a consequence, there is again pressure to reduce the fuel sulfur content. However, these levels are already being lowered (see “Fuels” below), and at such levels, the engine oil begins to be a significant

contributor to exhaust “sulfur” content. A debate has therefore arisen regarding the future level of lubricant sulfur, and diesel engine manufacturers have already expressed interest in lubricants with a sulfur level as low as 0.2%—considerably below the current value of ~1% (Mainwaring, R., Shell Global Solutions, Private Communication, January 2008).

In 1999, the European Union (EU) issued emission requirements for heavy-duty diesels that anticipated significant reductions in NO_x , CO, unburnt hydrocarbons, and particulates over the period from 2001 to 2008. The greatest challenge was to lower NO_x while at the same time reducing particulates as measures to correct the former normally resulted in an increase in the latter. In addition, in reducing NO_x , the efficiency of the diesel engine would be impaired, and the result would be an increase in fuel consumption and CO_2 emissions. However, a technique called selective catalytic reduction (SCR) has now been developed and adopted by several engine manufacturers in the EU [175]. This involves injecting an aqueous solution of urea ($\text{CO}(\text{NH}_2)_2$) into the exhaust stream where it degrades to carbon dioxide and ammonia (NH_3). The NH_3 then reduces the NO_x to nitrogen (N_2) and water on a tungsten/vanadium catalyst. It is obviously important to avoid NH_3 being released into the atmosphere, and another catalyst is required to oxidize any residual NH_3 while avoiding oxidation of the nitrogen.

To date, SCR (low NO_x but high particulates) has generally been favored over diesel particulate filters (high NO_x but low particulates) for reducing emissions by many EU manufacturers. It allows engines to operate more efficiently—indeed sufficiently so as to more efficiently and more than offsets the cost of the urea. However, although it is an effective technique, there are concerns about its size, weight, guaranteed availability throughout Europe, and its efficacy at the lower temperatures encountered in the exhaust of light-duty applications. These problems have so far prevented its application to passenger cars. The effects on pollution if urea is not used in a system designed for its use and how the solution would be made available to the ordinary motorist are currently the subject of further investigation and debate.

3.12 FUELS

- As a result of the concern regarding the direct and indirect impacts of fuel sulfur on engine emissions, there is pressure to reduce the sulfur content. In the EU, a limit of 50 ppm maximum sulfur in diesel fuel was introduced in 2005, with a further reduction to 10 ppm in 2008 for gasoline engines and in 2009 for diesel engines. At such low levels, it may be necessary to restore the lubricity of the fuel by additives, and incorporating a small amount of phosphorus has been shown to be effective [176].
- Considerable concern currently surrounds carbon dioxide emission and its connection with global warming. Within the EU, the auto producers have reached a voluntary agreement with the commission to achieve a carbon dioxide emission target of 140 g/km by 2008 with a further reduction to 130 g/km by 2012. This will encourage a move toward more fuel-efficient vehicles, particularly those that are smaller and lighter, and perhaps also to thinner lubricants requiring even better AW protection.

In the United States, the Senate has ruled that carbon dioxide emission from trucks are a pollutant rather than a “by-product” of combustion. This is expected to promote reductions in carbon dioxide levels and hence encourage the use of lower viscosity, more fuel-efficient diesel engine oils (Mainwaring, R., Shell Global Solutions, Private Communication, January 2008).

3.13 CONCLUSIONS

Ashless phosphorus-containing additives are available in a wide range of structures and performance. Although most are used as AW and EP additives for industrial oils, they can also function as antioxidants, rust inhibitors, metal passivators, and detergents. In some cases, the multifunctionality

can be found within the same molecule. Their advantageous physical properties—for example, low color and odor and good solubility for other additives—make them attractive components for additive packages. However, although the future looks bright in industrial oil applications in view of current pressure on sulfur and chlorine (mainly as a result of environmental concerns), the potential in automotive engine oil remains uncertain due to the current downward pressure on phosphorus. In fuels, the question is whether the reduced level of sulfur will require replacement by other AW additives and, if so, whether phosphorus can be incorporated without adversely affecting other properties (e.g., catalyst efficiency).

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APPENDIX A: EARLY PATENT LITERATURE ON PHOSPHORUS-CONTAINING COMPOUNDS

NEUTRAL PHOSPHATES

U.S. Patent 2,723,237, Texas Oil Co.

NEUTRAL PHOSPHITES

As AW/EP Additives

British Patent 1,052,751, British Petroleum (chloreethyl phosphite and a chlorparaffin)

British Patent 1,164,565, Mobil Oil Corp. (alkyl or alkenyl phosphite and a fatty acid ester)

British Patent 1,224,060, Esso Research and Engineering Co.

U.S. Patent 2,325,076, Atlantic Refining Co.

U.S. Patent 2,758,091, Shell Development Co. (haloalkyl or haloalkarylphosphites)

U.S. Patent 3,318,810, Gulf Research & Development Co. (phosphites and molybdenum compounds)

As Antioxidants

U.S. Patent 2,326,140, Atlantic Refining Co.

U.S. Patent 2,796,400, C.C. Wakefield & Co.

ACID PHOSPHATES/PHOSPHITES

British Patent 1,105,965, British Petroleum Co Ltd. (acid hydrocarbyl phosphite and phosphates or thiophosphates or phosphoramidates)

British Patent 1,153,161, Nippon Oil Co.
 U.S. Patent 2,005,619, E. I. du Pont de Nemours
 U.S. Patent 2,642,722, Tide Water Oil Co.
 French Patent 797,449, E.I. du Pont de Nemours

PHOSPHONATES

British Patent 823,008, Esso Research and Engineering Co. (dicarboxylic acid and either a haloalkane phosphonate, a haloalkyl phosphate or phosphite and optionally a neutral alkyl or aryl phosphate)
 British Patent 884,697, Shell Research Ltd. (dialkenyl phosphonates)
 British Patent 899,101, British Petroleum Co. (amino phosphonates)
 British Patent 993,741, Rohm and Haas Co. (aminoalkane phosphonates)
 British Patent 1,083,313, British Petroleum Co. (amino phosphonates)
 British Patent 1,247,541, Mobil Oil Corp. (Dialkyl-*n*-alkylphosphonate or alkylammonium salts of dialkylphosphonates)
 U.S. Patent 2,996,452, US Sec of Army (di-(2-ethylhexyl) lauroxyethyl phosphonate)
 U.S. Patent 3,329,742, Mobil Oil Corp. (diaryl phosphonates)
 U.S. Patent 3,600,470, Swift & Co. (hydroxy or alkoxy phosphonates and their amine salts)
 U.S. Patent 3,696,036, Mobil Oil Corp. (tetraoctyl-(dimethylamino) methylene diphosphonate)
 U.S. Patent 3,702,824, Texaco Inc. (hydroxyalkylalkane phosphonate)

ALKYL- AND ARYLPOLYETHYLENEOXY-PHOSPHORUS COMPOUNDS

U.S. Patent 2,372,244, Standard Oil Dev. Co.

AMINE SALTS

British Patent 705,308, Bataafsche Petroleum Maatschappij (substituted monobasic phosphonic acid and amine salts thereof)
 British Patent 978,354, Shell International Research (alkali metal-amine salt of a halohydrocarbyl phosphonic acid)
 British Patent 1,002,718, Shell International Research (alkylamine salt of diaryl acid phosphate)
 British Patent 1,199,015, British Petroleum Co. Ltd. (quaternary ammonium salts of dialkyl phosphates)
 British Patent 1,230,045, Esso Research and Engineering Co. (quaternary ammonium salts of alkyl phosphonic and phosphonic acids)
 British Patent 1,266,214, Esso Research and Engineering Co. (neutral phosphate and a neutral alkylamine hydrocarbyl phosphate)
 British Patent 1,302,894, Castrol Ltd. (tertiary amine phosphonates)
 British Patent 1,331,647, Esso Research and Engineering Co. (quaternary ammonium phosphonates)
 U.S. Patent 1,936,533, E. I. du Pont de Nemours. (triethanolamine salts)
 U.S. Patent 3,553,131, Mobil Oil Corp. (tertiary amine phosphonate salts)
 U.S. Patent 3,668,237, Universal Oil Products Co. (tertiary amine salts of polycarboxylic acid esters of bis(hydroxyalkyl)-phosphinic acid)

PHYSICAL MIXTURES OF PHOSPHORUS AND SULFUR AND CHLORINE COMPOUNDS

British Patent 706,566, Bataafsche Petroleum Maatschappij (a phosphorus compound, e.g., a trialkyl phosphate, a glycidyl ether and a disulphide)
 British Patent 797,166, Esso Research and Engineering Co. (TCP and a metal soap of a sulphonic acid)
 British Patent 841,788, C.C. Wakefield & Co. Ltd. (chlorinated hydrocarbon, a disulphide, and a dialkyl phosphite)
 British Patent 967,760, The Distillers Co. Ltd. (disulphides, chlorinated wax, and a haloalkyl ester of an oxy-acid of phosphorus)
 British Patent 872,899, Esso Research and Engineering Co. (trialkyl phosphates and chlorinated benzene)
 British Patent 1,222,320, Mobil Oil Corp. (diorganophosphonate and a sulphurized hydrocarbon or sulphurized fat)

- British Patent 1,287,647, Stauffer Chemical Co. (phosphonates or halogenated alkylphosphates, sulphurised oleic acid, and sebacic acid)
- British Patent 1,133,692, Shell International (TCP and triphenylphosphorothionate)
- British Patent 1,162,443, Mobil Oil Corp. (neutral or acid, alkyl or alkenyl phosphite, and a sulphurized polyisobutylene, triisobutylene, or a sulphurized dipentene)
- U.S. Patent 2,494,332, Standard Oil Dev. Co. (thiophosphates and TCP)
- U.S. Patent 2,498,628, Standard Oil Dev. Co. (sulfurized/phosphorized fatty material and TCP or tricresyl phosphite)
- U.S. Patent 3,583,915, Mobil Oil Corp. (di(organo)phosphonate, and an organic sulphur compound selected from sulphurized oils and fats, a sulphurized monoolefin or an alkyl polysulphide)

MISCELLANEOUS PHOSPHORUS COMPOUNDS

- British Patent 1,035,984, Shell Research Ltd. (diaryl chloralkyl phosphate or thiophosphate)
- British Patent 1,193,631, Albright & Wilson Ltd. (hydroxylalkyl disphosphonic acid/alkylene oxide reaction products)
- British Patent 1,252,790, Shell International Research (pyrophosphonic and pyrophosphinic acids and their amine salts)
- U.S. Patent 3,243,370, Monsanto Co. (phosphinylhydrocarbyloxy phosphorus esters)
- U.S. Patent 3,318,811, Shell Oil Co. (diacid diphosphate ester)
- U.S. Patent 3,640,857, Dow Chemical Co. (tetrahaloethyl phosphates)

APPENDIX B: ADDITIONAL LITERATURE AND PATENT REFERENCES ON THE MECHANISM AND PERFORMANCE OF PHOSPHORUS-CONTAINING ADDITIVES

NEUTRAL PHOSPHATES

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4 Detergents

Syed Q. A. Rizvi

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4.1 INTRODUCTION

Modern equipment must be lubricated to prolong its lifetime. A lubricant* performs a number of critical functions. These include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage [1]. Lubricant comprises a base fluid and an additive package. The primary function of the base fluid is to lubricate and act as a carrier of additives. The function of additives is either to enhance an already-existing property of the base fluid or to add a new property. The examples of already-existing properties include viscosity, viscosity index, pour point, and oxidation resistance. The examples of new properties include cleaning and suspending ability, antiwear performance, and corrosion control. The extent of the desirability of various properties differs from lubricant to lubricant and largely depends on the conditions of use. Automotive use, for example, requires lubricants with good oxidation resistance, suitable low- and high-temperature viscosities, high-viscosity index (i.e., minimum loss in viscosity with an increase in temperature), and good cleaning and suspending ability. Conversely, the use as nonautomotive lubricants, such as industrial and metalworking lubricants, emphasizes oxidation resistance, antiwear performance, corrosion control, and cooling ability.

One of the most critical properties of the automotive lubricants, especially engine oils, is their ability to suspend undesirable products from thermal and oxidative degradation of the lubricant. Such products form when the by-products of fuel combustion, such as hydroperoxides and free radicals, go past piston rings into the lubricant and, being reactive species, initiate lubricant oxidation. The resulting oxidation products are thermally labile and decompose to highly polar materials with a tendency to separate from the bulk lubricant and form surface deposits and clog small openings. The former will lead to malfunctioning of the closely fitted surfaces, such as those between pistons and cylinder walls, and the latter will impair oil flow to parts needing lubrication. The separation tendency of these products relates to their high polar to nonpolar ratio [2], which makes them less soluble in largely nonpolar base oil. A lubricant with high-oxidation resistance, due to the quality of the base fluid or the presence of a good oxidation inhibitor additive package, will slow down the formation of these undesirables.

* The terms “lubricant” and “oil” are interchangeable and are different from the terms “base oil” and “base fluid.” Lubricant and oil imply base oil or a base fluid plus additives.

Oxidation inhibitors, detergents, and dispersants make up the general class of additives called *stabilizers* and *deposit control agents*. These additives are designed to control deposit formation, either by inhibiting the oxidative breakdown of the lubricant or by suspending the harmful products already formed in the bulk lubricant. Oxidation inhibitors intercept the oxidation mechanism, and dispersants and detergents perform the suspending part [3,4]. *Detergents* are the topic of this chapter, and *dispersants* are the topic of the subsequent chapter. Detergents are metal salts of organic acids that frequently contain associated excess base, usually in the form of carbonate. Dispersants are metal-free and are of higher molecular weights than detergents. The two types of additives work in conjunction with one another.

The final products of combustion and lubricant decomposition include organic and inorganic acids, aldehydes, ketones, and other oxygenated materials [4,5]. The acids have the propensity to attack metal surfaces and cause corrosive wear. Detergents, especially basic detergents, contain reserve base that will neutralize the acids to form salts. Although this decreases the corrosive tendency of the acids, the solubility of the salts in the bulk lubricant is still low. The organic portion of the detergent, commonly called *soap*, has the ability to associate with the salts to keep them suspended in the bulk lubricant. However, in this regard, detergents are not as effective as dispersants because of their lower molecular weight. The soap in detergents and dispersants also has the ability to suspend nonacidic oxygenated products such as alcohols, aldehydes, and resinous oxygenates [4]. The mechanism by which this occurs is depicted in Figure 4.1.

Dispersants and detergents together make up the bulk, ~45 to 50%, of the total volume of the lubricant additives manufactured. This is a consequence of their major use in engine oils, transmission fluids, and tractor hydraulic fluids; all of which are high-volume lubricants [6].

As mentioned earlier, detergents neutralize oxidation-derived acids as well as help suspend polar oxidation products in the bulk lubricant. Because of this, these additives control rust, corrosion, and resinous buildup in the engine. Like most additives, detergents contain a surface-active polar functionality and an oleophilic hydrocarbon group, with an appropriate number of carbon atoms to ensure good oil solubility [2]. Sulfonate, phenate, and carboxylate [7] are the common polar groups present in detergent molecules. However, additives containing salicylate and thiophosphonate functional groups are also sometimes used.

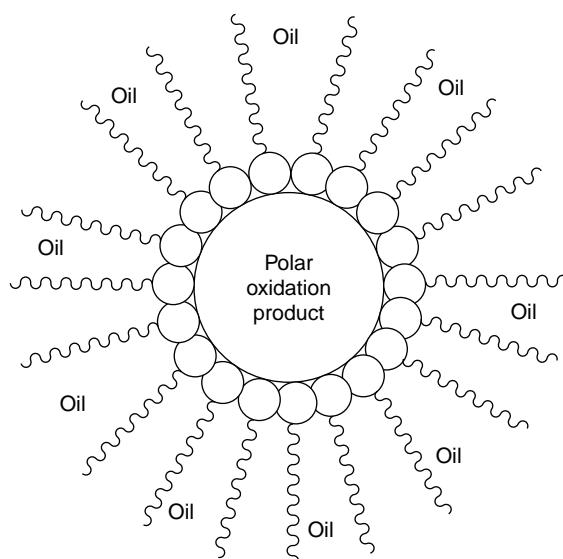


FIGURE 4.1 Oil suspension of polar oxidation products.



a and *c* = 1 and *b* = 2, if the metal M is monovalent; *a* and *c* = 2 and *b* = 1, if the metal M is divalent

FIGURE 4.2 General formulas for detergents. (Adapted from Rizvi, S.Q.A., Additives and additive chemistry., *ASTM Manual on Fuels and Lubricants*.)

4.2 DETERGENT TYPES

Detergents are the metal salts of organic acids. The acids normally used to synthesize these compounds include arylsulfonic acids such as alkylbenzenesulfonic acids and alkynaphthalenesulfonic acids [8–11]; alkylphenols [12–16]; carboxylic acids such as fatty carboxylic acids, naphthenic acids, and petroleum oxidates [17–20]; and alkenylphosphonic and alkenylthiophosphonic acids [21–23]. Sometimes, a mixture of different types of acids is also employed [24]. The reaction of these acids with inorganic bases, such as metal oxides, metal hydroxides, and metal carbonates, results in the formation of salts [7]. The quantity of the metal used may be equal to (stoichiometric amount) or in excess of the exact amount necessary to completely neutralize the acid functionality. The presence of metal in stoichiometric amount results in the formation of the neutral salt, often referred to as a neutral detergent or soap. If the metal is present in excess, the detergents are called *basic*, *overbased*, or *superbased* [7,25]. It is important to note that basic detergents appear as clear homogeneous fluids, the same as neutral detergents, because the excess metal is present in a colloidal form [26]. The general formulas for metal sulfonates, metal phenates, and metal carboxylates are presented in Figure 4.2.

The excess base in basic detergents may be present as metal hydroxide, metal carbonate, or both. For neutral detergents, *x* and *y* in the formulas in Figure 4.2 are zero. For low overbased detergents, such as those with a base number of about 50 or less, *x* may be zero and *y* may be a low number, or both *x* and *y* may be low numbers. This implies that slightly overbased detergents are either carbonate-free or contain a mixture of both the hydroxide and the carbonate. Highly overbased detergents invariably have a large amount of carbonate as the reserve base. That is, in their case, *y* is low and *x* is very high. In some cases, *x* can be as high as 20, or more. In summary, the excess base per equivalent of acid in metal hydroxide-containing detergents is generally lower than that in metal carbonate-containing detergents.

4.3 DETERGENT PARAMETERS

Detergents are described chemically in terms of their metal ratio, percent sulfated ash, degree of overbasing or conversion, soap content, and total base number (TBN) [7].

The *metal ratio* is defined as the total equivalents of metal per equivalent of acid. The *percent sulfated ash* is the ash produced when the detergent is treated with sulfuric acid and burned. All organic material in the detergent burns, leaving behind the metal sulfate ash. Sulfate ash results from the reaction of metal compound with sulfuric acid either directly, as with metal hydroxide and metal carbonate, or through the oxidative degradation of the metal sulfonate. Detergents are not the only additives that result in sulfate ash. Other metal-containing additives in the lubricant also contribute toward it. Such additives include metal carboxylates and metal dialkyldithiophosphates such as zinc dialkyldithiophosphate. The former compounds are sometimes used as friction modifiers and corrosion inhibitors, and the latter compounds are commonly used as oxidation inhibitors and antiwear agents. Because the metal compounds can lead to the formation of the inorganic material

(ash) on combustion, a formulator must know the metal content of a formulation to offset any problem that might occur. This is because the lubricant travels past piston rings into areas that experience flame and high temperatures, such as the top land and the groove behind the top ring; it burns to produce ash. Ash is undesired because it is believed to initiate deposit formation. Sulfated ash is one of the methods used to assess the metal content of a lubricant, and the methods to determine this are described in the ASTM Standards D 482 and D 874 [27].

The *degree of overbasing* is the number of equivalents of the metal base per equivalent of the acid substrate. This is usually expressed as *conversion*, which indicates the amount of inorganic material relative to that of organic material. Conversion is expressed as the number of equivalents of base per equivalent of acid times 100 [7]. The *soap content* is the amount of neutral salt as a percent of detergent composition.

The TBN of the detergent reflects its ability to neutralize acids. For basic sulfonate and phosphonate detergents, only the overbased portion of the detergent, that is, the carbonate and the hydroxide (see Figure 4.2), possesses this capability. The neutral metal sulfonates and phosphonates, that is, soaps, lack this ability. However, for basic carboxylates, salicylates, and phenates, soaps also possess the acid-neutralizing ability. This is because, unlike sulfonates and phosphonates that are strong acid-strong base salts, metal carboxylates, metal salicylates, and metal phenates are strong base-weak acid salts. This makes them Lewis bases, hence the acid-neutralizing ability.

Let us try to calculate the detergent parameters for a detergent of a hypothetical molecular formula $(RSO_3)_vCa_w(CO_3)_x(OH)_y$.^{*} In this formula, v , w , x , and y denote the number of sulfonate groups, the number of calcium atoms, the number of carbonate groups, and the number of hydroxyl groups, respectively. The *metal ratio*, the total equivalents of metal per equivalent of acid, for such a detergent equals to $2w/v$. The coefficient 2 signifies the divalent nature of calcium. For metals such as sodium and potassium, which are monovalent, the ratio equals to w/v . The degree of overbasing or conversion, which is metal ratio times 100, is $(w \times 100)/v$ for monovalent metals and $(2w \times 100)/v$ for divalent metals. Neutral detergents, or soaps, have a conversion of 100 because the ratio of equivalents of base to the equivalents of acid is 1. *Soap content* for such a detergent can be calculated using the following equation:

$$\text{Percent soap} = \frac{\text{formula weight } [(RSO_3)_2Ca] \times 100}{\text{effective formula weight}} \quad (4.1)$$

The effective formula weight is the weight of all the atoms that make up the formula $(RSO_3)_vCa_w(CO_3)_x(OH)_y$ plus the diluent, if present. The diluent can be the incidental alkylate that does not get sulfonated or the diluent oil that is intentionally added. If one must add oil, most of it is added to reactants at the beginning of the reaction, especially during the manufacture of basic detergents. The presence of diluent is believed to facilitate micelle formation, thereby making the process more efficient. Adding oil after the reaction is not as effective.

The TBN indicates a detergent's ability to neutralize acids. In additives and formulated lubricants, the TBN is expressed as mg KOH/g of additive [27]. The method to determine base numbers is described in the ASTM Standard D 974 [28]. For sulfonate and phosphonate detergents, it can be calculated by using the number of equivalents of excess metal after salting the acid, that is $(2w - v)$, according to Equation 4.2.

$$\text{TBN (mg KOH/g)} = \frac{(2w - v) \times 56,100}{\text{effective formula weight}} \quad (4.2)$$

* The correct formula for such a detergent is $(RSO_3)Ca.xCaCO_3.yCa(OH)_2$.

To calculate the base number of monovalent metal-derived sulfonates, one must use only $(w - v)$ in Equation 4.2. For divalent metal-derived carboxylate, salicylate, and phenate detergents, Equation 4.3 is to be used.

$$\text{TBN (mg KOH/g)} = \frac{(2w) \times 56,100}{\text{effective formula weight}} \quad (4.3)$$

For monovalent metal salt of this type, the numerator will be $w \times 56,100$. As mentioned earlier, the *percent sulfated ash* is the quantity of solid metal sulfate that results when the detergent is treated with sulfuric acid and the mixture ignited. Theoretical sulfated ash for divalent and monovalent metals can be calculated using the following equations. Equation 4.4 is for divalent metals, and Equation 4.5 is for monovalent metals.

$$\text{Percent sulfated ash} = \frac{w \times \text{molecular weight of } \text{M}_2\text{SO}_4 \times 100}{\text{atomic weight of metal M} \times \text{effective formula weight}} \quad (4.4)$$

$$\text{Percent sulfated ash} = \frac{0.5w \times \text{molecular weight of } \text{M}_2\text{SO}_4 \times 100}{\text{atomic weight of metal M} \times \text{effective formula weight}} \quad (4.5)$$

4.4 DETERGENT SUBSTRATES

Various organic acids are used to synthesize detergents. These include alkylaromatic sulfonic acids, alkylphenols, alkylsalicylic acids, fatty carboxylic acids, and alkenylphosphonic acids. Alkylaromatic sulfonic acids, such as alkylbenzenesulfonic acids and alkynaphthalenesulfonic acids, are made by reacting the respective alkylbenzenes and alkynaphthalenes with a sulfonating agent. The alkylaromatic starting materials are made through alkylation of aromatics—benzene and naphthalene [29–33]. To make synthetic sulfonates, benzene or naphthalene is first alkylated and then sulfonated. The alkylating agent is either an alkyl halide or an olefin. The olefins can be α -olefins, internal olefins, or olefin oligomers such as polypropylene and polyisobutylene. An acid catalyst is usually required. One may choose from many acids. These include mineral acids such as sulfuric acid and phosphoric acid, Lewis acids such as aluminum chloride and boron trifluoride, organic acids such as methanesulfonic acid, and mixtures thereof [32,33]. Some of the inorganic acids such as sulfuric acid are also available on a solid support, such as Fuller's earth or silica. Unlike other catalysts that require neutralization at the end of the reaction, these catalysts just require filtration to remove them. Zeolites and related mixed-metal oxides also enjoy the same advantage as the solid alkylation catalysts [30,31]. Another class of catalysts, exemplified by Amberlysts®, is aromatic polymer-derived sulfonic acids [31,34]. Although they have the advantages of being insoluble, hence easier to remove, and of multiple use, they have the disadvantage of being expensive. It is important to note that not all catalysts have equal effectiveness in all alkylations.

Alkylaromatic sulfonic acids are derived either from the sulfonation of alkylaromatics, such as alkylbenzenes and alkynaphthalenes, or from petroleum refining. The alkylbenzenes and alkynaphthalenes are converted into respective sulfonic acids by reacting them with a sulfonating agent. The acids thus obtained are called *synthetic* sulfonic acids. Alkylbenzenesulfonic acids are also available from petroleum refining. These are referred to as *natural* sulfonic acids. Detergents made from synthetic sulfonic acids are called *synthetic* sulfonates and those made from natural sulfonic acids are called *natural* or *petroleum* sulfonates.

The steps involved in making synthetic sulfonic acids are shown in Figure 4.3. The degree of branching in alkylbenzenes and alkynaphthalenes, commonly called the *alkylate*, increases as we go from α -olefins to internal olefins to olefin oligomers. More branching of the alkylate implies

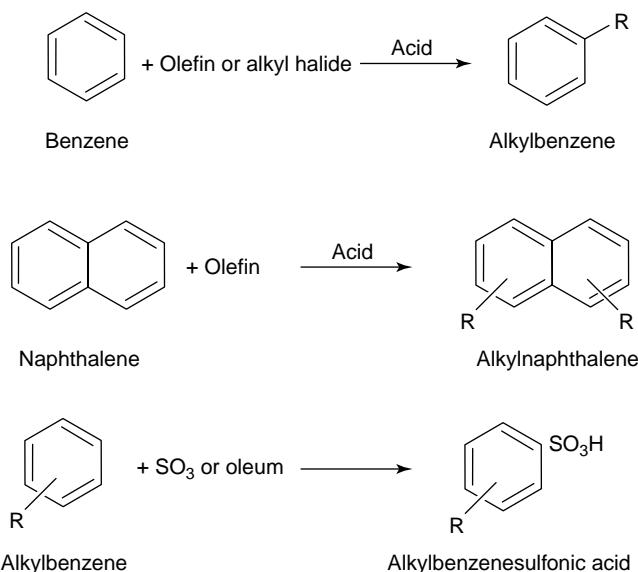


FIGURE 4.3 Synthesis of sulfonic acid substrates.

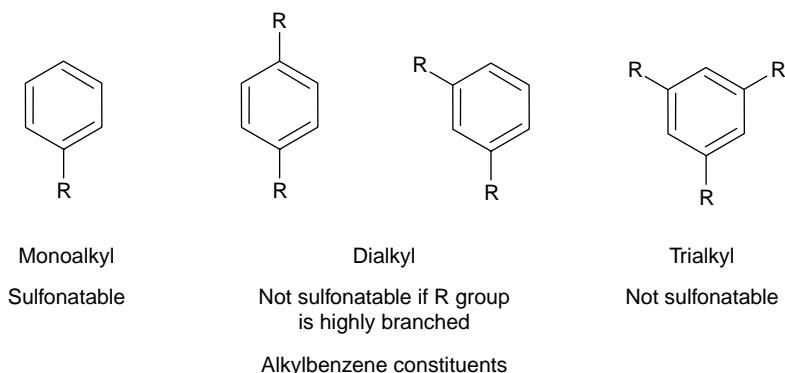


FIGURE 4.4 Alkylbenzene structures.

somewhat less-efficient sulfonation but better oil solubility of the final sulfonate detergent. The common reagents used to sulfonate alkylaromatics are sulfur trioxide, fuming sulfuric acid or oleum, and chlorosulfonic acid [35]. Oleum is 15–30% sulfur trioxide dissolved in concentrated sulfuric acid. In general, the alkylate is dissolved in a hydrocarbon solvent, such as hexane or heptane, and reacted with the sulfonating reagent. One obtains a mixture of a monosulfonic acid and disulfonic or higher sulfonic acids. The latter must be removed because of the high polarity of their metal salts, hence potentially lower oil solubility. This can be easily achieved by water washing. The disulfonic and higher sulfonic acids are also undesired because, when reacted with polyvalent metals, they have the tendency to make polymeric salts that are usually of low lubricant solubility as well.

Not all components of the alkylate are sulfonatable. In the case of alkylbenzenes, the species that do not sulfonate easily include polyalkylated benzenes, such as trialkylbenzene, or highly branched dialkylbenzenes. Their sulfonation difficulty is primarily a consequence of the steric crowding of the sulfonatable positions. Monoalkylbenzenes do not suffer from this drawback and hence sulfonate easily. In general, the sulfonation of branched alkylbenzenes is slower than linear alkylbenzenes. In the case of alkylbenzenes, Figure 4.4 shows structures that are sulfonatable and those that are not.

With naphthalene, however, steric factors are not as important because of its bicyclic nature. The alkyl groups are likely to be attached to different aryl rings, except for very highly alkylated naphthalenes. Commercial NA-SUL® products are based on alkylnaphthalene chemistry.

During petroleum refining, crude mineral oil is washed with a sulfonating agent such as sulfur trioxide or oleum [36]. Crude mineral oil contains reactive unsaturated compounds containing multiple bonds and alkyl aromatics. These react with sulfur trioxide to form sulfonic acids. This is a desirable step because oils containing unsaturates and aromatics have a greater susceptibility toward oxidative breakdown, which could lead to the formation of increased deposits. If this occurs, it is likely to lead to equipment malfunction [5,23,37–42]. An analogous process is used to manufacture medicinal-quality white oil from petroleum. In the subsequent reaction, the sulfonic acid fraction is reacted with sodium hydroxide to convert the acids into sodium salts. These salts are washed with water to extract *green acid* soaps, which are used in many consumer products. The residual water-insoluble material is then extracted with alcohol. This results in the isolation of *mahogany acid* soaps, which are useful in making detergent additives. The process is summarized in Figure 4.5.

Alkylphenols are made in a manner analogous to alkylbenzenes, that is, by alkylating phenol with an olefin in the presence of an acid catalyst. The preferred catalysts are sulfuric acid, aluminum chloride, and boron trifluoride [39–42]. The alkylphenols can be either converted directly into their neutral or basic salts or further reacted with sulfur or sulfur dichloride to form sulfur-bridged alkylphenols and with formaldehyde to form methylene-bridged alkylphenols. This is shown in Figure 4.6.

Alkylsalicylic acids are prepared from alkylphenols by reacting the alkali metal, especially potassium, phenates with carbon dioxide. The reaction is known as the Kolbe–Schmitt reaction [43]. Like the natural sulfonate process, this process yields alkali metal salts.

These must be either neutralized with a mineral acid to free acids to use them to make detergents or reacted directly with a metal halide, such as calcium chloride or magnesium chloride, to make the calcium or magnesium soaps [44].

Alkenylphosphonic and alkenylthiophosphonic acid detergents are only rarely used. The acids are prepared by reacting polyisobutylene of varying molecular weights with phosphorus pentasulfide and the subsequent hydrolysis of the resulting adduct [45,46]. The adduct is believed to result from an ene-type addition of phosphorus pentasulfide to polyolefin. This type of addition does not result in the loss of the double bond, but it shifts the double bond down the carbon chain. Unless steric factors hinder the reaction, at least theoretically, the ene product can react with another molecule of phosphorus pentasulfide. This process can extend further. The adduct is hydrolyzed by the use of steam. One obtains a complex mixture of acids that include fully hydrolyzed (sulfur-free)

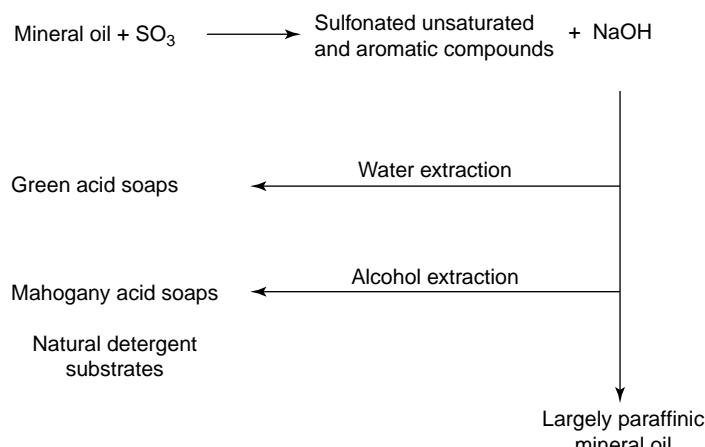


FIGURE 4.5 Isolation of *natural* sodium sulfonates.

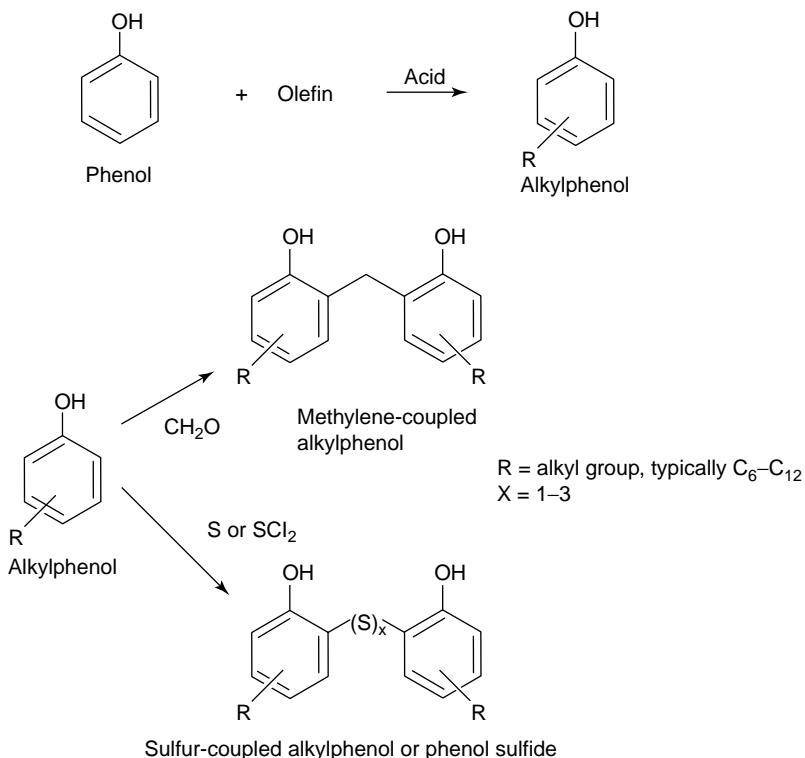


FIGURE 4.6 Synthesis of alkylphenol substrates.

alkenylphosphonic acids and partially hydrolyzed (contain residual sulfur) alkenylthiophosphonic acids. The reactions to synthesize alkylsalicylic acids and alkenylphosphonic and thiophosphonic acids are shown in Figure 4.7.

Recently, the development of basic detergents that are not derived from organic acids has been reported [47,48]. Substrates that can be overbased include organic amines and polyamines, ethers, and organic sulfides (sulfurized olefins). Only alkali metal-derived overbased materials have been reported.

4.5 SYNTHESIS OF NEUTRAL AND BASIC DETERGENTS

To make detergents, the organic acids are reacted with a metal base, such as a metal oxide or a metal hydroxide. In general, the reaction between the organic acid and the inorganic base is not good because of poor contact between the two reactants. A number of compounds, called *promoters*, are used to facilitate salt formation and the subsequent carbonation or a related reaction. Common promoters include ammonium hydroxide; low-molecular-weight carboxylic acids, such as formic acid and acetic acid; low-molecular-weight alkylphenols; and other polar compounds, such as nitroalkanes and imidazolines. A comprehensive list of such agents is provided elsewhere [49]. Most of these reagents are used in combination with water, except for high-temperature overbasing reactions where water will not stay in. In such cases, alcohols, such as 2-ethylhexanol or iso-octyl alcohol, and alkylphenols that have high boiling points are used. When water is present as part of the promoter system, it either is added or results from the neutralization reaction. The promoters are surfactants, that is, they contain a hydrophilic moiety, such as a hydroxyl group or a carboxylic acid functionality and a reasonably sized alkyl group to impart a somewhat hydrophobic character to the molecule.

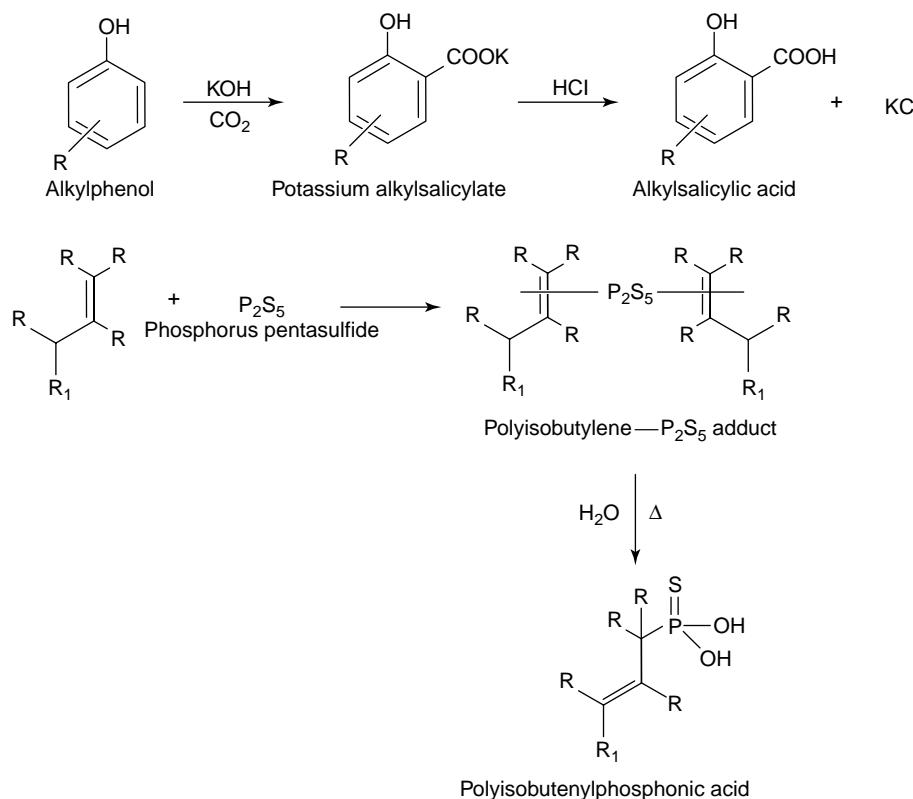


FIGURE 4.7 Synthesis of alkylsalicylic acids and alkenylphosphonic acids.

Not all promoters are effective for all overbasing reactions, and one has to experiment to select the right promoter system. For low-temperature overbasing ($\leq 100^{\circ}\text{C}$), alcohol–water mixtures are commonly used; for high-temperature overbasing ($\geq 100^{\circ}\text{C}$), low-molecular-weight alkylphenols are used. The structure of the final detergent from the two processes is believed to be different and hence the performance in certain tests. The role of promoters in the overbasing reaction is not well understood. One explanation regarding their role is based on their preferential reaction with the base to form an alkoxide or a phenoxide. This species then transfers the metal to the substrate, thereby facilitating salt formation and overbasing. The other explanation is based on their acting as a surfactant and a wetting agent. This improves contact between the base and the substrate, thereby assisting the reaction to occur. The second explanation is definitely more plausible than the first. However, in high-temperature overbasing reactions, usually carried out under anhydrous conditions, the first explanation may have merit.

Although a number of metals can be used to make neutral salts (soaps), only a few metals have the ability to result in oil-soluble basic detergents. The common metals that can be used for this purpose include lithium, sodium, and potassium in group I and magnesium, calcium, strontium, and barium in group II of the periodic table. Aluminum is the only overbasable metal in group III. Overbased salts of transition metals such as zinc, copper, cadmium, molybdenum, copper, manganese, cobalt, nickel, and iron, from sulfonic acids, alkylphenols, and naphthenic acids are also reported in the patent literature [19,50,51]. The ability to overbase relates to a metal's base strength: the higher the basic character, the easier it is to overbase. For group I metals, where basic character increases from lithium to sodium to potassium, it is easier to overbase potassium than lithium. In group II metals, the basic character increases from magnesium to calcium to strontium to barium; hence, it is easier to overbase barium than magnesium.

Various detergents derived from metal anions other than hydroxide and carbonate are reported in the patent literature. The anions include sulfites, sulfates, thiosulfates, borates, and phosphates [32,49,52–55]. These detergents are obtained either from the carbonate detergent by displacing the carbonate anion with the alternative anion or by using the anion precursor during overbasing. For example, one can obtain metal sulfite overbased detergent either by blowing sulfur dioxide during overbasing or by displacing carbon dioxide in a carbonate detergent with sulfur dioxide. The resulting metal sulfite detergent can be oxidized to a sulfate detergent by using an oxygen source, such as oxygen gas or peroxide, or to a thiosulfate detergent by reacting it with elemental sulfur [49,52,53]. Borate and phosphate overbased compositions can be made using boric acid or phosphoric acid during the reaction [54,55].

Common commercial detergents are derived from calcium, magnesium, sodium, and barium. The metals are listed in order of preference. As mentioned, neutral detergents are made by reacting the acid substrate with a stoichiometric amount of the metal base, and overbased detergents are made by reacting the substrate with an excess amount of base in the presence of carbon dioxide. To make calcium and magnesium salts from natural sulfonic acids and alkylsalicylic acids, one must convert commercially available alkali metal (sodium and potassium) salts (see Figures 4.5 and 4.7) into free acids by reacting them with a mineral acid and then reacting the acids with magnesium oxide or calcium hydroxide. Alternatively, alkali metal salts can be converted directly into magnesium and calcium salts through a double-decomposition reaction with a metal halide, as shown in Figure 4.8. To make the *natural* sulfonate detergent, one must react the mahogany acid soap with a metal halide such as calcium chloride. The reaction converts the sodium sulfonate soap into calcium sulfonate, which can be overbased if desired. Because of the extensive branching, *petroleum-derived* sulfonates have better oil solubility than *synthetic* sulfonates of similar molecular weight. Figure 4.9 presents the idealized structures of neutral detergents.

To make overbased detergents, one can use either a two-step process or a one-step process. Generally, the one-step process is preferred over the two-step process. In the two-step process, the neutral salt or the soap is made first, which is subsequently overbased. In the one-step process, the excess metal base is charged to the reaction; once the neutral salt formation is complete, carbon dioxide blowing (carbonation) of the reaction is initiated. When carbon dioxide uptake stops, the reaction is considered complete and it is worked up to isolate the product. Figure 4.10 summarizes the two processes. For making overbased natural sulfonates and alkylsalicylates, one can double-decompose alkali metal salts *in situ* by reacting with a metal halide and overbasing. The alkali metal halide by-product need not be removed until the overbasing is complete. It comes out during the final filtration, which is employed to remove any unreacted excess base and other particulate materials.

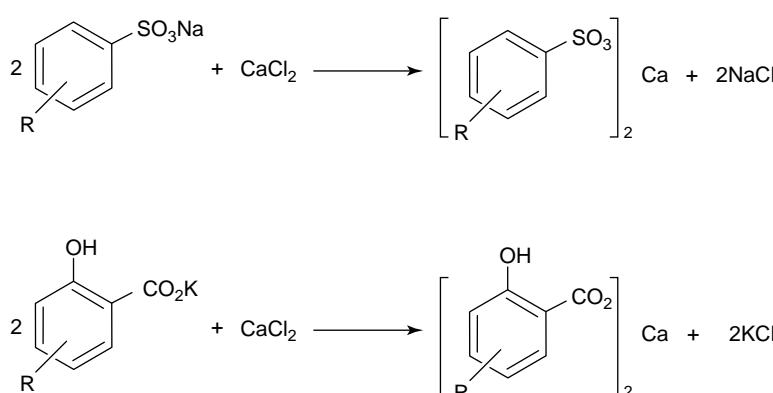
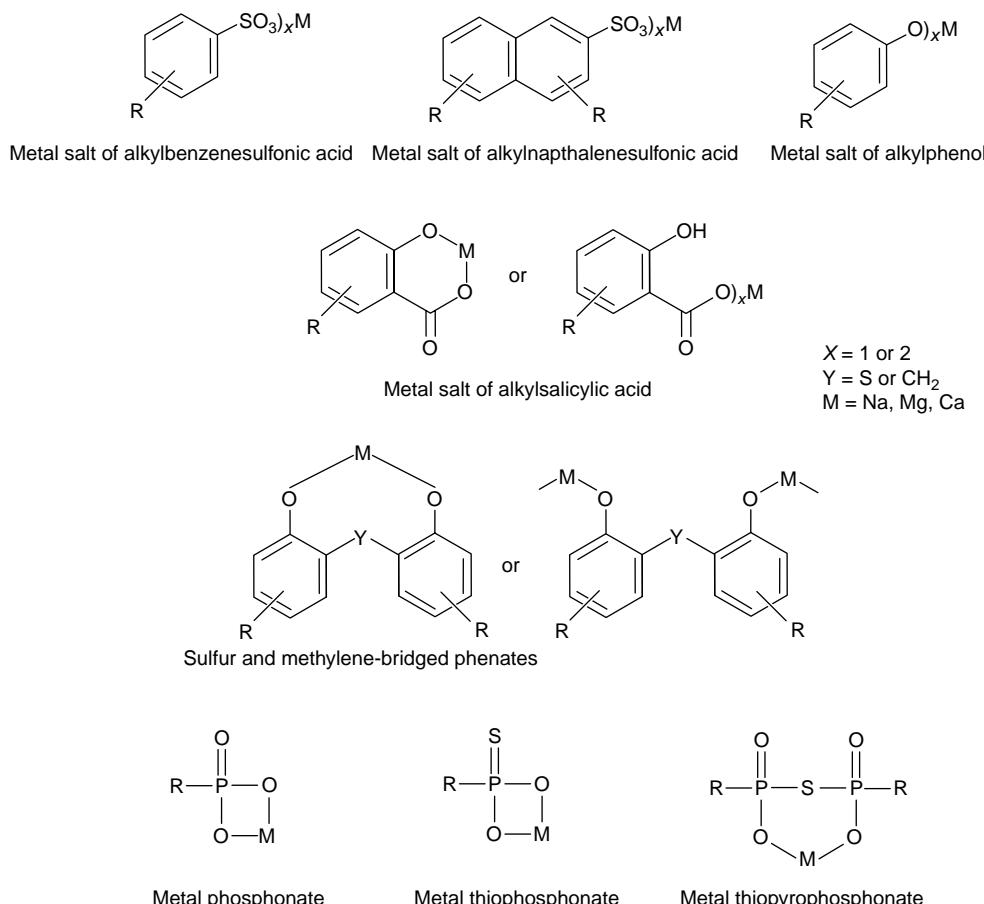
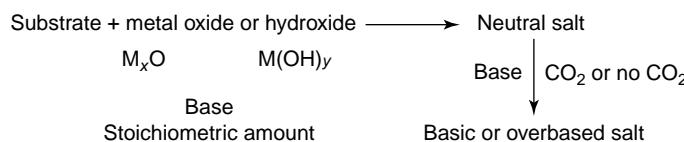
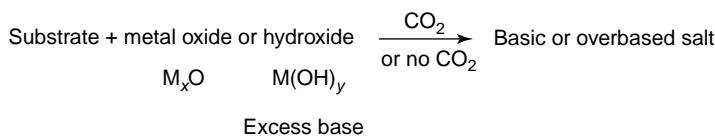


FIGURE 4.8 Double-decomposition reaction.

**FIGURE 4.9** Idealized structures of neutral salts (soaps).Two-step process:One-step process:Basic salts = neutral salts • M_xO, M(OH)_y or M_xCO₃

M = Na, Mg, Ca, or Ba

x = 1 and y = 2 for Mg, Ca, and Ba (divalent metals)

x = 2 and y = 1 for Na (monovalent metal)

FIGURE 4.10 Processes to make basic detergents.

As mentioned, common metals that can be used to make neutral or basic detergents include sodium, potassium, magnesium, calcium, and barium. Calcium and magnesium find most extensive use as lubricant additives, with a preference for calcium due to its lower cost. The use of barium-derived detergents is being curbed due to concerns for barium's toxicity. Technically, one can use metal oxides, hydroxides, and carbonates to manufacture neutral (nonoverbased) detergents; for nonoverbased detergents, oxides and hydroxides are the preferred bases. Sodium hydroxide, calcium hydroxide, and barium hydroxide are often used for sodium, calcium, and barium detergents. For magnesium detergents, however, magnesium oxide is the preferred base.

During the synthesis of calcium detergents, overbasing is usually stopped before all the metal base is converted into calcium carbonate. As a result, the excess base is present as a mixture of calcium hydroxide and calcium carbonate. The calcium carbonate predominates because, if the reaction is overblown with carbon dioxide, the amorphous calcium carbonate, which is desired, is converted into crystalline calcium carbonate. Of low solubility in the overbased system, crystalline calcium carbonate falls out of solution, and one obtains an oil-insoluble gel-like product. Although such products are of little use as lubricant additives, they are useful as rheology control agents in coatings. The challenge is to make them on a consistent basis. Lubrizol supplies such products derived from alkylbenzenesulfonic acids as its Ircogel® product line. Gelled carboxylates and solid calcium micellar complexes have also been reported in the patent literature [56–58].

Basic detergents contain reserve base, which is entrained into the detergent in a colloidal form. The base, such as the carbonate, is believed to be encapsulated by soap molecules. In this arrangement, the polar head group (sulfonate, phenate, or carboxylate) of the soap associates with the carbonate, and the hydrocarbon portion of the soap associates with the oil (see Figure 4.11). The base neutralizes acids that result from oxidation of the fuel and the lubricant and from the oxidation and thermal decomposition of thermally labile additives.

Some detergents are marketed as neutral or nonoverbased. However, most of them have a small amount of reserve base present. In other words, they are overbased to some degree. This implies that no effort was made to overbase them, and their reserve base is due to the presence of the unreacted base used to make them. For example, commercially available neutral sulfonates have a TBN of 30 or less, and the base is commonly present as a hydroxide such as calcium hydroxide. Conversely, *basic* or overbased detergents have a much higher base number, that is, they typically have a TBN of 200–500, and the base is commonly present as a metal carbonate.

Calcium-based phenate detergents are easier to make than magnesium-based detergents because alkylphenols are weak acids, and their reaction with magnesium oxide, a weak base, is not facile. To make the neutral salt, one must react the alkylphenol with a strong base such as

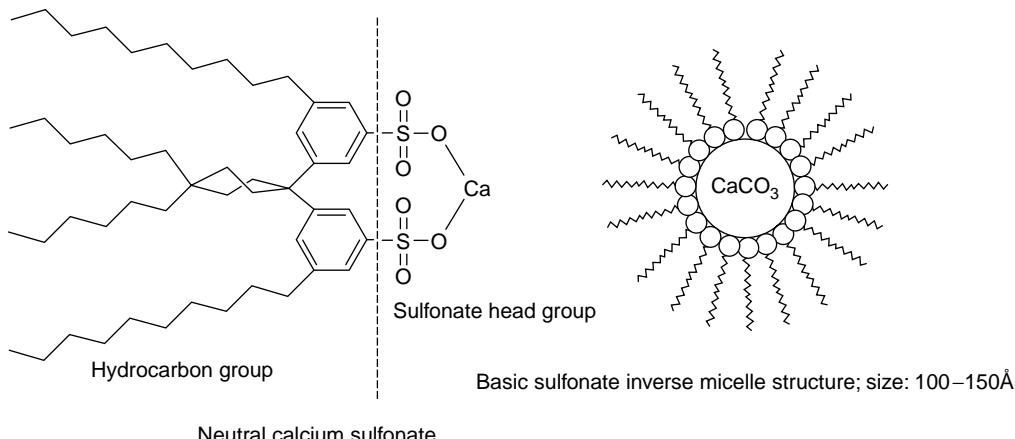


FIGURE 4.11 Micelle structure of detergents.

magnesium alkoxide. This reagent can be prepared by reacting magnesium metal with an excess of highly reactive alcohol such as methanol. However, this method is hazardous because of the hydrogen gas by-product and costly because of the price of the magnesium metal. Once the neutral salt or soap formation occurs, the excess alcohol is exchanged for an inert solvent, such as toluene or mineral oil, before overbasing. Alternatively, one can use a high-temperature overbasing procedure using a low-molecular-weight alkylphenol as a promoter [59]. In the case of methylene or sulfur-bridged phenols that are more acidic than regular alkylphenols, the reactivity toward magnesium oxide is not a problem. And these compounds form neutral and overbased magnesium salts without difficulty. Neutral and basic calcium phenates from alkylphenols, bridged or unbridged, are easy to make because calcium hydroxide, being a stronger base, reacts with them readily. Other acids, that is, alkylsalicylic acids, fatty carboxylic acids, and alkenylphosphonic acids, react with calcium and magnesium bases without any problem.

The synthetic sequences used to make common types of neutral and carbonate overbased detergents are outlined in Figures 4.12 through 4.17. Sulfonate, salicylate, and carboxylate detergents are commercially available as calcium and magnesium salts, and phosphonates are available as calcium salts. Some specialty sulfonates, for example, NA-SUL BSB®, are also available as barium salts. Phenate detergents are commonly available as calcium salts, and phosphonate detergents are available as both calcium and barium salts. Basic calcium sulfonates make up ~65% of the total detergent market, followed by phenates at ~31%.

4.6 TESTING

Detergents are used in engine lubricant formulations to perform two key functions. One is to neutralize the acidic by-products of lubricant oxidation and thermal decomposition, and the other is to suspend neutral but highly polar-oxygenated species in the bulk lubricant.

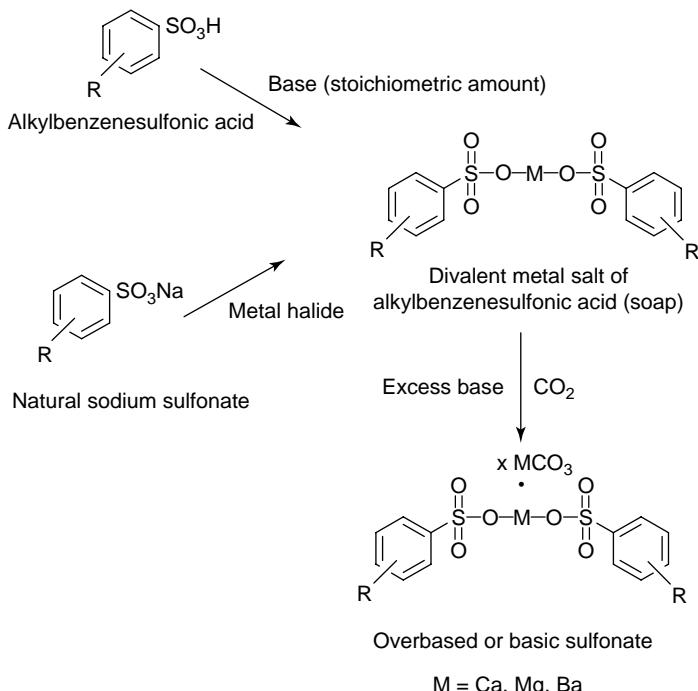


FIGURE 4.12 Synthesis of neutral and basic metal sulfonates.

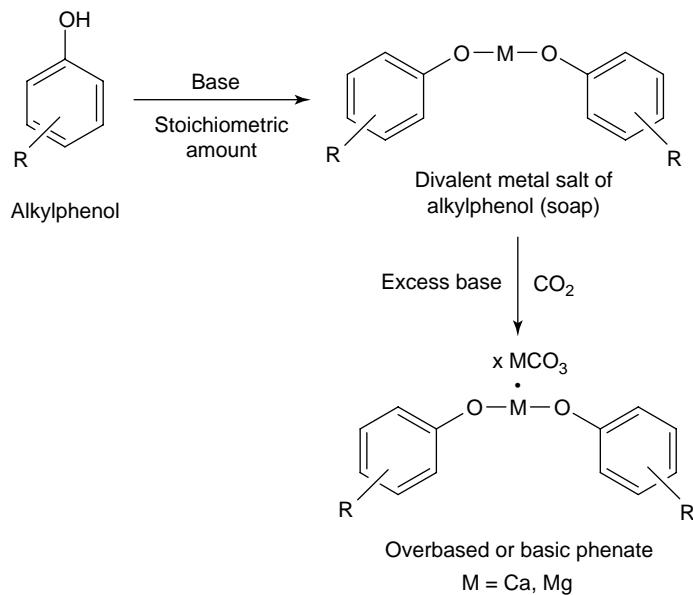


FIGURE 4.13 Synthesis of neutral and basic metal phenates.

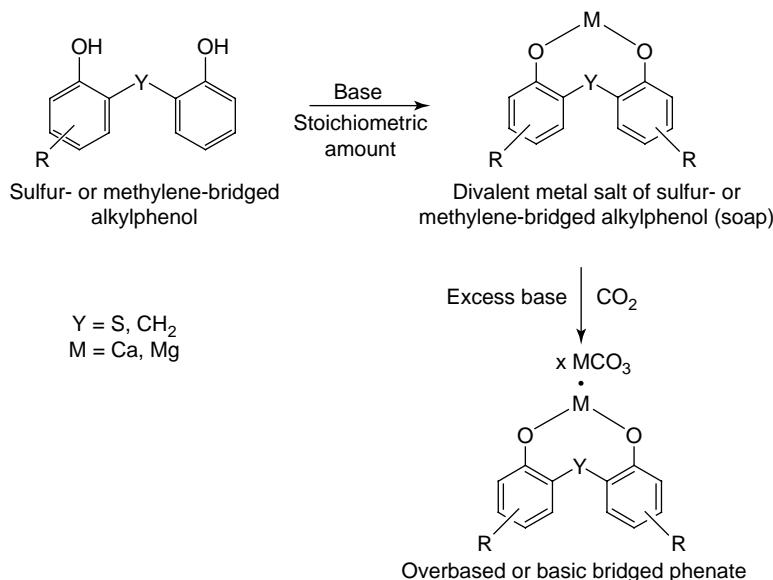
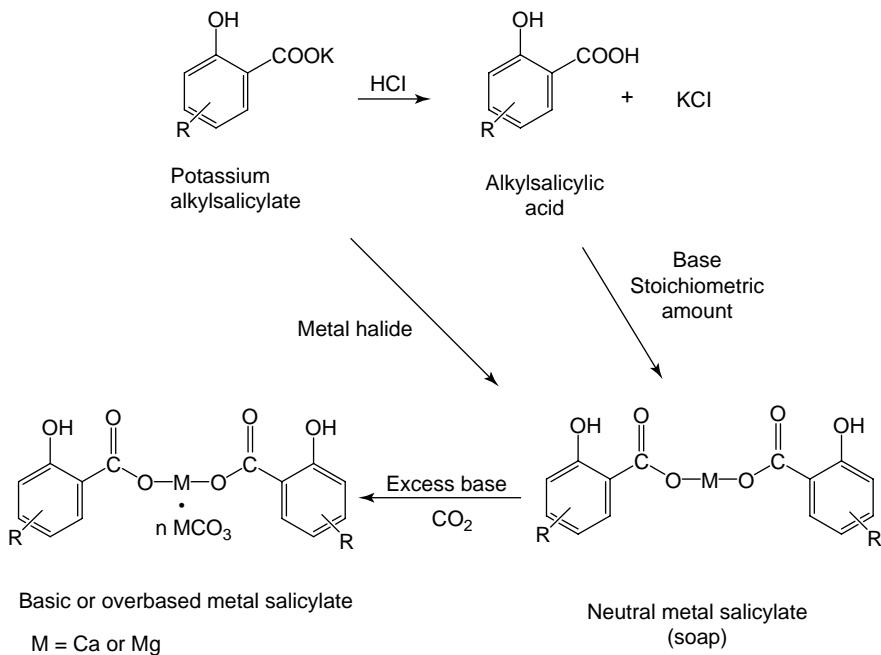
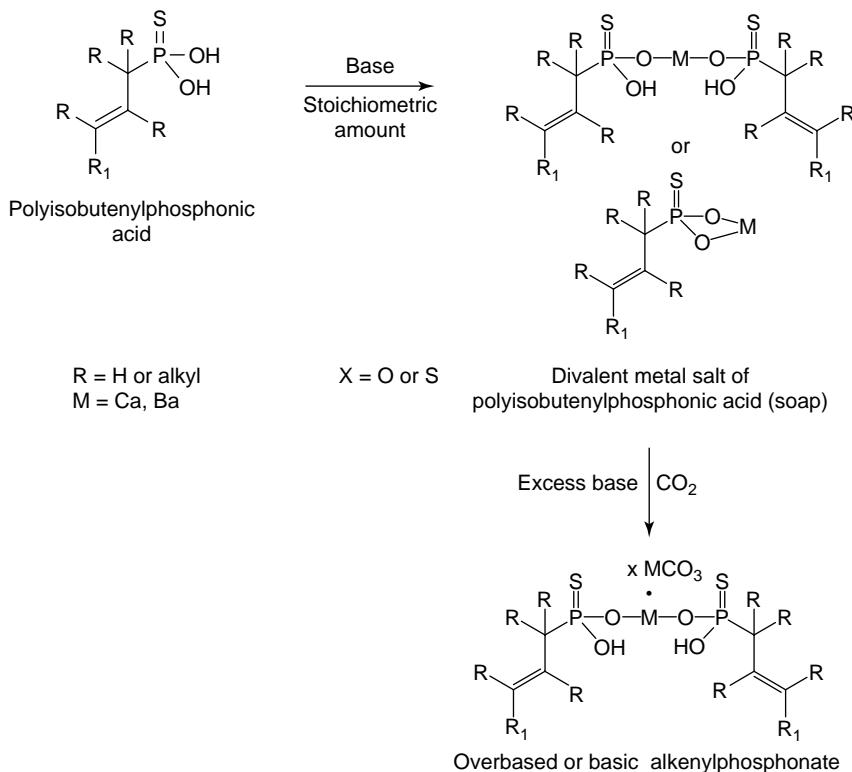


FIGURE 4.14 Synthesis of neutral and basic bridged metal phenates.

All components of a lubricant—base oil, additives, and viscosity modifier—oxidize because of their organic nature. Oxidation of the API group I base oils is more facile than that of the group II and group III base oils, primarily because of the presence of aromatic and sometimes olefinic components. These compounds oxidize to form hydroperoxides and radicals [6]. These species are highly reactive and start the oxidation chain reaction. The result is the oxidative breakdown of all components of the lubricant to highly oxygenated polar species, which are of low lubricant solubility. Because of this, these materials, both acidic and neutral, tend to separate on surfaces, thereby

**FIGURE 4.15** Synthesis of neutral and basic metal salicylates.**FIGURE 4.16** Synthesis of neutral and basic phosphonates.

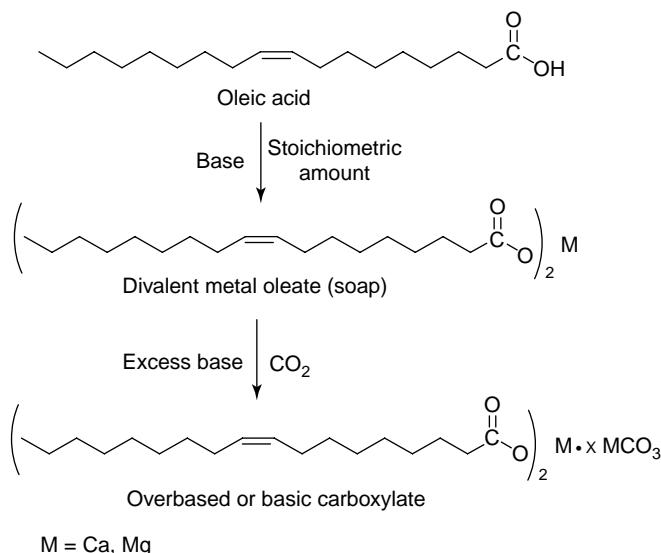


FIGURE 4.17 Synthesis of neutral and basic fatty carboxylates.

impairing the proper functioning of the various equipment parts. The acidic materials such as sulfur oxides, and organic acids resulting from lubricant oxidation can attack metal surfaces and cause corrosion. Sulfur oxides and sulfuric acid result from the combustion of fuel sulfur or the oxidation of sulfur-containing additives, such as sulfurized olefins or zinc dialkyldithiophosphates. The function of the detergent in this case is to neutralize these acids, thus causing corrosion. The reserve base in detergents primarily performs this function. The soap portion keeps oil-insoluble polar products suspended in oil.

Phenates, sulfurized phenates, and salicylates can also act as oxidation inhibitors because of the presence of the phenol functionality. Phenols are well known for their oxidation-inhibiting action [5]. Detergents are also effective corrosion inhibitors, especially basic detergents [25,26], because they not only neutralize corrosive acidic products but also form surface films that isolate metal surfaces from corrosive agents [6]. The carbonate portion in the detergent performs acid neutralization, and the soap portion forms the protective surface film. NA-SUL 729® and NA-SUL CA-50® are examples of commercial corrosion inhibitors belonging to this class of additives. The tests that evaluate rust and corrosion are described elsewhere [3,6]. Detergents derived from fatty carboxylic acids are good friction modifiers, primarily because of the linear structure of their soaps [6].

Detergents find primary use in engine oils, which are responsible for more than 75% of the total consumption. The detergent level in marine diesel engine oils is the highest because marine engines use high-sulfur fuel, which leads to highly acidic combustion products such as sulfuric acid. The lubricants for these engines therefore require the base reserve of highly overbased detergents.

A variety of proprietary and industry-established tests are used to determine a detergent's effectiveness in lubricants. For gasoline engine oils to be used in North America, these include the CRC L-38, TEOST (Thermo-Oxidation Engine Oil Simulation Test [60]), ASTM Sequence IIIE/IIIF, and ASTM Sequence VE/VG tests. For European gasoline engines, in addition to performance in the ASTM Sequence IIIE/IIIF and VE/VG Engine tests, performance in Peugeot TU3M High-Temperature Test and MB M111 Black Sludge Test is also required. These tests are part of the ACEA 2002 Standard. The standard also includes a sulfated ash limit that directly affects the amount of detergent used in formulations since it is the primary contributor to sulfated ash.

The efficacy of diesel engine oils for North American use is evaluated by the use of both the single-cylinder and the multicylinder engine tests. Single-cylinder tests include CRC L-38 and

Caterpillar 1K, 1M-PC, 1N, 1P, and 1R engine tests. CRC L-38's viscosity requirement, an imprecise measure of a detergent's effectiveness, is a part of the API CG-4 standard. Caterpillar 1K test is a part of the API CF-4, API CH-4, and API CI-4 standards. Caterpillar 1M-PC is a part of the API CF, CF-2, and the U.S. Military's MIL-PRF-2104G specifications. Caterpillar 1N is a part of the API CG-4, API CI-4, and the U.S. Military's MIL-PRF-2104G specifications. Caterpillar 1P is a part of the API CH-4 specification, and caterpillar 1R is a part of the API CI-4 specification. The pass ratings for these tests require meeting the overall appearance of the cylinder and its parts, which are expressed in terms of weighted demerits, percent top groove fill, ring side clearance loss, top land heavy carbon, oil consumption, and stuck rings. All these parameters are related to deposits on the piston and its parts. The multicylinder tests that determine the effectiveness of a detergent include Detroit Diesel 6V92TA engine test (a part of the API CF-2 and MIL-PRF-2104G specifications) and Mack M11 engine test (a part of the API CH-4 and CI-4 specifications). These two tests evaluate a detergent's ability to prevent deposit-related port plugging and engine sludge, respectively. For European use, oils must pass the requirements of tests such as VW1.6L TC diesel, XUD11BTE, VVDI, MB OM 364 LA, and MB OM 441 LA. These tests evaluate ring sticking, piston cleanliness, viscosity increase, and filter plugging. It is important to note that technically most of these tests evaluate the combined effectiveness of the detergent and the dispersant. The performance of the individual additive is hard to unravel. Detergents find additional use in automatic transmission fluids and tractor hydraulic fluids. In this case, the primary function of these additives is not to neutralize acids or to minimize deposit formation, but to alter the frictional properties of these fluids. This is critical if the fluids are to perform effectively as driveline lubricants.

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5 Dispersants

Syed Q. A. Rizvi

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5.1 INTRODUCTION

Lubricants are composed of a base fluid and additives. The base fluid can be mineral, synthetic, or biological in origin. In terms of use, petroleum-derived (mineral) base fluids top the list, followed by synthetic fluids. Base oils of biological origin, that is, vegetable and animal oils, have not gained much popularity except in environmentally compatible lubricants. This is because of the inherent drawbacks these base oils have pertaining to their oxidation stability and low-temperature properties. Additives are added to the base fluid either to enhance an already-existing property, such as viscosity, of a base oil or to impart a new property, such as detergency, lacking in the base oil. The lubricants are designed to perform a number of functions, including lubrication, cooling, protection against corrosion, and keeping the equipment components clean by suspending ordinarily insoluble contaminants in the bulk lubricant [1]. Although for automotive applications all functions are important, suspending the insoluble contaminants and keeping the surfaces clean are the most critical. As mentioned in Chapter 4 on “detergents,” this is achieved by the combined action of the detergents and the dispersants present in the lubricant. Dispersants differ from detergents in three significant ways:

1. Dispersants are metal-free, but detergents contain metals, such as magnesium, calcium, and sometimes barium [2]. This means that on combustion detergents will lead to ash formation and dispersants will not.
2. Dispersants have little or no acid-neutralizing ability, but detergents do. This is because dispersants have either no basicity, as is the case in ester dispersants, or low basicity, as

is the case in imide/amide dispersants. The basicity of the imide/amide dispersants is due to the presence of the amine functionality. Amines are weak bases and therefore possess minimal acid-neutralizing ability. Conversely, detergents, especially basic detergents, contain reserve metal bases as metal hydroxides and metal carbonates. These are strong bases, with the ability to neutralize combustion and oxidation-derived inorganic acids, such as sulfuric and nitric acids, and oxidation-derived organic acids.

3. Dispersants are much higher in molecular weight, approximately 4–15 times higher, than the organic portion (soap) of the detergent. Because of this, dispersants are more effective in fulfilling the suspending and cleaning functions than detergents.

As mentioned in Chapter 4, dispersants, detergents, and oxidation inhibitors make up the general class of additives called *stabilizers* and *deposit control agents*. The goal of oxidation inhibitors is to minimize the formation of deposit precursors, such as hydroperoxides and radicals [3,4]. This is because these species are reactive, and they attack the hydrocarbon base oil and additives, which make up the lubricant, to form sludge, resin, varnish, and hard deposits. The goal of the dispersant and the soap portion of the detergent is to keep these entities suspended in the bulk lubricant. This not only results in deposit control but also minimizes particulate-related abrasive wear and viscosity increase. When the lubricant in the equipment is changed, the deposit precursors and the deposit-forming species are removed with the used oil.

The dispersants suspend deposit precursors in oil in various ways. These comprise the following:

- Including the undesirable polar species into micelles.
- Associating with colloidal particles, thereby preventing them from agglomerating and falling out of solution.
- Suspending aggregates in the bulk lubricant, if they are formed.
- Modifying soot particles so as to prevent their aggregation. The aggregation will lead to oil thickening, a typical problem in heavy-duty diesel engine oils [5,6].
- Lowering the surface/interfacial energy of the polar species to prevent their adherence to metal surfaces.

5.2 NATURE OF DEPOSITS AND MODE OF THEIR FORMATION

A number of undesirable materials result from the oxidative degradation of various components of the lubricant. These are base oil, additives, and the polymeric viscosity modifier, if present. In engine oils, the starting point for the degradation is fuel combustion, which gives rise to hydroperoxides and free radicals [7]. The compounds in the fuel that are most likely to form peroxides, hydroperoxides, and radicals include highly branched aliphatics, unsaturates such as olefins, and aromatics such as alkylbenzenes. All these are present in both gasoline and diesel fuels. American Society for Testing and Materials (ASTM) test methods D 4420 and D 5186 are used to determine the aromatic content of gasoline and diesel fuels, respectively [8]. The fuel degradation products (peroxides, hydroperoxides, and radicals) go past the piston rings into the lubricant as blowby and, because they are highly energetic, attack largely the hydrocarbon lubricant. Again, the highly branched aliphatic, unsaturated, and aromatic structures are among those that are highly susceptible. ASTM Standard D 5292 is commonly used to determine the aromatic content of the base oil [8]. The reaction between the contents of the blowby and these compounds results in the formation of the lubricant-derived peroxides and hydroperoxides that either oxidatively or thermally decompose to form aldehydes, ketones, and carboxylic acids [3,4,9]. Acids can also result from the high-temperature reaction of nitrogen and oxygen, both of which are present in the air-fuel mixture; the oxidation of the fuel sulfur; and the oxidation, hydrolysis, or thermal decomposition of additives such as zinc dialkyl-dithiophosphates. The reaction between nitrogen and oxygen to form NO_x is more prevalent in diesel

engines and gasoline engines that are subjected to severe service, such as long-distance driving for extended periods. The NO_x formation initiates when the temperature reaches 137°C [10,11]. Zinc dialkyldithiophosphates are commonly used as oxidation inhibitors in engine oils [12,13]. All these acids are neutralized by basic detergents to form inorganic metal salts and metal carboxylates. These compounds are of low hydrocarbon solubility and are likely to fall out of solution.

The aldehydes and ketones undergo aldol-type condensation in the presence of bases or acids to form oligomeric or polymeric compounds. These can further oxidize to highly oxygenated hydrocarbons, commonly referred to as *oxygenates*. The oxygenates are usually of sticky consistency, and the term *resin* is often used to describe them [14]. Resin is either the basic component in or the precursor to all types of deposits. Common types of deposits include varnish, lacquer, carbon, and sludge [15,16]. Varnish, lacquer, and carbon occur when resin separates on hot surfaces and dehydrates or polymerizes to make tenacious films. The quantity and the nature of deposits depend on the proximity of the engine parts to the combustion chamber. The parts closer to the combustion chamber, such as exhaust valve head and stem that experience approximate temperatures of 630–730°C [17,18], will develop carbon deposits. The same is true of the combustion chamber wall, piston crown, top land, and top groove, which are exposed to approximate temperatures of 200–300°C. Carbon deposits are more common in diesel engines than in gasoline engines and result from the burning of the liquid lubricating oil and the high-boiling fractions of the fuel that adhere to hot surfaces [19].

As we move away from these regions to the low-temperature regions, such as the piston skirt, the deposits are not heavy and form only a thin film. For diesel engine pistons, this type of deposit is referred to as *lacquer*; for gasoline engine pistons, this type of deposit is called *varnish*. The difference between lacquer and varnish is that lacquer is lubricant-derived and varnish is largely fuel-derived. In addition, the two differ in their solubility characteristics. That is, lacquer is water-soluble and varnish is acetone-soluble [15]. Lacquer usually occurs on piston skirts, on cylinder walls, and in the combustion chamber, whereas varnish occurs on valve lifters, piston rings, piston skirts, valve covers, and positive crankcase ventilation (PCV) valves.

The coolest parts of the engine, such as rocker arm covers, oil screen, and oil pan, that are exposed to temperatures of $\leq 200^\circ\text{C}$ experience sludge deposits. Sludge can be watery or hard in consistency, depending on the severity of service. If the service is extremely mild and of short duration, as in the case of stop-and-go gasoline engine operation, the sludge is likely to be watery or mayonnaiselike [15]. This type of sludge is called low-temperature sludge, which occurs when the ambient temperature is $< 95^\circ\text{C}$. The high-temperature sludge is more common in diesel engines and gasoline engines with long, continuous operation. This type of sludge occurs when the ambient temperature is $> 120^\circ\text{C}$ and is hard in consistency. In the former case, the engine does not get hot enough to expel combustion water, which stays mixed with oil, imparting sludge, a mayonnaiselike appearance. In the latter case, however, the ambient temperature is high enough to expel water, thereby resulting in hard sludge. Sludge is common in areas that experience low oil flow, such as crankcase bottoms and rocker boxes.

Another component of the combustion effluent that must be considered is soot. Soot not only contributes toward some types of deposits such as carbon and sludge, but it also leads to a viscosity increase. These factors can cause poor lubricant circulation and lubricating film formation, both of which will result in wear and catastrophic failure. Soot is particulate in nature and results from the incomplete combustion of the fuel and of the lubricating oil from the crankcase that might enter the combustion chamber by traveling past the piston rings [20]. Fuel-derived soot is a chronic problem in the case of diesel engines because diesel fuel contains high-boiling components that do not burn easily. In addition, diesel engine combustion is largely heterogeneous, with poor air–fuel mixing, hence poor combustion [20]. Soot is made of hydrocarbon fragments with some of the hydrogen atoms removed. The particles are charged and hence have the tendency to form aggregates. When aggregates occur on surfaces, such as those of the combustion chamber, soot deposits result. These deposits are soft and flaky in texture. If these occur in oil, lubricant experiences an increase in viscosity. A soot-related viscosity increase usually requires the presence of polar materials in oil that

have the ability to associate with soot. These can be additives or polar lubricant oxidation and degradation products. Carbon deposits are lower in carbon content than soot and, in most cases, contain oily material and ash. This makes knowledge of the ash-forming tendency of a lubricant important to a formulator. This concern was addressed in Chapter 4.

When soot associates with resin, one gets either resin-coated soot particles or soot-coated resin particles [16]. The first type of particles results when resin is in excess, and the second type results when soot is in excess. The amount of soot in resin determines the color of the deposits: the higher the soot, the darker the deposits. Sludge results when resin, soot, oil, and water mix [9].

Deposit formation in gasoline engines is initiated by NO_x and oxidation-derived hydroperoxides that react with hydrocarbons in the fuel and the lubricant to form organic nitrates and oxygenates [14,21]. Being thermally unstable, these species decompose and polymerize to form deposits. The deposits typically include resin, varnish, and low-temperature sludge. In diesel engines, however, soot is an important component of the deposits, which include lacquer, carbon deposits, and high-temperature sludge [16]. Typically, carbon deposits are of high metal content, which is mainly due to the presence of detergent additives in the lubricant [22,23].

Detailed mechanism of deposit formation in engines is described elsewhere [24,25]. The mechanism is based on the premise that both the lubricant and the fuel contribute toward deposit formation. The role of the blowby, NO_x , and high-temperature oxidative and thermal degradation of the lubricant, described earlier, are substantiated [24]. The importance of oxygenated precursors—their decomposition, condensation, and polymerization to form deposits—is also supported. The deposit precursors consist of approximately 15–50 carbon atoms and contain multiple hydroxy and carboxy functional groups. Because of the polyfunctionality, these molecules have the ability to thermally polymerize to high-molecular-weight products [14,16]. As mentioned earlier, soot associates with polar oxidation products in oil to cause a viscosity increase. Viscosity increase can also occur in gasoline engine oils that have little or no soot. This happens when the oxygen content of the precursors is low and the resulting polymer is of low molecular weight and of good oil solubility [14]. This phenomenon is commonly referred to as *oil thickening* [6]. Conversely, if the oxygen content of the precursors is high, the polymerization results in the formation of high-molecular-weight products of low lubricant solubility. Such products constitute resin, which is of low oil solubility and separates on surfaces. If the surfaces are hot, subsequent dehydration and polymerization lead to the formation of varnish, lacquer, and carbon deposits. It is important to note that deposits are a consequence of lubricant oxidation that accelerates once the oxidation inhibitor package in the lubricant is exhausted.

Three other internal combustion engine problems—oil consumption, ring sticking, and corrosion and wear—are also related to lubricant degradation. Oil consumption is a measure of how much lubricant travels past piston rings into the combustion chamber and burns. A certain minimum amount of the lubricant is necessary in the vicinity of the piston rings to lubricate cylinder walls and cylinder liners and hence facilitate piston movement and minimize scuffing. However, if too much lubricant ends up in the combustion chamber, serious emission problems will result. Modern piston designs, such as articulated pistons and pistons with low crevice volume, allow just enough lubricant to minimize scuffing, but without adversely contributing to emissions [26,27]. Other parameters that affect oil consumption include the integrity of pistons and cylinders and the viscosity, volatility, and sealing characteristics of the lubricant. Pistons with stuck rings and out-of-square grooves and cylinders with increased wear will result in a poor seal between the crankcase and the combustion chamber [15]. As a consequence, a larger amount of blowby will enter the crankcase and increase the rate of lubricant breakdown. This will complicate the situation further. Ring sticking occurs when sticky deposits form in the grooves behind the piston rings. This is a serious problem because it not only results in a poor seal but also leads to poor heat transfer from the cylinder to the wall. If not controlled, this will result in nonuniform thermal expansion of the pistons, loss of compression, and ultimately the failure of the engine [15]. The wear of pistons and the cylinders is undesired for the same reasons. Wear of engine parts is either corrosive or abrasive. *Corrosive wear* arises from the attack of fuel sulfur-derived products, such as sulfur oxides or sulfuric acid, or the acidic by-products of

lubricant oxidation and degradation, such as carboxylic and sulfonic acids. Fuel sulfur-derived piston ring wear and cylinder wear are serious problems in large, slow-speed marine diesel engines that use a high-sulfur fuel. Corrosive wear is controlled by the use of lubricants with a base reserve, that is, those containing a large quantity of basic detergents. This was discussed in Chapter 4. *Abrasive wear* results from the presence of the particulate matter, such as large soot particles, in the lubricant. Dispersants are crucial to the control of soot-related wear.

5.3 DEPOSIT CONTROL BY DISPERSANTS

Fuel and lubricant oxidation and degradation products, such as soot, resin, varnish, lacquer, and carbon, are of low lubricant (hydrocarbon) solubility, with a propensity to separate on surfaces. The separation tendency of these materials is a consequence of their particle size. Small particles are more likely to stay in oil than large particles. Therefore, resin and soot particles, which are the two essential components of all deposit-forming species, must grow in size through agglomeration before separation. Growth occurs either because of dipolar interactions, as is the case in resin molecules, or because of adsorbed polar impurities such as water and oxygen, as is the case in soot particles. Alternatively, soot particles are caught in the sticky resin. Dispersants interfere in agglomeration by associating with individual resin and soot particles. The particles with associated dispersant molecules are unable to coalesce because of either steric factors or electrostatic factors [28]. Dispersants consist of a polar group, usually oxygen- or nitrogen-based, and a large nonpolar group. The polar group associates with the polar particles, and the nonpolar group keeps such particles suspended in the bulk lubricant [16]. Neutral detergents, or soaps, operate by an analogous mechanism.

5.4 DESIRABLE DISPERSANT PROPERTIES

Dispensing soot, deposit precursors, and deposits is clearly the primary function of a dispersant. Dispersants, in addition, need other properties to perform effectively. These include thermal and oxidative stability and good low-temperature properties. If a dispersant has poor thermal stability, it will break down, thereby losing its ability to associate with and suspend potentially harmful products. Poor oxidative stability translates into the dispersant molecule contributing itself toward deposit formation. Good low-temperature properties of a lubricant are desired for many reasons: ease of cold cranking, good lubricant circulation, and fuel economy. Base oil suppliers have developed a number of ways to achieve these properties. The methods they use include isomerization of the base stock hydrocarbons through hydrocracking and the use of special synthetic oils as additives. Since dispersant is one of the major components of the engine oil formulations, its presence can adversely affect these properties, which must be preserved.

5.5 DISPERSANT STRUCTURE

A dispersant molecule consists of three distinct structural features: a *hydrocarbon group*, a *polar group*, and a connecting group or a *link* (see Figure 5.1). The hydrocarbon group is polymeric

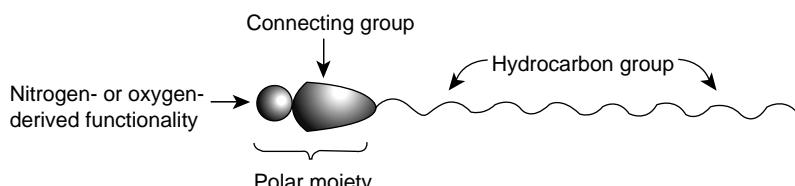


FIGURE 5.1 Graphic representation of a dispersant molecule.

in nature, and depending on its molecular weight, dispersants can be classified into *Polymeric dispersants* and *dispersant polymers*. Polymeric dispersants are of lower molecular weight than dispersant polymers. The molecular weight of polymeric dispersants ranges between 3,000 and 7,000 as compared to dispersant polymers, which have a molecular weight of 25,000 and higher. Although various olefins, such as polyisobutylene, polypropylene, polyalphaolefins, and mixtures thereof, can be used to make polymeric dispersants, the polyisobutylene-derived dispersants are the most common. The number average molecular weight (M_n) of polyisobutylene ranges between 500 and 3000, with an M_n of 1000–2000 being typical [29]. In addition to M_n , other polyisobutylene parameters, such as molecular weight distribution and the length and degree of branching, are also important in determining the overall effectiveness of a dispersant.

Substances obtained through a polymerization reaction, especially those made by using an acid catalyst or a free-radical initiator, often contain molecules of different sizes. Molecular weight distribution, or polydispersity index, is commonly used to assess the heterogeneity in molecular size. Polydispersity index is the ratio of weight average molecular weight (M_w) and M_n , or M_w/M_n [30–32]. These molecular weights are determined by subjecting the polymer to gel permeation chromatography (GPC). The method separates molecules based on size [33]. The larger molecules come out first, followed by the next size. When the molecules are of the same size, M_w/M_n equals 1 and the polymer is called a *monodisperse polymer*. The polymers with an index >1 are called *polydisperse polymers*. For most applications, monodispersity is desired. Polyisobutylene, derived from acid-catalyzed polymerization reaction, typically has a polydispersity index between 2 and 3. This will impact many of the dispersant properties described below.

Dispersant polymers, also called dispersant viscosity modifiers (DVMs) and dispersant viscosity index improvers (DVIIIs), are derived from hydrocarbon polymers of molecular weights between 25,000 and 500,000. Polymer substrates used to make DVMs include high-molecular-weight olefin copolymers (OCPs), such as ethylene–propylene copolymers (EPRs), ethylene–propylene–diene copolymers (EPDMs), polymethacrylates (PMAs), styrene–diene rubbers (SDRs) of both linear and star configurations, and styrene–ester polymers (SEs).

The polar group is usually nitrogen- or oxygen-derived. Nitrogen-based groups are derived from amines and are usually basic in character. Oxygen-based groups are alcohol-derived and are neutral. The amines commonly used to synthesize dispersants are polyalkylene polyamines such as diethylenetriamine and triethylenetetramine. In the case of DVMs or dispersant polymers, the polar group is introduced by direct grafting, copolymerization, or by introducing a reactable functionality. The compounds used for this purpose include monomers such as 2- or 4-vinylpyridine, *N*-vinylpyrrolidinone, and *N,N*-dialkylaminoalkyl acrylate and unsaturated anhydrides and acids such as maleic anhydride, acrylic acid, and glyoxylic acid. The details of these reactions are described in Section 5.6, which deals with the dispersant synthesis. Amine-derived dispersants are called nitrogen or amine dispersants, and those that are alcohol-derived are called oxygen or ester dispersants [28]. Oxygen-derived phosphonate ester dispersants were popular at one time, but their use in engine oils is now restrained because of the phosphorus limit. Phosphorus limit pertains to its tendency to poison noble metal catalysts used in catalytic converters. Formulators prefer to take advantage of the phosphorus limit by using zinc dialkyldithiophosphates, which are excellent oxidation inhibitors and antiwear agents. In the case of amine dispersants, it is customary to leave some of the amino groups unreacted to impart basicity to the dispersant. The reasons for this are described in Section 5.7.

5.6 DISPERSANT SYNTHESIS

Since it is not easy to attach the polar group directly to the hydrocarbon group, except in the case of olefins that are used to make DVMs, the need for a connecting group or a link arises. Although many such groups can be used, the two common ones are phenol and succinic anhydride. Olefin, such as polyisobutylene, is reacted either with phenol to form an alkylphenol or with maleic anhydride

to form an alkenylsuccinic anhydride. The polar functionality is then introduced by reacting these substrates with appropriate reagents.

5.6.1 THE HYDROCARBON GROUP

Polyisobutylene is the most common source of the hydrocarbon group in polymeric dispersants. It is manufactured through acid-catalyzed polymerization of isobutylene [34,35]. Figure 5.2 depicts the mechanism of its formation. In Figure 5.2, polyisobutylene is shown as a terminal olefin, whereas in reality it is a mixture of various isomers. Those that predominate include geminally disubstituted (vinylidene), trisubstituted, and tetrasubstituted olefins. Figure 5.3 shows their structure and the possible mechanism of their formation. Polyisobutylenes of structures I and II result from the loss of a proton from carbon 1 and carbon 3 of the intermediate of structure V. Polyisobutylenes of structures III and IV result from the rearrangement of the initially formed carbocation, as shown in Figure 5.3. The reactivity of these olefins toward phenol and maleic anhydride varies. In general, the more substituted the olefin, the lower the reactivity, which is a consequence of the steric factors. Similarly, the larger the size of the polyisobutyl pendant group, that is, the higher the molecular weight, the lower the reactivity. This is due to the dilution effect, which results from low olefin-to-hydrocarbon ratio. As mentioned earlier, polyisobutylene is the most commonly used olefin. One of the reasons for its preference is its extensive branching. This makes the derived dispersants to possess excellent oil solubility, in both nonassociated and associated forms. However, if the hydrocarbon chain in the dispersant is too small, its lubricant solubility greatly suffers. Because of this, the low-molecular-weight components in polyisobutylene are not desired. This is despite their higher reactivity. These must be removed, which is carried out through distillation. Alternatively, one can minimize the formation of these components by decreasing the amount of the catalyst during polymerization and by lowering the polymerization reaction temperature.

A new class of dispersants derived from ethylene/ α -OCP with an Mn of 300–20,000 has also been reported, primarily by the Exxon scientists [36,37]. Such dispersants are claimed to have superior low- and high-temperature viscometrics than those of the polyisobutylene-derived materials.

As mentioned earlier, dispersant polymers are derived from EPRs, styrene–butadiene copolymers, polyacrylates, PMAs, and styrene esters. The ethylene–propylene rubbers are synthesized by Ziegler–Natta catalysis [38]. The styrene–butadiene rubbers are synthesized through anionic polymerization [38]. Polyacrylates and PMAs are synthesized through polymerization of the monomers using free-radical initiators [38]. Styrene esters are made by reacting styrene–maleic

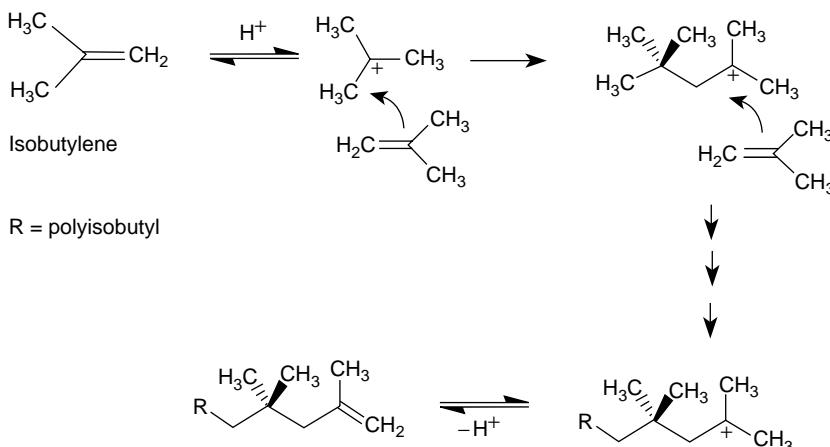


FIGURE 5.2 Acid-catalyzed polymerization of isobutylene.

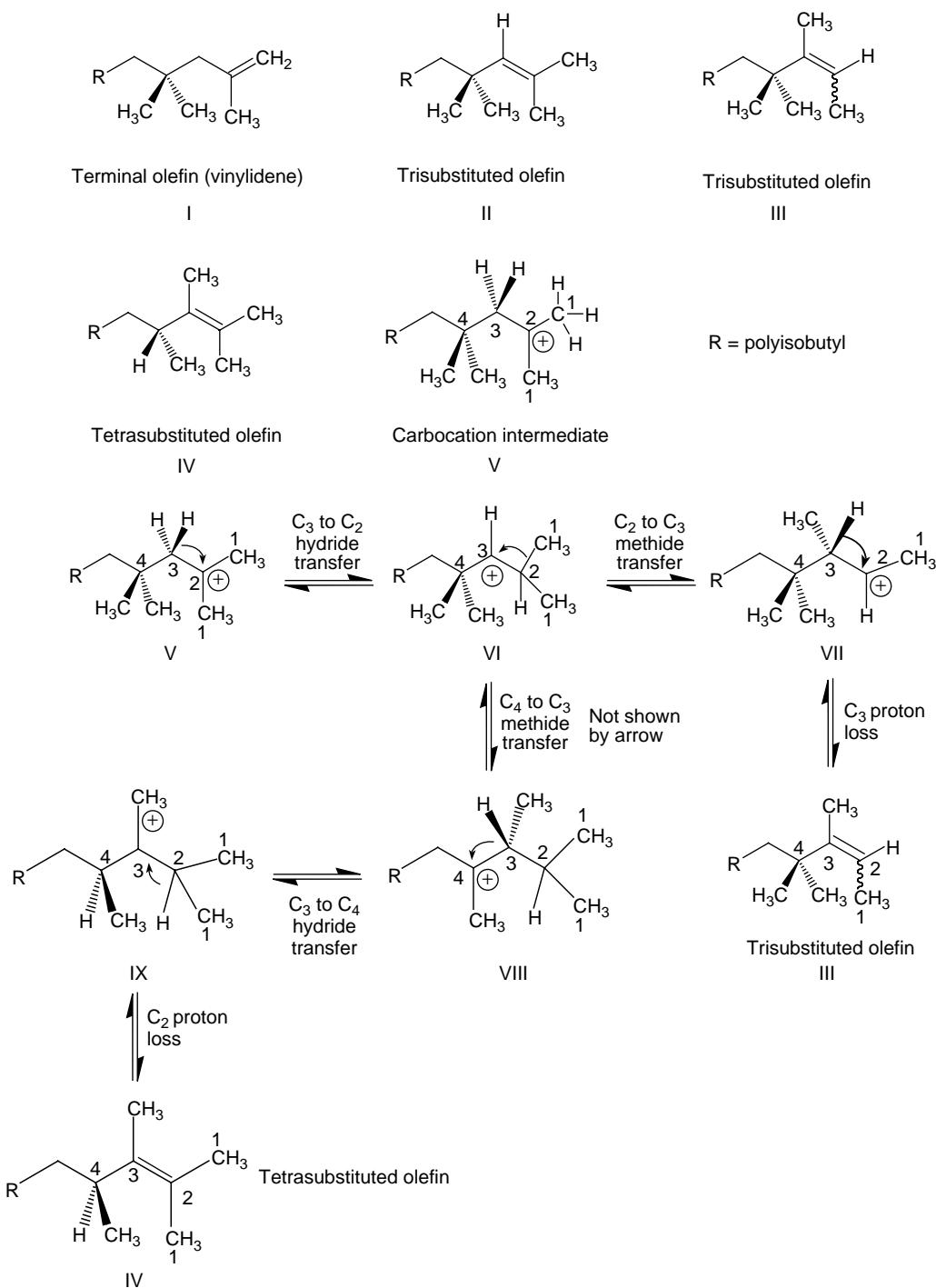


FIGURE 5.3 Polyisobutylene structures and the mode of their formation.

anhydride copolymer or styrene–maleic anhydride–alkyl acrylate terpolymer with alcohols, usually in the presence of a protic acid, such as sulfuric or methanesulfonic acid, catalyst. Since complete esterification of the anhydride is hard to achieve, the neutralization of the residual carboxylic acid anhydride is carried out by alternative means [38–40].

5.6.2 THE CONNECTING GROUP

As mentioned in Section 5.5, succinimide, phenol, and phosphonate are the common connecting groups used to make dispersants. Of these, succinimide and phenol are the most prevalent [2]. Succinimide group results when a cyclic carboxylic acid anhydride is reacted with a primary amino group. Alkenylsuccinic anhydride is the precursor for introducing the succinimide connecting group in dispersants. Alkenylsuccinic anhydride is synthesized by reacting an olefin, such as polyisobutylene, with maleic anhydride [2]. This is shown in Figure 5.4.

The reaction is carried out either thermally [29,41,42] or in the presence of chlorine [43]. The thermal process involves heating the two reactants together usually $>200^{\circ}\text{C}$ [29,41,42], whereas the chlorine-mediated reaction with a mixture is carried out by introducing chlorine to react containing polyisobutylene and maleic anhydride [43–48]. Depending on the manner in which chlorine is added, the procedure is either *one-step* or *two-step* [44]. If chlorine is first reacted with polyisobutylene before adding maleic anhydride, the procedure is considered two-step. If chlorine is added to a mixture of polyisobutylene and maleic anhydride, it is a one-step procedure. The one-step procedure is generally preferred.

The chlorine-mediated process has several advantages, which include having a low reaction temperature, having a faster reaction rate, and working well with internalized or highly substituted olefins. The low reaction temperature minimizes the chances of thermal breakdown of polyisobutylene and saves energy. The major drawback of the chlorine process is that the resulting dispersants contain residual chlorine as organic chlorides. Their presence in the environment is becoming a concern because they can lead to the formation of carcinogenic dioxins. A number of strategies are reported in the literature to decrease the chlorine content in dispersants [49–54]. The thermal process does not suffer from the presence of chlorine, although it is less energy-efficient and requires the use of predominantly a terminal olefin, that is, the polyisobutylene of high vinylidene content.

The mechanism by which the two processes proceed is also different [46,47,50–52]. The thermal process is postulated to occur through an ene reaction. The chlorine-mediated reaction is postulated to proceed through a Diels–Alder reaction. The mechanism of the diene formation is shown in Figure 5.5. Chlorine first reacts with polyisobutylene 1 to form allylic chloride II. By the loss of the chloride radical, this yields the intermediate III, which through C₄ to C₃ methyl radical transfer is converted into the intermediate IV. A C₃ to C₄ hydrogen shift in the intermediate results in the formation of the radical V. This radical can lose hydrogen either from C₄ to yield the diene VI or from C₅ to result in the diene VII. The resulting dienes then react with maleic anhydride through a 4 + 2 addition reaction, commonly called a Diels–Alder reaction [55], to form alkenyltetrahydrophthalic anhydrides [50,52]. These reactions are shown in Figure 5.6.

These anhydrides can be converted into phthalic anhydrides through dehydrogenation by using sulfur [50–52]. These compounds can then be transformed into dispersants by reacting with polyamines and polyhydric alcohols [51,52]. During the thermal reaction of polyisobutylene with maleic anhydride, that is, the ene reaction, the vinylidene double bond moves down the chain to the next carbon. Since thermal reaction requires a terminal olefin, further reaction of the new olefin with another mole of maleic anhydride will not occur if the double bond internalizes, and

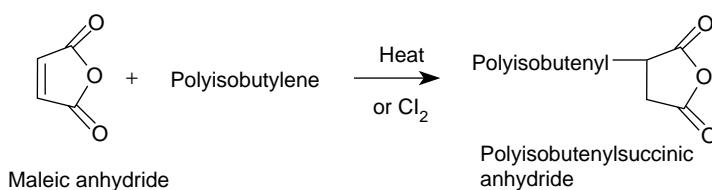


FIGURE 5.4 Alkenylsuccinic anhydride formation.

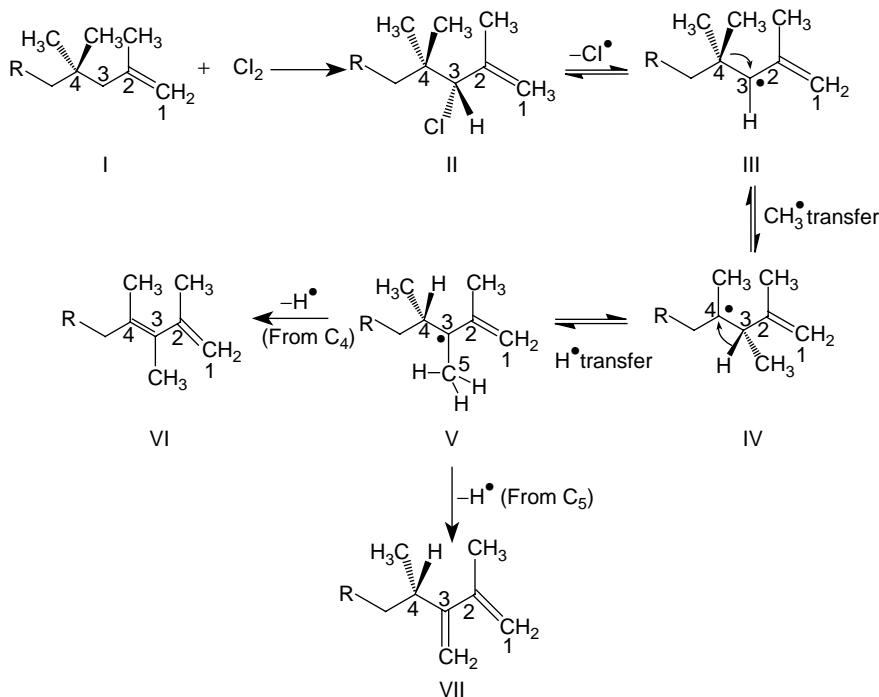


FIGURE 5.5 Mechanism of chlorine-assisted diene formation.

the reaction will stop at this stage. This is shown in reaction 5.3 of Figure 5.6. If the new double bond is external, the reaction with another molecule of maleic anhydride is possible [45]. This is shown in reaction 5.4.

For dispersants, polyisobutylphenol is the alkylphenol of choice. It is synthesized by reacting polyisobutylenes with phenol in the presence of an acid catalyst [56–58]. Lewis acid catalysts, such as aluminum chloride and boron trifluoride, are often employed. Boron trifluoride is preferred over aluminum chloride because the reaction can be carried out at low temperatures, which minimizes acid-mediated breakdown of polyisobutylene [58]. This is desired because dispersants derived from low-molecular-weight phenols are not very effective. Other catalysts, such as sulfuric acid, methanesulfonic acid, and porous acid catalysts of Amberlyst® type, can also be used to make alkylphenols [59,60]. Polyisobutylene also reacts with phosphorus pentasulfide through an ene reaction, as described in Chapter 4. The resulting adduct is hydrolyzed by the use of steam to alkenylphosphonic and alkenylthiophosphonic acids [2,3]. The methods to synthesize alkylphenols and alkenylphosphonic acids are shown in Figure 5.7.

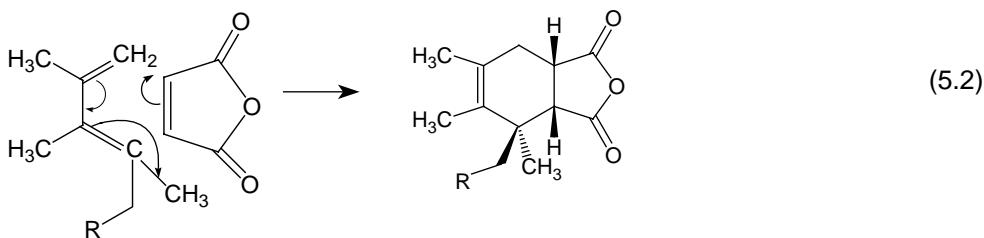
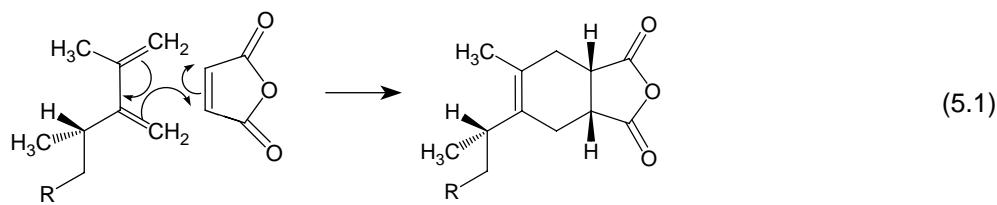
A new carboxylate moiety derived from glyoxylic acid to make dispersants has been reported in the literature [61–65]. However, at present, no commercial products appear to be based on this chemistry.

5.6.3 THE POLAR MOIETY

The two common polar moieties in dispersants are based on polyamines and polyhydric alcohols. The structures of common amines and alcohols used to make dispersants are shown in Figure 5.8.

The polyamines are manufactured from ethylene through chlorination, followed by the reaction with ammonia [66]. The reaction scheme is given in Figure 5.9. As shown, polyamines

Diels–Alder reaction



Ene reaction

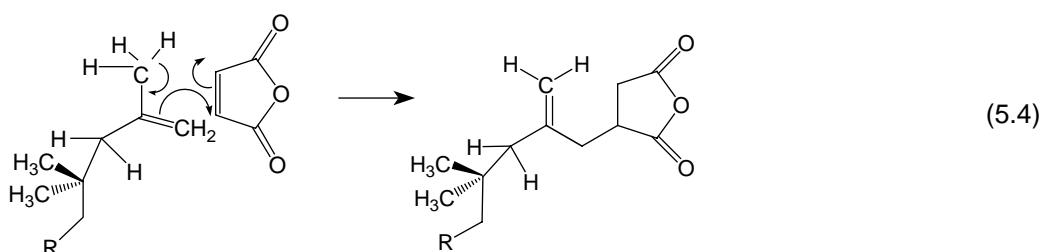
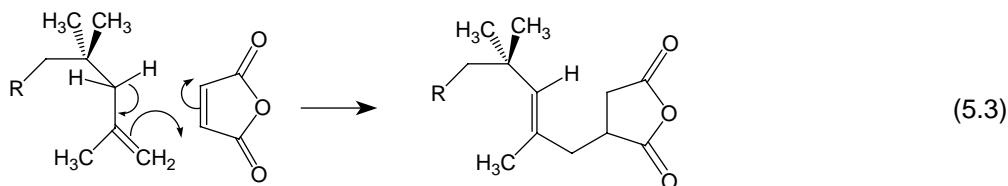


FIGURE 5.6 Mechanism of alkenylsuccinic anhydride formation.

contain piperazines as a by-product. Examining the structures of various amines, one can see that they contain primary, secondary, and tertiary amino groups. Each type of amino group has different reactivity toward alkenylsuccinic anhydride. The primary amino group reacts with the anhydride to form a cyclic imide, the secondary amino group reacts with the anhydride to form an amide/carboxylic acid, and the tertiary amino group does not react with the anhydride at all [67].

However, it can make a salt if a free carboxylic acid functionality is present in the molecule, as is the case in amide/carboxylic acid. These reactions are shown in Figure 5.10. New high-molecular-weight amines derived from phosphoric acid–catalyzed condensation of polyhydroxy compounds, such as pentaerythritol, and polyalkylene polyamines, such as triethylenetetramine, are known [68]. These amines are claimed to form high total base number (TBN) dispersants with

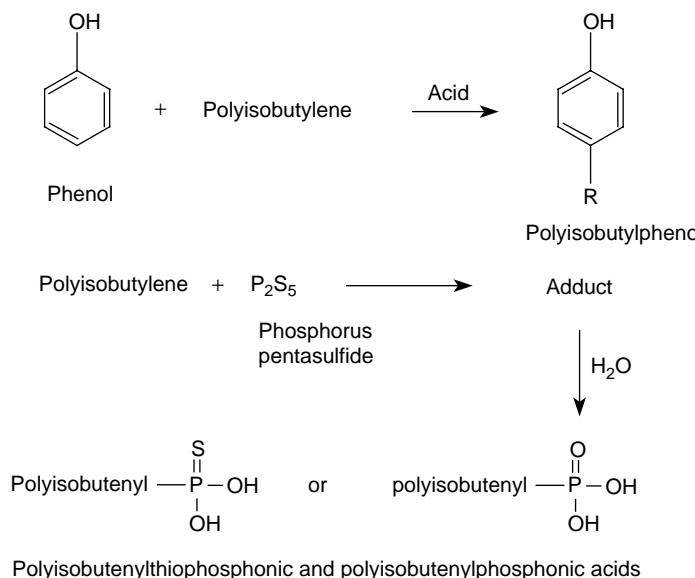


FIGURE 5.7 Synthesis of alkylphenols and alkenylphosphonic acids.

low free-amine content and better engine test performance than dispersants made from conventional polyamines.

Imide and ester dispersants are made by reacting polyamines and polyhydric alcohols with alkenylsuccinic anhydrides. The reaction typically requires a reaction temperature between 130 and 200°C to remove the resulting water and complete the reaction [44]. As mentioned earlier, imide dispersants are made by the use of polyalkylene polyamines, such as diethylenetriamine and triethylenetetramine. Many polyhydric alcohols can be used to make ester dispersants. These include trimethylolpropane, tris(hydroxymethyl)aminoethane, and pentaerythritol. When one uses tris(hydroxymethyl)aminoethane as the alcohol, one can obtain an ester dispersant with basicity. The reactions to make succinimide and succinate dispersants are depicted in Figure 5.11.

The alkylphenol-derived dispersants are made by reacting an alkylphenol, such as polyisobutylphenol, with formaldehyde and a polyamine [58,69]. The result is the formation of 2-aminomethyl-4-polyisobutylphenol. The reaction of ammonia or an amine, formaldehyde, and a compound with active hydrogen(s), such as a phenol, is called the *Mannich reaction* [70,71]. Hence, such dispersants are called Mannich dispersants. For making phosphonate dispersants, the common method is to react the free acid with an olefin epoxide, such as propylene oxide or butylene oxide, or an amine [2,72,73]. These reactions are shown in Figure 5.12. Salts derived from the direct reaction of amine and metal bases with olefin-phosphorus pentasulfide adduct are also known [74,75]. It is important to note that structures in figures are idealized structures. The actual structures will depend on the substrate (alkylphenol and alkenylsuccinic anhydride)-to-reactant (formaldehyde and polyamines) ratio.

Because of the polyfunctionality of the succinic anhydride group and of the amines and polyhydric alcohols, various dispersants can be made by altering the anhydride-to-amine or anhydride-to-alcohol ratios. These dispersants differ not only in their molecular weight but also in their properties. Polyfunctionality of the two reactants leads to dispersants, which have molecular weights that are three to seven times higher than expected if the two reactants were monofunctional.

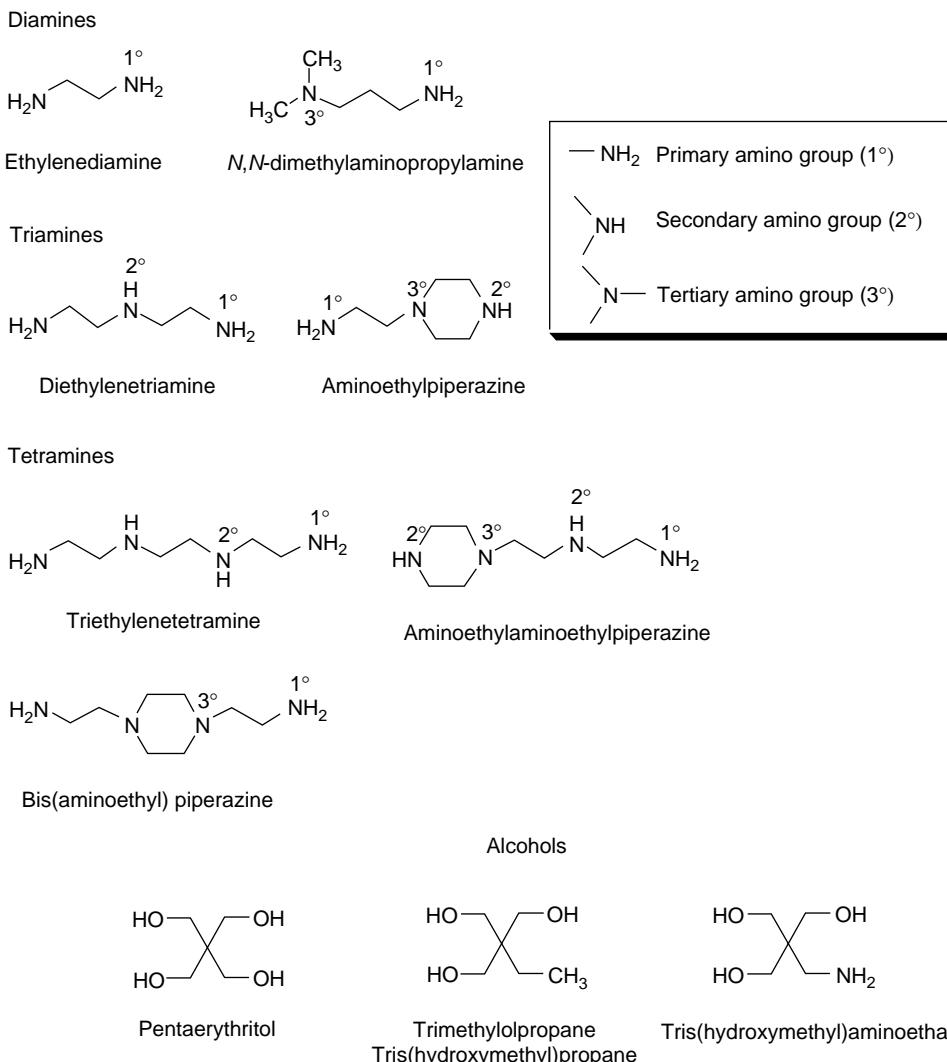


FIGURE 5.8 Amines and alcohols used to synthesize dispersants.

The methods to make DVMs are shown in Figures 5.13 through 5.15. These are synthesized by

- Grafting or reacting of a dispersancy-imparting monomer on an already-formed polymer, as in the case of EPRs and SDRs [76–84].
- Including such a monomer during the polymerization process, as in the case of polyacrylates and PMAs [85].
- Introducing a reactive functional group in the polymer that can be reacted with a reagent to impart dispersancy, as in the case of styrene–maleic anhydride copolymers [40,86–93].

Although most of the examples in Figures 5.13 through 5.15 pertain to the introduction of the basic nitrogen-containing moieties, neutral DVMs are also known in the literature. These are made by using nonbasic reactants, such as *N*-vinylpyrrolidinone, alcohols, or polyether-derived methacrylate ester [79,94,95]. Recently, dispersant viscosity-improving additives with built-in oxidation

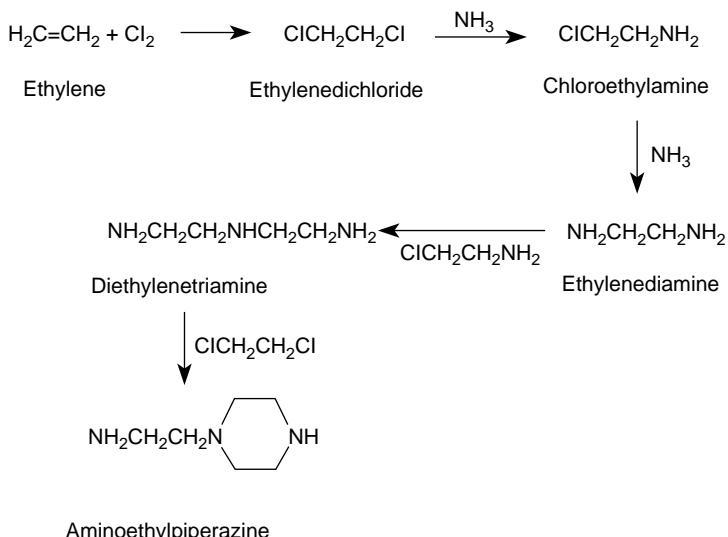


FIGURE 5.9 Manufacture of polyamines.

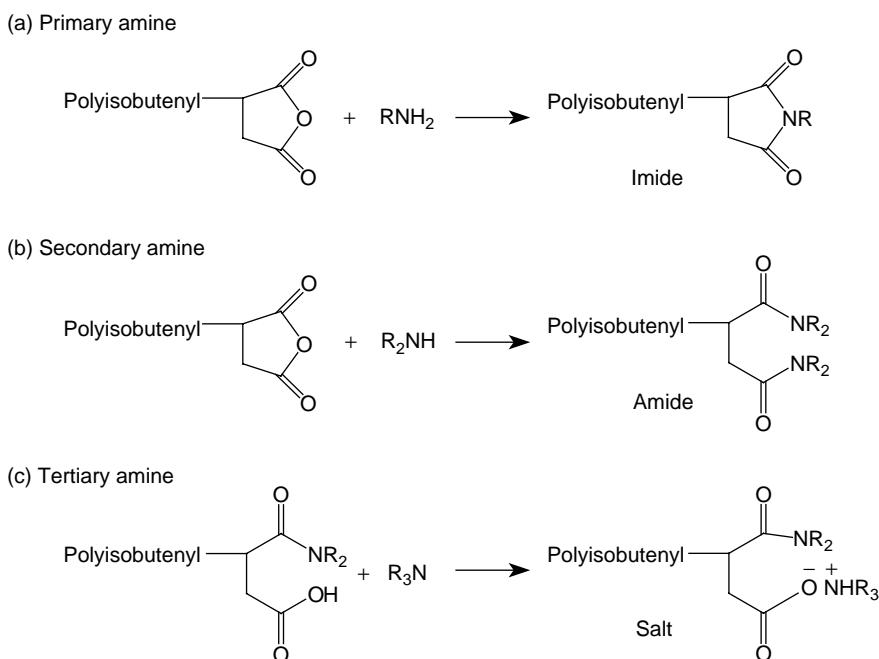


FIGURE 5.10 Amine-anhydride reaction products. (Based on Harrison, J.J., Ruhe, R., Jr., William, R., U.S. Patent 5,625,004, April 29, 1997.)

inhibiting and antiwear moieties have been reported in the patent literature [77,96,97]. Dispersant polymers containing oxidation-inhibiting moieties are commercially available from Texaco Chemical Company now part of Ethyl Petroleum Additives Company. As the examples show, grafting usually allows the introduction of the connecting group in the dispersant polymers at the same time as the polar moiety.

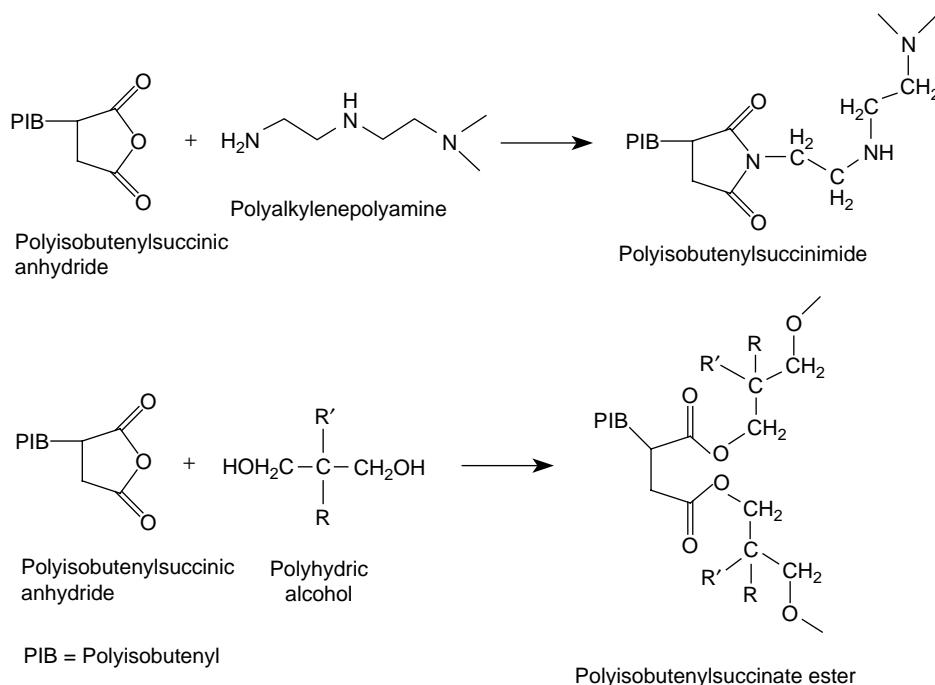


FIGURE 5.11 Synthesis of imide and ester dispersants.

5.7 DISPERSANT PROPERTIES

A dispersant consists of a hydrocarbon chain, a connecting group, and a polar functionality. Although each structural feature imparts unique properties to a dispersant, the dispersant's overall performance depends on all three. The overall performance is assessed in terms of its dispersancy, thermal and oxidative stability, viscosity characteristics, and seal performance. These criteria primarily relate to engine oils, where dispersants find major use.

5.7.1 DISPERSANCY

As mentioned, dispersancy pertains to a dispersant's ability to suspend by-products of combustion, such as soot, and lubricant degradation, such as resin, varnish, lacquer, and carbon deposits. The overall performance of a dispersant depends on all three of its structural features: the hydrocarbon chain, the connecting group, and the polar moiety. The molecular weight of the hydrocarbon group in a dispersant determines its ability to associate with undesirable polar species and suspend them in the bulk lubricant. For dispersants that have the same connecting group and the polar moiety, the lower the molecular weight, the higher the ability to associate with polar materials and the lower the ability to suspend them. Because of the trade-off between the two properties, the hydrocarbon chain must have the correct size and branching.

The size affects a dispersant's affinity toward polar materials, and branching affects its solubility, both before association and after association with the species, a dispersant is designed to suspend in oil. Experience has demonstrated that hydrocarbon groups containing 70–200 carbon atoms and extensive branching, as in the case of polyisobutylenes, are extremely suitable to design dispersants with good dispersancy. The hydrocarbon chains of larger size, even if the branching is similar, lead to dispersants with low affinity toward polar materials.

That is why dispersant polymers possess lower dispersancy than polymeric dispersants. However, since dispersant polymers have additional attributes, such as good thickening efficiency and

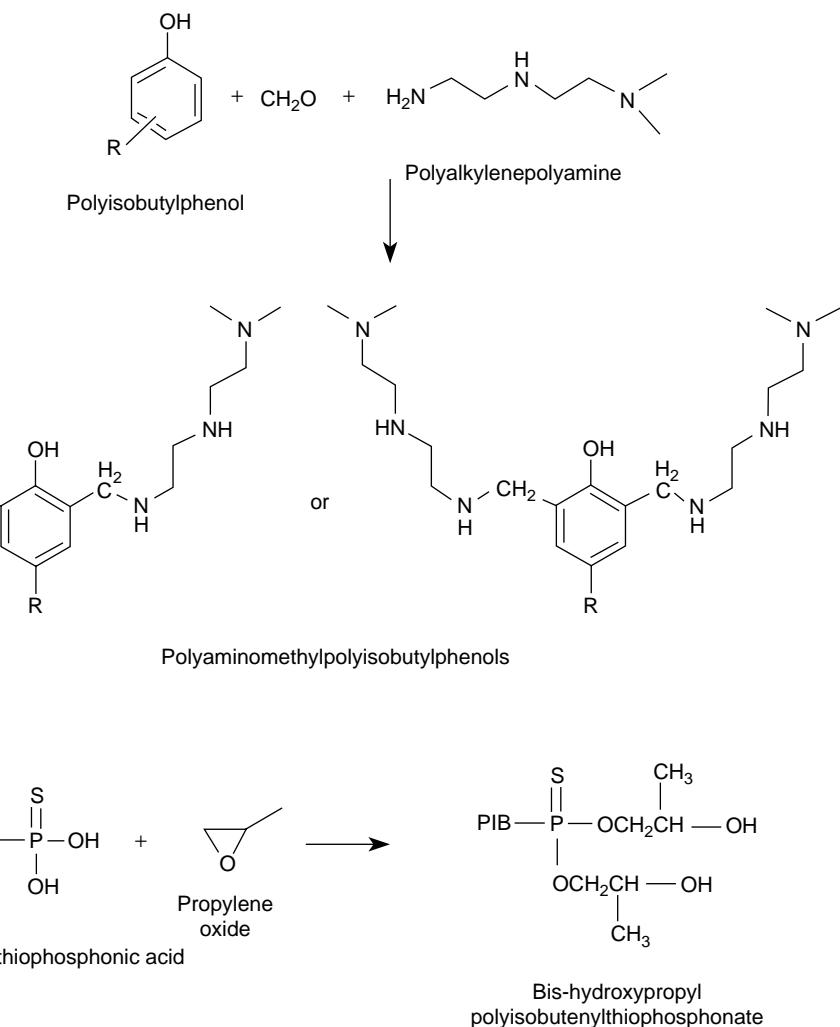


FIGURE 5.12 Synthesis of Mannich and phosphonate dispersants.

in some cases good thermal and oxidative stability, their use is advantageous. They usually replace additives, called viscosity modifiers, in the package. Since they impart some dispersancy because of their structure, the amount of polymeric dispersant in engine oil formulations is somewhat decreased [79,98].

Both the connecting group and the polar moiety are important to the dispersancy of the dispersant molecule. They must be considered together since both contribute toward polarity. In Mannich dispersants, the phenol functional group, and in imide and ester dispersants, succinimide, succinate, and phosphonate functional groups are also polar, the same as the amine and the alcohol-derived portion of the molecule. The polarity is a consequence of the electronegativity difference between carbon, oxygen, nitrogen, and phosphorus atoms. The greater the electronegativity difference, the stronger the polarity. This implies that groups that contain phosphorus–oxygen bonds are more polar than those containing carbon–oxygen bonds, carbon–nitrogen bonds, and carbon–phosphorus bonds. The electronegativity difference for such bonds is 1.4, 1.0, 0.5, and 0.4, respectively [99]. However, since dispersants have many bonds with various combinations of atoms, the overall polarity in a dispersant and its ability to associate with polar materials are not easy to predict.

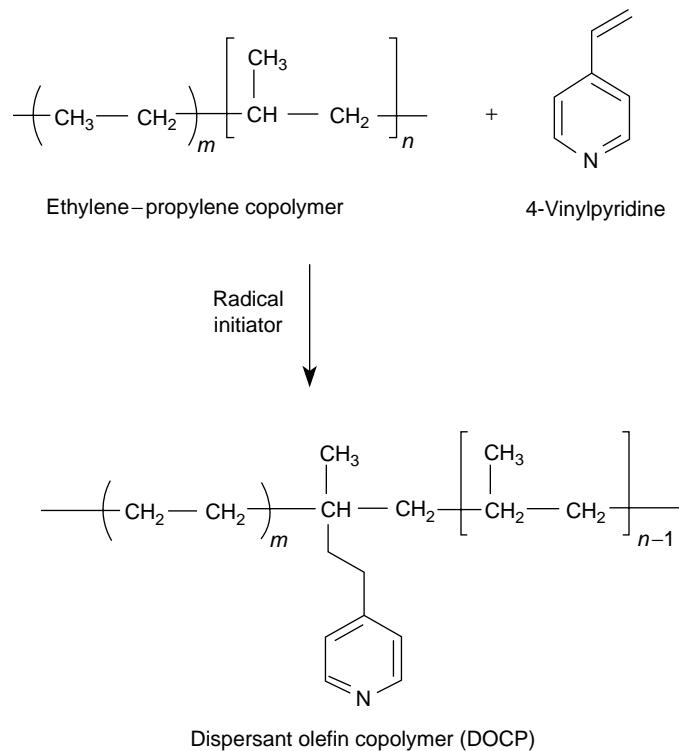


FIGURE 5.13 Dispersant viscosity modifier synthesis through grafting.

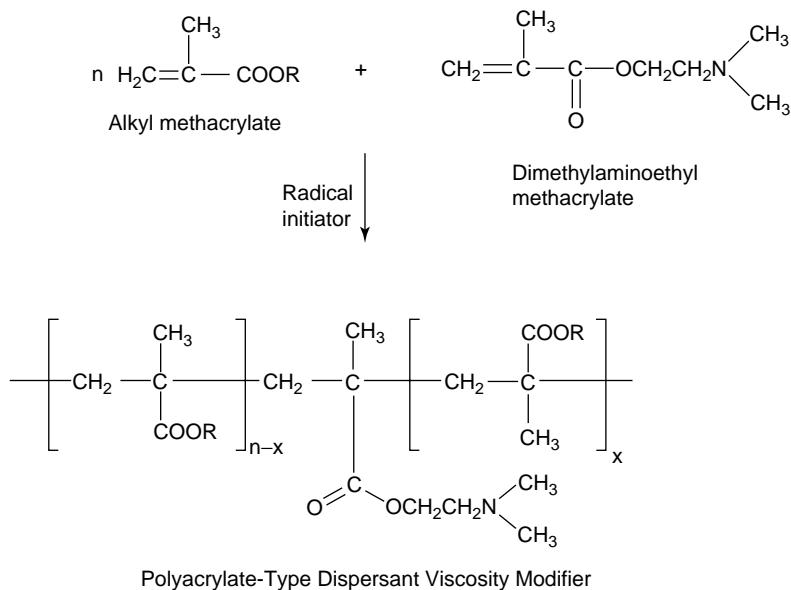


FIGURE 5.14 Dispersant viscosity modifier synthesis through copolymerization.

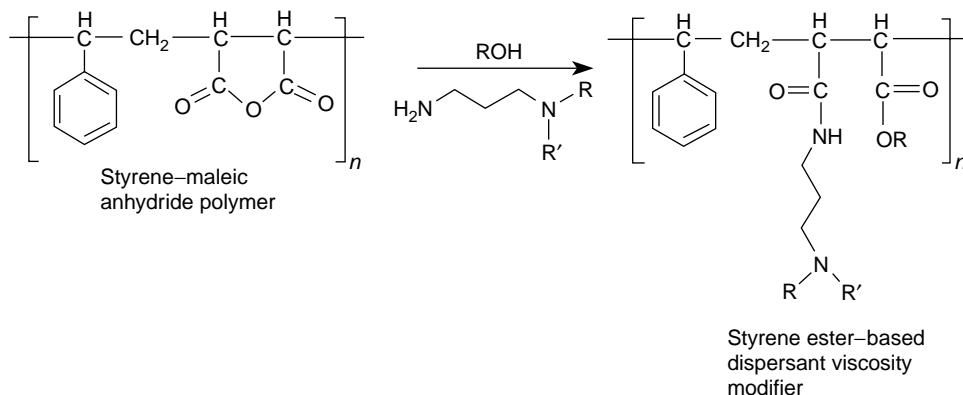


FIGURE 5.15 Dispersant viscosity modifier synthesis through chemical reaction.

Because some of the materials with which the dispersant associates are acidic, such as carboxylic acids derived from lubricant oxidation, the presence of an amine nitrogen is an advantage because of its basic character. Therefore, in certain gasoline engine tests, nitrogen dispersants are superior to ester dispersants. Ester dispersants are usually superior in diesel engine tests because of their higher thermo-oxidative stability. Mannich dispersants are good low-temperature dispersants; hence, they are typically used in gasoline engine oils.

As mentioned earlier, commercial polyisobutylenes have a molecular weight distribution. This will lead to dispersant structures of varying size, hence molecular weight. An optimum ratio between the molecular weight of the hydrocarbon chain and that of the polar functionality (polar/nonpolar ratio) is a prerequisite for good dispersancy. If a dispersant composition has an excessive amount of components with short hydrocarbon chains, that is, of low molecular weight, its associating ability increases, but its oil solubility suffers. This is likely to deteriorate its dispersancy, especially after associating with polar impurities. Such structures in dispersants are, therefore, undesired. Their formation can be minimized by using polyolefins of low polydispersity index, controlling the formation of low-molecular-weight components, removing such components through distillation [100], or postreacting with another reagent, preferably of the hydrocarbon type. Polyolefins of low polydispersity index (≤ 2) are available from BP and Exxon Chemical Company. Controlling the formation of low-molecular-weight components is exemplified by the use of boron trifluoride catalyst for making alkylphenols instead of aluminum chloride, which tends to fragment polyisobutylene. Removing the lower-molecular-weight components, although not easy, is possible at the precursor stage, which is before reacting with the alcohol or the amine. A number of reagents can be used for the postreaction [101]. Hydrocarbon posttreatment agents include polyepoxides [102], polycarboxylic acid [103], alkylbenzenesulfonic acids [104], and alkenylnitriles [105]. Whenever posttreated dispersants are used in engine oils, improved dispersancy, viscosity index credit, improved fluorocarbon elastomer compatibility, hydrolytic stability, and shear stability are often claimed.

5.7.2 THERMAL AND OXIDATIVE STABILITY

All the three components of the dispersant structure determine its thermal and oxidative stability, the same as dispersancy. The *hydrocarbon group* can oxidize in the same manner as the lubricant hydrocarbons to form oxidation products that can contribute toward deposit-forming species [4,9]. (This is described in Section 5.2.) Although the rate of oxidation is quite slow for largely paraffinic hydrocarbon groups, such as polyisobutyl group, it is quite high for those that contain multiple bonds, such as polyisobutenyl, and the benzylic groups. The benzylic functional group is present in styrene

butadiene and styrene ester-derived dispersant polymers. Purely paraffinic hydrocarbon groups that contain tertiary hydrogen atoms, such as EPRs, oxidize at a faster rate than those that contain only primary and secondary hydrogen atoms. Styrene isoprene-derived materials contain both benzylic and tertiary hydrogen atoms. This implies that highly branched alkyl groups, such as polyisobutyl and polyisobutetyl, have a higher susceptibility toward oxidation than linear or unbranched alkyl groups. Dispersant polymers with built-in oxidation-inhibiting moieties are known in the literature [77,78,96]. The polar moiety in an amine-derived dispersant is also likely to oxidize at a faster rate than the oxygen-derived moiety because of the facile formation of the amine oxide functional group on oxidation. Such groups are known to thermally undergo β -elimination [40], called the *cope reaction*, to form an olefin. This can oxidize at a faster rate as well as lead to deposit-forming polymeric products.

From a thermal stability perspective, the hydrocarbon group in the case of high-molecular-weight dispersant polymers, such as those derived from OCPs, is more likely to break down (unzip) than that derived from the low-molecular-weight polymers. Dispersants based on 1000–2000 molecular weight polyisobutylenes are relatively stable, except at very high temperatures that are experienced in some engine parts, such as near the top of the piston [17,18]. Thermal breakdown of the oxidized amine polar group is mentioned in the previous paragraph.

The chemical reactivity of certain dispersants toward water and other reactive chemicals present in the lubricant formulation is an additional concern. The most likely reaction site is the connecting group. The common connecting groups are amide and imide in amine-derived dispersants and ester in alcohol-derived dispersants. All three can hydrolyze in the presence of water [106], but at different rates. Esters are easier to hydrolyze than amides and imides. The hydrolysis is facilitated by the presence of bases and acids. Basic detergents are the source of the metal carbonate and metal hydroxide bases, which at high temperatures catalyze the hydrolysis reaction. Additives, such as zinc dialkyldithiophosphates, are a source of strong acids that result when these additives hydrolyze, thermally decompose, or oxidize. The fate of the ester-, amide-, and imide-type dispersant polymers, such as those derived from polyacrylates, PMAs, and styrene ester substrates, is the same. Some OCP-derived dispersant polymers, such as those obtained by grafting of monomers 2- or 4-vinylpyridine and 1-vinyl-2-pyrrolidinone [76,80], do not suffer from this problem since they do not contain easily hydrolyzable groups. Reactivity toward other chemicals present in the formulation is again prevalent in the case of ester-derived dispersants. Reaction with metal-containing additives, such as detergents and zinc dialkyldithiophosphates, can occur after hydrolysis to form metal salts. This can destroy the polymeric structure of a dispersant and hence its effectiveness. Some formulations contain amines or their salts as corrosion inhibitors or friction modifiers. Depending on the molecular weight and the ambient temperature, these can displace the polyol or sometimes the polyamine, thereby altering the dispersant structure, hence its properties.

5.7.3 VISCOSITY CHARACTERISTICS

The amount of dispersant in automotive engine oils typically ranges between 3 and 7% by weight [79], making it the highest among additives. In addition, dispersant is the highest molecular-weight component except the viscosity improver [107]. Both of these factors can alter some physical properties, such as viscosity, of the lubricant. A boost in the viscosity of a lubricant at high temperatures is desired, but at low temperatures it is a disadvantage. At high temperatures, the lubricant loses some of its viscosity [108], hence its film-forming ability, resulting in poor lubrication. Maintaining good high-temperature viscosity of a lubricant is therefore imperative to minimize wear damage. This is usually achieved by the use of polymeric viscosity modifiers [3,109]. Some dispersants, especially those that are based on high-molecular-weight polyolefins and have been oversuccinated partly fulfill this need [44]. Therefore, the amount of polymeric viscosity modifier necessary to achieve specific high-temperature viscosity is reduced. Unfortunately, dispersants that provide a viscosity advantage lead to a viscosity increase at low temperatures as well. The low-temperature viscosity requirements for engine oils have two components: *cranking viscosity* and *pumping*

viscosity [110]. Cranking viscosity is an indication of how easily the engine will turn over in extremely cold weather conditions. Pumping viscosity is the ability of the lubricant to be pumped to reach various parts of the engine. For cold weather operation, low to moderate cranking and pumping viscosities are highly desirable. Although pumping viscosity and the pour point can be lowered by the use of additives, called pour point depressants [3,13], lowering cranking viscosity is not easy. In the case of base oils, this is usually achieved by blending carefully selected base stocks. An ideal polymeric dispersant must provide high-temperature viscosity advantage without adversely affecting the cold-cranking viscosity of the lubricant. Dispersant polymers have the same requirement. Good high-temperature viscosity to cranking viscosity ratio in polymeric dispersants can be achieved by

- Carefully balancing the type and the molecular weight of the hydrocarbon chain [111]
- Choosing the optimum olefin to maleic anhydride molar ratio [112]
- Selecting the type and the amount of the polyamine used

In dispersant polymers this can be achieved by selecting (1) a polymer of correct molecular weight and branching and (2) a suitable pendant group. Dispersant polymers derived from medium-molecular-weight, highly branched structures, and ester-type pendant groups are best suited for use as additives. Examples include polyacrylate, PMA, and styrene ester-derived dispersants. These additives not only act as viscosity modifiers and dispersants but also act as pour point depressants, thereby improving the low-temperature properties of the lubricant.

A number of patents pertaining to dispersants with balanced high-temperature viscosities and low-temperature properties are reported in the patent literature [113–117]. A Mannich (alkylphenol) dispersant, derived from ethylene/1-butene polymers of Mn 1500–7500, has been claimed to possess improved dispersancy and pour point [113]. Another patent claiming the synthesis of a dispersant with superior dispersancy and pour point depressing properties has also been issued [114]. The dispersant is based on the reaction of maleic anhydride/lauryl methacrylate/stearyl methacrylate terpolymer with dimethylaminopropylamine, and a Mannich base was obtained by reacting *N*-aminoethylpiperazine, paraformaldehyde, and 2,6-di-*t*-butyl phenol. A number of patents describe the use of ethylene/ α -olefin/diene interpolymers to make dispersants [115–117]. These dispersants are claimed to possess excellent high- and low-temperature viscosities, as defined by VR'/VR . Here VR' pertains to the dispersant and VR pertains to the precursor, such as alkylphenol or alkenylsuccinic anhydride. VR' is the ratio of the -20°C cold-cranking simulator (CCS) viscosity (cP) of a 2% solution of dispersant in a reference oil to the 100°C kinematic viscosity (cSt) of the dispersant. VR is the ratio of the -20°C CCS viscosity (cP) of a 2% solution of precursor in the reference oil to the 100°C kinematic viscosity (cSt) of the precursor. The values of 2.0–3.9 for VR and VR' and of <1.11 for VR'/VR are considered suitable for balanced low- and high-temperature viscosities.

5.7.4 SEAL PERFORMANCE

Seals in automotive equipment are used for many purposes, the most prominent of which are to have easy access to malfunctioning parts to perform repair and to minimize contamination and loss of lubricant. Various polymeric materials are used to make seals. These include fluoroelastomers, nitrile rubber, polyacrylates, and polysiloxanes (silicones). Maintaining the integrity of seals is critical; otherwise, the lubricant will be lost, and wear damage and equipment failure will occur. The seals fail in a number of ways. They can shrink, elongate, or become brittle and thus deteriorate. The damage to elastomer seals is assessed by examining volume, hardness, tensile strength change, and the tendency to elongate and rupture [118]. Two primary mechanisms by which seal damage can occur include abrasion due to particulate matter in the lubricant and the attack of various lubricant components on the seals. The lubricant-related damage can occur when some of its components

diffuse into the seals. This will either cause a change in the seal's hardness, thereby leading to swelling and or elongation, or extract the plasticizer, an agent used to impart flexibility and strength to polymeric materials.

Abrasive damage is not common since most equipment has an installed lubricant filtration system. The lubricant-related damage, however, is of primary interest to us. The lubricant is a blend of base stocks and an additive package. Certain base stocks, such as those of high aromatics content or those that are of the ester type, have the tendency to extract the plasticizer because of their high polarity. Additives, however, have the ability to diffuse into the seal material and alter its properties as well as remove the plasticizer. Among additives, dispersants are the most implicated in causing seal damage, especially to fluoroelastomer (Viton[®]) seals. Although in many cases seal failure can be corrected by the use of additives, called the seal-swell agents, it is wise to eliminate such damage by prevention. Elastomer compatibility requirements are a part of the current United States, Association des Constructeurs Européens de l'Automobile (ACEA), and Japanese standards for engine oils and worldwide automotive transmission and tractor hydraulic fluid specifications [119]. Damage to seals is prevalent in the case of nitrogen dispersants. In general, the higher the nitrogen content, the higher the seal problems [118]. Rationally, these problems occur due to the presence of low-molecular-weight molecules in the dispersant. These include free amine either as such or in a labile form, such as an alkylammonium salt, or low-molecular-weight succinimides and succinamides. Because of their high polarity and smaller size, these molecules are more likely to diffuse into the seal material and alter its physical and mechanical properties [120]. It is believed that in the case of Viton seals, the loss of fluoride ions is responsible for seal deterioration. Removal of the free amine and of low-molecular-weight succinimides will improve seal performance. Alternatively, one can posttreat dispersants with reagents, such as boric acid and epoxides, which will either make such species innocuous or hinder their diffusion into the seal material. Many chemical treatments of dispersants, covered in Section 5.7.1, claim to improve seal performance of dispersants and crankcase lubricants that use them. These reagents react with seal-damaging amines and low-molecular-weight succinimides to make them harmless. Strategies other than those listed earlier are also reported in the patent literature [121–125].

5.8 PERFORMANCE TESTING

Engine oils account for almost 80% of the automatic transmission dispersant use. Other applications that use these additives include automatic transmission fluids, gear lubricants, hydraulic fluids, and refinery processes as antifoulants. Dispersants of relatively lower molecular weight are also used in fuels to control injector and combustion chamber deposits [126,127]. Such dispersants usually contain a polyether functionality [128].

Succinimide and succinate ester-type polymeric dispersants are used in gasoline and diesel engine oils, but the use of alkylphenol-derived dispersants, that is, of the Mannich type, is limited to gasoline engine oils. Dispersant polymers derived from ethylene-propylene rubbers, styrene–diene copolymers, and PMAs are also used in both gasoline and diesel engine oils. As mentioned earlier, dispersant polymers lack sufficient dispersancy to be used alone and hence are used in combination with polymeric dispersants. The PMA and styrene ester–derived dispersant polymers are used in automatic transmission fluids, in power-steering fluids, and, to a limited extent, in gear oils.

Additive manufacturers use various laboratory screen tests and engine tests to evaluate a dispersant's effectiveness. Many of the screen tests are proprietary, but all are developed around evaluating performance in terms of a dispersant's ability to disperse lamp black or used engine oil sludge. The laboratory engine tests are industry-required tests and include both gasoline engine and diesel engine tests. These are listed in International Lubricant Standardization and Approval Committee (ILSAC), American Petroleum Institute (API), ACEA 2002, Japanese Automobile Standards Organization (JASO), and Bureau of Indian Standards (BIS) standards. It is important

to note that the U.S. military and original equipment manufacturers (OEMs) have their own performance requirements, which are over and above those of the API. Although the details of various tests are available in these standards and elsewhere [119], the important engine tests that evaluate a dispersant's performance are listed in Tables 5.1 through 5.4.

TABLE 5.1
U.S. Gasoline Engine Tests

Engine Test	Engine Type	Evaluation Criteria
CRC L-38	CLR single-cylinder engine	Bearing corrosion, sludge, varnish, oil oxidation, and viscosity change
ASTM sequence IIIE	1987 Buick V6 engine	Sludge, varnish, wear, and viscosity change
ASTM sequence IIIF	1996 Buick V6 engine	Sludge, varnish, wear, and viscosity change
ASTM sequence VE	Ford Dual-Plug head four-cylinder engine	Sludge, varnish, and wear
ASTM sequence VG	Ford V8 engine	Sludge, varnish, and wear
TEOST	Bench test	Thermal and oxidative stability
High-temperature deposit test	Bench test	High-temperature deposits

TABLE 5.2
U.S. Diesel Engine Tests

Engine Test	Engine Type	Evaluation Criteria
Caterpillar 1K	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Caterpillar 1M-PC	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Caterpillar 1N	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Caterpillar 1P	Caterpillar single-cylinder engine	Piston deposits and oil consumption
Mack T-6	Multicylinder engine	Piston deposits, wear, oil consumption, and oil thickening
Mack T-7	Multicylinder engine	Oil thickening
Mack T-8	Multicylinder engine	Oil thickening
Mack T-9	Multicylinder engine	Soot thickening

TABLE 5.3
European Gasoline Engine Tests

Engine Test	Engine Type	Evaluation Criteria
ASTM sequence IIIE	Six-cylinder engine	High-temperature oxidation (sludge, varnish, wear, and viscosity increase)
ASTM sequence VE	Four-cylinder engine	Low-temperature sludge, varnish, and wear
Peugeot TU-3M high temperature	Four-cylinder single-point injection engine	Piston deposits, ring sticking, viscosity increase
M-B M111 black sludge	Four-cylinder multipoint injection engine	Engine sludge and cam wear
VW 1302	Four-cylinder carbureted engine	Piston deposits, varnish, wear, and oil consumption
VW T-4	Four-cylinder multipoint injection engine	Extended drain capability

TABLE 5.4
Current European Diesel Engine Tests

Engine Test	Engine Type	Evaluation Criteria
VW 1.6TC diesel intercooler	Four-cylinder engine	Piston deposits, varnish, and ring sticking
VW D1	Four-cylinder direct-injection engine	Piston deposits, viscosity increase, and ring sticking
Peugeot XUD11ATE	Four-cylinder indirect-injection engine	Piston deposits and viscosity increase
Peugeot XUD11BTE	Four-cylinder indirect-injection engine	Piston deposits and viscosity increase
M-B OM 602A	Five-cylinder indirect-injection engine	Engine wear and cleanliness
M-B OM 364A/LA	Four-cylinder direct-injection engine	Bore polishing, piston deposits, varnish, sludge, wear, and oil consumption
M-B OM 441LA	Six-cylinder direct-injection engine	Piston deposits, bore polishing, wear, oil consumption, valve train condition, and turbo deposits
MAN 5305	Single-cylinder engine	Piston deposits, bore polishing, and oil consumption
Mack T-8	Multicylinder engine	Soot-related oil thickening

As mentioned earlier, soot-related viscosity increase and deposit-related factors are the primary criteria for evaluating a dispersant's performance. Moreover, as commented in Chapter 4, neutral detergents (soaps) also help control deposits such as varnish, lacquer, sludge, and carbon. Therefore, besides the control of soot-related viscosity increase, which is the sole domain of dispersants, deposit control is the result of a joint performance of the detergent and the dispersant. However, in this regard, the dispersant plays a more prominent role.

Besides engine oils, transmission fluids are the primary users of dispersants. Certain parts of the transmission see very high temperatures, which lead to extensive lubricant oxidation. The oxidation products, such as sludge and varnish, appear on parts; for instance, clutch housing, clutch piston, control valve body, and oil screen components. This can impair the functioning of these parts. A turbohydramatic oxidation test (THOT) is used to determine a transmission fluid's oxidative stability.

Polymeric dispersants are useful in controlling sludge buildup [129]. When friction modification of the transmission fluid is the goal, either dispersants or their precursors, such as alkenylsuccinic acids or anhydrides, are used in combination with metal sulfonates [130–134]. In many such formulations, the borated dispersant and the borated detergent (metal sulfonate) are used.

Dispersants are used in gear oils to improve their properties also. Gear oils usually contain thermally labile extreme-pressure additives. Their decomposition by-products are highly polar, and dispersants are used to contain them to avoid corrosion and deposit formation [135,136]. Polymeric dispersants are used in hydraulic fluids to overcome wet filtration (Association Française de Normalisation [AFNOR]) problems, which is often required for HF-0-type fluids [137]. Filtration problems occur due to the interaction of water with metal sulfonate detergent and zinc dialkyldithiophosphate that are used as additives in hydraulic fluid formulations. Fouling is a common problem in many processes, including refinery processes. Fouling refers to the deposition of various inorganic and organic materials, such as salt, dirt, and asphaltenes, on heat-transfer surfaces and other processing equipment. This results in poor heat transfer, among other problems. Antifoulants are chemicals used in refinery operations to overcome fouling. Detergents and dispersants are often used for this purpose [138–140].

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Part 2

Film-Forming Additives

6 Selection and Application of Solid Lubricants as Friction Modifiers

Gino Mariani

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6.1 INTRODUCTION

Solid lubricants are considered to be any solid material that reduces friction and mechanical interactions between surfaces in relative motion against the action of a load. Solid lubricants offer alternatives to the lubricant formulator for situations where traditional liquid additives fall short on performance. An example is a high-temperature lubrication condition in which oxidation and decomposition of the liquid lubricant will certainly occur, resulting in lubrication failure. Another example is for situations that generate high loads and contact stresses on bearing points of mating surfaces, producing a squeeze-out of the liquid lubricant and a resulting lubricant starvation (see Figure 6.1).

Solid lubricants, used as a dry film or as an additive in a liquid, provide enhanced lubrication for many different types of applications. Typical hot-temperature applications include oven chain lubrication and metal deformation processes such as hot forging. Solid lubricants are also helpful for ambient-temperature applications such as drawing and stamping of sheet metal or bar stock. Solid lubricants are effectively used in antiseize compounds and threading compounds, which provide a sealing function and a friction reduction effect for threaded pipe assembly [1]. Applications involving low sliding speeds and high contact loads, such as for gear lubrication, also benefit from solid lubricants. The solid lubricant effectively provides the required wear protection and load-bearing performance necessary from gear oil, especially capable when used with lower-viscosity base oils.

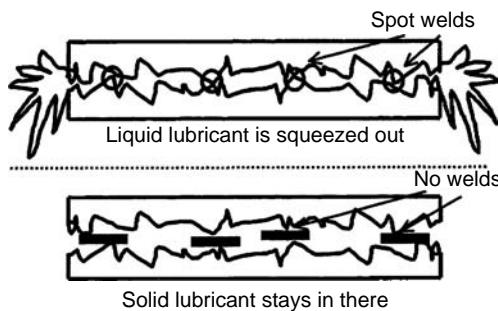


FIGURE 6.1 Contact stresses on bearing points of mating surfaces cause a squeeze-out.

Solid lubricants also assist applications where the sliding surfaces are of a *rough* texture or surface topography. Under this circumstance, the solid lubricant is more capable than liquid lubricants for covering the surface asperity of the mating surfaces. A typical application is a reciprocating motion that requires lubrication to minimize wear. Another application for solid lubricants is for cases where chemically active lubricant additives have not been found for a particular surface, such as polymers or ceramics. In this case, a solid lubricant would function to provide the necessary protection to the mating surfaces, which would normally occur due to the reaction of a liquid component with the surface [2].

Graphite and molybdenum disulfide (MoS_2) are the predominant materials used as solid lubricants. These pigments are effective load-bearing lubricant additives due to their lamellar structure. Because of the solid and crystalline nature of these pigments, graphite and MoS_2 exhibit favorable tolerance to high-temperature and oxidizing atmosphere environments, whereas liquid lubricants typically will not survive. This characteristic makes graphite and molybdenum disulfide lubricants necessary for processes involving extreme temperatures or extreme contact pressures.

Other compounds that are useful solid lubricants include boron nitride, polytetrafluoroethylene (PTFE), talc, calcium fluoride, cerium fluoride, and tungsten disulfide. Any one of these compounds may be more suitable than graphite or MoS_2 for specific applications. Boron nitride and PTFE are discussed along with graphite and molybdenum disulfide in this chapter.

What are the basic requirements for an effective solid lubricant? Five properties must be met in a favorable way [3].

1. *Yield strength.* This refers to the force required to break through the lubricant or deform its film. There should be high yield strength to forces applied perpendicular to the lubricant. This will provide the required boundary lubrication and protection to loads between the mating surfaces. Low yield strength of the film should be present in the direction of sliding to provide reduced coefficient of friction. This dependency on directional application of forces is considered an anisotropic property.
2. *Adhesion to substrate.* The lubricant must be formulated in a manner that maintains the lubricant film on the substrate for a sufficient period necessary for the lubrication requirements. The force of adhesion should exceed that of the sheer forces applied to the film. Any premature adhesion failure will result in a nonprotective condition between the two sliding surfaces that require lubrication.
3. *Cohesion.* Individual particles in the film of solid lubricant should be capable of building a layer thick enough to protect the high asperities of the surface and to provide a “reservoir” of lubricant for replenishment during consumption of the solid film (see Figures 6.2 and 6.3).
4. *Orientation.* The particles used must be oriented in a manner that parallels the flow of the stress forces and provide the maximum opportunity for a reduction in the coefficient of friction. For this to occur, it is necessary for the dimensions of the particles to be greatest in the direction of low shear.

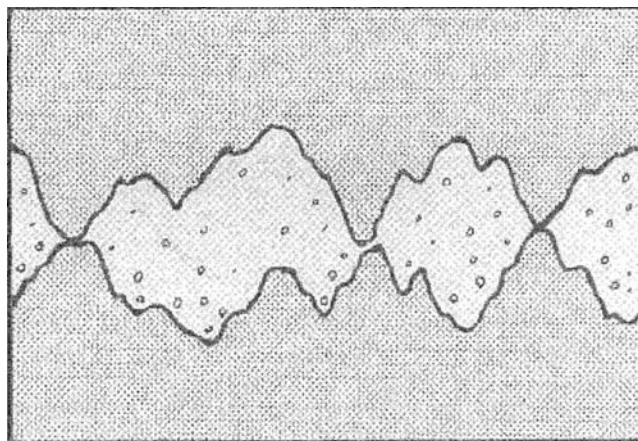


FIGURE 6.2 Surface asperities.

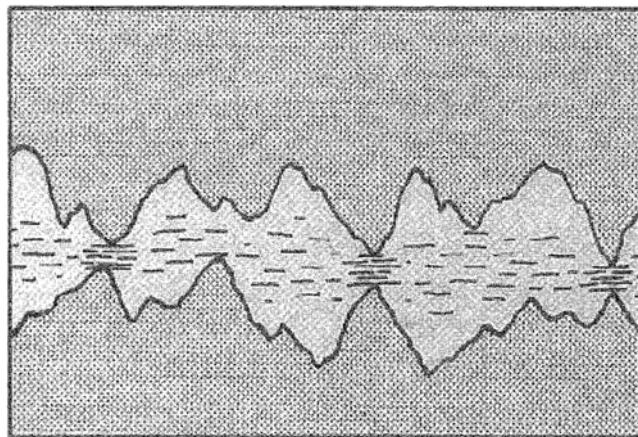


FIGURE 6.3 Burnished lubricant.

5. *Plastic flow.* The lubricant should not undergo plastic deformation when loads are applied directly perpendicular to the direction of motion. The solid should be able to withstand the intimate contact between the mating surfaces so that a continuous film of lubrication is maintained.

This chapter attempts to guide the formulator toward making successful choices in solid lubricants. It briefly summarizes the physical and chemical properties of the solid lubricant and discusses the merits of each type of major lubricant as well as the recommended application. The information will assist in understanding the chemistry of the lubricant and its general mechanism of lubrication.

6.2 SOLID LUBRICANT PROPERTIES

6.2.1 GRAPHITE

Graphite is most effective for applications involving high-temperature and high load-carrying situations. These capabilities make graphite the solid lubricant of choice for forging processes. Solid lubricants such as MoS_2 will oxidize too rapidly to be of any value at the typical hot-forging temperature range of 760–1200°C, although MoS_2 has a greater lubrication capability than graphite.

Why is graphite such a good lubricant? The answer lies in the platelet, lamellar structure of the graphite crystallite (see Figure 6.4). Graphite is structurally composed of planes of polycyclic carbon atoms that are hexagonal in orientation. Short bond lengths between each carbon atom within the plane are the result of strong covalent bonds (see Figure 6.4).

Weaker van der Waals forces hold together a number of planes to create the lattice structure. The *d*-spacing bond distance of carbon atoms between planes is longer and, therefore, weaker than the bond distance between carbon atoms within the planes. As a force is applied perpendicular to the crystallite, a strong resistance is applied against the force. This high yield strength provides the load-carrying capacity for the lubricant. Concurrent with the force applied perpendicular to the substrate is a sliding force applied parallel to the direction of sliding. The weak bond between the planes allows for easy shearing of the planes in the direction of the force. This creates a cleaving of the planes and results in friction reduction. The lamellar motion of graphite cleavage can be illustrated by the concept of a hand applying a force on a deck of playing cards as shown in Figure 6.5. Forces applied perpendicular to the deck are resisted by the stack's thickness

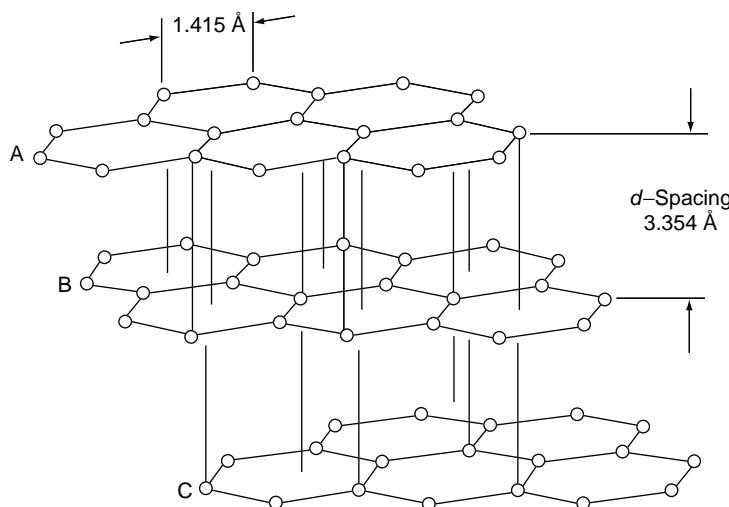


FIGURE 6.4 Structure of graphite.

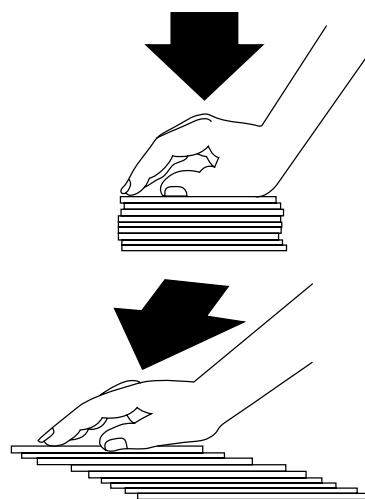


FIGURE 6.5 Representation of lamellar lubrication.

TABLE 6.1
Coefficients of Friction Provided by Graphite Films

Test Method	Graphite Film	Unlubricated Metal	Mineral Oil on Metal
Three-ball slider	0.09–0.12	0.16–0.18	0.15–0.17
Bowden–Leben machine	0.07–0.10	0.40	0.17–0.22

TABLE 6.2
Natural Graphite

	Amorphous	Crystalline Flake 1	Crystalline Flake 2
% Carbon	–85.0	90–95	96–98
% Sulfur	–0.30	0.15–0.20	0.10–0.70
% SiO ₂	6.0–7.0	0.20–0.30	0.05–0.2
% Ash	10–15	7–10	2.0–3.0
Mesh	–325	–325	–325

and yield strength. Yet, a far easier force is required to rupture the stack when the force is applied parallel along the face of the deck, resulting in the shearing of the cards.

The effects of the lamellar structure of graphite can be observed when sliding conditions are applied onto metal surfaces. Coefficient of friction data can be generated by various bench test methods for measuring the lubricity of sliding conditions. In comparison to unlubricated or oil-lubricated metal surfaces, graphite provides excellent lubricity [4]. This is summarized in Table 6.1.

6.2.1.1 Sources of Graphite

There are many types and sources of graphite. These sources influence the properties of the graphite, which affects the performance of the end product that uses graphite. Graphite is characterized by two main groupings: natural and synthetic.

Natural graphite is derived from mining operations worldwide. The ore is processed to recover the usable graphite. Varying quality of the graphite will be evident from the ore quality and the postmining processing of the ore. High-purity natural graphite will normally be highly lubricating and resistant to oxidation. This is due to the high degree of crystal structure and graphitization usually associated with naturally derived graphite.

Natural graphite of lesser quality is also available. A lower total carbon content and a lower degree of graphitization characterize the lesser quality. The end product is graphite that is more amorphous in nature, with a higher content of ash components, which are mostly oxides of silicon and iron. Lubrication functionality decreases as crystallinity and graphitization decrease. Lubrication functionality also decreases as total ash content of the graphite increases.

Commercially available natural graphite is provided in a variety of grades. The suitability of the grades depends on the intended application and economic constraints. Table 6.2 characterizes examples of commercially available natural graphite.

Selecting the type of natural graphite to use is based on the degree of lubrication required for the application, the particle size of the graphite necessary for the application, and the economic constraint. For situations where the lubrication demand is severe, a high-carbon crystalline flake or crystalline vein graphite is desired. The high degree of crystallinity and graphitization provides superior lubrication. A more economical alternative is the lower-carbon-content flake graphite.

TABLE 6.3
Synthetic Graphite

	Typical Values	
	Primary	Secondary
% Carbon	99.9	99.9
% Sulfur	Trace	0.01
% SiO ₂	0.02	0.05
% Ash	0.1	0.1

For most situations, these types of graphite perform adequately in lubricating conditions that do not require the purity and lubricity of higher-quality crystalline graphite. For occasions where only minor lubricity is needed and perhaps a more thermally insulating coating is required, amorphous graphite would be chosen. Amorphous graphite is also the least expensive of the commercially available natural graphite grades. Combining amorphous and crystalline graphite can also be done to modify the amount of lubrication to suit the requirements of the application.

Synthetic graphite is an alternative source for lubricating graphite. Synthetic graphite is characterized as primary or secondary grade (see Table 6.3). Primary grade is derived synthetically from production within an electric furnace, utilizing calcined petroleum coke as well as very high temperatures and pressures to produce the graphite. The result is usually a product of high purity and can approach the quality of natural graphite flake in terms of percent graphitization and lubrication capability.

Secondary synthetic graphite is derived from primary graphite that has been used for the fabrication of electrodes. This type of graphite is usually less lubricating than natural or primary grades of graphite because of its lesser degree of crystallinity and graphitization and the presence of binding agents and surface oxides that do not contribute to lubrication. Secondary synthetic graphite is perfectly capable of lubricating effectively for many applications that can afford a lesser degree of lubricity. The chief benefit in using secondary synthetic graphite is the cost, with the secondary graphite costing significantly less than primary-grade synthetic graphite or high-purity natural graphite.

6.2.1.2 Lubrication

Appropriate-quality graphite is able to meet the five criteria for an effective solid lubricant. Graphite possesses the necessary yield strength for successful lubrication. It is able to adhere sufficiently to metal surfaces due to its affinity to metal and its packing within and above the microstructure of the surface. Graphite has a burnishing capacity desirable for lubrication mechanisms that require a “memory” effect. Proper orientation of graphite particles is achieved by the natural tendency for the graphite crystal to orient itself parallel to the substrate and in the direction of lowest shear. The anisotropic characteristic of graphite lends itself well to its lubricating capability and friction reduction property. The planar orientation of the graphite particles on the substrate takes advantage of the anisotropic property. Proper orientation allows the lamellar functionality of graphite where easy shear is achieved along the crystal plane when sliding forces are put along the length of the particles. The high yield strength in graphite is maintained in the direction perpendicular to the direction of shear force, providing for the load-carrying capability.

Graphite is best suited for lubrication in a regular atmosphere. Water vapor is a necessary component for graphite lubrication. The role that adsorbed water vapor plays in the lubricating properties of graphite has been studied [5]. It is theorized that water vapor helps to reduce the surface energy of the graphite crystallite. The adsorption of a water monolayer onto the planar surface of

the graphite likely reduces the bonding energy between the hexagonal planes of the graphite to a level that is lower than the adhesion energy between a substrate and the graphite crystal. This allows for lamellar displacement of the graphite crystals when shear forces are applied to the graphite film. The result is a reduction of friction and corresponding lubrication. Because water vapor is a requirement for lubrication, graphite is usually not effective as a lubricant in a vacuum atmosphere.

The lubricating ability of graphite as a function of temperature is very good. Graphite is able to withstand continuous temperatures of up to 450°C in an oxidizing atmosphere and still provide effective lubrication. The oxidation stability of graphite depends on the quality of the graphite, the particle size, and the presence of any contaminants that might accelerate the oxidation. Graphite will also function at much higher temperatures on an intermittent basis. Peak oxidation temperatures are typically near 675°C. For these instances, modifying the composition of the graphite mixture may be necessary as a way to control its rate of oxidation.

The thermal conductivity of graphite is generally low. For example, primary-grade synthetic graphite has a conductivity of ~1.3 W/mK at 40°C. Amorphous graphite is even less conducting and is sometimes considered for providing some degree of thermal insulation for specific applications.

6.2.2 MOLYBDENUM DISULFIDE

Molybdenum disulfide is the second significant solid lubricant widely used in industry. It has been used since the early nineteenth century for lubrication applications. MoS₂, also known as molybdenite, is a mined material found in thin veins within granite. Lubricating-grade MoS₂ is highly refined by various methods to achieve a purity suitable for lubricants [6]. This purity usually exceeds 98%. MoS₂ is commercially available in a variety of particle size ranges. Table 6.4 lists basic properties for molybdenum disulfide. The low friction of MoS₂ is an intrinsic property related to its crystal structure, whereas graphite requires the adsorption of water to behave as an effective lubricant. Molybdenum disulfide achieves its lubricating ability with a mechanism similar to graphite. Just like graphite, MoS₂ has a hexagonal crystal lattice structure.

Sandwiches of planar hexagonal Mo atoms are interspersed between two layers of sulfur atoms. Similar to graphite, the bond strength between the hexagonal planes between the sulfur atoms are weak van der Waal-type bonds when compared to the strong covalent bond between molybdenum and sulfur atoms within the hexagonal crystal. Orientation of the MoS₂ crystallites is important if effective friction reduction is to be achieved. MoS₂ has anisotropic properties that are comparable to graphite. When a force is applied parallel along the hexagonal planes, the weak bond strengths between the planes allow for easy shearing of the crystal, resulting in a lamellar

TABLE 6.4
Characteristics of Hexagonal Molybdenum Disulfide

Property	Value
Bulk hardness	1.0–1.5 V
Coefficient of friction	0.10–0.15
Color	Blue-gray to black
Electrical conductivity	Semiconductor
Luster	Metallic
Melting point	>1800°C
Molecular weight	160.08
Service temperature	Up to 700°F
Specific gravity	4.80–5.0
Thermal conductivity	0.13 W/mK at 40°C

mechanism of lubrication. At the same time, the crystal structure and strong interplanar bond forces of MoS₂ allow for high load carrying against forces applied perpendicular to the plane of the crystal. This is necessary for the prevention of metal on metal contact for high-load applications such as gearbox lubrication.

MoS₂ scores well in the other criteria for an effective solid lubricant. It forms a strong cohesive film, that is smoother than the surface of the substrate on which it is bonded. MoS₂ film has sufficiently high adhesion to most metal substrates, which it successfully burnishes onto the wearing surfaces, thus minimizing metal wear and prolonging friction reduction. This characteristic is an exception, however, with titanium and aluminum substrates due to the presence of an oxide layer on the metal surface, which tends to reduce the tenacity of the MoS₂ film.

The lubrication performance of MoS₂ often exceeds that of graphite. It is most effective for high load-carrying lubrication when temperatures are <400°C. Another advantage of MoS₂ is that it lubricates in dry, vacuum-type environments, whereas graphite does not. This is due to the intrinsic lubrication property of MoS₂. On the contrary, the lubricating ability of MoS₂ deteriorates in the presence of moisture because of oxidation of MoS₂ to MoO₃. The temperature limitation of MoS₂ is due to similar decomposition issues of the material as that experienced with moisture. As MoS₂ continues to oxidize, MoO₃ content increases, which induces abrasive behavior and increases coefficient of friction for the surfaces to be lubricated.

The effectiveness of MoS₂ improves as contact forces increase on the lubricated surface. Burnished surfaces exhibit coefficient of friction reduction as a function of increasing contact forces [7]. In contrast, graphite does not necessarily exhibit this behavior. The frictional property of MoS₂ systems has been reported to be generally better than graphite in many instances, up to the service temperature limitations for the lubricant.

The particle size and film thickness of MoS₂ will affect lubrication. Generally, the particle size should be matched to the surface roughness of the substrate and the type of lubrication process considered. Too large a particle distribution may result in excessive wear and film reduction as mechanical abrasion is experienced. Too fine a particle size may result in accelerated oxidation in normal atmospheres as the high surface area of the particles promotes the rate of oxidation.

6.2.3 BORON NITRIDE

Boron nitride is a ceramic lubricant with interesting and unique properties. Its use as a solid lubricant is typically for niche applications when performance expectations render graphite or molybdenum disulfide unacceptable. The most interesting lubricant feature of boron nitride is its high-temperature resistance. Boron nitride has a service temperature of 1200°C in an oxidizing atmosphere, which makes it desirable for applications that require lubrication at very high service temperatures. Graphite and molybdenum disulfide cannot approach such higher service temperatures and still remain intact. Boron nitride also has a high thermal conductivity property, making it an excellent choice for lubricant applications that require rapid heat removal.

A reaction process generates boron nitride. Boric oxide and urea are reacted at temperatures from 800 to 2000°C to create the ceramic material. Two chemical structures are available: cubic and hexagonal boron nitride. As one might expect, the hexagonal boron nitride is the lubricating version. Cubic boron nitride is a very hard substance used as an abrasive and cutting tool component. Cubic boron nitride does not have any lubrication value. The hexagonal version of boron nitride is analogous to graphite and molybdenum disulfide. The structure consists of hexagonal rings of boron and nitrogen, which are connected to each other, forming a stack of planar hexagonal rings. As with graphite, boron nitride exhibits a platelet structure.

The bond strength within the rings is strong. The planes are stacked and held together by weaker bond forces. Similar to graphite and molybdenum disulfide, this allows for easy shearing of the planes when a force is applied parallel to the plane. The ease of shear provides the expected friction reduction and resulting lubrication. Concurrently, the high bond strength between boron

TABLE 6.5
Hexagonal Boron Nitride

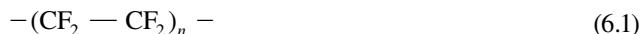
Property	Value
Coefficient of friction	0.2–0.7
Color	White
Crystal structure	Hexagonal
Density	2.2–2.3 g/cm ³
Dielectric constant	4.0–4.2
Dielectric strength	~35 kV/mm
Molecular weight	24.83
Service temperature	1200°C (Oxidizing atmosphere)
Thermal conductivity	~55 W/mK
Size (grades)	1–10 µm

and nitrogen within the hexagonal rings provides the high load-carrying capability that is necessary to maintain metal–metal separation of the substrates. Similar to MoS₂, boron nitride has intrinsic lubrication properties. Boron nitride effectively lubricates in a dry as well as a wet atmosphere. It is very resistant to oxidation, more so than either graphite or MoS₂, and maintains its lubricating properties up to its service temperature limit.

Commercial grades are available in a variety of purities and particle sizes. These varieties influence the degree of lubrication provided by boron nitride since particle size affects the degree of adhesion to substrate, burnishing ability, and particle orientation within a substrate. Impurities such as boric oxide content need to be considered with respect to the lubrication capability of boron nitride powder since this will influence the ability of the powder to reduce the coefficient of friction for an application. The variation in grades will also influence the thermal conductivity properties and ease of suspension in a liquid carrier. Table 6.5 summarizes typical properties for hexagonal boron nitride.

6.2.4 POLYTETRAFLUOROETHYLENE

Polytetrafluoro-ethylene (PTFE) has been in use as a lubricant since the early 1940s. Structurally, the polymer is a repeating chain of substituted ethylene with four fluorine atoms on each ethylene unit:



Contrary to the other lubricants discussed, PTFE does not have a layered lattice structure. The lubrication properties are at least partially the result of its high softening point. As frictional heat begins to increase from sliding contact, the polymer maintains its durability and is able to lubricate.

Various grades are produced and applied to specific applications as a result of the properties imparted by the grade. For example, molecular weight and particle size are two characteristics that can alter the performance of the polymer as a lubricant.

The critical characteristic of PTFE—the one it is widely known for [8]—is the outstandingly low coefficient of friction imparted by the molecule. PTFE has one of the smallest coefficients of static and dynamic friction than any other solid lubricant. Values as low as 0.04 for sliding conditions have been reported for various combinations of PTFE films on substrates [9]. The low-friction property is attributed to the smooth molecular profile of the polymer chains, which orient in a manner that facilitates easy sliding and slip. It is postulated that the PTFE polymer results in rod-shaped macromolecules, which can slip along each other, similar to lamellar structures.

TABLE 6.6
Typical Physical Properties of PTFE

Property	Value
Coefficient of friction (ASTM D1894)	0.04–0.1
Dielectric constant	2.1–2.4
Hardness	50–60 Shore D
Melting point	327°C
Service temperature	Up to 260°C
Specific gravity	2.15–2.20

Its chemical inertness makes it useful in cryogenic to moderate operating temperatures and in a variety of atmospheres and environments. Operating temperatures are limited to ~260°C due to the decomposition of the polymer.

One consideration in using PTFE is the cold weld property of the material. This could eliminate its use for some applications where extreme pressure is encountered. Such pressure may result in the destruction of the polymer particle and in the lubrication failure, as the PTFE congeals and fails to remain intact on the rubbing surface.

PTFE finds many uses in bonded film lubrication at ambient temperature. These applications include fasteners, threading compounds, and chain lubrication and engine oil treatments. PTFE is widely used as an additive in lubricating greases and oils, for both industrial and consumer applications (see Table 6.6 for basic properties).

Although difficult to accomplish due to the low surface energy of PTFE, colloidal dispersions of PTFE in oil or water can be produced. This is useful for applications requiring the stable suspension of PTFE particles in the lubricating medium such as for crankcase oil or hydraulic oil. The nature and feedstock of the PTFE influence the ability to create a stable, unflocculated dispersion, which is necessary for effective lubrication.

6.3 PREPARATION FOR LUBRICANT APPLICATION

For a lubricant to be effective, the solid has to be applied in a manner that provides an effective interface between the mating substrates that require wear protection or lubrication. Dry-powder lubrication can be used, but it is limited in its scope of application. In other words, the dry powder can be *sprinkled* onto the load-bearing substrate. By a combination of the rubbing action from sliding and the natural adhesion properties of the solid lubricant, some measure of attachment to the substrate will occur by burnishing to provide lubricating protection [10]. MoS₂ seems to function particularly well from this manner of application, as it has an effective burnishing capability.

The use of free powder has limitations. The films tend to have a short duration of service since adhesion is usually insufficient to provide any longevity for a continuous application. The use of dry powder also makes it difficult in many circumstances to accurately apply the lubricant to the place intended, with the possible exception of tumbling metal billets for achieving a coating over phosphated substrates.

This can be overcome by the use of bonded films. Bonded films will provide a strong adhesion to the substrate requiring protection. It also allows for a more controlled rate of film wear, which depends on the properties of the bonding agent and the film thickness of the bonded film. Bonded films can be achieved by a number of ways, all by use of secondary additives that promote a durable and longer-lasting film. The intended application will dictate the appropriate type of bonding agent. For applications of continual service, resin and polymer bonding agents are typically used. These include phenolic resins, acrylics, celluloses, epoxies, polyimides, and silicones. Some of the binders such as epoxies are

curable at room temperatures. Others such as the phenolic resins require elevated-temperature curing. Service temperature may be the limiting consideration for the chosen bonding agent.

To overcome service temperature limitations, alternative type bonding agents are also widely used. Most typical are inorganic salts such as alkali silicates, borates, and phosphates. These types of salts overcome temperature limitations of organic bonding agents, transferring the burden of temperature consideration to the solid lubricant. Conversely, the use of inorganic salts as bonding agents typically does not provide for a coating life that is as durable as an organic bonded coating. This usually limits the application to those requiring constant replenishment of the lubricant.

To facilitate the application of the solid lubricant, dispersion in a liquid is most commonly used. The liquid can be a solvent, oil, synthetic oil, or water. Suspension within a liquid allows for the easy and precise application of the solid lubricant to the intended areas that require protection. Compared to dry-powder application, film control is easily achieved through spray, dip, or flow methods onto the substrate. Environmental cleanliness is also improved since the solid particles are entrapped within a liquid matrix, preventing the airborne dispersion of the particles. For applications in which the solid lubricant is a secondary additive in a liquid, proper suspension is critical for achieving effective lubrication.

A consideration for liquid suspensions is that the shelf life of the lubricant is limited. Because the particles require suspension within a liquid carrier, eventual sedimentation of the solid lubricant will occur. This necessitates proper mixing procedures for the handling of the suspension to provide for consistent lubricant performance within the stated shelf life of the material. Adjustment to formulations with respect to dispersion and viscosity controls will influence the time it takes for the suspension to destabilize. The quality of the suspension will also determine how easily the settled pigment is redispersed with mild agitation (see Figure 6.6).

To create the suspension, the solid lubricant particles require treatment of the particle surface to make it amenable to suspension within the carrier liquid. This is similar to paint, where the colorant is chemically treated to provide the required dispersion characteristics and form what is considered a colloidal suspension (see Figure 6.7). This treatment is necessary to maximize the available particles for lubrication and provide the degree of dispersion stability required for the job. Without such treatment, particle agglomeration and rapid sedimentation will occur. This would negatively influence the application of the lubricant onto the substrate in a manner that creates an inferior and ineffective film. Wetting agents and suspending agents such as polymeric salts, starches, and polyacrylates are used to treat the surface of the solid lubricant to render it capable of suspension within the liquid carrier.

When creating the dispersion, the particle size distribution of the solid lubricant has to be considered. Small, submicron particles are easier to suspend and retain physical stability than large, coarse particles. To this end, milling action on the solid lubricant is usually necessary to alter the size distribution to the desired range of sizes (see Figure 6.8).

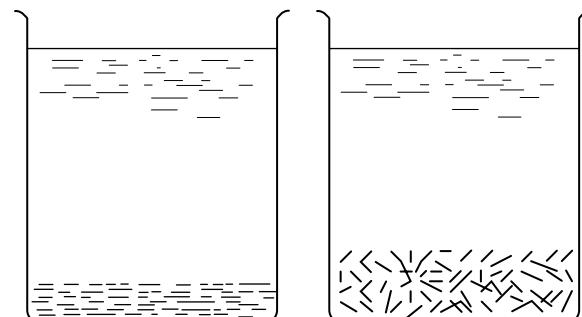


FIGURE 6.6 Particle sedimentation.

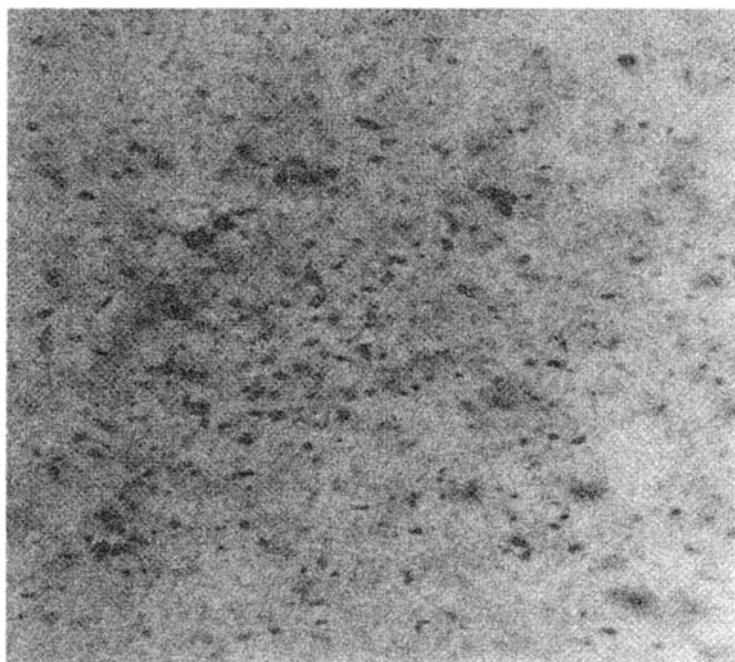


FIGURE 6.7 Colloidal dispersion.

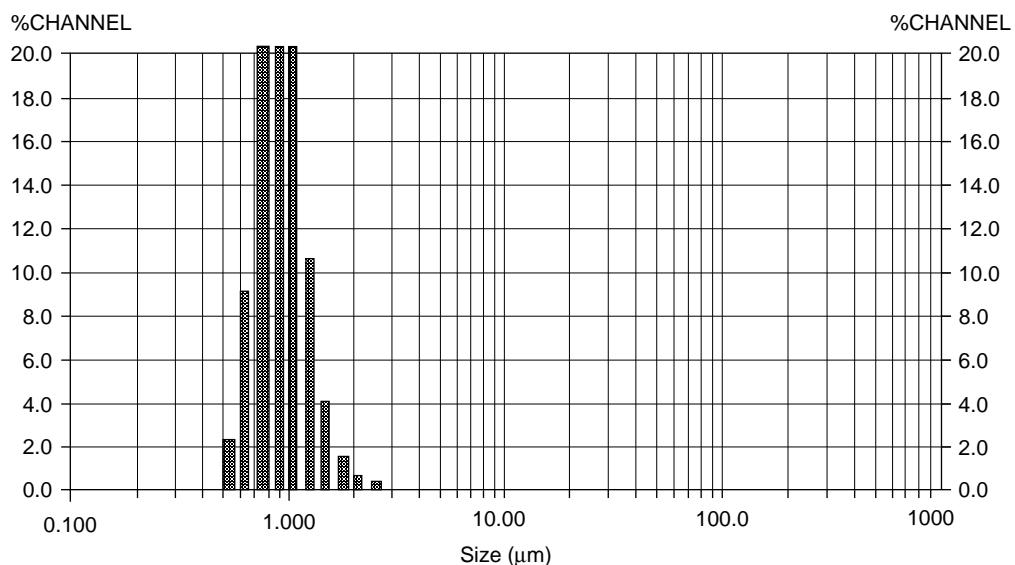


FIGURE 6.8 Particle size distribution of colloidal graphite suspension.

Fine sized particles are not necessarily the best distribution for a particular lubricating application (see Figure 6.9). Some consideration is required for the most beneficial particle size to match up with the surface roughness and nature of the application. This consideration could run contrary to what is the best particle size for dispersion stability. Therefore, some degree of compromise may be necessary to achieve a balance of dispersion stability and lubrication performance.

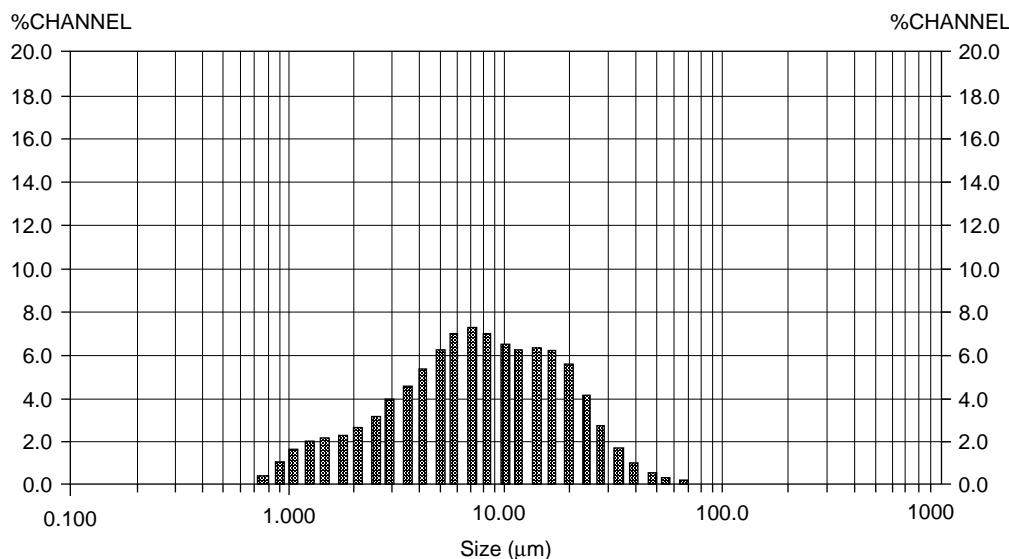


FIGURE 6.9 Coarse graphite particle size distribution.

Some type of substrate preparation for the load-bearing surface may be required to facilitate the application of the solid lubricant. This is usually necessary for metal deformation processes so that the film thickness, film uniformity, and durability of the applied lubricant on a billet will be robust enough to lubricate. Typical treatments of the surface include phosphating, peening, and shot blasting, which are especially useful for powder tumbling applications. With water-based dispersions, heating the substrate to some elevated temperature is often necessary to activate the bonding agents. Substrate heating serves a dual purpose: it facilitates the evaporation of the water carrier, and it also initiates the physical/chemical bonding of the film onto the substrate.

6.4 APPLICATIONS

Two major lubrication applications are considered here: metal wear protection lubrication and lubrication for plastic deformation of metal. The former concerns applications such as constant sliding or reciprocating motion, for example, gear, chain, or journal lubrication. The latter concerns applications where metal is under plastic flow, such as metal-forming or metal-cutting applications.

6.4.1 WEAR PROTECTION AND GENERAL LUBRICATION

Wear protection and general lubrication applications are meant to include processes requiring hydrodynamic lubrication, elastohydrodynamic lubrication, and boundary lubrication. Examples of such applications include chain lubrication, gear lubrication, and engine oil treatments. In essence, any application where repetitive sliding or rolling contact occurs between two surfaces can be considered under the umbrella of wear protection lubrication. The intention is for the lubricant to reduce the coefficient of friction and protect against wear (see Figure 6.10). The benefits include savings in power consumption and service life of the component and efficiency gains due to the increased uptime resulting from proper lubrication.

Solid lubricants are useful and required for applications and conditions when conventional liquid lubricants are inadequate. These conditions include the following:

1. High operating temperatures that eliminate or reduce the functionality of the liquid lubricant
2. Contact pressure of sufficient magnitude that breaches the integrity of the liquid lubricant

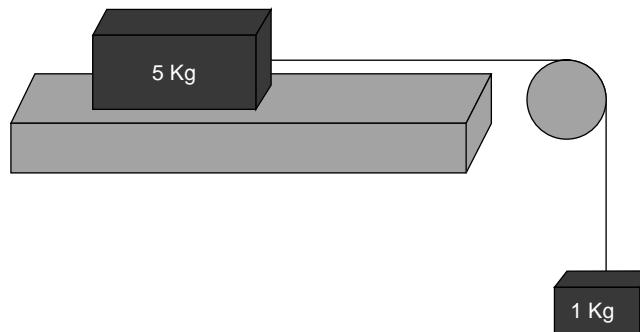


FIGURE 6.10 Lubrication of sliding surfaces—friction reduction.

TABLE 6.7
Worm Gear Dynamometer Tests

Description	Performance Parameters Output Torque = 113 N m		
	Mean Input Torque (N m)	Percent Efficiency	Mean Oil Sump Temperature (°C)
AGMA #8 gear oil	6.02	62.6	92.1
AGMA #8 gear oil + 1% colloidal MoS ₂ dispersion	5.92	63.6	95.5
AGMA #7 gear oil	6.05	62.3	93.6
AGMA #7 gear oil + 1% colloidal MoS ₂ dispersion	5.89	64.0	93.4
Synthetic PAG #2 oil	6.09	61.8	108.8
Synthetic PAG #2 oil + 1% MoS ₂ dispersion	5.79	65.1	88.4

Source: Pacholke, P.J., Marshek, K.M., Improved worm gear performance with colloidal molybdenum disulfide containing lubricants, ASLE paper presented at the 41st Annual Meeting in Toronto, Ontario, Canada, May 12–15, 1986.

3. Performance enhancement that extends the capability of the conventional liquid lubricant
4. Performance enhancement that extends the service life of the conventional liquid lubricant
5. Applications that undergo a “start/stop” routine
6. Applications that require low sliding speed but heavy bearing load
7. Applications that require “fool-proofing” for potential catastrophic lubrication failures that result from lubricant starvation

For successful incorporation of a solid lubricant as a secondary additive into liquid lubricants, a well-formulated colloidal dispersion is required. As an example, consider a case study where gear oil performance is enhanced above that of a conventional liquid lubricant by use of colloidal solids. The addition of 1% colloidal molybdenum disulfide to AGMA No. 7 and AGMA No. 8 gear oils reduced the break-in times and steady-state operating temperatures of low-viscosity synthetic oils as compared to nonfortified gear oils [11]. Table 6.7 summarizes a comparison of the performance of various blended gear oils to the measured output criteria as tested on a worm gear dynamometer.

Another example concerns the potential lubrication improvement from solid lubricants for friction-modified engine oils. Because of the burnishing property that solid lubricants such as colloidal graphite or colloidal MoS₂ would have on metal surfaces, friction reduction in engine and

axle components might be expected. Along with friction reduction, there should be a corresponding increase in fuel efficiency for motor vehicles. Various studies seem to support that conclusion. One report claims that in fleet trials conducted according to EPA 55/45 fuel economy testing with reference motor oils fortified with either MoS₂ or graphite, both in a colloidal dispersion, the fuel economy was improved by 4.5% [12]. In another fuel economy study using a fleet of taxicabs, the use of 2% colloidal graphite or colloidal MoS₂ in low-viscosity-formulated engine oils and rear axle lubricants improved the fuel economy by 2.5% [13].

The friction-reducing influence of colloidal graphite in oil is illustrated in one study by a dynamometer evaluation conducted on a 2.3 L engine [14]. The study indicates that graphite properly dispersed in an appropriate liquid lubricant will considerably reduce friction with the subsequent benefit of fuel economy savings.

Solid lubricants are also applied as bonded films for certain applications. For example, applications requiring a permanent or semipermanent lubricating film would require a bonded film. Bonded coatings are commonly formulated with MoS₂ or PTFE. One example would be for self-lubricating composites that require high-temperature stability, such as for what may be needed for engine piston ring protection [15]. Other examples that benefit from a bonded lubricant include fasteners, chains, and reciprocating mechanisms that require a persistent lubricating film. For these applications, PTFE stands out due to its low coefficient of friction. This is summarized in Table 6.8 by comparative coefficient of friction data for PTFE, graphite, and MoS₂, which are bonded onto cold-rolled steel substrates.

In assessing the lubrication potential for dispersed solid lubricants, some type of bench testing is utilized to characterize the apparent lubrication performance of the material. The most typical lubrication tests are Shell 4-Ball Wear method, Shell 4-Ball EP method, Falex Pin-Vee method, Plint Reciprocating method, Incline Plane method, and FZG Gear Lubrication method. In many cases, custom lubrication tests are developed for the specific application to be considered. When conducting bench testing for lubricant performance, correlation is best achieved when the mode of contact and conditions of the application are closely replicated by the bench test. The configuration of the contact points for the application is matched with a similar mode of contact for the bench test.

For an illustration of laboratory lubrication assessments, see Table 6.9 [16] to compare the empirical performance of the four solid lubricants dispersed in an oil carrier. The lubricants were tested according to two common methods of lubrication evaluation.

In this example, the dispersion of MoS₂ and PTFE provides effective load bearing, wear resistance, and coefficient of friction reduction when evaluated by a point-to-point contact (4-ball) and line-to-point contact (Falex Pin-Vee). Interpretation of any bench test result must be done carefully to ensure the validity of extrapolating the test performance to the actual application.

What criteria should be considered for an application when selecting the preferred or optimal solid lubricant? First, consider the service temperature for the application. This dictates which solid

TABLE 6.8
Coefficient of Friction for Bonded films

Coefficient of Friction ^a	
MoS ₂	0.23
Graphite	0.15
PTFE	0.07

^a Evaluated at room temperature, ASTM D4918.

Source: Watari, K., Huang, H.J., Turiyama, M., Osuka, A., Yamamoto, O., U.S. Patent 5,985,802, 11/16/99.

TABLE 6.9
Bench Lubrication Test Results

	Four-Ball Lubrication Test				Falex Lubrication Test		
	Wear ASTM D-4172		Extreme Pressure ASTM D-2783		Wear ASTM D-2670	EP ASTM D-3233	Coefficient of Friction
	20 kg mm	40 kg mm	Weld (kg)	Load Wear Index (kg)	Teeth	lb to Failure	Calculated
Base oil	0.678	1.060	126	17.20	Fail	875	0.159
With 1% colloidal graphite	0.695	0.855	160	18.7	78	1000	0.132
With 1% colloidal MoS ₂	0.680	0.805	200	24.3	8	4375	0.077
With 1% colloidal PTFE	0.50	0.84	200	29.04	10	4500+	0.0568
With 1% colloidal BN	0.37	0.72	126	19.9	Fail	500	0.1602

Source: Acheson colloids test data.

lubricant can be used. For example, MoS₂ generally has a higher load-carrying capability than graphite. Yet, at service temperatures above 400°C, MoS₂ degrades and loses its lubricating capacity. MoS₂ is, therefore, eliminated from consideration if the service temperature is above 400°C.

The second consideration is environment. Atmospheric restrictions will eliminate the use of certain solid lubricants. For example, a vacuum environment will eliminate the use of graphite. As mentioned previously, graphite requires adsorption of water molecules to its surface to function as an effective lubricant. MoS₂, on the contrary, as well as PTFE and boron nitride have intrinsic lubrication properties and do not require water molecules on their surface to provide friction reduction value.

The third criterion is the nature of the lubricant; either a liquid fortified with solid lubricant additives or a bonded solid lubricant film. Some pigments are easier to disperse in liquid than others. For example, graphite and MoS₂ are comparatively easier to disperse in liquids than PTFE and boron nitride. This is mostly due to particle size-reducing capability, surface energy, and surface chemistry of the solid lubricant.

The particle size of the pigment has an influence on lubrication performance. The size of the particulate and the size distribution of the particles should be optimized for the application (see Figure 6.11). For example, larger particles tend to give better performance for applications that are slow in speed or oscillating in nature.

Large particles also tend to give better performance on substrates where the surface roughness is relatively coarse.

A finer particle size tends to provide superior results for applications with constant motion and high speeds. Finer particles tend to function better where the surface roughness is relatively fine. Although not always predictable, the influence of particle size needs to be considered not only for dispersion requirements but also for the intended use application.

The fourth criterion involves cost-effectiveness of the lubricant. When the application conditions are met with two or more solid lubricants, cost will dictate the choice. Generally, graphite will be the least expensive. High-purity graphite is more expensive than lower-purity natural graphite or secondary synthetic graphite, which are more expensive than low-quality graphite. Molybdenum disulfide will be next, followed by PTFE and boron nitride as the more expensive solid lubricants. Cost-effectiveness for any of the solid lubricants will be influenced by the quality of the lubricant

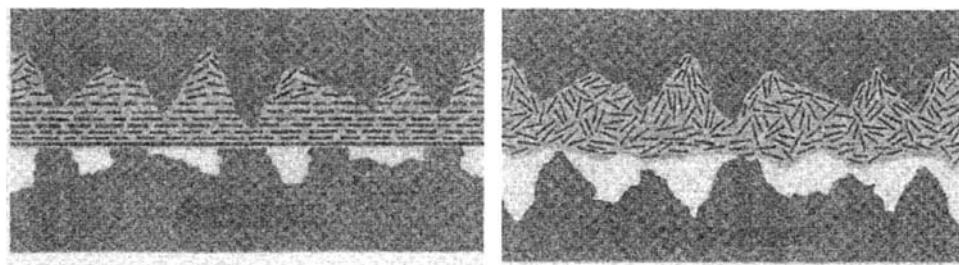


FIGURE 6.11 Orientation of solid lubricant particles in the direction of motion.

TABLE 6.10
Solid Lubricant Selection Comparison and Rating

Criteria	Graphite	MoS_2	PTFE	Boron Nitride
Normal atmosphere	1	1	1	1
Vacuum atmosphere	3	1	1	1
Ambient temperature	1	1	1	1
Continuous service temperature to 260°C in air	1	1	1	1
Continuous service temperature to 400°C in air	1	1	1	1
Continuous service temperature to 450°C in air	2	3	N/A	1
Burnishing capability	1	1	3	2
Hydrolytic stability	1	2	1	1
Thermal conductivity	2	3	3	1
Load-carrying lubrication	2	1	1	2
Friction reduction	2	2	1	3
Dispersability	1	1	3	2
Color	Black	Gray	White	White
Relative cost	1	2	2	3

Note: 1 = best, 2 = good, 3 = ok

and formulation that utilizes the lubricant. The effectiveness of the final formulation may prove that a costlier solid lubricant is more cost-effective in use. Table 6.10 attempts to rate the effectiveness of the solid lubricants for various criteria of application.

6.4.2 LUBRICATION FOR PLASTIC DEFORMATION OF METALS

Lubrication requirements for assisting metal deformation operations such as forging and metal drawing are far more demanding than those for wear lubrication. The metal movement process creates very fast metal flow and rapid new surface generation. This creates a demand for a lubricant to flow with the metal, remain adhered to the surface, maintain sufficient film cohesion to “meter” out the lubricant with the advancing metal, and interact rapidly with the newly formed metal surface. Metal-forming operations are inherently high-load and high-stress processes, which put a significant demand on protective lubrication.

Most applications are conducted at an elevated temperature region. Under this circumstance, conventional liquid lubricants fail to withstand the stresses for the application. Solid lubricants

are most appropriate for such applications because of their ability to withstand the operating temperatures, orient and adhere to the substrate surface, provide the coefficient of friction reduction necessary to promote metal flow, and provide the required load-carrying properties to prevent metal-on-metal contact. Indeed, most applications that involve plastic deformation of metal will utilize solid lubricants as either the primary or the secondary lubricant within a formulation.

What application criteria are used for determining the necessity for a solid lubricant? Severity of metal movement is the most significant factor. In cases where it is judged that metal movement would be considered extreme, solid lubricants will most likely be required. Application examples include forward, backward, and extreme lateral extrusion of metals. For example, forging of spindles, constant velocity (CV) joints, crankshafts, and hubs would fall in this category. For these and similar cases, liquid lubricant technology falls short of providing the necessary lubrication, coefficient of friction reduction, and die wear protection.

Once it has been determined that a solid lubricant is necessary, the temperature criteria need to be determined. Metalworking applications done at ambient temperature can utilize MoS_2 as the solid lubricant. MoS_2 has the best lubrication properties among the four lubricants discussed. In fact, for applications such as cold forging, MoS_2 is the preferred lubricant because of its ability to handle the very high load and stress applied onto the part being deformed.

In some cases, application of the MoS_2 is by dry-powder tumbling of the billets. Usually the billets are phosphated before applying powder to anchor the MoS_2 onto the surface and within the structure of the phosphate coating. The phosphate coating acts as an anchor for the powder and allows the lubricant to advance with the metal deformation. Table 6.11 compares forging performance for bare versus coated steel. Lubrication is improved as press tonnage falls and spike height of the forged billet increases.

Dry-powder tumbling is an effective application method for some cases. Other situations will require a more detailed and accurate depositing of MoS_2 film onto the substrate. This requires the use of a dispersed MoS_2 to provide a controlled coating thickness and particle size distribution considered appropriate for the job.

There may be instances where MoS_2 is not desirable—for example, environmental concerns or housekeeping issues. In these instances, PTFE or boron nitride would be appropriate. The white color of the pigments alleviates concerns regarding cleanliness of using graphite and molybdenum disulfide. Situations that require a reduction in emissions and material reactivity would favor boron nitride since PTFE will decompose at typical warm and hot forging temperatures. Both would effectively lubricate, with perhaps boron nitride faring better than PTFE for applications with significant metal flow.

PTFE can, however, stand out as a lubricant for cold metal-forming operations involving sheet stock and bar stock. The low coefficient of friction imparted by PTFE will provide the necessary lubrication to assist metal flow in a manner far better than boron nitride and much cleaner than graphite or molybdenum disulfide.

All the solid lubricants would be appropriate for bonded-film applications for metal deformation processes. Bonded films are desirable for sheet metal applications where coil or blank metal is

TABLE 6.11
Cold-Forging Lubrication

Sample	Press Tonnage	Spike Height (mm)
Bare steel	80.2	10.67
Bare steel + zinc phosphate	79.6	11.11
Bare steel + zinc phosphate + MoS_2	78.4	11.46

Source: Acheson Colloids test data.

prepared with a dry-film lubricant. When developing bonded-film lubricants, consider the formulation of effective binders and bonding agents so that the solid lubricant can function as intended.

For metalworking applications at elevated temperatures, the operating temperature will determine which solid lubricant can be used. All the solid lubricants mentioned would be suitable for temperatures up to 260°C. Above that temperature, PTFE will be eliminated from consideration due to its decomposition. MoS₂ will be suitable for applications up to 400°C in an oxidizing environment. Above that temperature, decomposition of MoS₂ will occur. Both graphite and boron nitride will lubricate effectively above an operating temperature of 400°C. Graphite is the predominant lubricant used for plastic deformation at elevated temperatures.

The use of graphite is common and preferred for what is considered warm- and hot-forging situations. The forging process is considered warm forging when billet temperatures are up to 950°C. The process is considered hot forging when billet temperatures exceed 950°C. In both cases, oxidation of graphite will occur. But the rate of oxidation depends on temperature and is regulated by the formulation and characteristics of graphite. Graphite quality, contaminants, crystallite size, and particle size will influence the rate of oxidation. The components of the finished formulation also play a role in controlling the oxidation rate of graphite, allowing it to survive for an appropriate length of time necessary for lubricating the process.

The type and quality of graphite play an important role in performance. Its consideration is the first step in a selection process. The first choice is to choose between natural and synthetic graphites. Often the choice is dictated by the degree of graphite quality suitable for the application. For instances where average lubrication is required, natural graphite of lesser quality can be used. More demanding lubrication will require the use of high-purity synthetic or natural graphite.

Selection of the particle size of graphite will vary depending on the intentions for the job. Particle size should be matched to the type of metal movement expected from the process, the surface roughness of the die and part, and the degree of stability required for the formulated lubricant. If a large particle distribution is desired, then concern about physical stability of the lubricant must be addressed. Rapid settling and hard packing of graphite could occur due to the large particle size if countermeasures are not taken. This would create handling costs and product inconsistency for the end user.

For most circumstances, high-quality graphite should be used so as to minimize performance inconsistency. The quality and characteristic of graphite can affect the lubricating performance. Table 6.12 illustrates a lubricity comparison of standard formulations produced with different graphites. In this example, the application is warm forging of steel. Actual forging of a steel billet generates lubrication data where the spike height is determined using preset forging press parameters (see Figure 6.12). A greater spike height and lower coefficient of friction suggest better lubrication from the coating.

Once the type of graphite to be used is selected, then the cost of the powder needs to be considered versus the benefit derived from its use. In general, high-purity natural or primary synthetic graphite will be costlier than secondary synthetic graphite. However, the performance benefit of using the higher-cost material may justify its selection for the application. Benefits normally associated with

TABLE 6.12
Graphite Influence on Forging Lubrication (800°C
Forging Temperature)

Graphite	Spike Height (mm)	Coefficient of Friction
A	1.5	0.05
B	1.3	0.08
C	1.1	0.10



FIGURE 6.12 Deformed billet and spike.

TABLE 6.13
Lubrication Comparison of Forging Lubricants (800°C Forging Temperature)

Lubricant	Spike Height (mm)	Coefficient of Friction
Graphite A	1.5	0.05
Graphite B	1.3	0.08
Nongraphite lubricant	0.7	0.15

the higher-cost materials are consistency, lubricating performance, and reduced oxidation rates of graphite.

The chosen graphite should be of a specific particle size distribution to derive certain benefits in performance. These benefits include the ease of dispersing graphite into a liquid carrier, the stability of graphite within the concentrated product, the application and film formation of the product onto the workpiece, and the optimized lubrication for the deformation process.

Forging processes normally require a temporary bond of the lubricant onto the workpiece and tool. This is achieved by the use of the type of bonding agents mentioned previously in this chapter. The use of dry powder or simple liquid–powder mixes will not perform adequately because of the poor adhesion onto the substrate.

To illustrate the value of graphite for hot-temperature metalworking applications, consider the example cited in Table 6.13. A comparison is made between two formulated graphite products and a nongraphite product tested under the same procedures of warm forging. In this example, the degree of spike height and coefficient of friction generated by the forging process are determined. The lower spike height and higher coefficient of friction for the nongraphite lubricant are indications of reduced lubrication capability in comparison to the graphite-containing materials.

In certain instances, graphite is not desirable due to either the operating temperature or concern about housekeeping and cleanliness. Hexagonal boron nitride is a capable alternative to graphite for these conditions. It is considered the “white graphite” due to its lamellar structure. It has a reasonably low coefficient of friction that approaches and sometime exceeds that of graphite. It is able to withstand operating temperatures up to 1200°C in oxidizing environments. This makes boron nitride an effective material for high-alloy isothermal forging, where extremely high temperatures

and long contact times are encountered. A profile of oxidation characteristics provides a comparison of oxidation stability between boron nitride and graphite (see Figure 6.13). The ability for boron nitride to remain intact at a very high temperature makes it ideal for applications that require a long residency time for lubricant coating.

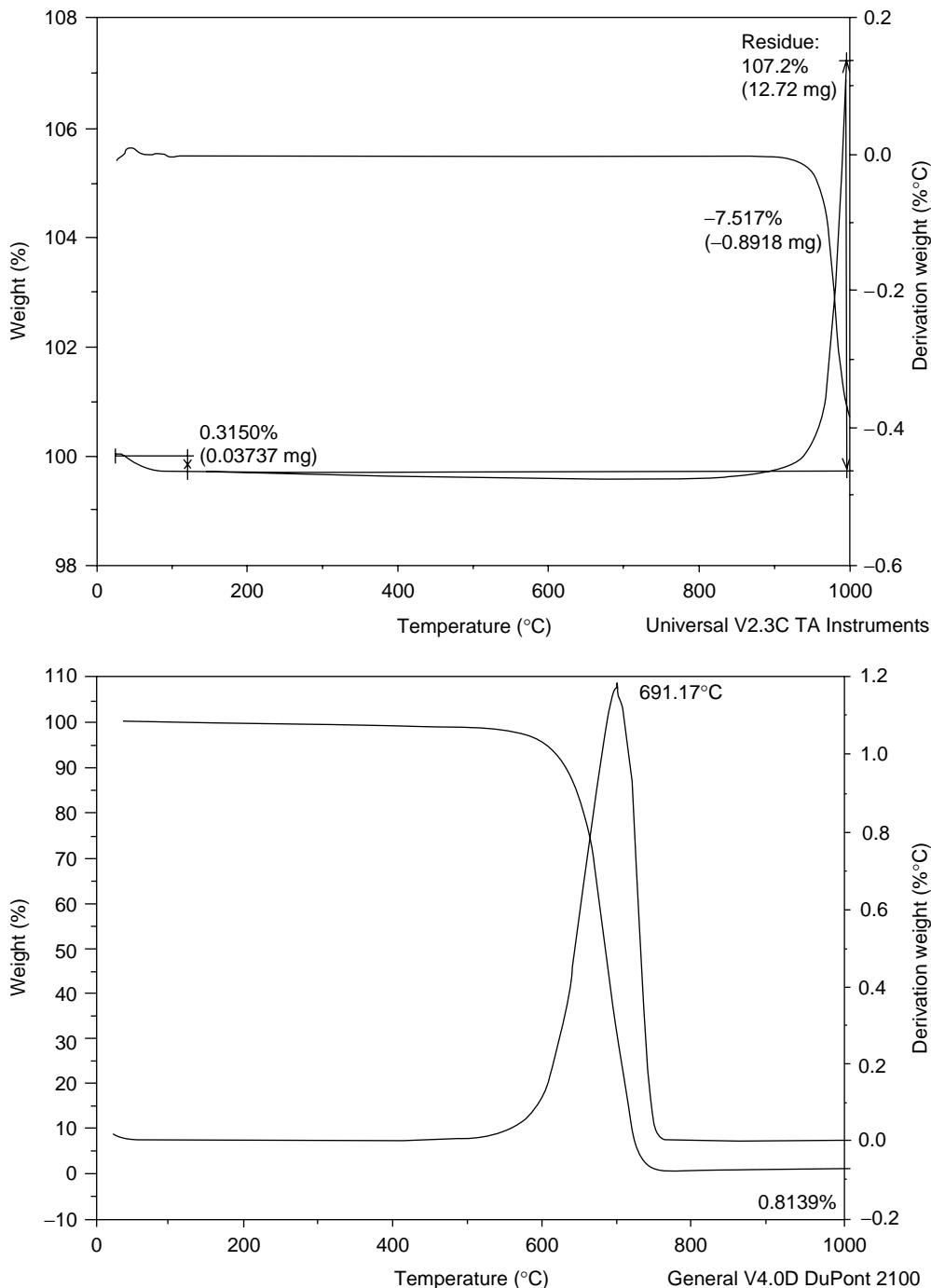


FIGURE 6.13 Comparison of peak oxidation temperatures of boron nitride and graphite. (From Acheson Colloids test data.)

Another advantage of using boron nitride is the heat conductivity property of the material. For applications that would require rapid heat dissipation, boron nitride serves quite well and is superior to graphite in that regard. Thermal conductivity values of boron nitride powder will vary depending on its quality. But, boron nitride in any of its grades is invariably more thermally conductive than graphite or MoS₂. Applications such as high-performance cutting oils are claimed to deliver benefits of enhanced lubrication and heat withdrawal when finely dispersed submicron particles of boron nitride are incorporated into the fluid [17].

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7 Organic Friction Modifiers

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7.1 INTRODUCTION

Friction modifiers (FMs) or friction reducers have been applied for several years. Originally, the application was for limited slip gear oils, automatic transmission fluids, slideway lubricants, and multipurpose tractor fluids. Such products made use of friction modification to meet requirements for smooth transition from static to dynamic condition as well as reduced noise, frictional heat, and startup torque.

Since fuel economy became an international issue, initially to reduce crude oil consumption, FMs have been introduced into automotive crankcase lubricants, as well, to improve fuel efficiency through the lubricant. In the United States, additional pressure is imposed on original equipment manufacturers (OEMs) by the corporate average fuel economy (CAFE) regulation.

Following the introduction of vehicle exhaust emission regulations in various regions around the world, emphasis on friction reduction further increased. This can be well understood if it is realized that 20–25% of the energy generated in an engine by burning fuel is lost through friction [1]. The biggest part is lost by friction on the piston liner/piston ring interface and a smaller part by bearing and valve train friction. It is predicted that in future engines the contribution of the piston group to engine friction will increase up to 50% [2].

Reduction of fuel consumption and emissions can be achieved through [3] engine design changes and modifications, such as

- Application of roller followers
- Use of coatings
- Surface modifications
- Material selection
- Fuel quality
- The engine lubricant

All these aspects are looked at and applied in the automotive industry. This chapter concentrates on the engine lubricant.

The need to measure fuel savings has led to the development of American Petroleum Institute (API) test sequences such as VI and VIA in the United States. Sequence VIB will be used for International Lubricant Standards Approval Committee GF-3. In Europe, a fuel economy test has been developed by Conseil Européen de Co-ordination pour le Développement des Essais de Performance des Lubrifiants et der Combustible pour Moteurs (CEC) (test number CEC L-54-T-96) for the Association des Constructeurs Européens d'automobiles A1 and B1 specifications using the DBM 111 engine. Both tests require that the candidate lubricant shows decreased fuel consumption relative to reference oil.

7.2 FRICTION AND LUBRICATION REGIMES

Friction is defined as *the resistance a body meets while moving over another body in respect of transmitting motion*. The friction coefficient is defined as

$$\frac{F_w}{F_n} \quad (7.1)$$

where F_w is the frictional force and F_n the normal force or load.

For a lubricated surface, the coefficient of friction is determined by the lubrication regime. In simple terms, the following three lubricant regimes can be distinguished:

1. Elasto-hydrodynamic lubrication (EHL) regime characterized by a (relatively) thick lubricant film [4]. The mating surfaces are far enough from one another to prevent metal-to-metal contact. The load on the system is completely carried by the lubricant film, and the viscosity of the lubricant determines the friction coefficient. Viscosity depends on temperature and pressure/viscosity coefficient.
2. Boundary lubrication (BL) regime characterized by a thin lubricant film [5]. Under high loads, high temperature, or with low viscosity oils, most of the lubricating film is squeezed out between the metal surfaces, and metal-to-metal contact occurs. The load is entirely carried by the metal asperities. A thin layer of absorbed or otherwise deposited molecules is necessary to prevent the two surfaces and their asperities from plowing into one another.
3. Mixed lubrication (ML) regime characterized by a lubricant film of intermediate thickness [6]. The two metal surfaces have come closer compared to hydrodynamic lubrication, and metal-to-metal contact occasionally occurs. The load is carried by both the lubricant and the asperities.

These regimes are related to the friction coefficient f by a lubricant parameter defined as

$$\frac{su}{F} \text{ or } \frac{su}{p} \quad (7.2)$$

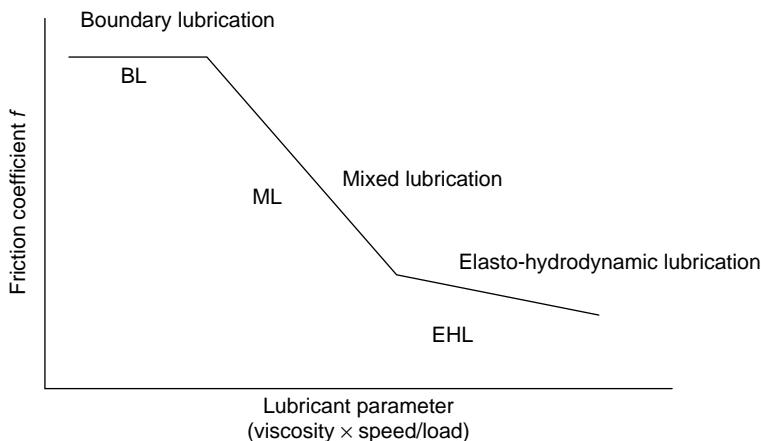


FIGURE 7.1 Stribeck curve at high contact pressure.

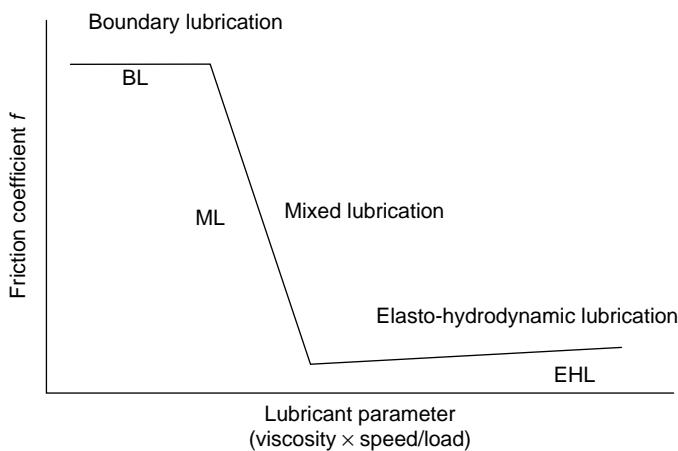


FIGURE 7.2 Stribeck curve at low contact pressure.

where

s = system speed

μ = lubricant dynamic viscosity

F = load (F_n)

p = contact pressure

The so-called Stribeck curve gives the relationship between f and these lubricant parameters. The shape of the Stribeck curve and the transitions from BL to ML and ML to EHL depend on a number of parameters such as material roughness (microgeometry), contact pressure, and lubricant viscosity. High contact pressure such as that present at point contacts leads to a different Stribeck curve as at line contact (lower contact pressure) (see Figures 7.1 and 7.2).

7.2.1 FRICITION REDUCTION THROUGH THE LUBRICANT

Engine friction originates from several components, that operate at different conditions of load, speed, and temperature. Hence, these components may experience various combinations of EHL, ML, and BL during engine operation. For each of these regimes, a number of factors govern engine friction.

Basically, two options to reduce friction and improve fuel efficiency come forward [7,8].

1. Use of low-viscosity engine oils (SAE 0W/5W-20/30) when fluid lubrication (EHL) is the governing factor [9–11]. Fluid lubrication is especially prevalent in the bearings. The gradual reduction of engine oil viscosity over the years has already brought significant fuel savings (see Figure 7.3).

In the preceding case, oil selection is crucial. In terms of frictional characteristics, one must emphasize low kinematic viscosity, high viscosity index, low “high-temperature, high-shear” (HTHS) viscosity, and a low-pressure/viscosity coefficient [12,13]. However, it has to be realized that other base fluid properties, such as volatility and thermal/oxidation stability, must not be ignored.

2. Addition of friction-reducing agents when BL and ML are the governing factors [14]. These are prevalent in the valve train and the piston group.

In the preceding case, additive system design is the crucial factor. One must emphasize selecting proper FMs and controlling additive–additive and additive–base fluid interactions.

To assess possible fuel economy improvements in the engine sequences prescribed, an overview of the lubrication regimes existing in various test engines is provided. The data those used for current and previous ILSAC specifications are given in Table 7.1.

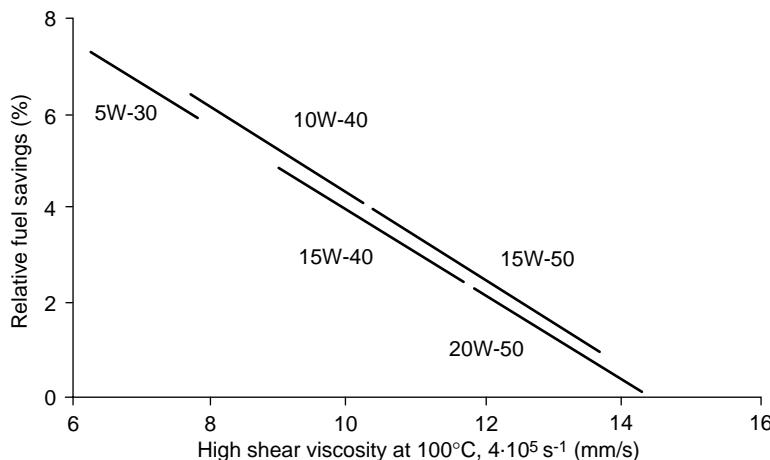


FIGURE 7.3 Relationship between SAE viscosity grades and fuel savings based on fleet car trials.

TABLE 7.1
Lubrication Regimes in API Sequences VI and VIA

	API Sequence VI (%)	API Sequence VIA (%)
Boundary lubrication	37	24
Mixed lubrication	15	4
Elasto-hydrodynamic lubrication	48	72

TABLE 7.2
Lubrication Regimes in the DB M111E Engine

	Frictional Loss (%)	Main Lubrication Regime
Valve train	25	Boundary lubrication
Piston assembly	40	Mixed lubrication
Bearings	35	Elasto-hydrodynamic lubrication

In Sequence VIA, which is prescribed for ILSAC GF-2, EHL is dominating, leading to a substantial effect of engine oil viscosity on fuel economy. Effects of FMs will be small due to the low presence of BL and ML conditions, which is due to the application of roller followers. Hence, the Sequence VIA test engine is often indicated as “a very expensive viscometer.”

This characterization of the Sequence VIA engine will be addressed by Sequence VIB, to be used for ILSAC GF-3, for which an engine, a bucket tappet sliding valve train will be used, leading to an increase of the BL and ML regimes [3].

In Europe, the M111 engine is used for the CEC L-54-T-96 fuel economy test, which is prescribed in the ACEA A1 and B1 engine oil specifications. Similar data as aforementioned are not available to the authors, but data given in a Shell paper [15] indicate the frictional loss occurring in this engine, which can be translated to lubrication regimes (Table 7.2).

On the basis of the relatively high amount of frictional loss in the valve train and piston assembly, the M111 engine should be sensitive to FMs. This is due to the use of four valves per cylinder to improve combustion efficiency and so to obtain more power from a given amount of fuel.

However, compared to other engine designs, the frictional loss in the M111E valve train will be higher. Provided that the higher-power output obtained from the four-valve assembly is significantly higher than that is lost by higher valve train friction, this approach is favorable with regard to fuel economy.

7.3 FRICTION MODIFIERS VERSUS ANTIWEAR/ EXTREME-PRESSURE ADDITIVES

A point of debate is often about the difference between FMs and antiwear/extreme-pressure (AW/EP) additives, especially when it is about FMs active at BL conditions. For a good understanding, this should be clarified; therefore, this section deals with the principal difference between these two additive categories [16].

AW/EP additives are types of compounds that provide good BL. Such materials have the capacity to build strong BL layers under severe load conditions. Hence, AW/EP additives protect closely approaching metal surfaces from asperities damaging the opposite surface. On the contrary, most AW additives have little friction-modifying properties.

The crucial differences between AW/EP and FM films are their mechanical properties. AW/EP films are semiplastic deposits that are difficult to shear off. Thus, under shearing conditions, their coefficient of friction is generally moderate to high. Conversely, FM lubricant films are built up of orderly and closely packed arrays of multimolecular layers, loosely adhering to one another and with the polar head anchored on the metal surface. The outer layers of the film can be easily sheared off, allowing for a low coefficient of friction.

TABLE 7.3
Lubrication Modes versus Friction Coefficient

Lubrication Mode	Friction Coefficient	Comparison
Nonlubricated surface	0.5–7	Dragging an irregular rock over rocky ground
AW/EP films	0.12–0.18	Dragging a flat stone over a flat rock
Friction-modified films	0.06–0.08	Ice skating
EHL	0.001–0.01	Hydroplaning

TABLE 7.4
FM Type and Mode of Action

Mode of Action/Type of FM	Products
Formation of reacted layers	Saturated fatty acids, phosphoric and thiophosphoric acids, sulfur-containing fatty acids
Formation of absorbed layers	Long-chain carboxylic acids, esters, ethers, amines, amides, imides
Formation of polymers	Partial complex esters, methacrylates, unsaturated fatty acids, sulfurized olefins
Mechanical types	Organic polymers

The difference between the two types of films and other lubrication modes is best illustrated by the data presented in Table 7.3.

7.4 CHEMISTRY OF ORGANIC FRICTION MODIFIERS

Organic FMs are generally long, slim molecules with a straight hydrocarbon chain consisting of at least 10 carbon atoms and a polar group at one end. The polar group is one of the governing factors in the effectiveness of the molecule as an FM. Chemically, organic FMs can be found within the following categories [16]:

- Carboxylic acids or their derivatives, for example, stearic acid and partial esters
- Amides, imides, amines, and their derivatives, for example, oleylamide
- Phosphoric or phosphonic acid derivatives
- Organic polymers, for example, methacrylates

Another classification can be given by mode of action and FM type (Table 7.4).

Owing to the different mode of actions, the mechanism of friction reduction varies for each category.

The next section further deals with details about their mode of action, and another section deals with the current chemistry used as well as specific products.

7.4.1 FRICTION MODIFIER MECHANISMS

7.4.1.1 Formation of Reacted Layers

Similar to AW additives, protective layers are formed by chemical reaction of the additive with the metal surface. However, the principal difference is that the reaction has to occur under the relatively

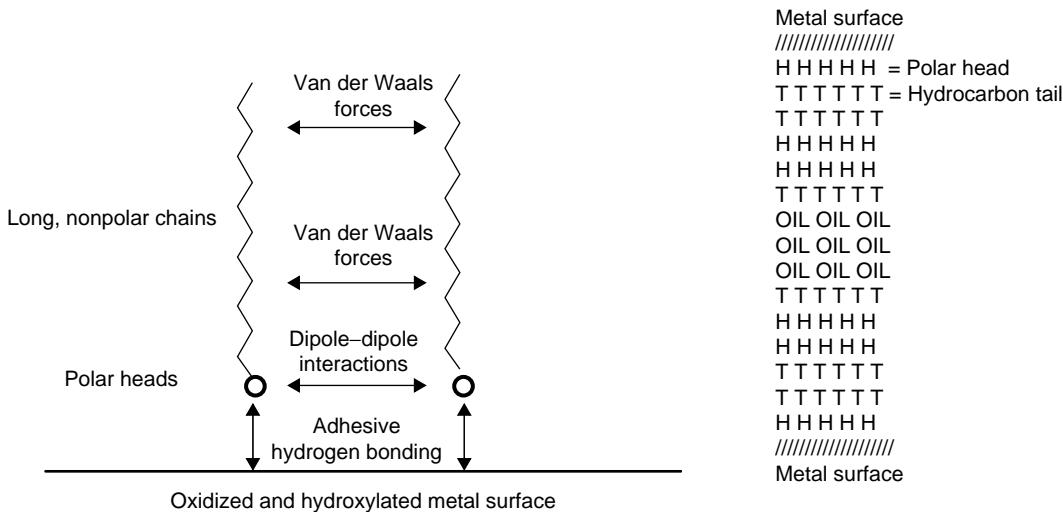


FIGURE 7.4 Organic FMs—formation of adsorbed layers.

FIGURE 7.5 Multilayer matrix of FM molecules.

mild conditions (temperature and load) of the ML regime. These conditions require a fairly high level of chemical activity as reflected by the phosphorus and sulfur chemistry applied.

An exception to this is stearic acid. Theoretically, the friction-reducing effect of stearic acid should decrease with increasing temperature due to desorption of the molecule from the metal surface. However, stearic acid experimentally shows a remarkable drop of friction with increasing temperature, which can only be explained by the formation of chemically reacted protective layers.

7.4.1.2 Formation of Absorbed Layers

The formation of absorbed layers occurs due to the polar nature of the molecules. FMs dissolved in oil are attracted to metal surfaces by strong absorption forces, which can be as high as 13 kcal/mol. The polar head is anchored to the metal surface, and the hydrocarbon tail is left solubilized in the oil, perpendicular to the metal surface (see Figure 7.4). Next the following steps occur:

1. Other FM molecules have their polar heads attracted to one another by hydrogen bonding and Debye orientation forces, resulting in dimer clusters. Forces are ~15 kcal/mol.
2. Van der Waals forces cause the molecules to align themselves such that they form multi-molecular clusters that are parallel to one another.
3. The orienting field of the absorbed layer induces further clusters to position themselves with their methyl groups stacking onto the methyl groups of the tails of the absorbed monolayer [17,18].

As a result, all molecules line up, straight, perpendicular to the metal surface, leading to a multi-layer matrix of FM molecules (see Figure 7.5).

The FM layers are difficult to compress but very easy to shear at the hydrocarbon tail interfaces, explaining the friction-reducing properties of FMs. Owing to the strong orienting forces, mentioned earlier, sheared-off layers are quite easily rebuilt to their original state.

The thickness and effectiveness of the absorbed FM films depend on several parameters, four of which are explained here.

1. *Polar group.* Polarity itself is not necessarily sufficient for adsorption; the polar group must also have hydrogen-bonding capability. Molecules with highly polar functional groups that are not capable of forming hydrogen bonds, such as nitroparaffins, do not adsorb.

Hence, these do not function as friction-reducing additives. However, polarity plays a major role among the various lateral surface interactions through strong electrostatic dipole–dipole interactions. These may be either repulsive or attractive, depending on the orientation of the adsorbed dipoles with respect to the surface [19].

2. *Chain length.* Longer chains increase thickness of the absorbed film, and the interactions between the hydrocarbon chains increase as well [18].
3. *Molecular configuration.* Slim molecules allow for closer packing as well as increased interaction between adjacent chains, leading to stronger films. Therefore, straight chains may be preferred.
4. *Temperature.* Temperature influences FM film thickness and tenacity. Adsorption of friction-reducing compounds to the metal surface does occur at relatively low temperatures. AW additives form protective layers by chemical reactions for which higher temperatures are needed.

If the temperature is too high, enough energy might be provided to desorb the friction-reducing molecules from the metal surface.

7.4.1.3 Formation of *In Situ* Polymers

The formation of low-friction-type polymer films can be considered a special case. Instead of the usual solid films, fluid films are formed under influence of contact temperature (flash temperature) and load. Another difference is that the polymers are developed at the interface between metal asperities without reacting with the metal surface.

The requirements of such polymers are

1. Polymers must have relatively low reactivity. Polymerization must be generated by frictional energy.
2. The polymers formed must be mechanically and thermally stable and should not be soluble in the lubricant.
3. The polymers must develop a strong bond to the metal surface either by absorption or by chemical bonding.
4. The formation and regeneration of films must be fast to prevent competitive adsorption by other additives.

Examples of polymer-forming FMs are

- Partial complex esters, for example, a sebacic acid/ethylene glycol partial ester methacrylates
- Oleic acid (olein), which may be explained through thermal polymerization (formation of dimers and higher oligomers)

7.5 CHEMISTRY OF OTHER FRICTION MODIFIERS

Within this group, the following categories can be distinguished by chemical type:

1. Metallo-organic compounds
2. Oil-insoluble materials

Classification by type appears in Table 7.5.

7.5.1 METALLO-ORGANIC COMPOUNDS

Molybdenum dithiophosphate, molybdenum dithiocarbamate, and molybdenum dithiolate as well as copper-oleate, copper-salicylate, and copper-dialkyldithiophosphate are examples of friction-reducing metallo-organic compounds.

TABLE 7.5
Classification of Other FMs

Types of FMs	Products
Metallo-organic compounds	Molybdenum and copper compounds
Mechanical types	Molybdenum disulfide, graphite, teflon (PTFE)

The mechanisms of operation of this class of products are not fully understood, but the following hypotheses are presented:

- Diffusion of molybdenum into the asperities
- Formation of polymer-type films
- *In situ* formation of molybdenum disulfide (most accepted hypothesis)
- Selective transfer of metal (copper) leading to the formation of thin, easy-to-shear metal films

7.5.2 MECHANICAL TYPES

In this group, the classical types such as graphite and molybdenum disulfide as well as some more recent FMs such as teflon (polytetrafluoroethylene, PTFE), polyamides, fluoridized graphite, and borates can be found. The friction-reducing mechanisms can be explained by

- The stratified structure and formation of easy-to-shear layers
- The formation of elastic or plastic layers on the metal surface

7.6 FACTORS INFLUENCING FRICTION-REDUCTION PROPERTIES

This section lists the main factors that impact friction-reducing properties.

1. *Competing additives.* Other polar additives with affinity to metal surfaces such as AW/EP and anticorrosion additives as well as detergents and dispersants may compete with FMs. This emphasizes that lubricant formulations have to be balanced carefully to achieve optimal performance.
2. *Contaminants.* Short-chain acids, which are formed by oxidative degradation of the lubricants, may compete at the metal surface, resulting in a loss of friction-modifying properties.
3. *Metallurgy.* The type of steel alloy used will affect the adsorption of FMs.
4. *Concentration.* Increase of FM concentration results in an increase of friction reduction up to a point above which improvements are marginal. Generally, the friction-reducing effect is most (cost-)effective at concentrations of ~0.25 to 1% for organic FMs and 0.05–0.07% for molybdenum dithiocarbamates.

7.7 FRICTION MODIFIERS: CURRENT PRACTICE

The most frequently used organic FMs include

1. Long-chain fatty amides, specifically oleylamide (Figure 7.6). This is a reaction product of olein (main component oleic acid, a straight-chain unsaturated C18 carboxylic acid) and ammonia (NH_3).

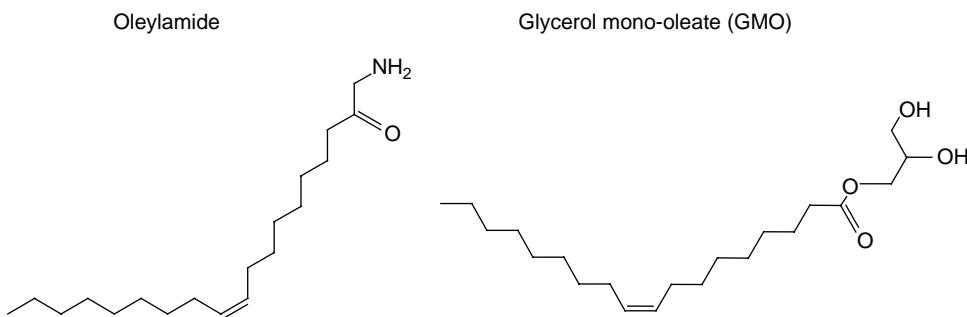


FIGURE 7.6 Organic FMs—structural drawings.

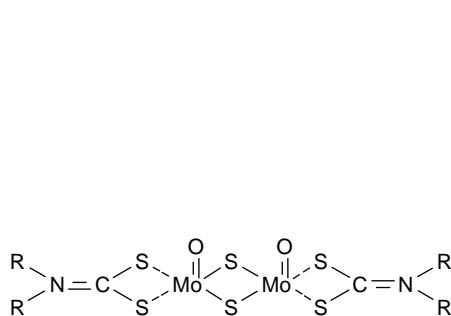


FIGURE 7.7 Molybdenum dithiocarbamate—structural drawing.

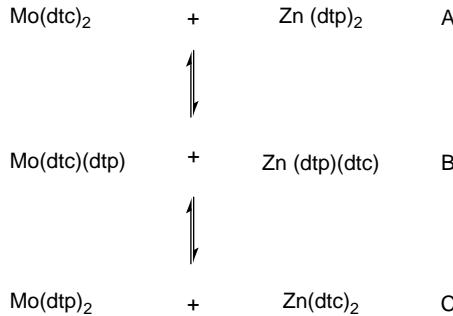


FIGURE 7.8 Molybdenum dithiocarbamate—exchange of functional groups.

- Partial esters, specifically glycerol mono-oleate (GMO) (Figure 7.6). GMO is a reaction product of glycerin (natural alcohol with three hydroxyl groups) and olein (as mentioned previously). Investigations have shown that the alpha version (terminal hydroxyl groups esterified) is the active component rather than the beta one (middle hydroxyl group esterified). Special production techniques are required to manufacture high-alpha-containing products.

The mode of action of both product groups is based on the formation of adsorbed layers that can easily be sheared off, leading to reduced friction. It is expected that further research will result in new and improved types to cope with more severe requirements with regard to friction retention over time.

Within the group of metallo-organic compounds, molybdenum dithiocarbamate [Mo(dtc)₂] seems almost exclusively to be used to obtain friction reduction (Figure 7.7). Research [7,20] has shown that the friction-reducing activity of Mo(dtc)₂ is based on the exchange of functional groups with zinc dialkyldithiophosphates [Zn(dtp)₂] (Figure 7.8).

It was found that oxidation affects these exchange reactions significantly and that the most effective friction reduction is achieved at the later stages of oxidation when the concentrations of the single-exchange product [Mo(dtc)(dtp)] and the double-exchange product [Mo(dtp)₂] are high. When both products are nearly consumed by oxidation, friction reduction ceases.

7.8 FRICTION MODIFIER PERFORMANCE

Literature suggests that FMs act both in the BL and ML regimes [7,16,21]. Their mode of action should depend on FM chemistry and prevailing engine conditions. It is further suggested that organic FMs are most active in the mixed regime, whereas metallic types are predominantly active

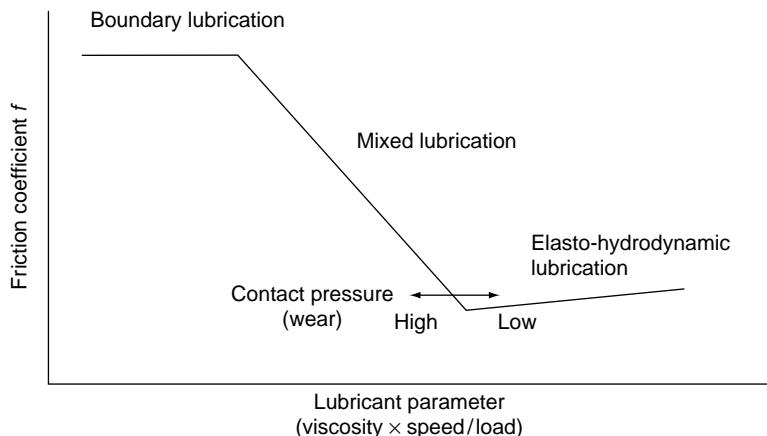


FIGURE 7.9 Influence of wear/contact pressure on ML/EHL transition.

in the BL regime. Recent investigations by the authors, carried out with a pin-on-ring tribometer, showed that it is likely that organic FMs act predominantly in the BL regime as well.

Tests were carried out with CEC reference oil RL 179/2, which is applied in the CEC L-54-T-96 fuel economy test. RL 179/2 is a formulated 5W/30 engine oil that does not contain any FM and that has a proven fuel economy benefit CEC round-robin tests.

Frictional behavior was investigated by establishing stabilized Stribeck curves. By determining these, both boundary and mixed friction can be investigated. Stabilized Stribeck curves are obtained by measuring the coefficient of friction over a speed range from ~ 0.0025 to 2 m/s at appropriate steps. A number of runs are carried out until two consecutive runs give a good match. Usually, after four runs, the curve has stabilized, meaning that process roughness has stabilized to a large extent.

Performance criteria in considering the results are frictional level in the BL and ML regimes in combination with specimen wear. The reason for looking at wear is that this parameter corresponds with contact pressure, which in turn influences the ML/EHL transition.

The relationship between wear and contact pressure is given by the expression

$$\frac{F_n}{A} = p \quad (7.3)$$

where

F_n = normal force (load)

A = wear scar

p = contact pressure

Consequently, a high-wear scar leads to a lower contact pressure, and a lower contact pressure does shift the ML/EHL transition in the Stribeck curve to the left (see Figure 7.9).

7.8.1 STRIBECK CURVE DETERMINATIONS

Stabilized Stribeck curves have been determined with a pin-on-ring tribometer at which the ring was a 100Cr6 stainless steel ring with a 730 mm diameter. These rings are high-quality materials used in standard bearings and therefore easily available. The pin used was a cylinder from the same material with an 8 mm diameter, also used in bearings. To get proper line contact, the cylinders have been provided with *flexible* ends to allow full alignment with the ring.

Ring roughness, R_a , was $\sim 0.15 \mu\text{m}$, although the cylinder was very smooth. Hence, the roughness of the ring determined the shape of the Stribeck curve, specifically the BL/ML transition. The load (normal force $F_n = 100 \text{ N}$) was chosen such that heat development in the contact zone was negligible, so that the viscosity was constant. Hence, it was possible to determine the Stribeck curve only as a function of speed. The temperature chosen was 40°C .

The following graph (Figure 7.10) shows comparative data for RL 179/2 as well as this oil with addition of 0.5% GMO and addition of 0.5% of organic FMs A and B. (A and B are products with both free and esterified hydroxyl groups.)

All the FMs studied here show a significant reduction of the friction coefficient in the BL regime. Organic FMs A and B show a reduction in the mixed regime as well. On first sight this looks favorable.

The next graph (Figure 7.11) shows the wear, taken at similar sliding distances.

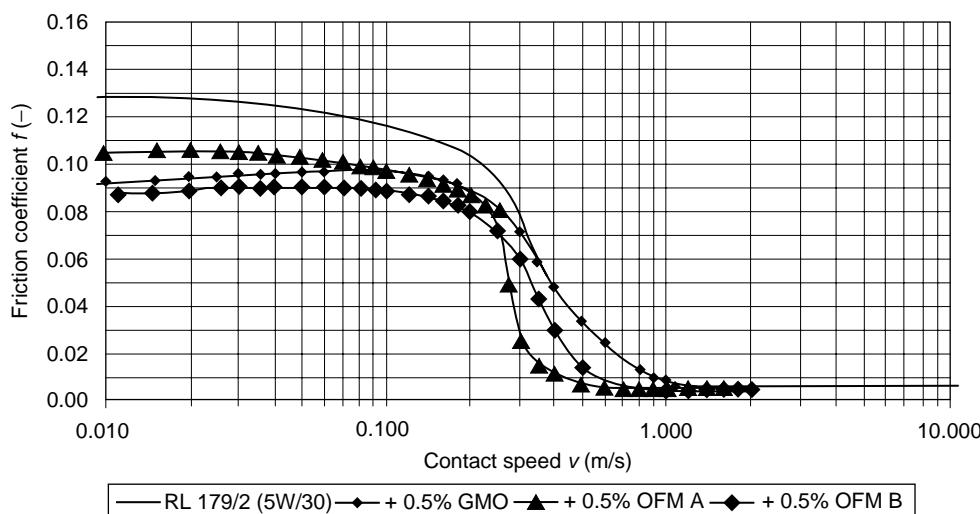


FIGURE 7.10 Stribeck curves of CEC RL 179/2 plus organic FMs.

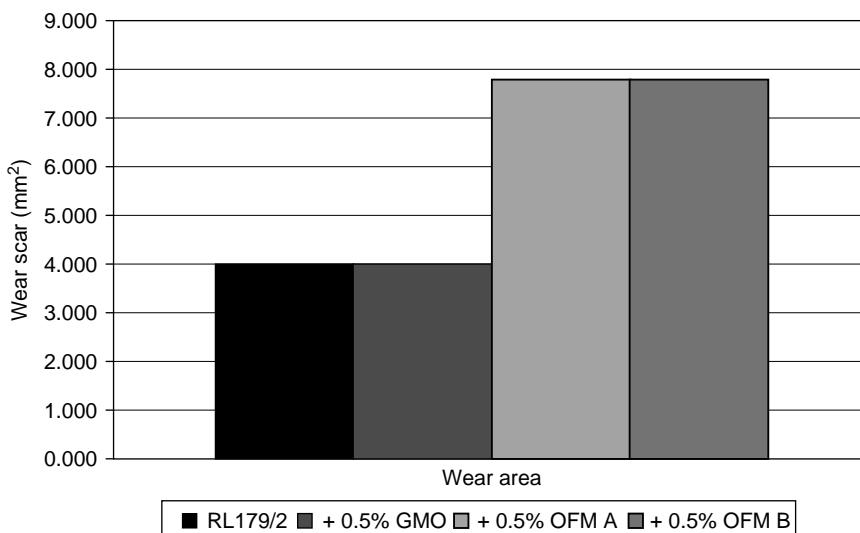


FIGURE 7.11 Wear scars of CEC RL 179/2 plus organic FMs.

The wear of the oil containing A and B is twice as high as those of the reference oil and that oil with addition of 0.5% GMO. Consequently, the contact pressure p is twice as low as those of the others and is what makes the ML/EHL transition shift to the left.

Thus it seems that organic FMs are predominantly active in the BL regime and that the shifts observed in the mixed regime are likely to be caused by other phenomena that must not be ignored.

7.8.2 FRICTION AS A FUNCTION OF TEMPERATURE

Another aspect of FM performance is friction as a function of temperature. Temperature plays an important role with regard to adsorption/desorption phenomena as for the formation of adsorbed layers as well as regarding those of reacted layers.

The graph in Figure 7.12 shows the frictional behavior of some organic FMs as a function of temperature, using the pin-on-ring tribometer as before with the same specimens and configuration. Again, CEC reference oil RL 179/2 was used, and the speed chosen (0.03 m/s) assured operation well within the BL regime.

All the organic FMs studied show a significant friction reduction over the temperature range tested. GMO and oleylamide perform best, and the optimum adsorption seems to be obtained at $\sim 70^\circ\text{C}$. At higher temperatures, desorption may start to occur as well as some kind of competition with other surface-active additives, leading to a higher coefficient of friction. Oleylamide, however, continues to show high friction-reducing properties at elevated temperatures.

Figure 7.13 shows a comparison between organic FM GMO and metallic-type FM molybdenum dithiocarbamate. Two sources of the latter were used at a concentration equivalent to 0.07% molybdenum.

GMO and the molybdenum dithiocarbamates show a marked performance difference. Although GMO is active over a wide temperature range, the molybdenum dithiocarbamates start to reduce friction at temperatures of 120°C and above only. This has to be considered as an induction period that can be explained by the necessary exchange of ligands between molybdenum dithiocarbamate and zinc dialkyldithiophosphate (see Section 7.7). Once molybdenum dithiocarbamate has “lighted off,” a fast drop of friction is noticed. At the end of the test cycle 140°C , the system has not stabilized and the friction coefficient might decrease further.

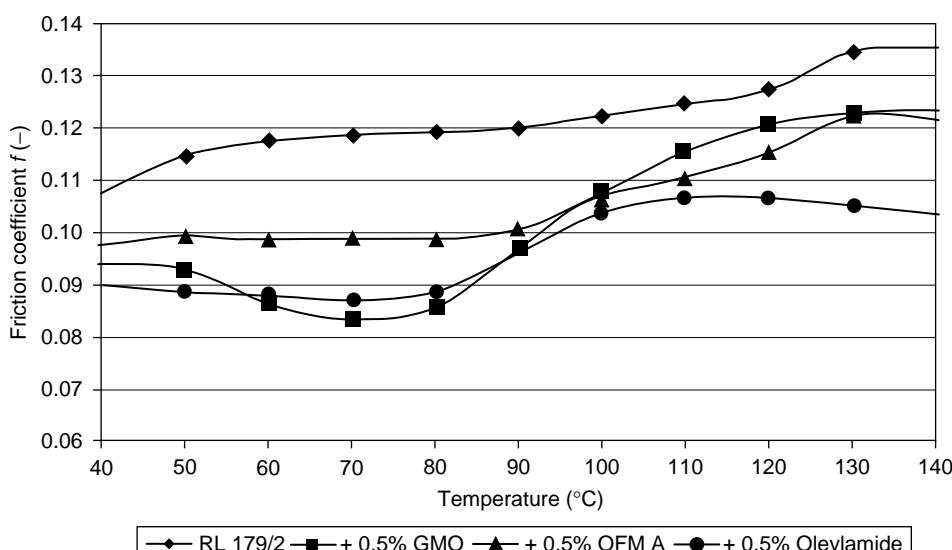


FIGURE 7.12 Friction coefficient versus temperature—CEC RL 179/2 plus organic FMs.

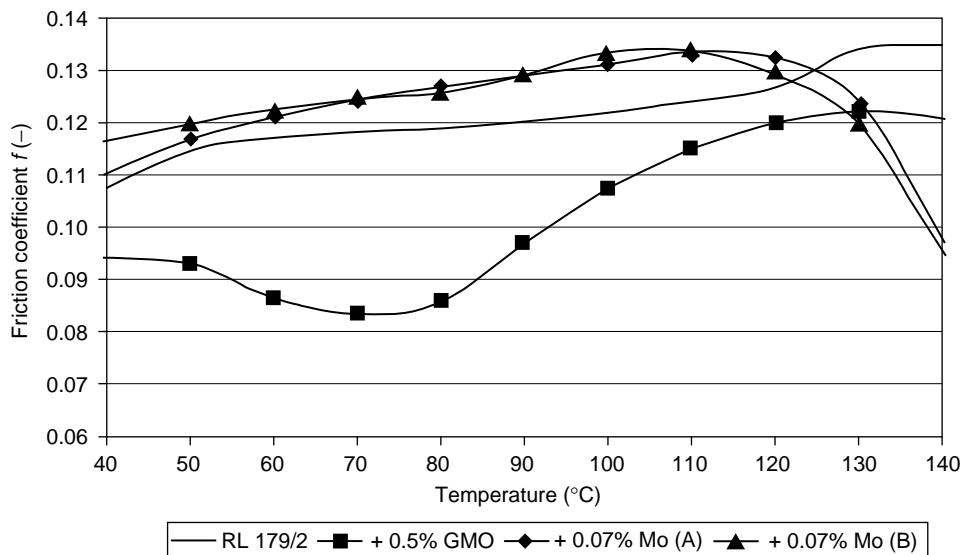


FIGURE 7.13 Friction coefficient versus temperature—CEC RL 179/2 plus molybdenum dithiocarbamates.

The difference in friction-modifying characteristics between organic FMs and molybdenum dithiocarbamate suggests that it might be beneficial to use a combination of these materials.

7.9 CONSEQUENCES OF NEW ENGINE OIL SPECIFICATIONS AND OUTLOOK

Although initial fuel economy requirements were focused on fresh oil only, new engine oil specifications will address fuel economy longevity as well. A good example is Sequence VIB, which has been developed for the ILSAC GF-3 specification.

Sequence VIB includes aging stages of 16 and 80 h to determine fuel economy as well as fuel economy longevity. These aging stages are equivalent to 4000–6000 mi of mileage accumulation required before the EPA metro/highway fuel economy test. That test is used in determining CAFE.

To obtain engine oil formations that are optimized with regard to fuel economy longevity, high requirements are demanded for base oil selection and additive system design [3,7,22]. These requirements are

- To minimize the increase of viscosity thereby maintaining a low electrohydrodynamic friction coefficient
- To maintain low boundary/mixed friction

A minimum increase of viscosity can be obtained by base fluid selection (in terms of volatility, oxidation stability, and antioxidant susceptibility) and selection of antioxidants and their treat level. The market is already anticipating requirements by increasing the production capacity of groups II (HIVI) and III (VHVI) base fluids and by increased interest in groups IV (PAOs) and V (a.o. esters) base fluids.

To achieve low friction under BL and ML conditions, the use of effective friction-reducing additives is needed. To maintain low boundary and mixed friction over time, it is necessary to prevent consumption of these additives by processes such as oxidation and thermal breakdown. Therefore, selecting suitable antioxidant systems for molybdenum compounds and organic FMs and developing organic FMs with highest thermal/oxidative stability will be key for high fuel economy longevity and a successful application in engine oil formulations.

Further studies on the mechanisms of FM action, for example, through molecular modeling techniques, could also speed up the development of optimized additives and additive systems. Apart from frictional properties, other important tribological parameters such as wear rate and surface-metal geometry should be investigated as well. In most papers studied, this seems to be ignored, although all three parameters should be considered in relation to one another.

7.10 BENCH TESTS TO INVESTIGATE FRICTION-REDUCING COMPOUNDS

Several bench tests can be thought of to investigate the frictional properties of base fluids and formulated products. In recent literature [8,23,24], the following test equipment has been used:

1. The high-frequency reciprocating rig (HFRR) to measure boundary friction. Although originally developed to measure diesel fuel lubricity, the equipment can be successfully applied to measure lubricant properties as well.

Frequency	10–200 Hz
Stroke length	20–2000 µm
Load	0–1000 g
Ambient temperature	200°C

A 6 mm diameter ball is the upper specimen and a 3 mm thick smooth disk with a 10 mm diameter is the lower specimen. HFRR specifications are the test conditions that the authors applied to screen FMs; these include a 40 Hz frequency, a stroke of 1000 µm, and a 400 g load.

2. A mini traction machine (MTM) to measure mixed and (E)HD friction, for example, by the determination of Stribeck curves. The MTM rig is capable of measuring at either constant or varying slide/roll ratios if required.

Speed range	Up to 5 m/s
Slide/roll ratio	0–200% (Full rolling to full sliding)
Load	0–75 N
Ambient temperature	150°C

Standard specimens are a 19.05 mm diameter ball as upper specimen and a 50 mm diameter disk as lower specimen. Both are manufactured from AISI 52100 bearing steel. The standard disk is smooth, which allows measurement of mixed-film and full-film friction. Alternatively, rough disks are available for measurements in the BL regime. MTM specifications are the test conditions that the authors applied to test FMs; these comprise a speed range of 0.001–4 m/s, a 30 N load, and a 200% slide/roll ratio.

3. An optical rig provided with a disk coated with a spacer layer to measure EHD film thickness. Such a rig enables film-thickness measurements down to <5 nm with a precision between 1 and 2 nm.

Some other literature refers to the low-velocity friction apparatus (LVFA). Alternative reciprocating rigs may be suitable as well.

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Part 3

*Antiwear Additives and
Extreme-Pressure Additives*

8 Ashless Antiwear and Extreme-Pressure Additives

Liehpao Oscar Farng

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8.1 INTRODUCTION

To optimize the balance between low wear and low friction, machine designers specify a lubricant with a viscosity sufficient to generate hydrodynamic or elastohydrodynamic oil films that separate the machine's interacting surfaces, but not too high to induce excessive viscous drag loss. In practice, the various contact types in a machine, the incidence of operating conditions beyond the design range, and the pressure to improve efficiency by reducing oil viscosity conspire to reduce oil film thickness below the optimum. The high spots, or asperities, on the interacting surfaces then start to interact with one another, initially through micro-elastohydrodynamic lubrication (EHL) films, and at the end through direct surface contact, resulting in increased friction and the likelihood of surface damage. Antiwear and extreme-pressure (EP) additives are added to lubricating oils to decrease wear and prevent seizure under such conditions.

A common way to demonstrate the viscosity optimization is shown in Figure 8.1; this is known as a Stribeck curve. The curve is a composite of a boundary friction curve and a viscous friction curve that decreases as viscosity and, therefore, film thickness increase and that increases as viscosity and speed increase, respectively. A good operating target is represented slightly to the right of the minimum in the curve. Improving the surface finish of contacting surfaces can move the minimum in the curve to a lower viscosity range, saving energy but increasing the cost of components. The hardening or coating of surfaces can increase their durability under increased levels of contact with lower viscosity, but again at an increase in component cost. Notwithstanding these component manufacturing improvements, the need for antiwear and EP additives will continue, but the nature of their chemistry is likely to change due to environmental constraints, component material developments, and the continuing increase in severity of machine operating conditions.

The distinction between antiwear and EP additives is not clear-cut. Some are classed as antiwear in one application and EP in another, and some have both antiwear and EP properties. To add to the confusion, EP additives come in mild and strong flavors, and some are only effective in low-speed, high-load situations and others only in high-speed, high-temperature applications. Generally, antiwear additives are designed to deposit surface films under normal operating conditions and thereby reduce the rate of continuous, moderate wear, whereas EP additives are expected to react rapidly with a surface under severe distress and prevent more catastrophic modes of failure such as scuffing (scoring), galling, and seizure. Recently, it has been suggested that EP additives be renamed as antiscuffing additives, since there is no *pressure*

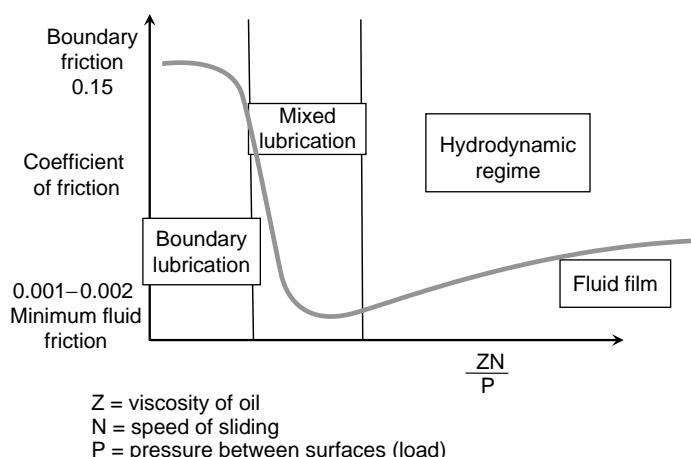


FIGURE 8.1 Regions of lubrication—Stribeck curve.

distinction between them and antiwear additives; only an expectation of a performance boost under severe conditions. EP/antscuffing additives tend to be very reactive, and some can have adverse effects on oxidative stability of oils, can be corrosive to nonferrous materials, and can reduce the fatigue life of bearing and gear surfaces. They should only be used when severe distress is a distinct possibility.

Antiwear additives function in various ways. Some deposit multilayer films thick enough to supplement marginal hydrodynamic films and prevent asperity contact altogether. Some develop easily replenishable monolayer films that reduce the local shear stress between contacting asperities and are preferentially removed in place of surface material. Others bond chemically with the surface and slowly modify surface asperity geometry by controlled surface material removal until conditions conducive to hydrodynamic film generation reappear.

EP additives are designed to prevent metal–metal adhesion or welding when the degree of surface contact is such that the natural protective oxide films are removed and other surface-active species in the oil are not reactive enough to deposit a protective film. This is most likely to occur under conditions of high-speed, high-load, or high-temperature operation. EP additives function by reacting with the metal surface to form a metal compound such as iron sulfide. They act in a manner similar to that of antiwear additives, but their rate of reaction with the metal surface and therefore the rate of EP film formation are higher and the film itself is tougher. Some EP additives prevent scoring and seizure at high speed and under shock loads; others prevent ridging and rippling in high-torque, low-speed operations. In both cases, EP additives and surface metal are consumed, and a smoother surface is created with an improved chance of hydrodynamic action, resulting in less local distress and lower friction. In the absence of such additives, heavy wear and distress well beyond the scale of surface asperities would occur, accompanied by very high friction.

A wide variety of antiwear and EP additives are commercially available, and many other chemicals with antiwear and EP functionality have been reported in the literature and in patents. To be commercially viable, additives must be adequately soluble in lubricant formulations and reasonable in cost, must neither overly reduce the lubricant's oxidative stability nor increase the corrosivity of metals contacted by the lubricant [1–3]. Lead naphthenates were extensively used early in the industry's history, but environmental concerns have led to their virtual disappearance. Similarly, chlorine-containing additives are in decline. Zinc dialkyldithiophosphates (ZDDPs or ZnDTPs) are the best known and most widely used antiwear additives in engine oils, transmission fluids, and hydraulic oils. However, the concern for phosphorus poisoning of automotive catalysts and for zinc as an environmental contaminant has resulted in a pressure to find metal- and phosphorus-free replacements for both automotive and industrial applications. This has resulted in a move toward ashless antiwear and EP additives, and this chapter covers these additives in terms of their chemistry, properties, and performance characteristics, applications, marketing, sales, and outlook.

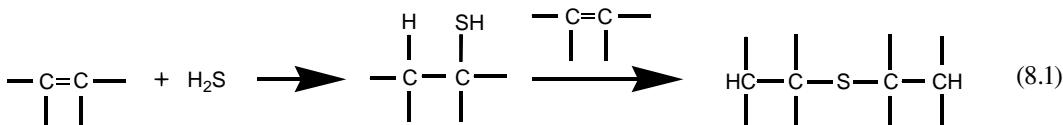
8.2 CHEMISTRY, PROPERTIES, AND PERFORMANCE (CLASSIFIED BY ELEMENTS)

8.2.1 SULFUR ADDITIVES

Sulfur-containing additives are used to provide protection against high pressure, metal-to-metal contacts in boundary lubrication. The magnitude of the EP activity is a function of the sulfur content of the additive; high-sulfur-content additives are usually more effective EP agents than are low-sulfur-content additives. The sulfur content of the additive must be balanced against requirements for thermal stability and noncorrosiveness toward copper-containing alloys. The additive's composition and structure represent a chemical compromise between conflicting performance requirements. In general, any compound that can break down under an energy-input stress, such as heat, and allow for a free sulfur valence to combine with iron would do well as an antiwear and EP additive. Sulfur additives are probably the earliest known, widely used EP compounds in lubricants.

Sulfurization by addition of sulfur compounds [elemental sulfur, hydrogen sulfide, and mercaptans] to unsaturated compounds has been known to the chemical industry for years [4–8]. The two most common classes of additives are called sulfurized olefins [9,10] and sulfurized fatty acid esters [11], because they are produced from reactions of olefins and naturally occurring or synthetic fatty acid esters with sulfur compounds.

In the absence of initiators, the addition to simple olefins is by an electrophilic mechanism; and Markovnikov's rule is followed. However, this reaction is usually very slow and often cannot be done or requires very severe conditions unless an acid catalyst is used. In the presence of free radical initiators, H₂S and mercaptans add to double and triple bonds by a free radical mechanism, and the orientation is anti-Markovnikov. By any mechanism, the initial product of addition of H₂S to a double bond is a mercaptan, which is capable of adding to a second molecule of olefin, so that sulfides are often produced (reaction 8.1):

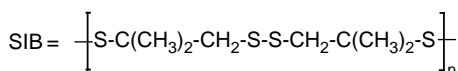
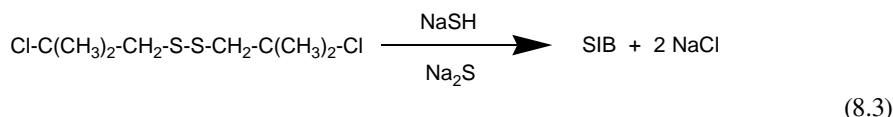
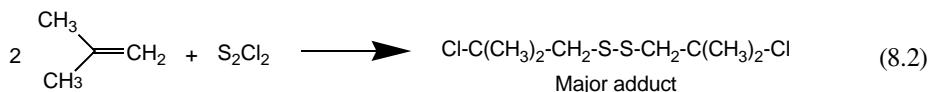


8.2.1.1 Sulfurized Olefins

Sulfurized olefins are prepared by treating an olefin with a sulfur source under proper reaction conditions. The more the sulfur used, the higher is the sulfur content. Suitable olefins preferably include terminal olefins and internal olefins, mono-olefins and polyolefins. However, to provide adequate oil solubility, the olefin should provide a carbon chain of at least four carbon atoms. Accordingly, suitable alpha olefins are butenes, pentenes, hexenes, and preferably higher alpha olefins such as octenes, nonenes, and decenes. Isobutylene is a very unique olefin that not only exhibits very high reactivity toward sulfur reagents (high conversion rate) but also can produce sulfurized products having very good stability and lubricant compatibility. Therefore, sulfurized isobutylene (SIB) has been by far the most cost-effective, widely used EP additive in lubricants.

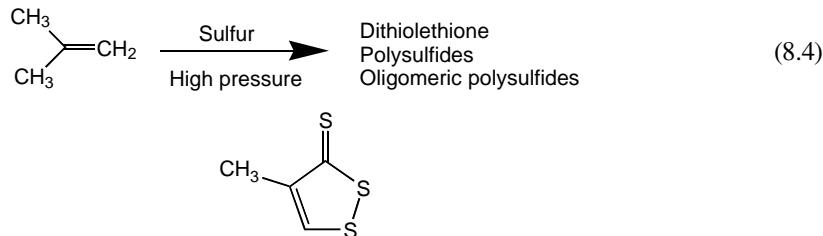
8.2.1.1.1 Chemistry and Manufacture

Initially, sulfurized olefins were synthesized through a two-step chloride process, and often, the products were referred to as “conventional sulfurized olefins.” Sulfur monochloride and sulfur dichloride were used in the first step to produce chlorinated adducts, and then the adducts were treated with an alkali metal sulfide in the presence of free sulfur in an alcohol–water solvent, followed by further treatment with an inorganic base (reactions 8.2 and 8.3) [12]. The final product is a light yellow–colored fluid with oligomeric monosulfides and disulfides as the main compositions, as typified by reactions 8.2 and 8.3.



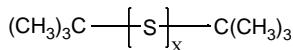
The manufacture of conventional sulfurized olefins involves sulfur monochloride, and the final product contains some residual chlorine. The process also generates aqueous waste with halogen- and sulfur-containing by-products that must be disposed of. Chlorine in lubricants and other materials is increasingly becoming an environmental concern because chlorinated dioxins can be formed when chlorine-containing materials are incinerated. Chlorinated waxes have been eliminated from many lubricants for this reason. Residual chlorine content is also becoming a major concern in many areas of the world. Germany currently has a 50 ppm maximum limit on the chlorine content of automotive gear oils. This requirement is a problem for automotive gear oil suppliers as well as additive suppliers if their technology is based on conventional sulfurized olefins, since the residual chlorine content is a consequence of the chemistry required to manufacture conventional sulfurized olefins. By fine-tuning the manufacturing process, the chlorine content of conventional sulfurized olefins may be reduced from a typical 1500 ppm to <500 ppm. However, manufacturing changes to reduce the residual chlorine content will probably slow the production process, require additional capital investments, and possibly generate more aqueous waste.

In the late 1970s, the high-pressure sulfurized isobutylene (HPSIB) process was developed to replace the conventional, low-pressure chlorine process. HPSIBs are usually mixtures of di-*tert*-butyl trisulfides, tetrasulfides, and higher-order polysulfides [13–16]. Some HPSIBs contain oligomeric polysulfides of poorly defined composition or other materials such as 4-methyl-1, 2-dithiole-3-thione (Structure A, [8,17], and reaction 8.4). The higher-order polysulfides generally favor EP activity at the expense of oxidative stability and copper corrosivity compared to the monosulfides and disulfides of conventional sulfurized olefins. In the absence of other reagents, the straight reaction of elemental sulfur and isobutylene results in a dark-colored liquid that contains a significant amount of dithiolethiones (thiocarbonates). 4-Methyl-1, 2-dithiole-3-thione is a pseudoaromatic heterocyclic compound. Owing to its rigid ring structure, dithiolethiones can be easily precipitated as yellowish solids that cause severe staining problems. Therefore, dithiolethione is often not a desirable side product in SIB.



STRUCTURE A

In the presence of various catalysts (or basic materials), such as aqueous ammonia, alkali metal sulfides, or metal dithiocarbamates, amounts of dithiolethiones (Structure A) and oligomeric polysulfides can be reduced, and low-molecular-weight polysulfides ($X = 2$ to 6 in Structure B) are the predominant products [18].



STRUCTURE B

The use of hydrogen sulfide in the high-pressure sulfurized olefin process can ease the reaction complexity and also yield high-quality, low-molecular-weight polysulfides. The compositions of products prepared from this process usually have good clarity, low odor, light color, and high EP activity. Hydrogen sulfide is a very foul smelling and toxic gas. It leads to collapse, coma, and death as result of respiratory failure within a few seconds after one or two inhalations. Liquefied hydrogen sulfide has a high vapor pressure that requires additional, adequate protective equipment. There are considerable risks associated with its routine use on an industrial scale, but hydrogen

sulfide is a low-cost, commodity chemical, which can often offset the additional costs for safe use. High-pressure sulfurized olefins can also be prepared with reagents that generate hydrogen sulfide within the reactor during the course of the reaction. Direct handling of hydrogen sulfide is thus avoided, but there can be processing penalties, usually in the area of aqueous waste handling. Performance wise, high-pressure sulfurized olefins could replace conventional sulfurized olefins in suitable applications. A decision to manufacture high-pressure sulfurized olefins by one process or another will require a careful assessment of acceptable risks versus economic requirements.

Other olefins or mixed olefins are also used in the preparation of various sulfurized olefins. Among these, di-*tert*-nonyl and di-dodecyl trisulfides and penta-sulfides are very popular additives. Diisobutylene (2,4,4-trimethyl-1-pentene) is also used extensively to make higher-viscosity sulfurized products. In addition, sulfurized hydrocarbons such as sulfurized terpene, sulfurized dicyclopentadiene, or sulfurized dipentene olefin, and sulfurized wax are also widely used due to low raw material costs.

8.2.1.1.2 Applications and Performance Characteristics

Sulfurized olefins played a key role in establishing superior ashless sulfur/phosphorus (S/P) additive systems for lubricating automotive and industrial EP gear oils in the late 1960s [19–21]. The early EP gear oil additives were clearly dominated by chlorine, zinc, and lead, which had difficulty in adequately protecting heavy-duty equipment. On the contrary, the S/P gear oil additive technology, based on ashless and chlorine-free components, possesses very good thermal-oxidative stability and rust inhibition (CRC L-33 and ASTM D665B); therefore, this is a significant performance improvement over the metal- and chlorine-based technologies.

Sulfurized olefins function mainly through thermal decomposition mechanisms. Sulfur prevents contact between interacting ferrous metal surfaces through the formation of an intermediate film of iron sulfide. By doing this, sulfur usually decreases the wear rate but accelerates the smoothing of the surfaces. This smoothing actually helps reduce the wear rate. Furthermore, a higher percent of active sulfur in a molecule increases the chances of reaction with the metal surface and favors EP (antsizeizure) more than antiwear properties. Thus, SIB is mainly a strong antiscuffing additive, with outstanding scuffing protection properties (e.g., CRC L-42 performance). Table 8.1 shows coefficients of friction and dimensions with respect to metal surface, oil molecules, and sulfide layers. It can be seen that the friction coefficients of the sulfide layers are about half of those for metal-to-metal surfaces. The sulfide layers retard the welding of the moving metal surfaces, but do not prevent wearing. Particles of iron sulfide are constantly sloughed off from the metal surface. This wear can be determined by an analysis of the lubricating oils (residual iron content), and subsequent sludge formation can be controlled by the use of dispersants.

Besides heavy-duty gear oil applications [22], sulfurized olefins have also found usefulness in other lubricant areas, such as metal processing oils, greases, marine oils, and tractor transmission oils.

TABLE 8.1
Typical Surface Characteristics

Surface	Coefficient of Friction
Steel:steel	0.78
FeS:FeS	0.39
Copper:copper	1.21
CuS:CuS	0.74
Material	Dimension (Å)
Size of oil molecules	50
Size of sulfide layers	3000
Surfaces with <i>superfinish</i>	1000

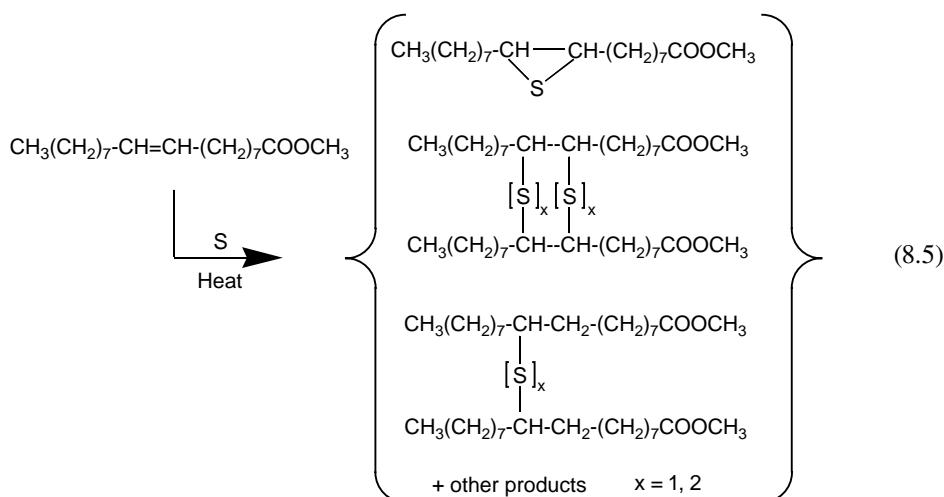
8.2.1.2 Sulfurized Esters and Sulfurized Oils

The oldest widely used sulfur-based additive that is still found in commercial lubricants is sulfurized lard oil (SLO), a sulfurized animal triglyceride. In 1939, H. G. Smith made one of the most important discoveries in the history of lubricant additives. He found that sulfurized sperm whale oil (SSWO) was more soluble in paraffinic base oils, even at low temperatures, and had a much higher thermal stability than SLO. Thus, over 60 years ago, he recognized that the improved stability of sulfurized sperm oil resulted from its monoester structure, compared with the triester structure of SLO. With long-chain monoesters, the sulfur has little potential to form bridges between the molecules, as it does when triglycerides are being sulfurized. SSWO is an excellent boundary lubricant and is highly resistant to gumming, resin formation, or viscosity increase, when subjected to high temperature and high pressure [23]. Unfortunately, from a lubricant cost-performance viewpoint, this additive is no longer available due to restrictions on the use of sperm whale oil. Sulfurized jojoba oil, an expensive alternative, is available; it is also a mixture of long-chain alcohol fatty acid compounds. All these sulfurized fats or esters are usually manufactured to contain 10–15% sulfur and are often good antiwear and mild EP agents.

8.2.1.2.1 Chemistry and Manufacture

Sperm oil is a waxy mixture of esters of fatty alcohols and fatty acids with a small amount of triglycerides. After the separation of solid waxes by filtration or centrifuge, a liquid wax remains, consisting mainly of an ester of oleic alcohol and oleic acid. Such a structure could not be better for sulfurizing purposes.

Similar to sulfurized olefins, sulfurized esters can be made by either direct sulfurization with elemental sulfur or sulfurization with hydrogen sulfide under superatmospheric pressures. Nowadays, they are mainly made from vegetable oils having one or more double bonds. Sulfurized esters are made from unsaturated fatty acids such as oleic acid, and esterified with an alcohol such as methanol. Frequently the sulfurization of fats is made in the presence of an olefin, preferably of long chain, and the resulting commercial product is a mixture of the two types. Equation 8.5 shows a typical example of sulfurization of methyl oleate with elemental sulfur. When sulfurized with hydrogen sulfide, products usually possess light color and lower odor.



8.2.1.2.2 Properties, Performance Characteristics, and Applications

The load-carrying property of sulfurized oils is directly linked to the amount of active sulfur in the additive. Percent of active sulfur (which is believed to provide EP activity) and total sulfur can be determined by proper analytical methods, and the difference is the percent of inactive sulfur.

The more the active sulfur present, the higher the load-carrying property. However, there is also a direct correlation between active sulfur and copper corrosivity—the more the active sulfur, the poorer the copper corrosion protection. More active sulfur can also lead to cleanliness and stability challenges. Therefore, the ultimate product properties for a specific lubricant product will dictate which sulfurized products to use.

Although the sulfur content may not be as high as in many sulfurized olefins, sulfurized esters are attractive for their exceptionally good frictional properties in many applications. This is because combining sulfur with fat in a lubricant additive provides a synergistic effect. In this instance, the fat provides reduced friction, and sulfur provides wear and EP protection. Of all the elements, sulfur probably gives the best synergistic results in combination with other components and organic compounds. As to EP characteristics, sulfurized esters have a surface activity conferred by a small amount of their normal free fatty acids. These are polar species that tend to be absorbed in layers of molecular dimensions at the metal interface. The interposition of such films is effective in preventing metal seizure under conditions of EP or under conditions tending to displace the lubricating film between the bearing surfaces. Here, film strength and EP phenomena are often used synonymously. Film strength implies that metal-to-metal contact and welding are prevented as a result of the film formation (or replenishment) by the chemical reaction of the metal and an EP additive. Also, fatty oils and sulfurized fatty oils because of their affinity for metal surfaces are less easily displaced from metal surfaces by water than are mineral oils.

The ferrophilic ester groups improve the EP properties. Depending on the molecular structure and its polarity, the surface activities vary. Since the surface activity or polarity of the substances used for sulfurization plays an equally decisive role in lubricating action, it should be taken into serious consideration when one formulates a product for a specific application. Comparing sulfurized triglycerides (e.g., SLO) with sulfurized monoesters (e.g., SSWO), the EP properties of the triglycerides are better. Two factors may be responsible for this phenomenon: (1) as the triester structure is more ferrophilic, hydrogen bridging may occur; (2) as triglycerides decompose at high temperatures to form acrolein moieties during the lubrication process, the polymerized acrolein film can add strength to the sulfide film and improve the EP characteristics. However, this EP activity of triglycerides has limited value due to their poor stability and oil solubility. Stability tests at elevated temperatures show faster and heavier sludging for SLO than for SSWO. Therefore, a proper balance of all properties is an essential part of product formulations.

Sulfurized fats or esters are used extensively in lubricants such as metalworking fluids, tractor-transmission fluids, and greases.

8.2.1.3 Other Sulfur Additives

Elemental sulfur provides good EP properties; however, it leads to corrosion. It dissolves in mineral oils up to certain levels depending on the type of base oils. Low polarity paraffinic/naphthenic type group II and III base oils usually have very limited solubility of elemental sulfur. Sulfurized aromatics such as dibenzyl disulfide, butylphenol disulfide, diphenyl disulfide, or tetramethyldibenzyl disulfide generally containing less-active sulfur improve the EP characteristics of lubricants only moderately; they are therefore used predominantly in combinations with other sulfur or phosphorus-containing EP additives [24,25]. Other sulfur carriers such as sulfurized nonylphenol, dialkyl thiodipropionates ($S[CH_2CH_2C(=O)OR]_2$), derivatives of thioglycolic acid esters ($HS-CH_2C(=O)OR$), derivatives of thiosalicylic acid, and trithians are also available [26]. However, materials with low sulfur content are usually less active as antiwear/EP additives, but more effective as antioxidants.

8.2.2 PHOSPHORUS ADDITIVES

Phosphorus-containing additives are used to provide protection against moderate to high pressure, metal-to-metal contacts in boundary lubrication and EHL. Unlike sulfur additives, where their EP activity must be balanced against performance requirements for thermal stability and mild

corrosivity toward copper-containing alloys, phosphorus additives usually possess very good corrosivity control. Owing to totally different mechanisms involved in surface film formation rates and film strengths, phosphorus additives cannot replace sulfur additives in many applications and vice versa. Typically, phosphorus additives are extremely effective in applications with slow sliding speeds and high surface roughness.

8.2.2.1 Phosphate Esters

Phosphate esters have been produced commercially since the 1920s and have gained importance as lubricant additives, plasticizers, and synthetic base fluids for compressor and hydraulic oils. They are esters of alcohols and phenols with a general formula $O=P(OR)_3$, where R represents alkyl, aryl, alkylaryl, or very often, a mixture of alkyl and aryl components. The physical and chemical properties of phosphate esters can be varied considerably depending on the choice of substituents, and these can be selected to give optimum performance for a given application. Phosphate esters are particularly used in applications that benefit from their high-temperature stability and excellent fire-resistance properties in addition to their adequate antiwear properties [27].

8.2.2.1.1 Chemistry and Manufacture

Phosphate esters are produced by reaction of phosphoryl chloride with alcohols or phenols as shown in reaction 8.6.



Early production of phosphate esters was based on the so-called crude cresylic acid fraction or tar acid derived by distillation of coal tar residues. This feedstock is a complex mixture of cresols, xylenols, and other heavy materials and includes significant quantities of *ortho*-cresol. The presence of high concentrations of *ortho*-cresol results in an ester that has been associated with neurotoxic effects, and this has led to the use of controlled coal tar fractions, in which the content of *ortho*-cresol and other *ortho*-*n*-alkylphenols is greatly reduced. Phosphate esters using coal tar fractions are generally referred to as *natural* as opposed to *synthetic*, where high-purity raw materials are used.

The vast majority of modern phosphate esters are *synthetic*, using materials derived from petrochemical sources. For example, *t*-butylated phenols are produced from phenols by reaction with butylene. The reaction of alcohol or phenol with phosphoryl chloride yields the crude product, which is generally washed, distilled, dried, and decolorized to yield the finished product. Low-molecular-weight trialkyl esters are water-soluble, requiring the use of nonaqueous techniques. When mixed alkylaryl esters are produced, the reactant phenol and alcohol are added separately. The reaction is conducted in a stepwise process and the reaction temperature is kept as low as possible to avoid transesterification reactions from taking place.

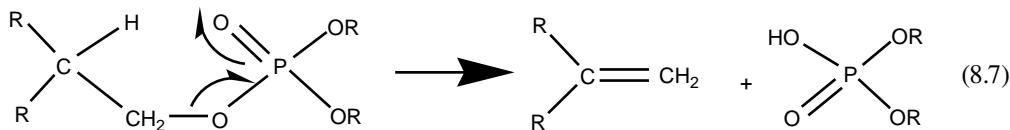
The most commonly used phosphate esters for antiwear performance features are tricresyl phosphates (TCP), trixylenyl phosphates (TXP), and tributylphenyl phosphates (TBP).

8.2.2.1.2 Physical and Chemical Properties

The physical properties of phosphate esters vary considerably according to the mix and type of organic substituents, the molecular weights, and structural symmetry, all proving to be particularly significant. Consequently, phosphate esters range from low-viscosity, water-soluble liquids to insoluble high-melting solids.

As mentioned previously, the use of phosphate esters as synthetic base fluids arises mostly from their excellent fire resistance and superior lubricity, but is limited due to their hydrolytic and thermal stability, low-temperature properties, and viscosity index. Although phosphate esters are widely used as antiwear additives for lubricants, the concerns about hydrolytic stability, thermal stability, and of course, satisfactory antiwear properties are equally important. In that sense, triaryl phosphates are dominant over trialkyl phosphates, because their hydrolytic–thermal stability is much better.

The thermal stability of triaryl phosphates is considerably superior to that of the trialkyl esters, which degrade thermally by a mechanism analogous to that of the carboxylic esters (reaction 8.7).



With respect to hydrolytic stability, aryl phosphate esters are superior to the alkyl esters. Increasing chain length and degree of branching of the alkyl group leads to considerable improvement in hydrolytic stability. However, the more the substituent is sterically hindered, the more difficult it is to prepare the ester. Alkylaryl phosphates tend to be more susceptible to hydrolysis than the triaryl or trialkyl esters.

The low-temperature properties of phosphate esters containing one or more alkyl substituents tend to be reasonably good. Many triaryl phosphates are fairly high-melting point solids, but an acceptable pour point can be achieved by using a mixture of aryl components. Coal tar fractions, used to make natural phosphate esters, are already complex mixtures and give esters with satisfactory pour points.

Phosphate esters are very good solvents and are extremely aggressive toward paints and a wide range of plastics and rubbers. When selecting suitable gasket and seal materials for use with these esters, careful consideration is required. The solvency power of phosphate esters can be advantageous in that it makes them compatible with most other common additives and enables them to be used as carriers for other less-soluble additives to generate additive slurry.

8.2.2.2 Phosphites

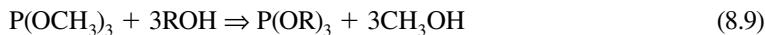
Phosphites are the main organophosphorus compounds used to control oxidative degradation of lubricants. They eliminate hydroperoxides and peroxy and alkoxy radicals, retard the darkening of lubricants over time, and also limit photodegradation. In addition to their important role as antioxidants, phosphites are also found to be useful antiwear additives. Dialkyl hydrogen phosphites and diaryl hydrogen phosphites are neutral esters of phosphorus acid. These materials have two rapid equilibrating forms: the keto form, $(\text{RO})_2\text{P}(=\text{O})\text{H}$, and the acid form, $(\text{RO})_2\text{P}-\text{O}-\text{H}$. Physical measurements indicate that they exist substantially in the keto form, associated in dimeric or trimeric groupings by hydrogen bonding. Trialkyl phosphites and triaryl phosphites are neutral trivalent phosphorus esters. These materials are clear, mobile liquids with characteristic odors.

8.2.2.2.1 Chemistry and Manufacture

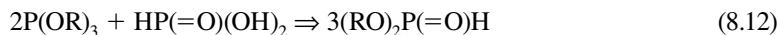
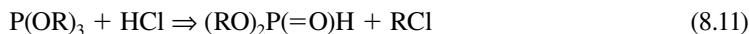
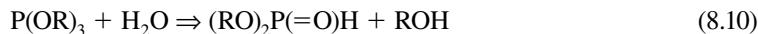
Phosphites are produced by reaction of phosphorus trichloride with alcohols or phenols as given by



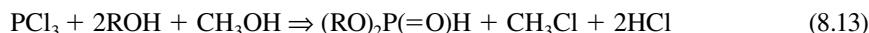
When mixed alkylaryl phosphites are produced, the reactants phenol and alcohol are added separately with the reaction temperature being controlled carefully. High-molecular-weight phosphites can be produced from transesterification reaction of either alcohols or phenols with trimethyl phosphite under catalytic (acidic) conditions.



With acid catalyzed hydrolysis, dialkyl or diaryl hydrogen phosphites can be produced from trialkyl or triaryl phosphites as shown in reactions 8.10 through 8.12.



By carrying out the preceding reactions in the presence of hydrogen chloride acceptors such as pyridine, the isolation of mono, di, and trialkyl phosphites is feasible. However, with alcohols of normal reactivity, the product is often mainly dialkyl hydrogen phosphite. This can be made in up to 85% yield, by adding PCl_3 to a mixture of methanol and a higher alcohol at low temperature. The methyl and hydrogen chlorides are then removed by heating under reduced pressure on a steambath.



The commonly used phosphites available in the marketplace are dimethyl hydrogen phosphite, diethyl hydrogen phosphite, diisopropyl hydrogen phosphite, dibutyl hydrogen phosphite, bis(2-ethylhexyl) hydrogen phosphite, dilauryl hydrogen phosphite, bis(tridecyl) hydrogen phosphite, dioleyl hydrogen phosphite, trisnonylphenyl phosphite, triphenyl phosphite, triisopropyl phosphite, tributyl phosphite, triisoctyl phosphite, tris(2-ethylhexyl) phosphite, trilauryl phosphite, triisodecyl phosphite, diphenylisodecyl phosphite, diphenylisoctyl phosphite, phenyldiisodecyl phosphite, ethylhexyl diphenyl phosphite, and diisodecyl pentaerythritol diphosphite.

8.2.2.2 Chemical and Physical Properties

Phosphites tend to hydrolyze when exposed to humidity in the air or moisture in the lubricant. The extent of hydrolysis depends on the moisture content of the ambient atmosphere, the temperature, and the duration of exposure. Generally, liquid phosphites are more stable than solids because of the reduced surface area available for moisture pickup. But hydrolysis can be minimized if proper precautions, such as dry nitrogen atmosphere, cool storage, and use of tight seals, are observed. The lower dialkyl hydrogen phosphites hydrolyze in both acidic and alkaline solutions to monoalkyl esters and phosphorus acid. Rates of hydrolysis normally decrease with increasing molecular weight. The lower esters of trialkyl phosphites are rapidly hydrolyzed by acids; however, they are relatively stable in neutral or alkaline solutions. In general, the hydrolytic stability of the trialkyl phosphites increases with molecular weight.

Since the dialkyl hydrogen phosphites are predominately in the keto form, they are somewhat resistant to oxidation and do not complex with cuprous halides. Both of these reactions are characteristic of trivalent organic phosphorus compounds [28–30]. These esters are relatively resistant to reaction with oxygen and sulfur, but react quite readily with chlorine and bromine giving the corresponding dialkyl phosphorohalides ($(\text{RO})_2\text{P}(=\text{O})\text{X}$ where $\text{X} = \text{Cl}$ or Br) [27].

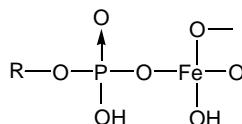
The hydrogen atom of the dialkyl hydrogen phosphites is replaceable by alkali but is not acidic in the usual sense. The alkali salts are readily obtainable by reaction of ester with metals. In contrast with the parent compound, these salts readily add sulfur to form the corresponding phosphorothioates. Sodium salts of phosphites can be reacted with alkyl chlorides to produce alkyl phosphonates. These salts react with halophosphites to produce pyrophosphites and with chlorine or bromine to yield the corresponding hypophosphates. Dialkyl hydrogen phosphites add readily to ketones, aldehydes, olefins, and anhydrides, and these reactions are catalyzed by bases and free radicals. This type of reaction provides an excellent method for preparing phosphonates.

Sulfur reacts readily with trialkyl or triaryl phosphites to form corresponding trialkyl or triaryl phosphorothioates, which are also very useful antiwear additives. The reaction of trialkyl phosphites with halogens is an excellent method for preparing dialkyl phosphorohalides. Acyl halides and most polyfunctional primary aliphatic halides can be used. Triisopropyl phosphite provides a unique means for preparation of unsymmetrical phosphonates and diphosphonates because the by-product isopropyl halide reacts very slowly and thereby does not compete with the primary reaction.

8.2.2.2.3 Applications and Performance Characteristics

Dialkyl (or diaryl) hydrogen phosphites, besides being excellent antiwear agents, are considered the most potent form of phosphorus, suited to high-torque, low-speed operations. This is the area where antiwear processes are taken to the extreme and is one of the most important sections of the EP performance spectrum. Sulfur can be quite incapable of giving protection under such conditions. Only a phosphorus source, if active enough and in sufficient concentration, can help here. Conversely, phosphorus components are of little use in high-speed and shock operations where sulfur components can be excellent. Dialkyl or diaryl phosphites are also potent antioxidants.

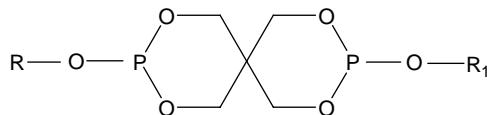
With dialkyl phosphites, it has been reported that oxidation produces a phosphate anion, which tends to act as a bridging ligand to form an oligomeric iron (III) complex, that is, an iron oxide complex resembling Structure C.



STRUCTURE C

However, there is also a weak, high-viscosity, nonsolid film that increases the overall thickness of the total film at high speeds [24,31].

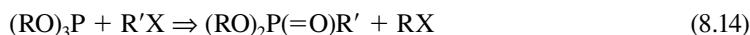
Dialkyl phosphites are widely used in gear oils, automatic transmission fluids (ATF), and many other applications. Spiro bicyclodiphosphites are also reported to be used in continuously variable transmission fluids [32] (Structure D).



STRUCTURE D

8.2.2.3 Dialkyl Alkyl Phosphonates

Dialkyl alkyl phosphonates [$\text{R}-\text{P}(\text{=O})(\text{OR}')_2$] are stable organic phosphorus compounds that are miscible with ether, alcohol, and most organic solvents. Besides being used as additives in solvents and low-temperature hydraulic fluids, they can also be used in heavy metal extraction, solvent separation, and as preignition additives to gasoline, antifoam agents, plasticizers, and stabilizers. Dialkyl alkyl phosphonates are prepared from either dialkyl hydrogen phosphites or trialkyl phosphites as described in reactions (Michaelis–Arbuzov reaction).



In principle, the thermal isomerization of all phosphites to phosphonates can be carried out. The stability of these compounds varies greatly; however, depending on the nature of the R group, other products may be formed during heating. For R = methyl, complete conversion occurs at 200°C in 18 h, but for R = butyl, the compound is stable at 223°C. It is thought by some that isomerization of phosphites may be possible only if traces of phosphonate are already present as an impurity [33].



8.2.2.4 Acid Phosphates

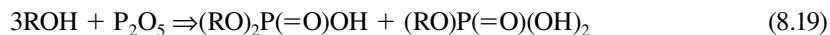
Acid phosphates are also potent additives, useful in similar areas of antiwear and EP to the dialkyl phosphites. Orthophosphoric (monophosphoric) acid (H_3PO_4), the simplest oxyacid of phosphorus, can be made by reacting phosphorus pentoxide with water. It is widely used in fertilizer manufacture. Orthophosphoric acid has only one strongly ionizing hydrogen atom and dissociates according to the following reaction



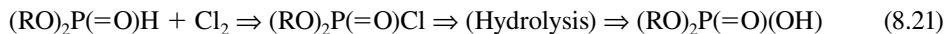
Since the first dissociation constant, $K_1 (7.1 \times 10^{-3})$, is much larger than the second ($K_2 = 6.3 \times 10^{-8}$), very little of the $H_2PO_4^-$ produced in the first equilibrium goes on to dissociate according to the second equilibrium. Even less dissociates according to the third equilibrium since the third constant K_3 is very small ($K_3 = 4.4 \times 10^{-13}$). The acid gives rise to three series of salts containing these ions, for example, NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 .

8.2.2.4.1 Chemistry and Manufacture

Alkyl (aryl) acid phosphates are made from alcohol (phenol) and phosphorus pentoxide. Generally, a mixture of monoalkyl (aryl) and dialkyl (aryl) phosphates is produced.



Pure monoalkyl or dialkyl (aryl) phosphates can be synthesized through different reaction routes as follows:



8.2.2.4.2 Properties, Performance Characteristics, and Applications

Phosphoric acids tend to hydrolyze further when exposed to humidity. The extent of hydrolysis depends on the moisture content of the ambient atmosphere and the duration of exposure. Wherever possible, phosphoric acids should be handled in a dry nitrogen atmosphere to prevent hydrolysis. Therefore, for applications where incidental moisture contact is inevitable, acid phosphates are not recommended.

Acid phosphates are used as rust inhibitors and antiwear additives. However, they are not as widely used as their amine-neutralized derivatives, for example, amine phosphates.

8.2.3 SULFUR-PHOSPHORUS ADDITIVES

Sulfur-phosphorus additives are used to provide protection against moderate to high pressure, metal-to-metal contacts in boundary lubrication, and EHL. Metallic sulfur-phosphorus additives, such as zinc dithiophosphates (ZnDTPs), are the most important antiwear/EP components used in engine oils. Ashless sulfur-phosphorus additives are used less extensively, and the most commonly available S/P additives in the marketplace are based on chemistries of dithiophosphates, thiophosphates, and phosphorothioates. Other important applications of S/P compounds are in matches, insecticides, flotation agents, and vulcanization accelerators.

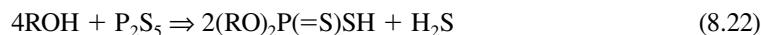
8.2.3.1 Ashless Dithiophosphates

Numerous patents were issued on the use of phosphorodithioic acid esters in lubricating oils in the early days. U.S. Patent 2,528,732 describes alkyl esters of phosphorodithioic acid. U.S. Patent 2,665,295

describes the *S*-terpene ester, whereas U.S. Patent 2,976,308 describes an anti-Markovnikov addition of phosphorodithioic acid ester to various olefins, both aromatic and aliphatic. Amine dithiophosphates and other novel dithiophosphate esters are reported in the literature [34–38]. Coupling with vinyl pyrrolidinone, acrolein or alkylene oxides (to make hydroxyl derivatives) are also known [39–41].

8.2.3.1.1 Chemistry and Manufacture

Similar to metallic dithiophosphates, ashless dithiophosphates are also based on phosphorus pentasulfide (P_2S_5) chemistry. They can be prepared from the same precursor of ZnDTP, dithiophosphoric acid (reaction 8.22) through the reaction of alcohol (or alkylphenol) and P_2S_5 .



The dithiophosphoric acids are further reacted with an organic substrate to generate ashless derivatives. Typical organic substrates are compounds such as olefins, dienes, unsaturated esters (acrylates, methacrylates, vinyl esters, etc.), unsaturated acids, and ethers. The efficiency and stability of the ashless dithiophosphates very much depends on components used in their manufacture and the reaction conditions.

The most common ashless dithiophosphate used in the marketplace is a dithiophosphate ester made from ethyl acrylate and *o,o*-diisopropyl dithiophosphoric acid as described in the following:



Treatment of terpenes, polyisobutylene (PIB), or polypropylene (PP) with phosphorus pentasulfide and hydrolysis give thiophosphonic acids [$R-P(=S)(OH)_2$, where R = PIB, terpenes, or PP]. They can be further reacted with propylene oxide or amines to reduce acidity. However, this type of additive belongs to the same class of chemicals called ashless dispersants. Hence, they can be dual functional dispersants with improved antiwear/EP properties.

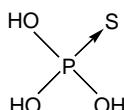
8.2.3.1.2 Applications and Performance Characteristics

Unlike ZnDTP, ashless dithiophosphates are usually not as versatile, and therefore cannot be considered as multifunctional additives. Although ashless dithiophosphates have fairly good antiwear and EP properties, their anticorrosion properties are not as good as ZnDTP. This is closely related to the stability and decomposition mechanisms of ashless dithiophosphates. Relatively weak corrosion protection also limits their application at high concentrations in engine oils as well as some industrial oils.

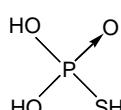
Ashless dithiophosphates can be useful in metalworking fluids, automotive transmission fluids (ATF), gear oils, greases, and non-zinc hydraulic fluids [42,43].

8.2.3.2 Ashless Phosphorothioates and Thiophosphates

Numerous esters of the phosphorothioic acids are known. In salts and esters of these oxygen/sulfur (O–S) acids, there may be a preferred location of the multiple bonds, but in general, this is not well known. Thus in principle, there are two series of possible acids, each of which might give rise to salts and esters as described in the following:



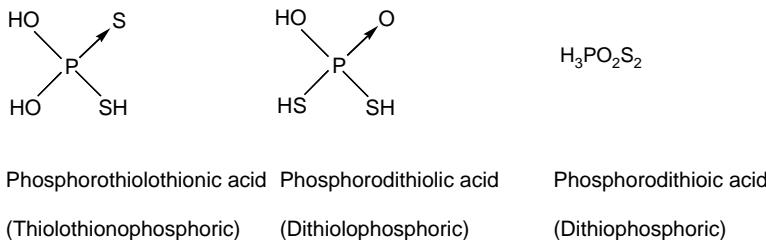
Phosphorothionic acid
(Thionophosphoric)



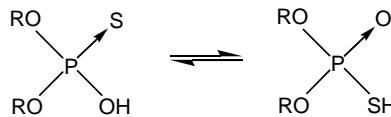
Phosphorothiolic acid
(Thiolophosphoric)



Phosphorothioic acid
(Thiophosphoric)



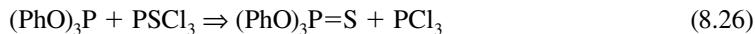
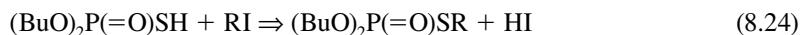
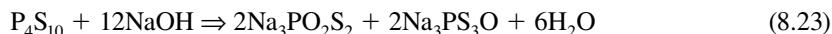
The “thionic” acids contain the group P=S, whereas the “thiolic” acids contain the group P-SH. The term “thioic” is often used when the molecular form is unknown or when specification is not desired. One form of these acids is usually more stable than the other, and it may not be possible to prepare both esters as, for example, the isomers of phosphorothioic acid.



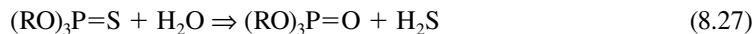
In the case of some esters, the thiol form is the most stable, but the phenyl ester exists 80% in thiono, $(PhO)_2P(=S)OH$, and 20% in thiolo, $(PhO)_2P(=O)SH$ forms. The equilibrium of these compounds is liable to be dependent on the nature of the R groups, the solvent used, and even the concentration. Intermolecular hydrogen bonding may be expected to play a part in such equilibrium [33].

8.2.3.2.1 Chemistry and Manufacture

The creation of a compound with a phosphorus–sulfur linkage can often be carried out simply by heating the appropriate phosphorus compound with sulfur [44]. Likewise, the replacement of oxygen by sulfur in compounds containing P–O linkages can also be achieved simply by heating them with P_2S_5 . Inorganic phosphorothioates (thiophosphates) are usually prepared from sulfur-containing phosphorus compounds. They are produced during the hydrolytic breakdown of phosphorus sulfides and are often themselves unstable in water. They hydrolyze to the corresponding oxy compounds with the evolution of H_2S . Phosphorus–sulfur compounds are often thermally less stable than their oxy analogues. A few examples are listed as follows:



Hydrolysis of phosphorothioate esters results in a progressive loss of sulfur as hydrogen sulfide (H_2S) and its replacement by oxygen.



8.2.3.2.2 Applications and Performance Characteristics

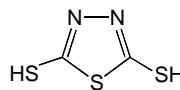
It has been known for many years that sulfur compounds form a film of iron sulfide, and phosphorus compounds form iron phosphate, on the mating metal surfaces. Generally, the films formed from sulfur sources such as SIB are expected to contain FeS , $FeSO_4$, as well as organic fragments from

the additive decomposition. With phosphorus sources, such as dialkyl phosphites, films containing FePO_4 , FePO_3 , as well as organic fragments are expected. When both sulfur and phosphorus are present, both elements contribute to the nature of the film, and which one predominates depends on the S/P ratio, the decomposition mechanisms, and the operating conditions, for example, high speed and shock or high torque/low speed.

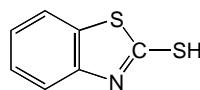
Ashless phosphorothioates are widely used as replacements for metallic dithiophosphates in many lubricant applications where metal is less desirable [43,44]. Phosphorothioates are often present (generated *in situ*) in lubricant formulations when both sulfur and phosphorus additives are used. Aryl phosphorothioates provide good thermal stability and good antiwear/EP properties as evidenced by their strong FZG performance.

8.2.4 SULFUR–NITROGEN ADDITIVES

Sulfur and nitrogen-containing additives are used to provide protection against moderate to high pressure, metal-to-metal contacts in boundary lubrication, and EHL. Both open chain and heterocyclic compounds have attracted a considerable amount of research effort to explore their potential as antiwear and EP additives. Among open chain additives, dithiocarbamates are the most widely used. Other additives, such as organic sulfonic acid ammonium salts [45], and alkyl amine salts of thiocyanic acid [46] are reported in the literature, but are of relatively low commercial value. Nitrogen and sulfur-containing heterocyclic compounds, such as 2,5-dimercapto-1,3,4-thiadiazole (DMTD, Structure E), 2-mercaptop-1,3-benzothiazole (MBT, Structure F), and their derivatives, have been used for many years as antioxidants, corrosion inhibitors, and metal passivators; generally at relatively low concentrations.



STRUCTURE E



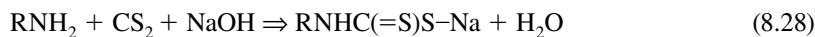
STRUCTURE F

8.2.4.1 Dithiocarbamates

The dithiocarbamates, the half amides of dithiocarbonic acid, were discovered as a class of chemical compounds early in the history of organosulfur chemistry [47,48]. The strong metal-binding properties of the dithiocarbamates were recognized early, by virtue of the insolubility of metal salts and the capacity of molecules to form chelate complexes. Other than applications in lubricant areas, dithiocarbamates have been used in the field of rubber chemistry as vulcanization accelerators and antiozonants.

8.2.4.1.1 Chemistry and Manufacture

Organic dithiocarbamates can be made by a one-step reaction of dialkylamine, carbon disulfide, and an organic substrate. The organic substrate is preferably an olefin, diene, epoxide, or any other unsaturated compounds as exemplified in the literature [49,50]. Organic dithiocarbamates can also be made through a two-step reaction involving ammonium or metal dithiocarbamate salts and organic halides [51]. In the case of their ammonium salts, N-substituted dithiocarbamic acids, $\text{RNHC}(=\text{S})\text{SH}$ or $\text{R}_2\text{NC}(=\text{S})\text{SH}$, are formed by reaction of carbon disulfide with a primary or secondary amine in alcoholic or aqueous solution before they are further reacted with ammonia. To conserve the more valuable amine, it is a common practice to use an alkali metal hydroxide to form the salt.



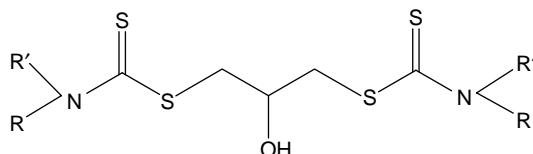
The dithiocarbamic acid can be precipitated from an aqueous solution of dithiocarbamate by adding strong mineral acid. The acids are quite unstable but can be held below 5°C for a short time.

The most common additive, methylene bis-dibutyl dithiocarbamate, is prepared from sodium dibutyl dithiocarbamate and methylene chloride.

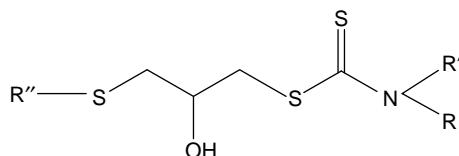


8.2.4.1.2 Applications and Performance Characteristics

Unlike metallic dithiocarbamates that have been widely used in lubricants, ashless dithiocarbamates have only been gaining more attention recently. Relatively high cost is certainly a major factor in limiting wider use. The success of metallic dithiocarbamates also overshadows their ashless counterpart. Certain metallic dithiocarbamates, such as molybdenum dithiocarbamates, offer exceptionally good frictional properties that cannot be matched by their ashless analogues also. However, ashless dithiocarbamates have been found to be versatile, multifunctional additives in a few areas. They can be effective antiwear/EP additives as well as good antioxidants and metal deactivators [52–55], (Structures Ga and Gb). They tend to generate less sludge or deposits than mostly metallic additives and they are very compatible with various base oils.



STRUCTURE Ga



STRUCTURE Gb

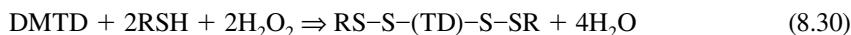
8.2.4.2 Dimercaptodiadiazole and Mercaptobenzothiazole Additives

Additives derived from DMTD and 2-mercaptopbenzo-thiazole (MBT) are well documented in the literature. Owing to strong ring stability (partial aromaticity and resonance delocalization), balanced sulfur–nitrogen distributions, and reactive mercaptan groups, both heterocyclic compounds can be versatile core molecules to make many useful additives with many beneficial characteristics, such as improved thermal/oxidative stability and reduced corrosivity. Unfortunately, some potentially good reactions are hampered by the limited solubility of DMTD and MBT in common petrochemical solvents. Therefore, a suitable sample preparation procedure is very critical to help achieve desirable antiwear/EP additives.

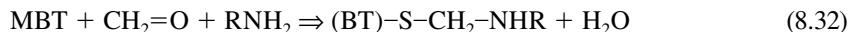
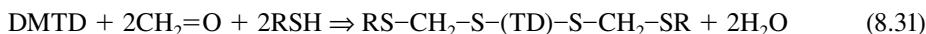
8.2.4.2.1 Chemistry and Manufacture

Many differing organic reactions can be applied to functionalize the mercaptan groups of DMTD and MBT. Oxidative coupling reactions involving other alkyl mercaptans can bring in additional sulfur for EP performance and additional alkyl chains for improved solubility [56]. (Addition reactions with organic compounds containing activated double bonds can link DMTD or MBT heterocyclic core molecules with long chain esters, ketones, ethers, amides, and acids together [57–60]). Likewise, ring opening with epoxides to generate alcohol derivatives is also known [61]. Direct amine salts formation and linking alkyl amines through Mannich base condensation are also extensively studied [62–64]. A number of examples are listed in reactions 8.30 through 8.33, where TD is the abbreviation for the thiadiazole moiety and BT is for the benzothiazole moiety.

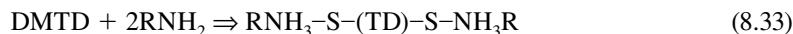
Oxidative coupling



Mercapto alkylation and Mannich alkylation



Amine salt formation



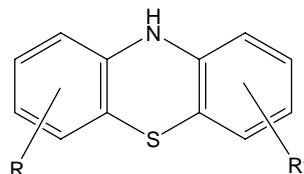
8.2.4.2.2 Applications and Performance Characteristics

MBT is a light yellow powder with limited solubility in hydrocarbons. It is more soluble in aromatic solvent (~1.5% in toluene), polar solvents, and highly aromatic oils. MBT is used as a copper corrosion inhibitor in fuels as well as a corrosion inhibitor/deactivator in numerous industrial lubricants such as heavy-duty cutting and metalworking fluids, hydraulic oils, and lubricating greases. DMTD is also a light yellow powder with very limited solubility in hydrocarbons. It is considered a versatile chemical intermediate suitable for making various oil-soluble derivatives.

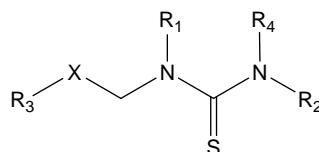
Both MBT and DMTD derivatives are widely used as copper passivators and nonferrous metal corrosion inhibitors. Some proprietary load-carrying additives are substituted MBT and DMTD compounds that are used in various applications either as a component or as a part of additive packages with a specific purpose [65,66]. In the absence of any phosphorus moiety in MBT and DMTD, their oil-soluble derivatives are suitable for replacing zinc dithiophosphates in some lubricant applications. For example, a commercial, high-density, powder-like MBT and DMTD derivatives is used as a dual functional antioxidant/EP agent in greases.

8.2.4.3 Other Sulfur–Nitrogen Additives

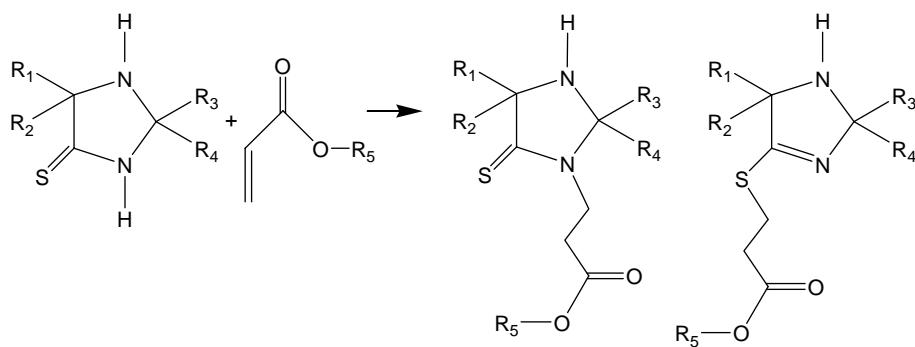
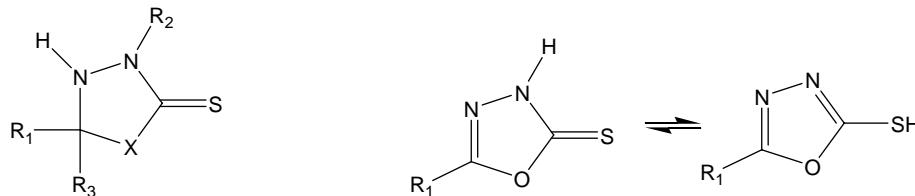
In addition to DMTD, MBT, and dithiocarbamate additives, there are other sulfur–nitrogen-containing additives available in the marketplace or reported in the literature. Among these, phenothiazine derivatives (Structure H, PTZ), substituted thiourea additives (Structure I, TU), thionoimidazolidine derivatives (Structure J, TIDZ), thiadiazolidine and oxadiazole (ODZ) derivatives (Structures K and L), thiuram monosulfides, thiuram disulfides, and benzoxazoles are of particular interest because they are all sulfur- and nitrogen-rich molecules [67–73]. Thiuram disulfides, chemically similar to dithiocarbamates, can be used in the rubber industry as vulcanizers. 2-Alkyldithio-benzoxazoles also offer good frictional properties in addition to strong antiwear/EP properties [74].



STRUCTURE H, PTZ



STRUCTURE I, TU

**STRUCTURE J, TIDZ****STRUCTURE K, TDZL****STRUCTURE L, ODZ**

8.2.5 PHOSPHORUS–NITROGEN ADDITIVES

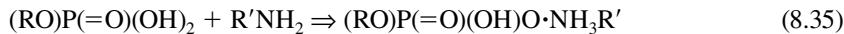
Phosphorus–nitrogen additives are used to provide protection against moderate to high pressure, metal-to-metal contacts in boundary lubrication, and EHL. Ashless phosphorus–nitrogen additives are used as dual functional antiwear/antirust extensively, and those that are most commonly available in the marketplace are based on chemistries of amine dithiophosphates, amine thiophosphates, amine phosphates, and phosphoramides.

8.2.5.1 Amine Phosphates

Amine phosphates are by far the most important phosphorus–nitrogen-containing additives used in lubricants. In fact, they are multifunctional additives possessing very good antirust properties as well as antiwear/EP properties.

8.2.5.1.1 Chemistry and Manufacture

Amine phosphates are produced by treating acid phosphates with alkyl or aryl amines. Under various conditions, neutral, overbased, and underbased amine phosphates can be synthesized. If mixed mono- and dialkyl acid phosphates are used as starting materials, mixed mono and dialkyl amine phosphates are produced. The final additives usually possess high total acid number (TAN) and high total base number (TBN), although reaction adducts are considered fairly neutral. It is known that a complete neutralization of both phosphoric acid groups in monoalkyl acid phosphates with amines cannot be easily achieved, and therefore, under normal conditions, a partially neutralized amine phosphate is formed.



8.2.5.1.2 Applications and Performance Characteristics

Amine phosphates are extensively used in industrial oils, greases, and automotive gear oils. They offer very good rust protection as demonstrated in various bench rust tests (ASTM D665 and CRC L-33). They also show very good antiwear/EP characteristics (Four-Ball Wear and Four-Ball

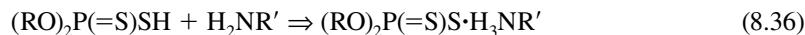
EP, FZG, Timken, and CRC L-37). Since amine phosphates are very polar species, they interact strongly with other additive components, making their performance very dependent on the formulation. Hence, extra attention is needed when amine phosphates are used.

8.2.5.2 Amine Thiophosphates and Dithiophosphates

Amine thiophosphates and amine dithiophosphates can be found in engine oils and industrial oils where zinc dithiophosphates and other nitrogen-containing additives are used, either as decomposition products or as *in situ*-produced products. They are critical to the lubricant performance because of their high activity toward metal surfaces.

8.2.5.2.1 Chemistry and Manufacture

Amine thiophosphates are produced by reacting thiophosphoric acid with alkyl or aryl amines [75]. Likewise, amine dithiophosphates are synthesized from dithiophosphoric acid and amines.



8.2.5.2.2 Applications and Performance Characteristics

Amine thiophosphates and dithiophosphates are also multifunctional additives providing good rust inhibition and antiwear properties. Owing to their high activity and low stability, amine thiophosphates and dithiophosphates are not as extensively used as either amine phosphates or metallic dithiophosphates. A detailed study of their antiwear mechanisms suggested that a tribofragmentation process is involved [76,77]. Relatively poor corrosion control is one area of concern that needs attention. With proper formulation adjustments, it is quite feasible to overcome certain intrinsic weaknesses and apply both chemistries to various lubricant products.

8.2.5.3 Other Phosphorus–Nitrogen Additives

There are many other phosphorus–nitrogen-containing ashless antiwear additives reported in the literature. Some are proprietary technologies, and their commercial status is unknown. Organophosphorus derivatives of benzotriazole (BZT) are a group of additives based on triazole and dialkyl or dialkylphenyl phosphorochloridate chemistry [78]. Arylamines and dialkyl phosphites can be coupled through a Mannich condensation reaction to form unique phosphonates that are used as multifunctional antioxidant and antiwear additives [79]. Bisphosphoramides are also reported [80].

8.2.6 NITROGEN ADDITIVES

Nitrogen-containing additives are used to provide rust inhibition and cleanliness features in various lubricant applications. For example, nitrogen-containing ashless dispersants are a key component for engine oils, and alkoxylated amine compounds are used in lubricating greases to provide corrosion inhibition [81]. Furthermore, arylamines are widely used as antioxidants due to their ability to terminate radical chain propagation and decompose peroxides. Very few nitrogen additives alone are considered effective antiwear/EP additives, and their performance is either very specific to industrial applications or fairly dependent on product formulations. However, when used in combination with other sulfur, phosphorus, or boron additives, nitrogen-containing additives can be very effective supplements to enhance antiwear/EP performance.

8.2.6.1 Chemistry, Manufacture, and Performance

Several novel chemistries are available in the literature for nitrogen-only antiwear additives. Among these, dicyano compounds were tested and they exhibited very good Four-Ball Wear activities [82]. Polyimide-amine salts of styrene–maleic anhydride copolymers are also reported as antiwear additives; however, high additive concentrations (5–10%) are needed [83]. Alkoxylated amines (Structure M) and mixtures of fatty acid, fatty acid amide, imide or ester derived from substituted

TABLE 8.2
SAE 5W-20 Prototype Motor Oil Formulation

Component	Formulation A (wt%)
Solvent neutral 100	22.8
Solvent neutral 150	60
Succinimide dispersant	7.5
Overbased calcium phenate detergent	2
Neutral calcium sulfonate detergent	0.5
Rust inhibitor	0.1
Antioxidant	0.5
Pour point depressant	0.1
OCP VI improver	5.5
Antiwear additive ^a	1

^a In the case of no antiwear additive present in the formulation, solvent neutral 100 is put in its place at 1.0 wt%.

TABLE 8.3
Four-Ball Wear Results

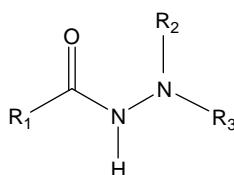
Compound	Formulation	Wear Scar Diameter (mm)
No antiwear additive	A	0.73 (0.74) ^a
1.0 wt% ZDDP	A	0.50 (0.51)
0.5 wt% ZDDP	A	0.70 (0.67)
5-Heptadecenyl-1,3,4-oxadiazole	A	0.38 (0.38)
5-Heptyl-1,3,4-oxadiazole	A	0.54 (0.56)
5-Heptadecenyl-2,2-dimethyl-1,3,4-Oxadiazole	A	0.7
5-Heptadecenyl-2-furfuryl-1,3,4-Oxadiazole	A	0.38 (0.39)

^a Duplicated runs.

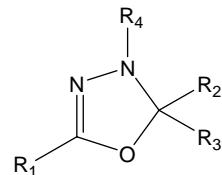
succinic acid or anhydride have been identified to be good fuel lubricity additives [84] (Structure M). Alkyl hydrazide additives possessing two adjacent nitrogen atoms have also been claimed to exhibit good antiwear properties [85] (Structure N). Products of nitrogen heterocycles, such as ODZ (Tables 8.2 and 8.3 for performance evaluations), BZT, tolyltriazole (TTZ), alkyl succinhydrazide (SHDZ), and borated hydroxypyridine (BHPD) (Structures O, P, Q, R, S, respectively), with pendant alkylates, amines or carboxylic acids have been found to be effective antiwear additives in both lubricants and fuels [86–92]. Although triazoles are costly chemicals, they have unique geometric structures that contribute to high surface film-forming efficiency.



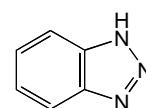
STRUCTURE M



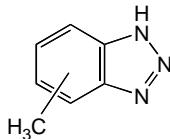
STRUCTURE N (AHDZ)



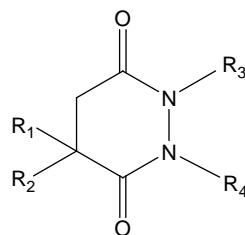
STRUCTURE O (ODZ)



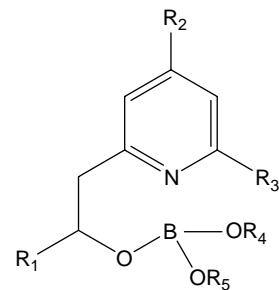
STRUCTURE P (BZT)



STRUCTURE Q (TTZ)



STRUCTURE R (SHDZ)



STRUCTURE S (BHPD)

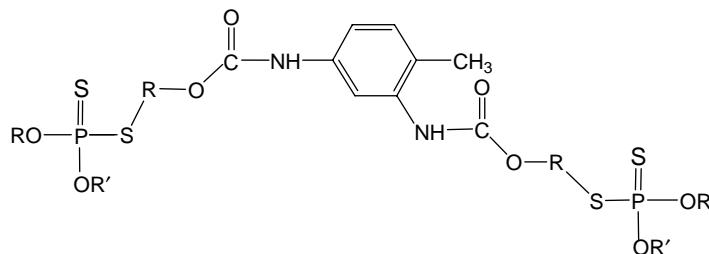
Both BZT and TTZ derivatives are also effective copper deactivators at low concentrations. Therefore, these types of additives indeed have dual functions. They find applications in industrial oils, greases, and fuels.

Table 8.2 lists a prototype engine oil formulation used for the evaluation of ODZ additives where various ODZs can be blended at 1 wt% in place of the same amount of light base oil. Table 8.3 lists the Four-Ball Wear performance data where a series of ODZs were evaluated against 0.5 wt% and 1 wt% ZDDP. As demonstrated, those ODZ additives exhibited fairly good antiwear properties in this bench test [86].

8.2.7 ADDITIVES WITH MULTIPLE ELEMENTS

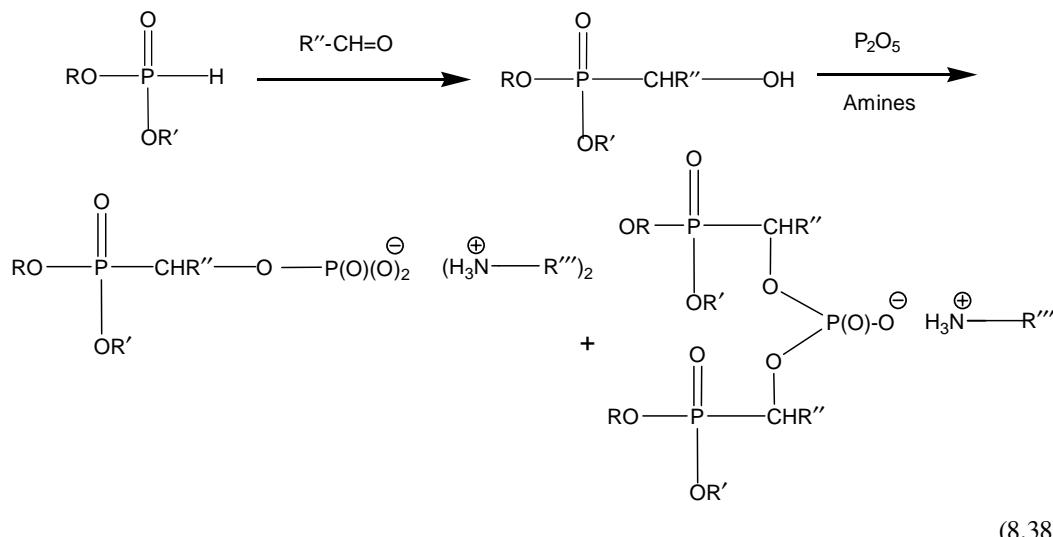
Complex additives with multiple elements can be derived from various S/P, sulfur/nitrogen, phosphorus/nitrogen, and many other traditional additive building blocks. As a result, molecules with more than four, five, six, or even more elements are created (S/P/N/B in addition to C/H/O). Derivatization frequently adds a degree of complexity, yet provides a chance of achieving better synergisms among all critical elements that can not only satisfy the performance needs but also help neutralize any potentially added costs associated with the new chemistry under development.

Many examples are available in the literature as well as in the marketplace, such as amine salts of dithiophosphates and thiophosphates (Section 8.2.5.2); borated derivatives of dithiophosphates [41], dithiocarbamates [50], and dimercapto-thiadiazole [93]; urethane derivatives of dithiophosphates [94] (Structure T); and reaction adducts of dialkyl phosphites, sulfur, and acylated amines [95].



STRUCTURE T

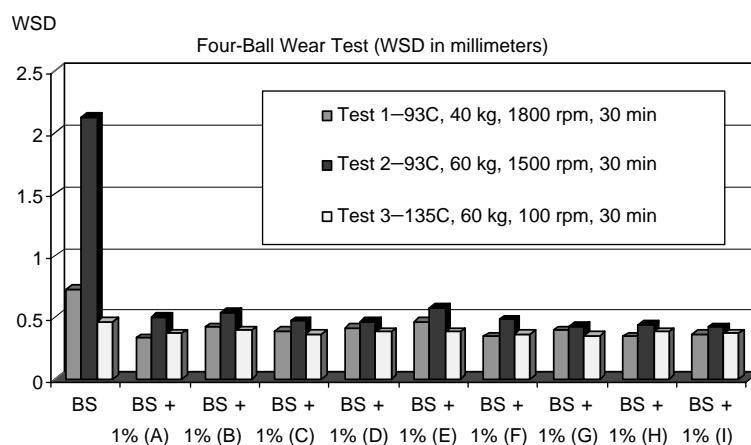
Several complex additives have different chemistries involved with the same element in a single molecule to attain strong synergisms. As exemplified in the following case, where both phosphite chemistry and phosphate chemistry are incorporated into the same molecule, greater antiwear performance can be achieved ([96]; reaction 8.38).



The synergistic antiwear performance of the aforementioned complex phosphorus additives are illustrated in Chart 8.1. Nine different analogues were synthesized and tested at 1 wt% in base oils using three different conditions in the Four-Ball Wear test. As demonstrated, they all exhibit exceptionally good antiwear properties.

8.2.8 HALOGEN ADDITIVES

Chlorine was one of the earliest antiwear and EP elements used in the lubricant industry. Chlorine-containing additives are still used in cutting oils and related metalworking lubricants, in combination with sulfur additives. Iodine was mentioned in aluminum-processing lubricants for wear control. Fluorine, in perfluorinated compounds, is well known to reduce wear and especially friction.



All tested additives (A–J) were derived from dibutyl phosphite, butyraldehyde, and a selected amine at various molar ratios. A and B: using Primene JMT at different ratios, C and D: using Adogen 183 at different ratios, E, G, and I: using Duomeen O at different ratios, F and H: using bis 2-EH amine at different ratios.

CHART 8.1 Complex phosphorus additives. (BS, base stock; WSD, wear scar diameter.)

The chlorine compounds act and function in that they coat the metal surface with a metal chloride film under the influence of high pressure at point of lubrication and in the presence of traces of moisture. FeCl_2 melts at 672°C and has low shear strength when compare with steel.

The effect of chlorine compounds depends on the reactivity of the chlorine atom, temperature, and concentration. Hydrogen chloride formed in the presence of larger quantities of moisture can cause severe corrosion of the metal surfaces. As the corrosion hazards increase along with the EP properties with increasing reactivity of the chlorine atoms, a compromise must be found in the development of chlorine-containing additives.

Chlorinated paraffins such as trichlorocetane represent a group of important EP additives used in the past. They can significantly increase the load stages in the FZG test with increasing concentration. The chain length has practically very little influence on the EP effect; on the contrary, the load-carrying capacity increases with increasing degree of chlorination. In practice, chlorinated paraffins with ~40 to 70 wt% chlorine are used; however, they are sensitive to moisture and light and can easily evolve hydrogen chloride [97]. Compounds such as phenoxy-propylene oxide, amines, or basic sulfonates neutralize hydrogen chloride and thus act as stabilizers.

Good results are also obtained with chlorinated fatty acids and their derivatives; particularly those with trichloromethyl groups in the end position, since the additives with CCl_3 groups are particularly effective.

Owing to their high stability, chlorinated aromatics have less favorable EP properties than the chlorinated aliphatics. Alkylaromatics with chlorinated side chains improve the load-carrying capacity much more than those chlorinated in the ring; the efficiency increases with the number of carbon atoms in the side chain. Chlorinated fatty oils and esters as well as chlorinated terpenes and amines have also been patented as EP additives.

Sulfur–chlorine additives were found to be satisfactory for gear lubrication in passenger cars in the mid-1930s. Apparently, this type of additive could satisfy the high-speed and moderate-load operation of passenger cars used in that time period. When sulfur and chlorine are combined in the organic molecule, sulfur somewhat reduces the corrosive tendency of chlorine; on the contrary, the EP properties of the combined moieties are improved in comparison with the individual compounds. Chlorinated alkyl sulfides, sulfurized chloronaphthalenes, chlorinated alkyl thiocarbonates, bis-(*p*-chlorobenzyl) disulfide, tetrachlorodiphenyl sulfide, and trichloroacrolein mercaptals [$\text{Cl}_2\text{C}=\text{CCl}-\text{CH}(\text{SR}')-\text{SR}''$, where R' and R'' are alkyl or aryl] must be mentioned in this class. Reaction products of olefins and unsaturated fatty acid esters with sulfur chlorides contain highly reactive β -chlorosulfides, which due to their reactive chlorine and sulfur atoms give very good EP agents, yet show more or less strong corrosive tendencies. However, severe wear was frequently encountered in truck axles where performance under high-torque, low-speed conditions is of greater importance. Later on, the presence of chlorine, although a good EP agent, was found to be detrimental to lubricant thermal stability. Hence, for the past 30 years, chlorine has not been used in gear oils.

Chlorinated trioleyl phosphate, condensation products of chlorinated fatty oils with alkali salts of dithiophosphoric acid diesters, and reaction products of glycols with PCl_3 are examples of chlorine–phosphorus additives used in earlier years.

The most serious drawback for chlorine antiwear and EP additives is in the environmental area. Legislation around the industrial world limits the chlorine content of many lubricants to parts per million. Therefore, except for the cutting oil industry, which is also under pressure to change, chlorine additives are not considered a viable option for modern lubricants.

8.2.9 NONTRADITIONAL ANTIWEAR/EXTREME-PRESSURE ADDITIVES

Traditional sulfur, phosphorus, and halogen-related compounds are considered to be the dominant antiwear/EP additives in the marketplace. However, as environmental concerns escalate, the future trends will favor products that diminish potential hazard and disposal problems. Recent clean fuel

activities are driving sulfur levels toward 10–50 wt ppm ranges. Subsequently, the petroleum industry is favoring lower sulfur lubricants since sulfur is also known to poison the catalytic system used for NO_x reduction. Therefore, the use and development of nontraditional antiwear additives is becoming more valuable.

A number of nonsulfur, nonphosphorus ashless antiwear additive technologies have been reported in the literature [98–102]. Among these, high hydroxyl esters (HHE), dimer acids, hydroxyamine esters, acid anhydrides, cyclic amides, and boron derivatives are recognized as leading technologies. Graphite and polytetrafluoroethylene (PTFE) possess excellent friction reduction properties and indirectly contribute some antiwear/EP characteristics. However, both materials need to be dispersed in the oil as they have very limited lubricant solubility, which hampers their usefulness. Organic borates are considered as effective friction modifiers, antioxidants, and cleanliness agents. Recent studies indicate that some borates can be good antiwear additives. Potassium borates have been used in gear oils for years, but these types of metallic borates are outside the scope of this chapter. Esters are known to possess good lubricity properties. The properties can be further improved to offer antiwear characteristics through proper functionalization. Several companies have marketable products in this area.

8.3 MANUFACTURE, MARKETING, AND ECONOMICS

All major additive suppliers produce ashless antiwear and EP additives that are available as components and packages. Following is a list of major producers (arranged in alphabetical order).

- Afton Corporation
- Akzo Nobel
- Atofina Chemicals (former Elf Atochem NA and Pennwalt Corporation)
- BASF
- Chemtura (former Great Lakes Chemical's Durad Division)
- Ciba Specialty Chemicals
- Chevron Corporation (Oronite Division)
- Clariant
- Dover Chemical (former Keil Chemical Division, Ferro)
- Dow Chemical (former Angus Division)
- Elco Corporation (Detrex)
- FMC
- Hampshire Chemical Corporation (former Evans Chemetics)
- ICI America (Uniqema)
- Infineum International Limited
- Lubrizol Corporation
- Polartech
- Rhein Chemie
- Rhodia (former Albright & Wilson)
- Zeneca

Ashless antiwear and EP additives are supplied in various chemistries, including single and multiple blends formulated to maximize performance and minimize adverse effects (e.g., dropout and corrosion). Product designations vary by chemical class and concentration. Many of them are formulated into additive packages according to applications, such as passenger car engine oils, heavy diesel engine oils, automotive transmission oils, automotive gear oils, hydraulic fluids, and others. Since the product offering information can be supplier-specific, it is recommended to contact the suppliers directly or go to their corresponding Web site for further information.

There has been some consolidation in the additive business, but the market has not changed much as a result. Following are the major changes by year.

1992	Ethyl acquired Amoco Petroleum Additives (U.S.) and Nippon Cooper (Japan)
1996	Ethyl acquired Texaco Additives Company
1997	Lubrizol bought Gateway Additives (Spartanburg, South Carolina)
1999	Infineum, the new petroleum additives enterprise, a joint venture between Exxon Chemical, Shell International Chemicals Ltd., and Shell Chemical Company, unveiled its new corporate identity and became fully operational on January 1, 1999 (the largest merge of additive companies in history)
1999	Crompton completed a merger with Witco
2001	Texaco Oil merged into Chevron Oil whereas Chevron Chemical Oronite Division was kept intact
2003	Dover Chemical acquired the Keil Chemical petroleum additives business from Ferro Corporation
2004	Ethyl Corporation transformed into NewMarket Corporation, the parent company of Afton Chemical Corporation and Ethyl Corporation to maximize the potential of its operating divisions—petroleum additives and tetraethyl lead fuel additive business
2005	Chemtura was formed by the merger of Crompton and Great Lakes Chemical Corporation
2007	Chemtura bulked up its specialty lubricants business with the assets of Kaufman Holdings Corporation, parent company of Anderol and Hatco

Since most lubricant additives are produced through batch processes, consolidation can lead to improved operations and reduced costs (e.g., reducing plant idle time with better chemical manufacturing management systems). There are still many manufacturing facilities using equipment and procedures that are 30–40 years old. Hence, any investments in automation and continuous processing for a plant will be a competitive advantage. However, the business is so cost-competitive that most suppliers have difficulties in justifying major capital expenditures.

8.4 EVALUATION EQUIPMENT/SPECIFICATION

8.4.1 LUBRICANT SPECIFICATIONS

Lubricant components and formulated products are manufactured as per the rigid specifications in petroleum refineries and lubricant blending plants, and must also meet detailed commercial, industrial, and military specifications. As an example, the U.S. Military has rigid specifications for automotive lubricants, although the automotive manufacturers have similarly rigid but not necessarily the same specifications to assure quality and consistency of lubricant manufacture. In addition, there are performance specifications that must be met from such original equipment manufacturers (OEMs) as farm machinery and other off-highway automotive equipment. These specifications are designed to enable the user to select appropriate lubricants and to be assured of adequate performance over a specified service life.

The industry is, for the most part, adequately self-regulating with minimal government input concerning performance specifications. The most elaborate system for developing and upgrading lubricant and fuel specifications is for automotive lubricants. The American Society of Testing and Materials (ASTM), the Society of Automotive Engineers (SAE), and the American Petroleum Institute (API) all have defined roles in determining specifications for products such as passenger car motor oils and heavy-duty motor oils. These three organizations, working together in the United States, are known as the Tripartite. Extending internationally, the International Lubricant Standardization and Approval Committee (ILSAC) is also active in all phases of engine lubricant category development.

In other product categories, lubricant and additive suppliers, OEMs, and industry trade associations work together to determine performance requirements and product specifications. In addition to the three industry organizations mentioned earlier, the National Lubricating Grease Institute (NLGI), the National Marine Manufacturers Association (NMMA), the American Gear Manufacturers Association (AGMA), the Society of Tribologists and Lubrication Engineers (STLE), and other groups, associations, and key equipment builders can influence lubricant specifications.

In addition to meeting all military and industrial specifications, many leading lubricant marketers and finished lubricant suppliers develop their own internal specifications to be used for new product launching, competitive product analysis, and future product development. Proprietary field-testing is an integral part of the overall new lubricant product development processes and is often the most critical step to assure technical success and customer satisfaction for new products.

8.4.2 ADDITIVE SPECIFICATIONS

Specifications for antiwear/EP additives focus primarily on application, base oil compatibility, and quantification of elemental constituents. In addition, specifications typically identify specific and critical performance standards for applications. Common specifications for antiwear/EP additives are shown in Table 8.4.

In addition to typical specifications as reported in the Certificate of Analysis (C of A) from additive suppliers, individual lubricant marketers often prefer to conduct their own internal additive specifications, such as infrared analysis and key performance testing.

8.4.3 TEST METHODS AND EQUIPMENT

In the United States, a number of bench and advanced tests were developed and approved by ASTM, and these tests have gained widespread reception throughout the industry. However, there are also a few selected lab-bench and advanced tests that were developed and approved only by specific OEMs, but represent certain critical and desirable performance features (Figures 8.2 and 8.3). This chapter is not intended to cover all evaluation tests in detail, but rather to illustrate a few representative tests to highlight the key assessment criteria.

- Four-Ball Wear and EP Test.* This tester was developed to evaluate the antiwear, EP, and antiweld properties of lubricants. It is a simple bench test machine designed to measure the protection a lubricant provides under conditions of high unit pressures and various sliding velocities. The Four-Ball Wear tester consists of four 1.5 in. diameter steel balls arranged in the form of an equilateral tetrahedron. The three lower balls are held immovably in a

TABLE 8.4
Typical Specifications for Antiwear and EP Additives

Chemical Class	Property	Performance Test
Amine phosphates	Percent of nitrogen, phosphorus, and TAN/TBN	Four-Ball Wear, Four-Ball EP, FZG, rust/oxidation test
Methylene bis-dialkyl dithiocarbamate	Percent of sulfur, nitrogen, and residual chlorine, amine	Four-Ball EP, FZG, Falex EP, oxidation/corrosion test
Sulfurized lard, esters, fatty acids	Percent of total sulfur	Four-Ball Wear, Four-Ball EP, stick-slip, Cu corrosion
	Percent of active sulfur	
Triphenyl phosphorothioate	Percent of sulfur, phosphorus, and melting point	Four-Ball EP, FZG, Falex EP, oxidation/corrosion test
Chlorinated paraffins, fatty acids	Percent of chlorine	Four-Ball Wear, Falex EP, Timken, Cu corrosion
	Acid value	

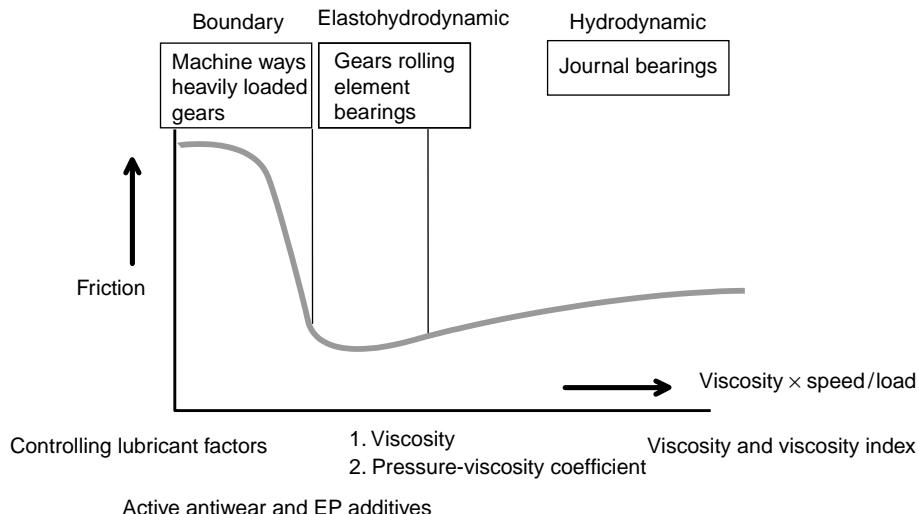


FIGURE 8.2 Lubrication regimes.

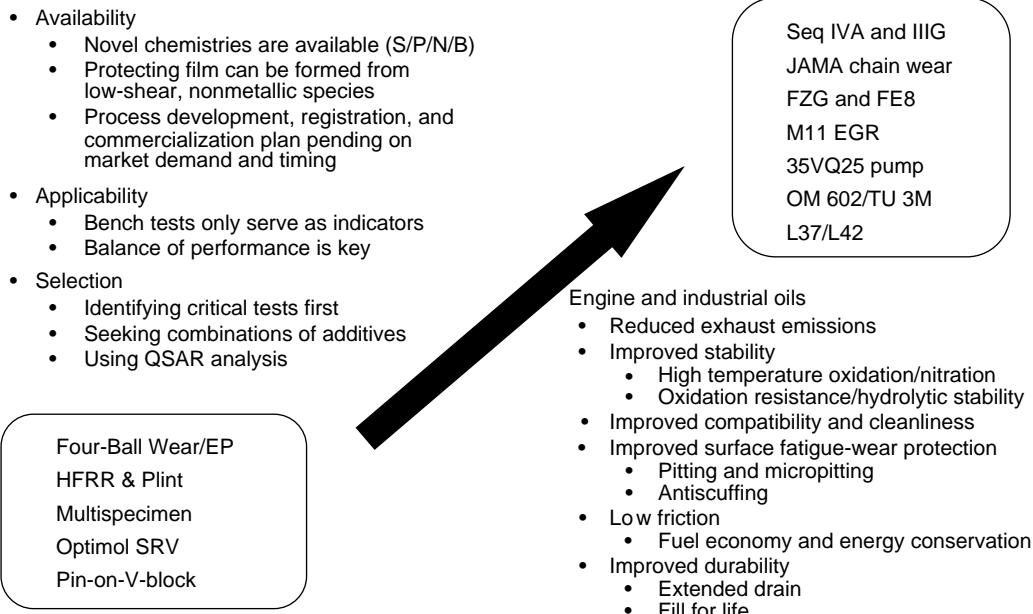


FIGURE 8.3 Ashless antiwear additives: availability, applicability, selection, and future needs.

clamping pot, while the fourth ball is made to rotate against them. Test lubricant is added in the test pot, covering the contact area of the test balls. During a test, wear scars are formed on the surfaces of the three stationary balls. The diameter of the scars depends on the load, speed, temperature, duration of run, and type of lubricant. The Four-Ball EP tester runs at a fixed speed of 1770 ± 60 rpm and has no provision for lubricant temperature control. A microscope is used to measure the wear scars. Two of the standard tests run on the Four-Ball machine are Mean-Hertz Load and Load-Wear Index. ASTM D 2596 covers the detailed calculation procedure of Load-Wear Index for greases and D-2783

for oils. These procedures involve the running of a series of 10 s tests over a range of increasing loads until welding occurs. From the scar measurements, the mean load (load-wear index) is calculated and it serves as an indicator of the load-carrying properties of the oil being tested.

2. *FZG Four-Square Gear Test Rig.* The FZG test equipment consists of two gear sets, arranged in a four-square configuration, driven by an electric motor. The test gear set is run in the test fluid, while increasing load stages (from 1 to 13) until failure. Each load stage is run for a 15 min period at a fixed speed. Two methods are used for determining the damage load stage. The visual rating method defines the damage load stage as the stage at which more than 20% of the load-carrying flank area of the pinion is damaged by scratches or scuffing. The weight loss method defines the damage load stage as the stage at which the combined weight loss of the drive wheel and pinion exceeds the average of the weight changes in the previous load stages by more than 10 mg. The test is used in developing industrial gear lubricants, ATFs, and hydraulic fluids to meet various manufacturers' specifications.
3. *Falex EP/Wear Tester.* The Falex test machine provides a rapid method of measuring the load-carrying capacity and the wear properties of lubricants. The test consists of rotating a test pin between two loaded journals (V-blocks) immersed in the lubricant sample. There are two common tests run in this machine: one is an EP test (subjecting a test lubricant to increasing loads until a failure occurs) and the other is a wear test (subjecting a lubricant to a constant load for a definite period of time while measuring the wear pattern).
4. *Timken EP Test.* This test provides a rapid method of measuring abrasion resistance and the load-carrying capacity of lubricants. A number of lubricant specifications require Timken "OK" loads above certain minimum values. The mode of operation consists of rotating a Timken tapered roller bearing cup against a stationary, hardened steel block. Fixed weights force the block into contact with the rotating cup through a lever system. The OK load is the highest load the cup and block can carry without scoring during a 10 min run. Timken abrasion tests are run under fixed loads for extended time periods, and the weight loss of the cup and block are a measure of the abrasion resistance of the lubricant.
5. *L-37 High Torque Test.* The CRC L-37 test operates under low-speed, high-torque conditions. It evaluates the load-carrying ability, wear stability, and corrosion characteristics of gear lubricants. The test differential is a Dana Model unit driven by a Chevrolet truck engine and four-speed transmission. A complete, new axle assembly is used for each test after a careful examination of gear tooth and bearing tolerance. After break-in at reduced load and high speed, the test continues for 24 h under low-speed (80 axle rpm) and high-torque conditions.
6. *L-42 High Speed Shock Test.* The CRC L-42 test is established to evaluate the antiscore performance of EP additives in gear lubricants under high-speed, shock load conditions. The test axle is a Dana Model unit driven by a Chevrolet engine through a four-speed truck transmission. The procedure requires five accelerations in fourth gear with inertia loading and 10 accelerations in third gear with dynamometer loading. The lubricant evaluation is based on the amount of scoring, and test results are expressed as percent tooth contact area scored.
7. *FAG FE-8 Test.* FAG developed this test frame to be a flexible *tribological* system to conduct tests over a wide range of operating conditions with different test bearings. Short-duration standardized tests have been developed for different applications. FAG also uses longer-term testing (e.g., fatigue) for comprehensive evaluations. The FE-8 gear oil test was developed specifically to evaluate the effectiveness of antiwear additives. The test runs under heavy load and low speed that forces the bearing to operate under boundary lubrication conditions.

Bearing Test Conditions

Bearings	Cylindrical roller/thrust loaded
Speed	7.5 rpm
Load	114 kN
Bearing temperature	Variable
Test duration	80 h

Other tests including Optimol SRV, Cameron-Plint, high-frequency reciprocating rig (HFRR), Falex multi-specimen, Vickers vane pump, Vickers 35-VQ-25 pump, and Denison high-pressure pump tests are also used widely in evaluation of various lubricants and greases. Appropriate field tests are also arranged in proprietary test sites to ensure good product quality and equipment compatibility/friendliness before the introduction of a new product into the marketplace.

On the engine oil side, the ILSAC is active in all phases of passenger car category development, and the SAE is the technical society for those with interest in transportation. Within the SAE is a Fuels and Lubricants Division/Engine Oil Technical Committee (TC-1) that serves as a forum for open discussion of technical issues related to current and future engine lubrication needs and standard development. With the introduction of GF-3 in 2001, the industry moved to a completely new set of engine tests for validation of passenger car engine oil performance. Although some new tests replaced previous tests, which were running out of parts, others provided a means to measure performance in new areas. The current category is GF-4, which superseded GF-3 in the summer of 2004.

Among the GF-4 tests, the most critical engine tests related to antiwear/EP performance are the Sequence IVA and the Sequence IIIG. The Sequence IVA is an ASTM designation of a test previously referred to as the KA24E, originally developed by the Japan Automotive Manufacturers Association. It is included to replace the wear component of the Sequence VE. The Sequence IVA is designed to evaluate an oil's ability to prevent cam lobe wear in slider valve train design engines operated at low temperature, short trip, and "stop and go" conditions (low-speed/low-temperature operation). Following is a list of the test conditions and specifications:

Engine	Nissan 2.4 L inline 4 cylinder
Engine speed	800 and 1500 rpm cycles
Engine torque	25 N m
Oil temperature	50–60°C
Cycle duration	50 min low speed/10 min high speed
Test length	100 h
7-Point cam lobe wear	120 µm maximum

The Sequence IIIG is a replacement for the Sequence IIIF and uses a current production version of the GM 3800 Series II V-6 engine. Special camshaft and lifter metallurgy and surface finishing are used to increase wear. The Sequence IIIG procedure is designed to evaluate the oil resistance to oxidation and wear in high-speed and high-temperature vehicle operation. The test conditions and specifications are summarized as follows:

Engine	GM 3800 Series II V-6 (231 CID)
Engine speed	3600 rpm
Engine load	250 N m
Valve spring load	205 lb
Oil temperature	150°C
Coolant temperature	115°C
Test length	100 h
Average cam and lifter wear	60 µm maximum

The next ILSAC category is ILSAC GF-5, which is targeted to be introduced around mid-2010. The ILSAC/Oil Committee has decided that the Sequence IIIG and Sequence IVA tests will be retained to ensure that acceptable wear protection is achieved in the upcoming ILSAC GF-5 category.

In the heavy-duty diesel engine oil area there are a number of industry standard engine tests that measure the wear performance. These tests required to meet both industry and engine manufacturer requirements such as API CJ-4 and various specifications from Caterpillar, Cummins, Detroit Diesel, Mack, and Volvo. The key wear tests assess the ability of an oil to control valve train or ring and liner wear under severe operating conditions, which include high-load duty cycles, use of exhaust gas recirculation, and high levels of soot contamination.

The API CJ-4 category requires three tests that include valve train wear as a pass/fail parameter. The Roller Follower Wear Test (ASTM D5966) is run in a 6.5 liter V-8 GM diesel engine; it was initially developed for the older API CG-4 category, which was developed for the introduction of low sulfur (500 ppm maximum) fuel. However, this test has remained as a requirement in all subsequent specifications. At the end of this 50 h test, the used oil soot level is typically 3.5 to 4.0%. The level of wear on the stationary pin in the hydraulic cam followers is measured. The Cummins ISB test (ASTM procedure in progress) was introduced as an industry requirement for API CJ-4. This 350 h test runs in a 5.9 liter in-line 6 cylinder engine running of ultra low sulfur (15 ppm maximum) diesel fuel. The first 100 h are run at steady-state conditions to generate 3.25% soot in the oil. The final 250 h are run under cyclic conditions to stress cam and tappet wear, which are the primary pass/fail criteria. The third diesel engine test that measure valve train wear is the Cummins ISM test (ASTM procedure in progress). The Cummins ISM is the third in a series of Cummins heavy-duty wear tests developed for API and engine builder diesel oil specifications. Similar to previous Cummins M11 HST (ASTM D6838) and Cummins M11 EGR (ASTM D6975) tests, the Cummins ISM alternates between 50 h soot generation and 50 h wear stages. This test runs for 200 h using 500 ppm sulfur diesel fuel. The used oil typically contains 6 to 7% soot, and the key pass/fail wear parameters are focused on the crossheads (bridges for the inlet and exhaust valves) and the adjusting screw for the fuel injectors.

The Mack T-12 test (ASTM D7422) measures ring and liner wear under severe operation using 15 ppm sulfur fuel. This 300 h test runs with a very high EGR rate for the first 100 h to generate 4.3% soot. During the final 200 h, the engine runs over-fueled at peak torque conditions to create a very severe environment for top ring weight loss and liner wear at the point of top ring reversal, which are the key wear parameters for this test.

8.5 OUTLOOK

The additives business has experienced an economic upturn in recent years, primarily due to the imbalance between demand and supply as a result of tight feedstock availability and increased demand in the Far East region. The basic chemicals used to produce additives are subject to short supply as new and large capacity has not been effectively added to the manufacturing side for several years. A number of natural disasters such as the hurricane Katrina certainly made the situation even worse. The additive suppliers have successfully passed the raw material costs to their customers resulting in escalated unit pricing and improved profitability. The increased volume demand has been neutralized by several factors, such as longer drain lubricants and the reduction of ash additives. Despite the push for new engine oils meeting more stringent requirements, a major rationalization is occurring because of the ability to use additives longer and the recycling of products in the industry. Consequently, the total additive volume demand is growing slowly. Ashless antiwear/EP additives are no different from other additives in terms of market demand.

Antiwear additives are a mature function class, and business opportunities in the next few years will be modest. The dominant position of zinc dithiophosphates in engine oils is gradually diminishing, but is not expected to be in jeopardy in the near term. Therefore, a total switch to ashless antiwear additives in engine oils is not likely to occur very soon, but minor changes are in progress.

The impetus for significantly improved lubricant additives is found on a number of fronts. Governmental and regulatory requirements continue to challenge the industry for improved products with lower toxicity. New engine developments, such as increased use of diamond-like carbon (DLC)-coated engine parts and ceramic components for wear resistance and higher contact temperatures, are on the horizon and present opportunities for antiwear additives that can function at very high operating temperatures. Space technology and other advanced transportation needs present new challenges to the industry. And, of course, there will always be a need for low product costs and ease of production.

Four particular developments may have a major impact on the lubricant industry in the near term: (1) a move toward low-sulfur hydroprocessed (groups II and III), sulfur-free gas-to-liquid (GTL) and synthetic (groups IV and V) base stocks; (2) the imminent trend toward lower ash, sulfur, and phosphorus in engine oils; (3) a desire to reduce or eliminate chlorine in lubricants, particularly in metalworking fluids; and (4) a move to eliminate heavy metals and achieve low ash or even ash-free in both engine and industrial oils.

To meet the growing needs for better thermal/oxidative stability and better viscometrics, synthetic base stocks such as polyalpha olefins, together with hydrotreated petroleum base stocks and GTLs are continuing to expand in all lubricant sectors. These types of materials have no aromatic hydrocarbons or greatly reduced amounts of aromatic hydrocarbons, which are potentially problematic for additive solvency; as a result of removing these solubilizing aromatics, the additives tend to precipitate out of the oil. This is particularly true for surface-active, polar components such as antiwear additives. Therefore, greater compatibility with nonconventional base stocks (groups II–IV) will be an essential requirement for all ashless antiwear/EP additives. Meanwhile, there are noticeable synergies identified among certain ashless antiwear/EP additives and nonconventional base stocks in a number of lubricant applications. Therefore, the choice of proper ashless additives will be vitally important.

Because of the large number of automobiles equipped with catalytic converters that are sensitive to phosphorus derived from zinc dithiophosphates in the crankcase oil (possible reduction of catalytic efficiency), strong needs exist for engine oils with lower phosphorus content. Initially, ILSAC GF-4 aimed to reduce phosphorus levels to as low as 0.05% (about one-half of the former GF-3 level), but settled on a maximum phosphorus level of 0.08% instead (a 20% reduction). In addition to phosphorus limits, GF-4 oils also offered improved oxidation stability (including nitration control), high-temperature wear discrimination, high-temperature deposits control and used oil pumpability [103].

As vehicle emission regulations become more challenging, increasing restrictions are likely to be placed on other lubricant elements besides phosphorus that can impact emission control systems. Sulfur and metals are also under scrutiny as sulfur is suspected as a poison of DeNO_x catalysts, and ash (from metals) may plug after-treatment particulate traps. Modern engine oils rely heavily on ZDDP to provide antiwear, antioxidation, and anticorrosion protection. Since ZDDP is rich in phosphorus, sulfur, and zinc, it becomes an obvious target for emission control. In fact, at former use level, ZDDP was almost solely accountable for more than two-thirds of sulfur and all the phosphorus and zinc present in engine oils, excluding sulfur from base oils. Oils with ZDDP at former levels could make it difficult for OEMs to optimize (for cost and life) their exhaust after-treatment systems. Therefore, the future trend will likely be toward further reduced ZDDP in engine oils providing that the performance integrity can be maintained through the use of alternate additives [104].

To satisfy performance requirements in terms of oxidation control and deposit levels, more antioxidants could be added to the engine oil formulation. These ashless antioxidants (hindered phenols and arylamines) may effectively compensate for the loss of oxidation protection due to the reduction in ZDDP concentrations. However, since ZDDP is such a cost-effective additive and is the sole antiwear component used in many engine oils, a reduction in ZDDP treat levels may not provide the needed wear protection. Recently, engine builders are requiring even greater antiwear protection, and more demanding test protocols are being put in place to ensure that lubricants can meet these more stringent specifications. Therefore, there is a strong need for advanced ashless antiwear systems to replace or supplement ZDDP to satisfy emission regulations while ensuring high levels of wear protection [105,106].

Not all phosphorus-containing additives behave the same in engine oils. Furthermore, even within the same ZDDP family, not all ZDDP respond the same to after-treatment devices as evidenced by their relative volatility performance. Data indicated that volatilized phosphorus showed very low statistical dependence on either oil volatility or phosphorus concentration in the fresh oil. Rather the data seemed to indicate that the chemistries of the phosphorus-containing additives and their formulation with other additives were the controlling cause of phosphorus volatility and, by extension, emission level. Selby's Phosphorus Emission Index (PEI) and Sulfur Emission Index (SEI) shed some insights into the volatility impact on emission issues and better S/P volatility control than the current ZDDP that is highly desired for future ashless antiwear additives [107–109].

Chlorine in lubricants and other materials is becoming an increasing environmental concern. Legislation around the industrial world limits the chlorine content of many lubricant products to 50 ppm or less. The Montreal Protocol mandated a gradual phase-out of the use of chlorine-containing refrigerants, such as hydrochlorofluorocarbon (HCFC) and chlorofluorocarbon (CFC), and replacement with alternative hydrofluorocarbons (HFC). Increased wear occurred in the refrigeration compressor when HFC refrigerants were substituted for CFC, and the cause of this increased wear was believed to be inferior antiwear capability of the alternative HFC refrigerant as the environmental gas, compared to that for CFC [110]. This offers some opportunities for the development of new ashless antiwear additives for refrigeration compressor oils.

The cutting oil industry is facing similar ecological pressures, and future changes to reduce or eliminate chlorine are expected. The most significant opportunity is perhaps driven by human health and waste disposal issues concerning the use of chlorinated paraffins. Chlorinated paraffins are used extensively as EP additives in metalworking fluids. The National Toxicology Program (NTP) listed chlorinated paraffins, derived from C12 feedstocks and chlorinated at 60%, as a suspect carcinogen. Although few metalworking fluids are formulated with this class of chlorinated paraffin, the image of chlorinated paraffins in general has suffered due to uncertainties about future NTP reclassification of all such additives.

Gear additives are another area of concern. Because of the problems associated with chlorine additives, their use in gear oils has been greatly reduced. However, a number of processes for making gear additives utilize chlorine or chlorine-containing reagents at some point in the reaction sequence. Small amounts of chlorine still remain in the final product. The complete removal of chlorine is therefore expected to become an important priority, but will be difficult to attain in the near future.

Finally, the use of metallic antiwear/EP additives is diminishing due to the influence of environmental concerns. Heavy metals are considered pollutants, and their presence is no longer welcomed in the environment. Given equal performance and costs, ashless antiwear additives will be preferred for many future lubricants.

In the future, the lubricant additive business will continue to grow and will need more ashless antiwear/EP additives [111]. Possible new markets include biodegradable lubricants, biodiesel fuel-friendly lubricants, advanced transportation lubricants, robotics, ceramics, and space technology lubricants. Traditional markets in engine oils, ATFs, marine, aviation, gear, hydraulic, circulating oils, metalworking, and other industrial lubricants are also expanding. Healthy growth for nonconventional base oils (groups II–V) is expected in many of these areas. Clearly advanced ashless antiwear additives with environment-friendly features, excellent stability, and unique performance properties, especially for nonconventional base oils, will be the additives of choice for increasingly demanding lubricant applications.

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9 Sulfur Carriers

Thomas Rosrucker and Achim Fessenbecker

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9.1 INTRODUCTION

In the lubricant industry, a great variety of sulfur-containing additives are known and in use today. We list only a few of the most common types:

- Sulfur carriers (sulfurized olefins, esters, and fatty oils)
- Sulfur/phosphorus derivatives (dithiophosphates, thiophosphonates, thiophosphites, etc.)
- Thiocarboxylic acid derivatives (dithiocarbamates, xanthogenates, etc.)
- Heterocyclic sulfur (mercaptobenzothiazoles, thiadiazoles, etc.)
- Sulfonates (Na-, Ca-salts of alkylbenzenesulfonic acids, nonylnaphthalenesulfonates, etc.)
- Others (sulfated fatty oils/Turkish red oils, sulfurchlorinated fatty oils, sulfur-linked phenols and phenates)

This long list gives a good impression of the versatility and importance of sulfur chemistry in lubricants. But as versatile their chemistry is, the range of applications of sulfur-containing lubricant additives is just as versatile. In this chapter, we try to review major aspects of a group of additives commonly known as *sulfur carriers*. This is a generic name that has been accepted in the marketplace

and used to summarize a group of additives that provide extreme-pressure (EP) and antiwear (AW) properties and are used in gear oils, metalworking fluids, greases, and engine oils. The vast majority of them are sulfurized fats, esters, and olefins. To distinguish them from other sulfur-containing products and avoid misunderstandings, a suitable definition of sulfur carriers is the following:

Sulfur carriers are a class of organic compounds that contain sulfur in its oxidation state 0 or -1 , where the sulfur atom is bound either to a hydrocarbon or to another sulfur atom

- That does not contain other hetero atoms except oxygen
- Produced by adding sulfur to all kinds of unsaturated, double-bond-containing compounds such as olefins, natural esters, and acrylates or by substitution reaction with reactive organic halides and alike

Lubricant additives fitting this definition are the main focus of this chapter.

Owing to the overwhelming versatility of sulfur chemistry, other sulfur-containing product groups cannot be discussed in depth but are mentioned in the context where appropriate.

Although this group of additives has been used in the lubricant industry for more than eight decades, sulfur carriers are not at all an endangered species. In fact, we are still seeing increasing usage today. This is partly due to continuous ongoing R&D work done in this area, which brings about innovation and product improvement. Also, many chemical aspects and applications are waiting to be discovered. Furthermore, sulfur carriers are essential additives for the solution of upcoming lubricant market requirements such as chlorinated paraffin substitution; heavy metal replacement; and health, safety, and environmental issues. Therefore, we expect to see substantial future growth of light-colored, low-odor, and odor-free sulfur carriers.

9.2 HISTORY

As we look back on more than 100 years of sulfurized compounds, the authors had to rely on literature sources for the time before 1950s. During the literature studies, it turned out that one of the most fruitful sources for the time period before 1950 is the review articles of Helen Sellei [1,2] published in 1949. Much of what follows is based on their content, but we have tried to reinterpret the information with today's background knowledge.

9.2.1 FIRST SYNTHESIS AND APPLICATION (1890–1918)

Sulfurized fatty oils have been commercially produced for more than 100 years. Long before they were used as additives in lubricants, they had become important additives for the rubber industry. The addition of 4–8% sulfur to an unsaturated natural oil such as rapeseed oil at high temperatures (120–180°C) gives a flexible, gummy polymer called *factis*. Sulfur undergoes an addition reaction to the double bonds of the natural oil and builds up a three-dimensional structure of sulfur bridges between the triglyceride molecules. This is comparable to the vulcanization process of latex, which results in *rubber*.

In the late nineteenth century, rubber was an expensive natural raw material, and with the rapid industrialization in general and the growing automobile industry in particular, rubber tires were needed in increasing amounts. It soon turned out that *factis* also provided special, positive properties to rubber goods during the vulcanization process. This was the starting point of smaller chemical factories producing additives for the rubber industry. In 1889, Carl Benz submitted the patent for the world's first automobile in Mannheim, Germany. In the same year and city, Rhein Chemie Rheinau GmbH was founded and started to produce sulfurized natural oils. Germany had seen a special national aspect to the industrial history of sulfurized fats and rubber before 1914. Because Germany had very few colonies, all rubber had to be imported. During the national tensions in the first decade of the twentieth century and subsequent trade boycotts, the search for alternatives

had been strongly pushed, leading to the development of synthetic rubber (*Buna*). Subsequently, because it was cheap and based on locally available raw materials, factis had found increasing use as rubber substitute and rubber diluent.

9.2.2 FIRST APPLICATION IN METALWORKING OILS (1920–1930)

In the very early days of modern lubrication, it had become known that sulfur is an important element to improve frictional properties and prevent seizure under high loads. Free sulfur and sulfur-containing heterocyclic molecules are known as part of natural crude oil (thiophenes, thioethers, etc.). In early refining technology, they were not removed effectively, especially from the higher-viscosity oils that were typically used for gear oils, which had up to 3–4% sulfur. This natural sulfur contributed to mild EP performance (antiwelding). After the positive effects of sulfur for lubricant oil formulations were recognized, the next step was to physically dissolve sulfur flower into the lubricant oil at elevated temperatures. This sulfur, however, is very reactive and corrosive against copper and its alloys. Also, sulfur flower has a limited solubility in mineral oil, which limits its maximum dosage and final EP performance achievable.

Sulfurized esters were first used in metalworking. For heavy-duty operations with a high degree of boundary lubrication conditions, it was realized that the addition of oil-soluble sulfur compounds had a tremendous effect on the performance. The first milestone literature that reports this effect was published in 1918 by the E.F. Houghton Corporation [3] for cutting oils. It is claimed that a mixture of lard oil, mineral oil, and wool fat treated with sulfur flower at elevated temperatures results in a sulfurized product that increases the performance of cutting oils enormously. In particular, the tool life is extended, and smoking of the coolant is reduced greatly due to friction and temperature reduction. These observations are still valid today and may be considered the starting point of the application of sulfur carriers as additives for lubricants.

In comparison with the solid, rubberlike material factis, which has been commercialized for several decades, Houghton Corporation's breakthrough was to produce a liquid fatty material that was soluble in mineral base oil at any ratio. It overcomes the solubility limits of sulfur flower and allows the adjustment of the EP performance level according to treat rate. They achieved this simply by using nonreactive mineral oil and wool wax as chain-breaking agents and diluent to control the polymerization reaction of lard oil to keep it liquid. From thereon, the use of sulfurized oils has become quite common in metalworking.

9.2.3 SULFURIZED COMPOUNDS FOR GEAR OILS AND OTHER LUBRICANTS (1930–1945)

Some years later, the idea of improving load-carrying capacity under high-pressure and high-temperature conditions had been picked up by automotive lubricant researchers and applied to oils for the newly constructed hypoid gear boxes. With the advent of hypoid gears in automotive applications in the 1920s and 1930s, wear and seizure under high-load conditions became a major technical problem that lubricant companies needed to solve. Most of the development work had been done within these lubricant companies, and the new technology had not been published in detail. However, the number of patents on sulfur compounds for lubricants developed very rapidly throughout the 1930s and 1940s.

- 1936 First patent review on EP lubricants [4]
- 1940 Patent review 1938–1939 [5]
- 1941 General publication on lubricating additives including an extensive patent bibliography [6]
- 1946 Review article on sulfurization of unsaturated compounds [7]

This clearly indicates that the ideas that had been invented and first applied by the metalworking people also worked for gears. Combinations of sulfurized products with lead soaps and lubricity

esters were the first high EP performance technology in gear oils. Many years later, Musgrave [8] stated in an article on hypoid gear oils that it was just by chance that the synergistic effect of sulfur with lead soaps had been discovered in the early 1930s.

An interesting historical dimension was added to the EP gear oil development during World War II. Most of the EP gear oil development occurred in the United States due to the great importance of automotive industry in the 1920s and 1930s. German gear oil technology was not as advanced as that of United States. Eyewitnesses report of frequent gear box failures of German tanks and heavy equipment during the attack against Russia. The reason was that in autumn Russian roads were turning into mud and the heavy vehicles were operated most of the time at maximum power. The only mildly additized gear oils were not just good enough to prevent scoring and welding.

9.2.4 SCIENTIFIC RESEARCH ON CHEMISTRY AND APPLICATION (1930–1949)

Between 1930 and 1950, the important basics of sulfur carrier technology had been developed. Patents from this period include most of today's raw materials and reaction pathways. Raw materials used were animal oils [3], vegetable oils/organic acids [9], pine oils [10,11], whale oil (sperm oil), acrylates, olefins [12], alcohols [13], synthetic esters [14], and salicylates [15]. Even thiocarbonates [16] and xanthogenates [17] were synthesized and used as organic, oil-soluble sulfur-containing EP additives.

Reaction pathways mentioned in patents mentioned earlier include

- Sulfur flower reaction with and without H_2S , aminic, and other suitable catalysts
- Sulfur chlorination with S_2Cl_2 [18]
- Organic halides with alkalipolysulfides
- Mercaptan route [19]

Important product properties that are still part of today's development work were also mentioned in that period:

- Stability of sulfurized products, for example, diisobutene [20]
- Active and inactive sulfur compounds
- Corrosive and noncorrosive compounds
- Light- and dark-colored derivatives
- High- and low-odor products

Parallel to new chemistry, the development of test machines for tribological research progressed quickly along with publications on mechanistic studies of additives. In 1931, at an API meeting, Mougay and Almen [21] presented the first chemical interpretation for the load-carrying capacity of sulfur-containing EP additives and their synergy with lead soaps. They attributed the performance to the formation of a separating film between the frictional partners—a theory generally accepted today in tribological science. In 1939, this film-forming theory of sulfur compounds was proven using the four-ball tester [22]. In 1938, Schallbock et al. published [23] standard-setting results on investigations in the field of metalworking. Empirical correlations were found among cutting speed, temperature, and tool life that are still valid. In 1946, synergistic effects of chlorinated additives with sulfur additives were explained based on a chemical reaction theory [24] under the aspect of newest generation hypoid gear formulations. Phosphorus additives (tricresylphosphate [25], zinc dialkyldithiophosphates [ZnDTP]), primary antioxidants (AOs) (phenyl- α -naphthylamine, butylated hydroxytoluene [BHT]), and detergent/dispersants [26] (salicylates) also joined the world of lubricant additives during this period and have been used since in combination with sulfur carriers.

Most of the development work at that time had been done in a deductive way in a trial-and-error approach. Theoretical explanations, tribological, and chemical modeling always trailed behind (looking back from today's point of view, it is quite astonishing that not so much has changed in 70 years).

9.2.5 SUMMARY OF THE PAST 50 YEARS

With the fundamentals of sulfur carriers being explored so early in lubricant additive history, the literature from 1950 until today concentrates around improvements in production procedures, combinations and synergies with other additives, improvement in product qualities, and search for special applications. The use of sulfur carriers has been extended from metalworking and automotive engine to industrial oils and greases. Ashless hydraulic oils may contain sulfurized EP additives for special applications. Now this product group is used throughout the lubricant oil industry.

Tribology has been defined as a particular field of scientific research, and several basic models of additive response have been worked out. A review article [27] in 1970 summarizes the state of the art at that time, including many literature references.

Until the 1950s, sulfur carriers were mostly made by the lubricant manufacturers. However, increasing environmental awareness, growing market, and the need for more specialized products brought about change. As the sulfurization process involves deep chemical knowledge and production know-how and includes extremely high safety risks, specialty chemical companies became active in this area. It is expected that the few lubricant companies that still produce a small quantity of black sulfurized fats in-house may discontinue sooner or later.

Since the 1950s, the sulfur carrier market was split into two segments: automotive and industrial. In automotive gear oil applications, sulfurized isobutene (SIB) soon became the standard EP product because it is high in sulfur content but low in corrosivity. The typical, rather strong smell of SIB is no real problem in this field of application because gear boxes are totally closed systems. In any open lube system, this EP technology is not acceptable. The big oil companies had their petrochemical subsidiaries (Mobil Chemical, BP Chemical, Shell Chemical, Exxon Chemical, Chevron Chemical, etc.) and added additive manufacturing as the market grew including SIB production units. So SIB production has always been the target for those companies with focus on automotive additives and lubricants. Over the decades, the SIBs have gone through changes in chlorine level due to environmental requirements [28]. Starting at 2–3% in the early days, today high qualities no longer contain chlorine because of a chlorine-free, high-pressure H₂S production processes. Also, the amount of active sulfur in SIBs has been reduced to improve the long-term abrasive wear of gear oil formulations in bearings and to meet today's *fill-for-life* requirements. But in principle, in automotive applications, the same sulfur chemistry is in use today as it was some 60 years ago.

The other big field of application of sulfurized EP additives is industrial lubrication. Traditionally this area is less regulated and restricted by Original Equipment Manufacturer (OEM) approvals, general specifications, and standards—it is particularly true for the metalworking market. Here much more differentiated, problem-solving additives have been and still are in use. This environment has generated a greater variety of smaller volume sulfur carriers that address strongly differentiated technical requirements of metalworking processes and grease applications. Subsequently smaller, more specialized chemical companies entered the lube additive business. The first products were dark in color, but as early as 1962, Rhein Chemie commercialized its first light-colored, low-odor sulfurized synthetic ester based on chlorine-free production technology (see Section 9.3.2).

A big milestone in the history of sulfur carriers has been the international banning of sperm oil (whale oil) in 1971. Up to this year, sperm oil and lard oil (pig fat) have been the dominant fatty raw materials for sulfur carriers. The sperm-oil-based products in particular showed excellent solubility and lubricity in addition to their sulfur-related EP properties. The extensive research activities of this period resulted in various patents [29,30]. The new raw materials turned out to be vegetable oils in combination with either synthetic esters or olefins.

Another aspect that strongly influenced the sulfur carrier market has been the change of refinery technology for base oils. The driving force behind was the necessity to improve environmental as well as health and safety aspects of the major refinery products: fuels. These requirements led to drastic reduction of aromatic components and sulfur content in fuels and subsequently of base oils. From a lubricant point of view, the reduction of aromaticity of the base oils had strong negative

impact on their solvency for additives and thus triggered intensive adjustment work on the additive producer's side including sulfur carrier manufacturers.

The reduction in sulfur content however has contributed substantially to the market growth of sulfurized additives. The reduction of naturally occurring sulfur in base oils through the desulfurization units now needs to be balanced for specific applications through the addition of synthetic, oil-soluble sulfur components to keep EP/AW properties as well as AO performance. This trend started in the 1970s but is getting stronger today with the increase in the availability of XHVI base oils/groups II and III as well as completely synthetic basestocks (polyalphaolefins [PAOs]).

In the late 1970s and early 1980s, a new class of sulfur carrier has been introduced into the industrial lubrication market: dialkylpolysulfides. They are based on C8, C9, or C12 olefins and contain up to 40% sulfur in a very reactive form. They can be looked at as liquid, oil-soluble sulfur flower. The starting point for the development of these additives was the requirement of many lubricant-blending companies for an alternative to sulfurization of base oils with sulfur flower. It is a very time-consuming step and may generate toxic gas (hydrogen sulfide, H₂S) and sulfur dropout during application. Sulfur flower can be dissolved in mineral oil just above its melting point of 115°C in concentrations of typically 0.4–0.6% and is used if appropriate in heavy-duty metalworking applications or running-in gear oils (see Section 9.5.1.3). The solution that has been offered from additive manufacturers has been the new class of organic polysulfides of light color and rather low odor. Diisobuteneptasulfide and *tert* nonyl- and dodecylpentasulfide have been introduced as easy to blend liquids and substitutes for sulfur flower. Today, these active type pentasulfides have become the most important and wide-spread class of sulfur carriers on the industrial oil side.

In 1985, it was found that sulfur carriers, preferably polysulfide types, show a strong synergistic EP/AW behavior when combined with high total base number (TBN) ASTM-D4739 sodium and calcium sulfonates [31]. This has become known as the *PEP technology* (passive EP) in neat oil metalworking. In the beginning, it was hoped that this combination would be a general and simple solution to upcoming chlorinated paraffin replacement issue that started in Western Europe and Scandinavia in the mid to late 1980s. But as it turns out today, the PEP technology can only partially match the universal properties of chlorinated paraffin formulations especially under low-speed/high-pressure operation conditions (for more details, see Section 9.5.4.2).

From the late 1980s to early 1990s, a totally new aspect of sulfurized esters and fats has gained substantial ground—the toxicology and ecotoxicology of these chemicals. Workers' safety, environmental compatibility, biodegradability, and similar requirements need to be addressed in industrial more than in automotive lubrication, because workers in machine shops often cannot avoid constant direct contact with the lubricant. The fact that the use of natural, renewable raw materials and optimized production procedures may give low-toxic and biodegradable sulfur carriers refreshed the interest of development chemists in these special, environmentally safe but classic additives.

The twenty-first century's central question of additive and lubricant R&D departments is how to further optimize energy efficiency and reduce friction. Again, sulfur carriers play a role. Spanning from engine oils to wind turbine gear boxes, formulators take advantage of their multipurpose character.

9.3 CHEMISTRY

9.3.1 CHEMICAL STRUCTURE OF SULFUR CARRIERS

For the majority of sulfur carriers, discrete structures are very hard to sketch for several reasons:

The raw materials are very often mixtures of isomers: in the case of olefins, for example, diisobutene, there are five main isomers; tetrapropylene shows some 35 components in the gas chromatogram (GC). Natural fatty oils have a distribution with mono-, double- and triple unsaturated acids with unsaponifiable matter.

Depending on the temperature, inter- or intramolecular bonding of sulfur occurs preferably. The catalyst directs the addition of sulfur in a certain way (Markovnikov, etc.).

It is a fact that sulfur carriers are technical products based on technical raw materials. In the following, the most typical structures of sulfur carriers based on different, contemporary raw materials are shown. Taking the rather complex reaction pathways of a sulfurization reaction into account, they necessarily are simplified model structures.

9.3.1.1 Sulfurized Isobutene

This is the standard EP additive for gear oils with typical sulfur contents in the range of 40–50% (Figure 9.1).

9.3.1.2 Active-Type Sulfurized Olefins

These are the polysulfide types of sulfur carriers that have been introduced as substitute for sulfuration of base oil and are widely used today in metalworking applications (Figure 9.2).

9.3.1.3 Inactive Sulfurized α -Olefins

These are used in noncorrosive lubricant applications ranging from metalworking, greases to even engine oil applications (Figure 9.3).

9.3.1.4 Sulfurized Synthetic Esters (Light Color)

These are widely used in metalworking and grease applications. Depending on the type of synthetic ester chosen, special properties such as low temperature stability/fluidity and low viscosity may be achieved (Figure 9.4).

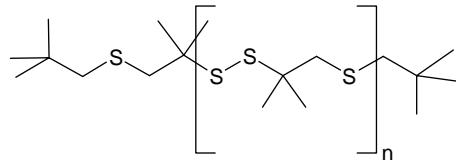


FIGURE 9.1 Sulfurized isobutene.

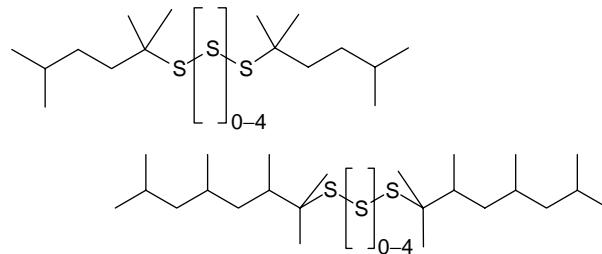


FIGURE 9.2 Sulfurized diisobutene, sulfurized tetrapropylene.

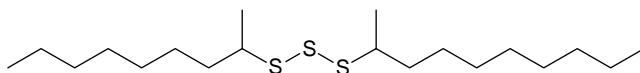


FIGURE 9.3 Inactive sulfurized α -olefins.

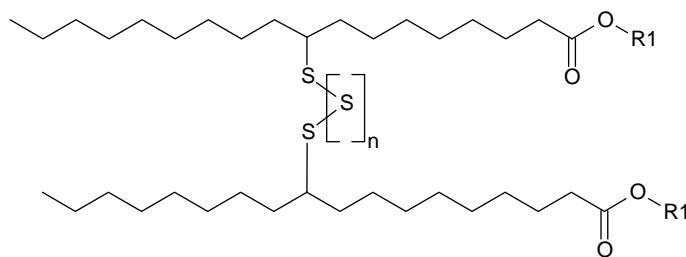


FIGURE 9.4 Sulfurized synthetic esters (light color).

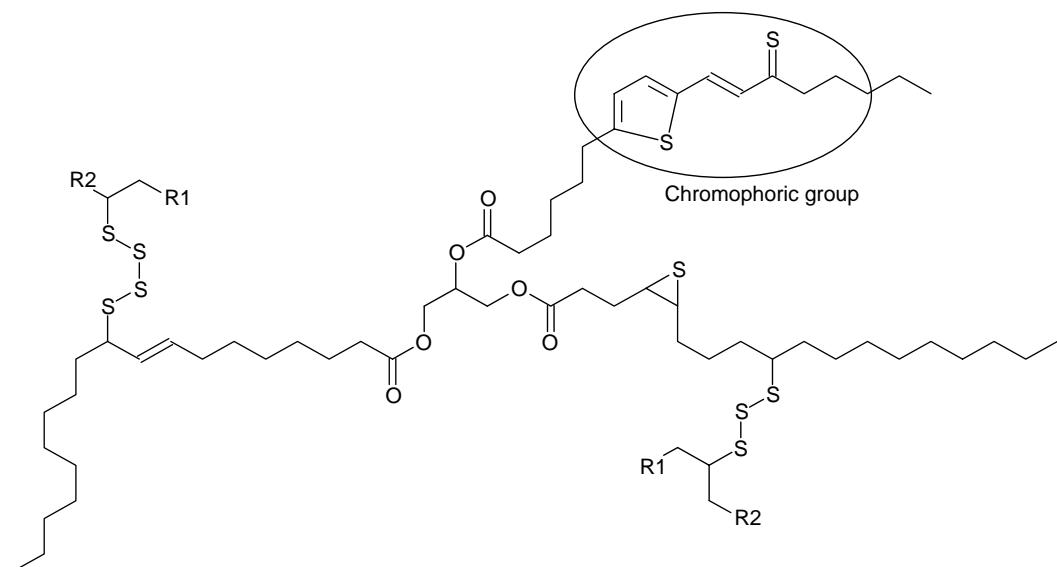


FIGURE 9.5 Sulfurized fatty oil (black color).

9.3.1.5 Sulfurized Fatty Oil (Black Color)

See Section 9.3.2.2 (Figure 9.5).

9.3.1.6 Sulfurized Fatty Oil/Olefin Mixture (Light Color)

This special group of sulfur carriers is outstanding in properties as they combine the positive effects of sulfurized olefins (e.g., hydrolytic stability, high sulfur content) with the excellent lubricity and film-forming properties of sulfurized fatty oils (Figure 9.6).

9.3.2 CURRENT COMMERCIAL PRODUCTION PROCESSES

9.3.2.1 General Aspects

In any current sulfurization process, the raw material is based on unsaturated compounds (olefins or unsaturated esters). All reactions are addition reactions to olefinic double bonds, and textbook chemistry applies to this kind of reaction (catalytic conditions, mechanisms, addition patterns—Markovnikov–anti-Markovnikov orientation).

Today's large-scale production technology in general avoids any halogen-containing reaction steps because there are low limits (maximum 30 ppm chlorine) in the final lubricants that may not be exceeded, for example, in automotive gear oils. Also, expensive removal/workup steps, for example, by washing, can be avoided if halogens are not used.

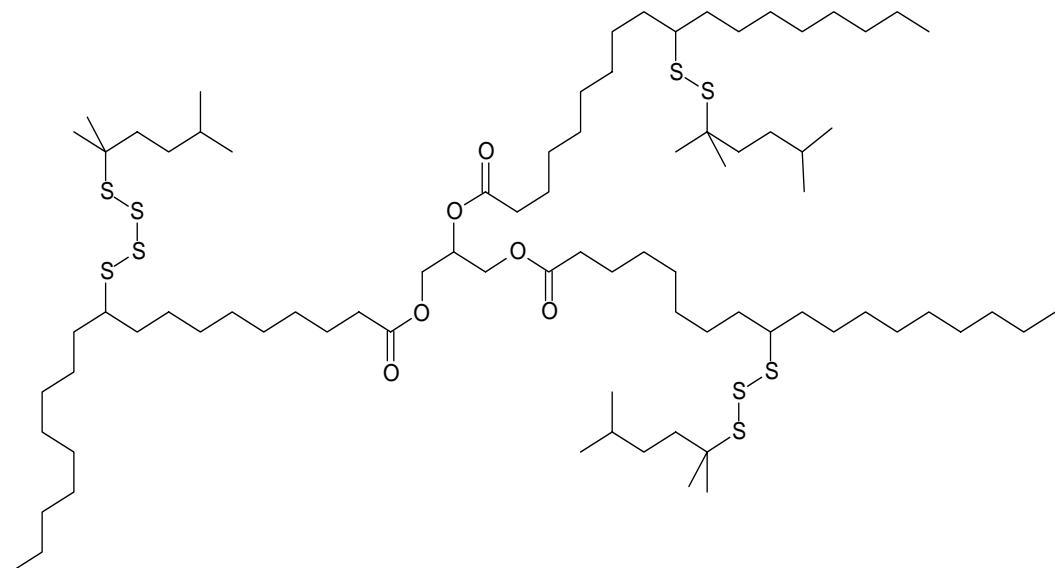


FIGURE 9.6 Sulfurized fatty oil/olefin mixture (light color).

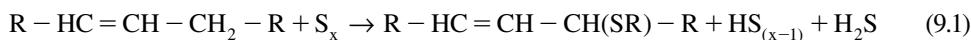
Any sulfurization process involves either the possible formation or the actual use of hydrogen-sulfide (H_2S), an extremely toxic and corrosive gas. The smell of H_2S is generally that of rotten eggs, which is offensive to the human nose. In earlier times, the H_2S released during the sulfurization reaction (see Section 9.3.2.2) was just vented through a chimney or, if at all, scarcely absorbed in alkaline scrubbers. Today, this procedure is no longer tolerated almost worldwide, and smaller factories that have not yet done so need to invest into expensive safety equipment. This is another reason why the smaller lubricant oil companies that still do a little bit of sulfurization are considering stopping. The processes are either pure batch or semicontinuous processes. For industrial applications, the volumes and varieties would not completely justify continuous productions.

9.3.2.2 Black Sulfurization

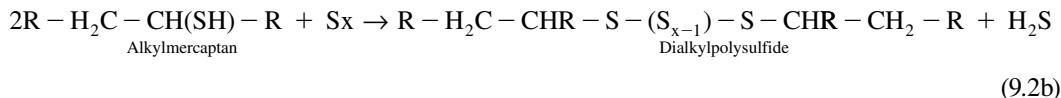
This is the simplest and oldest of all production technologies for sulfur carriers. The first patented sulfur carrier was done this way. The manufacturing equipment needs to withstand pressure above 1–2 bars (it may even be pressureless). Raw materials may be olefins as well as natural or synthetic esters with a certain degree of unsaturation. The other reactant introduced into the olefin-containing reaction vessel is sulfur flower. The mixture is heated above the melting point of sulfur. An uncatalyzed reaction starts to become exothermic above 150–160°C, with the evolution of substantial amounts of H_2S . Catalyzed reactions start just above the melting point of sulfur, in the range of 120–125°C. Typical catalysts are organic amines, metal oxides, and acids.

Mechanistic studies of this reaction have been reported [32] and are very complex. At temperatures between 120 and 160°C, intermolecular reactions are preferred. At 160–190°C, intramolecular reactions may be detected.

The first reaction step in this so-called black sulfurization process is the ring opening of the sulfur flower (S_8 -ring structure) and the subsequent oxidative attack of the sulfur on the vinylic protons (Equation 9.1). This quite uncontrolled reaction ends in the release of H_2S and the formation of vinylic mercaptans, vinylic thioethers, vinylic alkyl- and dialkylpolysulfanes, vinylic thioketones, and even sulfur-containing heterocycles (thiophenes, etc.).



A great part of the *in situ* generated H₂S does not leave the reaction mixture but is directly adsorbed by the double bonds, thus producing saturated alkylmercaptans (Equation 9.2a). They react further, oxidatively, with sulfur flower to generate alkyl- and dialkylsulfides with the release of more H₂S (Equation 9.2b).



The final product consists of a full range of organic sulfur derivatives. Some of them are still unsaturated, with isomerized double bonds and conjugated, chromophoric (color-deepening) sulfur compounds such as thioketones and thiophenes, which cause the product to be dark black in color and rather smelly. From an application point of view, these products exhibit EP/AW performance, but because of their remaining double bonds, they have the following negative characteristics:

- They will continue to polymerize during use and even under normal storage conditions.
- They are easily oxidizable and form residues on fresh metal surfaces/discoloration.
- They will cause a TAN increase within a short time in circulation systems and cause short oil drain intervals.
- They will even generate H₂S/mercaptan during high-temperature usage in lubricant systems (see Sections 9.4.2.1.7 and 9.4.2.1.2).

So today's main use of these black sulfurized products are total loss lubricants in which long-term stability and bad smell are not an issue. It is the cheapest way of making sulfurized additives.

9.3.2.3 High-Pressure H₂S Reaction

High-quality sulfur carriers, which have improved properties compared to the black materials, are produced today using high-pressure/high-temperature equipment. The handling of toxic H₂S under high-pressure conditions requires sophisticated handling techniques and safety measures. Furthermore, H₂S is an expensive gas. All these aspects contribute to significantly higher production costs compared to the simple black sulfurization.

In this process, the olefins, sulfur, and H₂S are added to a high-pressure-resistant reactor and heated to 120–170°C. The reaction is also catalyzed by amines, metal oxides, acids, etc. For low-boiling olefins such as isobutene, the pressure may go up as high as 50–60 bar. For higher-boiling olefins such as disisobutene, typical pressure is in the range of 2–15 bar. The presence of H₂S as reducing agent and strong nucleophile makes a total difference to the black sulfurization process. The oxidative attack of sulfur on the vinylic carbon–hydrogen (C–H) bond is effectively suppressed. The side reaction of the black sulfurization process becomes the main reaction here: the addition of H₂S to the double bonds to form mercaptans (Equation 9.2a) which then quickly react with sulfur in a redox reaction to form dialkyldi-, tri-, tetra-, and polysulfides and release 1 mol equivalent of H₂S (Equation 9.2b).

This procedure gives much more controlled reaction conditions and finally fewer side products. The most important effect of this reaction pathway is the fact that the double bonds are gone after the reaction and no conjugated systems with chromophore (color-deepening) properties can be formed. The sulfur carriers produced by this way are much more oxidatively stable, and they are of light color. This one-step process is an advantage in terms of total production time and turnover.

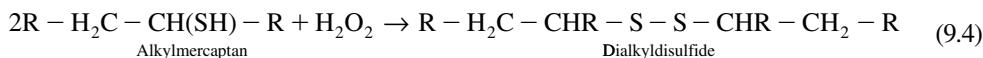
9.3.2.4 Mercaptan Route

Few producers synthesize sulfur carriers in a two-step process.

1. In the first step, H_2S is added to olefins under the catalytic action of Lewis acids. If strong activators such as BF_3 are used, the reaction takes place at as low as -20°C . Another procedure works at $60\text{--}90^\circ\text{C}$. The resulting alkylmercaptans are distilled from the reaction mixture and isolated as intermediates (Equation 9.3). The nonreacted olefins are circulated back to the reaction vessel.



2. The mercaptans are oxidized either with hydrogen peroxide (H_2O_2) (Equation 9.4a) to the dialkyldisulfides



or by stoichiometric amounts of sulfur to trisulfides (Equation 9.5) and polysulfides (Equation 9.6)



This may be summarized in the reaction shown in Figure 9.7.

This process is mainly applied to olefin-based sulfur carriers based on tri- and tetrapropylene as starting material because the resulting tertiary dodecylmercaptan may be used chemical intermediate and in other applications such as rubber processing as.

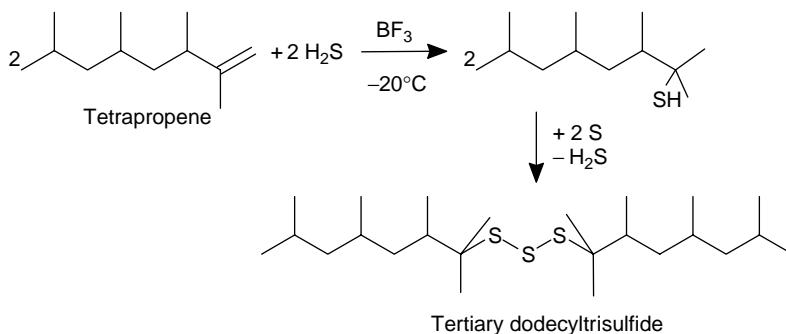


FIGURE 9.7 Summary of two-step process.

9.3.3 OTHER SYNTHETIC ROUTES

9.3.3.1 Sulfurchlorination Route

Sulfur carriers can be synthesized in a two-step process using disulfur dichloride and sodium sulfide solution (Figure 9.8). It had been widely used because it is a controlled way of adding discrete S_2 -bridges to double bonds with little side reactions occurring.



FIGURE 9.8 Sulfurchlorination reaction.

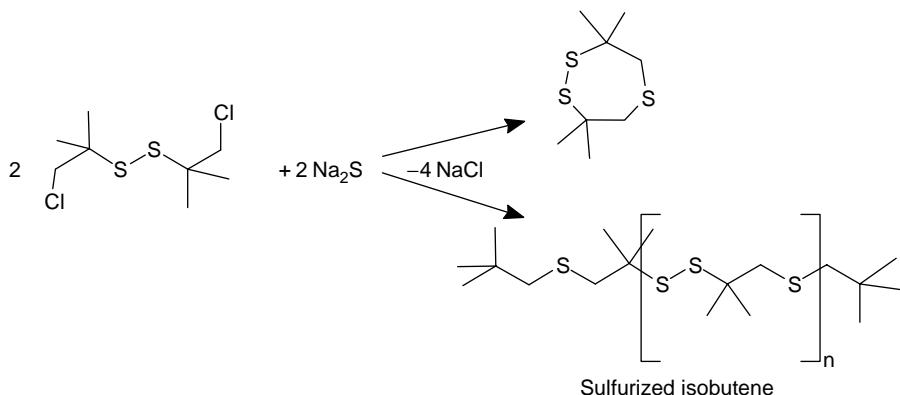


FIGURE 9.9 Dechlorination reaction.

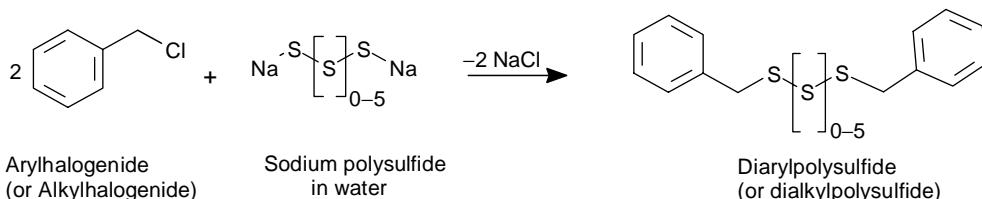


FIGURE 9.10 Dechlorination of arylhalogenides.

Step 1. Addition of disulfur dichloride to double bonds.

In case of fatty oil being used as olefin source, the resulting product is a sulfurchlorinated fatty oil useful as chlorine and sulfur-containing EP additives in metalworking. From a technical point of view, their biggest problem is the split-off of chlorine and subsequent severe corrosion problems that are difficult to control. From today's point of view, the presence of chlorine is not favorable anymore because of environmental concerns.

Step 2. Subsequent treatment of the sulfurchlorinated products with sodium sulfide (NaS_2) solution in water. It is a substitution reaction of sulfur versus chlorine (Figure 9.9). Inter-molecular linkage as well as ring closure may occur. The water-soluble sodium chloride is washed out.

9.3.3.2 Alkylhalogenide/ NaS_x

This process is closely related to the first step reaction discussed in Section 9.3.3.1. Starting materials may be alkyl- or arylhalogenides. As shown in Figure 9.10, it is possible to substitute halogens with sulfur using alkali sulfides. If Na_2S is used, monosulfides are generated. In case alkali polysulfide is applied, alkyl- or arylpolysulfides are the resulting derivatives.

This route has not found commercial interest as raw material costs are too high compared to other synthetic methods.

9.3.4 RAW MATERIALS

In principle, any single- or multi-double-bond-containing molecule may be sulfurized. Therefore, the list of olefinic raw materials is long. The list of sulfur-containing materials is rather short. It is mainly sulfur flower (S_8), hydrogen sulfide gas, some S_2Cl_2 , and some alkali polysulfide (e.g., NaS_x).

On the olefin side, patent literature reports of the following:

- Vegetable oils (soybean, canola, rapeseed, cottonseed, rice peel, sunflower, palm, tall oil, terpenes, etc.)
- Animal fats and oils (fish oils, lard oil, tallow oil, sperm oil, etc.)
- Fatty acids
- Synthetic esters
- Olefins (isobutene, diisobutene, triisobutene, tripropylene, tertapropylene, α -olefins, n -olefins, cyclohexene, styrene, polyisobutene, etc.)
- Acrylates, methacrylates
- Succinic acid derivatives, and more

The choice of commercially applied raw material is certainly limited to those compounds that have a reasonable price level and give certain performance benefits. Sulfur carriers based on low-boiling olefins (e.g., C4-types) are limited to closed lubricating systems due to the volatility of the decomposition products and associated offensive smell. For water-based lubricant oil systems, sulfurized fatty acids that can be easily emulsified and active types of olefins that cannot be hydrolyzed are preferred. In oil applications, one can find the full range of products.

9.4 PROPERTIES AND PERFORMANCE CHARACTERISTICS

9.4.1 CHEMICAL PROPERTIES

9.4.1.1 Effect of Additive Structure on Performance

9.4.1.1.1 Raw Materials

The additive structure is mainly influenced by the choice of the raw materials and the sulfurization method. A general overview of the performance properties of sulfurized products based on different raw materials is shown in Table 9.1.

9.4.1.1.2 Influence of Raw Materials on Extreme Pressure and Antiwear

The raw material determines the polarity and, therefore, the affinity of the product to a metal surface [33]. With increasing polarity, an increasing EP performance can be observed. Straight sulfurized

TABLE 9.1
Performance Properties of Sulfurized Products

	Ester		Triglyceride		Olefins	
	Inactive	Active	Inactive	Active	Inactive	Active
Extreme pressure	Fair	Good	Good	Very good	Low	Fair
Antiwear	Good	Low	Very good	Low	Good	Poor
Reactivity	Low	High	Low	High	Low	Very high
Cu corrosion	Low	High	Low	High	Low	High
Antioxidant	Good	Low	Good	Poor	Good	Poor
Lubricity	Fair	Fair	Very high	Very high	Poor	Poor

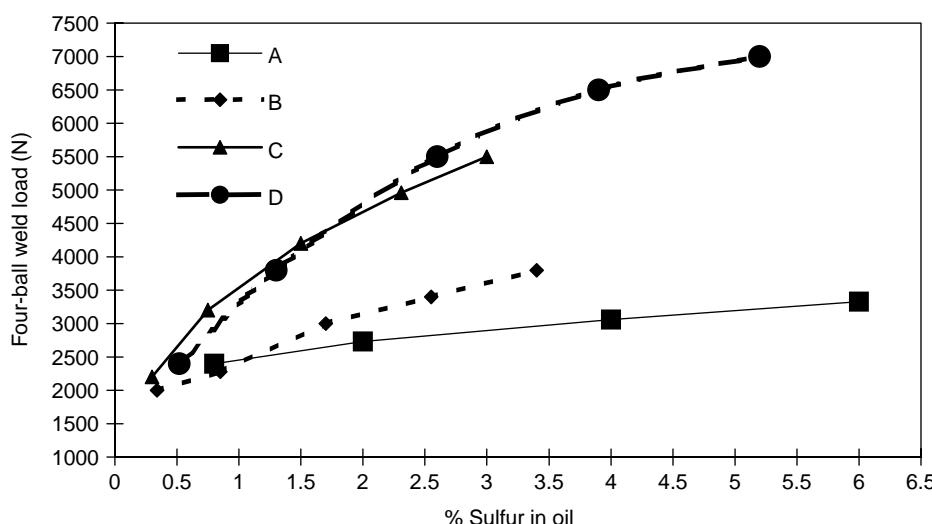
olefins are nonpolar and show a relative poor affinity for metal surfaces (see Section 9.4.2.1.4). As the polarity increases from olefin < ester < triglyceride, the EP performance increases in the same order. This behavior is demonstrated in a simple four-ball EP test. Chart 9.1 shows the four-ball weld load (DIN 51350 Part 2) of sulfurized additives over the sulfur level in oil. The products with a high polarity (C and D) show considerably higher EP loads than the nonpolar additives (A and B).

The content of active sulfur is only of minor importance on the EP performance, but the polarity and chemical structure play a major role.

9.4.1.1.3 Activity

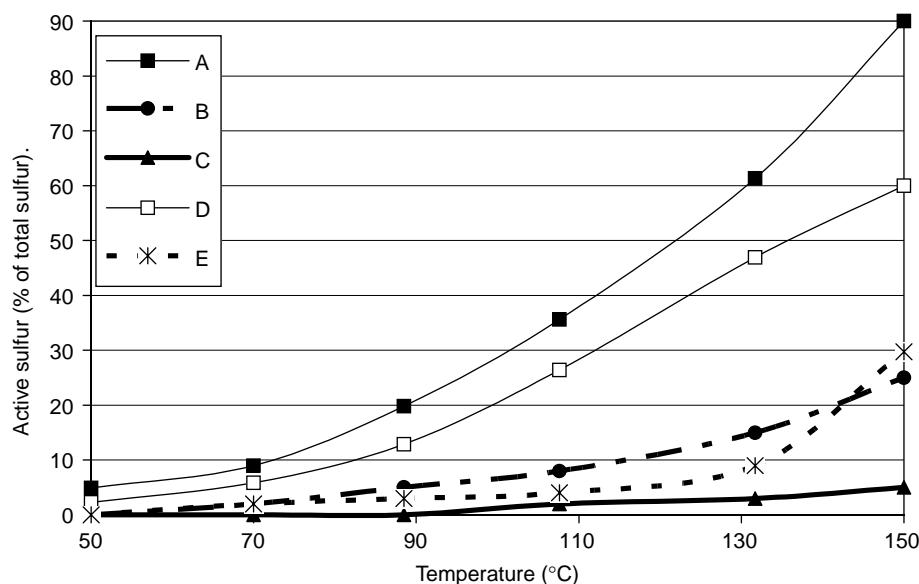
Active sulfur is the amount of sulfur available for a reaction at a certain temperature. A common method for its determination is ASTM D-1662 [34]. The amount of active sulfur is determined by reacting copper powder with the sulfurized product for 1 h at 149°C. Depending on the raw materials and on the sulfidation method, the active sulfur content can vary greatly. The activity is a function of the temperature. Chart 9.2 shows typical active sulfur contents of sulfurized products based on different chemistry and sulfidation methods.

The activity depends mainly on the sulfur chain in the molecule. Mono- and disulfides are not aggressive against yellow metals. Pentasulfides are highly reactive and, therefore, suitable for heavy-duty machining of steel. The long-term inhibition of these products against yellow metals is hardly possible. Long-chain sulfur bridges in polysulfides (A) are thermally less stable than short sulfur bridges, where sulfur is linked to the carbon atom of the raw material. For this reason, the reaction with the metal surface is possible at relatively low temperatures. Mono and disulfides show only a medium activity, because sulfur will be released only at higher temperatures [35]. The active sulfur at a given temperature is an indication of the ability of the product to provide sufficient reactive sulfur to form metal sulfides. Published work on the mechanism of the influence of



	Type	Total Sulfur	Active Sulfur	Activity (%)
A	Olefin	40	36	90
B	Ester	17	8	47
C	Triglyceride	10	0.5	5
D	Triglyceride	18	9	50

CHART 9.1 Influence of raw materials on EP performance.



	Type	Total Sulfur	Active Sulfur at 149°C
A	Olefin	40	36
B	Olefin	20	5
C	Triglyceride	10	0.5
D	Triglyceride	18	10.5
E	Olefin/Triglyceride	15	4.5

CHART 9.2 Active sulfur of various sulfurized products.

organosulfur compounds on the load-carrying properties of lubricating oils indicates that this is due to their ability to form sulfide films that are more easily sheared than the metallic junctions under EP conditions [36].

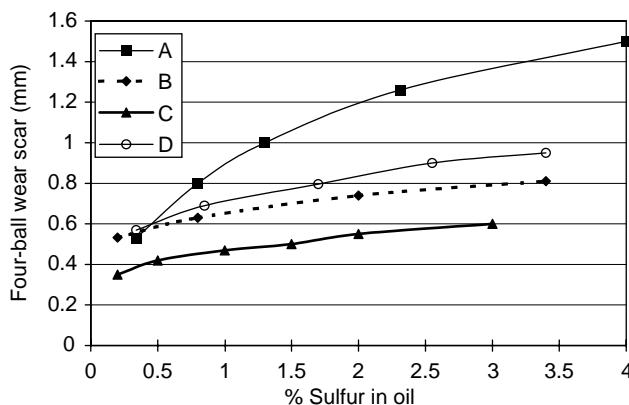
Therefore, active sulfur has a significant influence on the AW performance. Higher sulfur activity results in faster formation of the metal sulfide and higher wear. This performance is visualized in Chart 9.3. The chart shows the four-ball wear scar (DIN 51350 Part 3) of sulfurized products with various activities.

9.4.1.1.4 Copper Corrosion

ASTM D-130 [37] is a common method to determine the copper corrosion of additives. This copper corrosion does not necessarily reflect the activity of a sulfurized product, because very often yellow metal deactivators are used to mask the active sulfur.

The degree of copper corrosion depends on the amount of active sulfur and the presence of yellow metal deactivators. Inactive sulfurized products will show a long-term inactivity toward yellow metals, whereas active sulfur, masked with yellow metal deactivators, will react with the yellow metal as soon as the deactivator is consumed/reacted.

Therefore, the only statement that can be made is that a product will not stain copper under the given test parameters. This method is not suitable to determine the activity that is of major relevance for the performance of a sulfurized product (see Section 9.4.1.3).



	Type	Total Sulfur	Active Sulfur	Activity (ASTM D-1662)(%)
A	Hydrocarbon	40	36	90
B	Hydrocarbon	20	5	25
C	Triglyceride	10	0.5	5
D	Triglyceride	18	10.5	58

CHART 9.3 Influence of activity on AW performance.

9.4.1.1.5 Antioxidant

Sulfurized products with low active sulfur content are suitable to improve the AO behavior of lubricants. This is particularly important if hydrocracked, almost sulfur-free base fluids are used. During the synthesis of these oils, the natural sulfur (mainly heterocycles, inactive) is removed. The reintroduction of inactive sulfur carriers improves the oxidation stability, especially in combination with other secondary AOs.

9.4.1.1.6 Lubricity

Lubricity can be described as friction reduction under low-pressure conditions. Under these conditions, physical adsorbed lubricating films are effective (see Section 9.4.2.1.4). Inactive sulfurized triglycerides are widely used to improve the lubricity of a lubricant. In general, the lubricity of sulfur carriers increases with the polarity. Sulfurized olefin (no lubricity) < sulfurized ester (medium lubricity) < sulfurized triglyceride (high lubricity). Special products with enhanced lubricity are based on synergistic raw material blends such as triglyceride/long-chain alcohol, triglyceride/fatty acid, and triglyceride/olefin.

9.4.1.1.7 Color

The color of sulfurized compounds is mainly influenced by the production method and virtue of the raw materials. Light color is not only a matter of cosmetics but also a quality feature. Light-colored products manufactured with high-pressure hydrogen sulfide processes or by mercaptan oxidation do not have remaining unsaturated double bonds, and therefore, they show better oxidation stability in general.

9.4.2 PHYSICAL PROPERTIES

9.4.2.1 Effect of Additive Structure on Properties

9.4.2.1.1 Raw Materials

The selection of the raw materials and the production process determine the chemical structure of the compound. The physical properties of a sulfurized product are dependent on the chemical structure. An overview is given in Table 9.2.

TABLE 9.2
Physical Properties of Sulfurized Products

	Ester	Triglyceride	Olefin
Polymerization	Low	High	Very low
Solubility	Good	Fair-good	Very good
Polarity	Moderate	High	Low
Viscosity	Low	High	Very low
Biodegradability	Good	Excellent	Poor

9.4.2.1.2 Polymerization

During the sulfurization process, the molecules of the raw materials are linked through sulfur. Depending on the structure of the raw material, two or more raw material molecules will be linked. Triglycerides such as lard oil and soybean oil do polymerize and form solid, rubberlike products, if the polymerization is not controlled through chain terminators such as esters or olefins, containing only one double bond. Olefins with only one double bond do not polymerize. Two molecules are linked by a sulfur chain where length depends on the production process. Esters behave in a similar way but due to varying amounts of multiple unsaturated compounds in natural esters, some polymerization takes place. Dark sulfurized products not only show less oxidation stability compared with light-colored, completely saturated compounds but will also resume polymerization after the production process is finished.

9.4.2.1.3 Solubility

The solubility is mainly a function of the polarity of the product. As the polarity increases from olefin < ester < triglyceride, the solubility decreases. Polarity as well as the grade of polymerization determines the solubility. In general, sulfurized olefins have excellent solubility in solvents and all mineral oils. Depending on the sulfurization method, esters can exhibit good solubility even in group II and group III base oils if their polymerization grade is controlled during production. Sulfurized triglycerides are, in general, limited in their solubility due to their high polarity. But even more, the grade of polymerization plays a predominant role. A controlled reaction/polymerization can lead to light-colored products that will be soluble in paraffinic base oils, whereas uncontrolled polymerization will lead to dark-colored products, soluble only in oils with higher polarity and aromatic content such as, for example, naphthenic base oils.

9.4.2.1.4 Polarity

Polarity determines the adhesion of a sulfurized product to the metal surface. The polarity depends on the raw materials used for the sulfurization. The organic portion of the molecule is responsible for the polarity and the affinity of the sulfurized product to the metal surface [35]. As the polarity increases from sulfurized hydrocarbon < sulfurized ester < sulfurized triglyceride, the affinity (physical adsorption) to metal surfaces also increases. Therefore, sulfurized products based on triglycerides, fatty acids, or alcohols provide superior lubricity compared with sulfur carriers based on less polar esters or nonpolar olefins.

9.4.2.1.5 Viscosity

Viscosity of a sulfurized product depends on the type of raw material used for the sulfurization and polymerization grade. A higher degree of polymerization (molecular weight) results in higher viscosity. The raw materials determine the viscosity index (VI) of a sulfur carrier. Short-chain sulfurized olefins show low VIs, whereas sulfurized triglycerides have VI above 200.

9.4.2.1.6 *Biodegradability*

Depending on the raw materials and on the sulfurization process, sulfurized products cover the whole range from nonbiodegradable to readily biodegradable. Besides the raw material, the production technology plays a predominant role. Catalysts used, impurities in the raw materials, and side components formed during the synthesis have a strong influence on the biodegradability. Therefore, biodegradability cannot be predicted but has to be tested for every single product. Biodegradable sulfur carriers are available for various applications [38].

9.4.2.1.7 *Stability*

Storage stability is obtained by total reaction of the double bonds in the sulfur carrier and in eliminating H₂S and mercaptans. Especially mercaptans, but also H₂S, are left over from the sulfurization process. If H₂S or mercaptans are not removed completely, they will evaporate under severe conditions in the final application or even under unfavorable storage conditions. Mercaptans can react with the polysulfanes and thereby release H₂S. Depending on the raw materials and the type of sulfurization process, some sulfurized products continue to polymerize during storage. Especially triglycerides, sulfurized with flower of sulfur under atmospheric pressure, show a steady and sometimes very strong polymerization during storage.

9.5 COMPARATIVE PERFORMANCE DATA IN PERTINENT APPLICATION AREAS

9.5.1 METALWORKING

9.5.1.1 Cutting/Forming

In principle, we have to deal in all cutting processes with abrasive wear (i.e., cutting) and adhesive wear (i.e., build up edges). Depending on the particular process, the machining parameters, one of these wear types, play a dominant role. At low machining speeds, like in most of the forming operations, adhesive wear (cold welding), the formation of build up edges, and wear on the flank of the cutting edge are very often the limiting factors for tool life. At high machine speeds and increasing contact temperatures, the abrasive wear determines the tool life. The reactivity of additives depends on temperature and pressure. Field and laboratory tests showed that different types of sulfur carriers (same sulfur content but varying raw materials or production processes) lead to significantly different results in a metalworking operation [39].

9.5.1.2 Contribution of Sulfur Carriers to Metalworking

Sulfurized products can be designed to meet technical and ecological requirements in metalworking processes. They are used successfully for more than 80 years to avoid abrasive and adhesive wear and enhance lubricity. In cutting operations, their main function is to support the cut and to prevent wear of the tool, whereas in forming processes, sulfurized products should form a pressure-stable lubricant film and prevent adhesive wear.

9.5.1.3 Replacement of Sulfur Flowers

In the past, it was very common to dissolve sulfur flowers in metalworking fluids to obtain a high reactivity and good EP properties. This procedure is very cost-intensive because it has to be done under controlled temperature conditions below the melting point of sulfur and has several disadvantages such as limited solubility (maximum 0.8% S), limited stability (sulfur dropout), and high corrosivity toward yellow metals. Also, there is a risk of H₂S generation, a highly toxic gas well known because of its rotten-egg odor. Today, this process is widely substituted by using sulfurized products. If just reactivity is required, sulfurized olefins with high total and active sulfur content are

used, although it is possible to adjust almost any activity/lubricity ratio while using the combination of appropriate sulfurized products.

9.5.1.4 Copper Corrosion

Depending on the process and on the metals machined, corrosion control toward yellow metals can be a requirement. If inactivity (no staining) toward yellow metals is required, it is important to use either absolute inactive sulfurized products or medium-active sulfur carriers in combination with yellow metal deactivators. Active sulfurized products can be inhibited short term but will, in the long term, turn active again.

9.5.1.5 Substitutes for Chlorinated Paraffins

The driving forces for the replacement of chlorinated paraffins are mainly ecological and toxicological reasons. Users and waste oil disposal facilities have additional concerns over the corrosivity of the chlorinated paraffin decomposition products, primarily hydrochloric acid.

Chlorinated paraffins work because of their ability to form a highly persistent lubricating film even at low temperatures or moderate pressure. At high-temperature/high-pressure conditions, they decompose, and the formed hydrogen chloride forms metal chloride with the metals involved in the process [39].

Chlorinated paraffins can be substituted with sulfurized products. Depending on the main function of the chlorinated compound in the particular process used, lubricity, or activity, suitable sulfurized products are available, which can function as alternatives. The lubricity performance is mainly covered by highly polar, inactive sulfur compounds (see Section 9.4.1.1.6), whereas the activity will be covered by reactive sulfurized olefins or mixed sulfurized olefins/triglycerides.

9.5.1.6 Substitute for Heavy Metals

Heavy metals, particularly antimony, molybdenum, and zinc compounds are used as EP and AW additives in severe metalworking processes. Sulfur carriers have proven to be suitable substitutes, particularly when used with synergistic compounds such as polymer esters, phosphates, phosphites, dialkyldithiophosphates, and sulfonates.

9.5.1.7 Carbon Residue Reducing in Rolling Oils

Sulfur carriers are used in cold rolling of steel to prevent carbon residues build up on the surface of the metal sheets during the annealing process. Carbon residues are generated by oxidation/polymerization of additives used in rolling oils. Therefore, typical rolling oils contain sulfur-based anti-snakey edge and carbon-reducing additives [40]. Clean burning of the lubricant is important to obtain a clean metal surface that can be evenly coated in subsequent process steps.

Typical products used for this application are sulfurized olefins with low to medium activity or inactive sulfurized triglycerides.

9.5.1.8 Water Miscible Metalworking Products

Sulfurized products are used in water-miscible metalworking systems to provide EP performance and, depending on the type of sulfur carrier, lubricity. By far the biggest applications are soluble oils or emulsions. Standard sulfurized products are not water-soluble. Surfactants must be used to keep the sulfur carrier in the emulsion. Compared to applications in non-water-based systems, the water-based systems require hydrolytically stable products that can react at relatively low temperature. Therefore, active sulfurized olefins, preferably pentasulfides, are widely used for this application. Sulfurized esters and triglycerides are also used, especially if additional lubricity is required. Specialty sulfur carriers are reaction products of sulfurized fatty acids and sulfurized olefins. These sulfur carriers have good emulsifying properties with relatively high hydrolytic stability and activity.

Straight sulfurized fatty acids such as sulfurized oleic acid, are used in semisynthetic metalworking fluids. The sulfurized fatty acid will be reacted with alkaline compounds such as amines or potassium hydroxide to form a soap. This soap is water-dispersible and needs much less emulsifiers than a sulfurized olefin. However, hard water stability can become a problem with this type of sulfur carrier.

9.5.2 GREASE

High demands on load-carrying capacity of machine parts require the use of EP and AW additives to avoid material loss and the destruction of the surfaces of the friction partners. Older technology still uses typical gear oil sulfur carriers based on short-chain olefins such as isobutene. These sulfur carriers provide a high sulfur content, but their distinct, strong odor prohibits their use in open lubricating systems.

As it is almost impossible to mask the activity of sulfurized products in greases by using yellow metal deactivators or sulfur scavengers, inactive sulfurized products are widely used as EP additives in greases. Especially if the grease is designed for a wide application range, it is imperative that truly inactive sulfur carriers are used, because yellow metals are widely present as friction partners (e.g., brass cages in bearings). In addition, there are increasing demands on high-temperature stability for various grease types. This also calls for inactive, oxidation-stable sulfurized products. Typical sulfur carriers for greases are shown in Table 9.3.

Sulfurized products are also used to substitute heavy-metal-containing compounds, which are traditionally used as EP additives in greases. Besides their excellent performance, these heavy-metal-containing compounds show some weak points. Antimony and bismuth compounds are known to have some weakness regarding copper corrosion, and lead compounds are toxic. In the meantime, many of these products have been replaced by special sulfurized products either as a direct replacement or in combination with synergistic compounds such as zinc dialkyldithiophosphates, phosphate esters, or overbased sulfonates [41]. Sulfurized products are also used in greases for constant velocity joints (CVJ) [42]. They are very efficient in combination with molybdenum compounds (e.g., molybdenum dithiocarbamate [MoDTC], molybdenum dithiophosphate [MoDTP], Mo-organic salts) as a sulfur source to support the formation of lubricating, active molybdenum disulfide in the friction zone.

There is an increasing demand for EP greases for environmentally sensitive applications such as railroad wheel flange lubrication, railroad switches, and agricultural equipment such as tractors or cotton picker spindles. Some sulfurized products are biodegradable and show excellent ecological data [39]. Therefore, these products are used rather than heavy-metal-containing compounds to enhance EP and AW properties in such applications.

9.5.3 INDUSTRIAL OILS

An increasing variety of industrial fluids use sulfurized products as EP and AW additives.

TABLE 9.3
Typical Sulfurized Products for Greases

Type	Total Sulfur	Active Sulfur	Features
Triglyceride	8–12	0.5–3	Mainly inactive, limited EP performance
Triglyceride	13–15	4–7	Mainly active, hard to mask Cu corrosion long term, good EP
Olefin	45	10–15	High EP performance, very distinct odor, only for encapsulated systems
Triglyceride/olefin	15	4	Mainly inactive, high EP performance
Ester	9–11	1–3	Mainly inactive, limited EP performance, excellent low-temperature pumpability

9.5.3.1 Industrial Gear Oils

Typical sulfur carriers for this application are short-chain sulfurized olefins. Sulfurized Isobutene (SIB) or Sulfurized Diisobutene are widely used as EP additive in industrial gear oils. SIB is used for some decades as the EP additive of almost all industrial gear oil packages. The high sulfur content, combined with a relative low active sulfur level, is ideally suited to match the requirements. Unfortunately, these products have a very distinct odor and, depending on the manufacturing process, can contain chlorine compounds. Newer developments are based on sulfurized olefins with a longer chain length. Specialty products with additional demands on lubricity are based on sulfurized triglycerides or mixtures of sulfurized olefins and triglycerides.

9.5.3.2 Slideway Oils

Slideway oils are a special type of gear oils with very good anti-stick-slip properties. Besides the austere requirements on coefficient of friction, there are also demands on compatibility and demulsibility with metalworking emulsions. Inactive sulfurized triglycerides are suitable to reduce the coefficient of friction. Unfortunately, most of these products are easy to emulsify and will, therefore, not meet the requirements on demulsibility without extensive formulation work. Modern slideway oils are based on demulsifying sulfurized olefin/triglyceride-based products that have the advantages of low coefficient of friction, good demulsibility, and high EP loads.

9.5.3.3 Hydraulic Fluids

It is possible to use inactive sulfur carriers in hydraulic systems with only moderate requirements on thermal stability. Typical products are sulfurized olefins and triglycerides or mixtures thereof.

9.5.3.4 Multifunctional Lubricants

Multifunctional lubricants cover more than just one lubrication application. There are increasing demands for this lubricant type, especially in metalworking shops. As one lubricant will be used for different applications with sometimes very different requirements, it is important that multifunctional additives are used. Depending on the overall performance requirements, sulfur carriers are used as EP, AW, or lubricity additive (see Tables 9.1 and 9.2). Multifunctional lubricants are almost always a compromise in their formulation. For example, metalworking machines with combined gear oil/process oil sump require a fine-tuned additive, especially on the EP side. Sulfur carriers with a medium activity, additionally passivated with sulfur scavengers, are widely used for this application.

9.5.3.5 Agricultural Applications

Lubricants in agricultural applications can be spilled on soil because of either the machine design or leaks in hydraulic and gear systems. Therefore, there are increasing requirements on environmentally compatible or less harmless lubricants. Sulfurized products are ideally suited for this type of applications. They can be designed to meet performance and ecological requirements (e.g., biodegradability). A wide range of lubricants exists for outdoor equipment based on vegetable oils (e.g., soybean, canola, rapeseed, and sunflower oil).

Sulfur carriers for these applications are mainly based on vegetable oils and synthesized in strictly controlled manufacturing processes.

Typical sulfur carriers for agricultural applications are shown in Table 9.4.

9.5.3.6 Automotive Applications

It is disclosed in U.S. Patent Nos. 4,394,276 and 4,394,277 that various sulfur-containing alkane diols may be formulated with lubricating oils to effectively reduce fuel consumption in an internal combustion engine. Sulfurized products in general and inactive sulfurized, oxidatively stable

TABLE 9.4
Sulfur Carriers for Agricultural Applications

Sulfur Carrier Type	Application
Ester, inactive	Gear greases (NLGI class 000), cotton picker spindle lubricants
Triglyceride, inactive	Gear lubricants, hydraulic fluids, greases for bearing lubrication, chassis lubricants
Triglyceride, medium-active	Gear lubricants, chain saw, and bar saw lubricants
Olefin, inactive	Gear greases (NLGI class 000), cotton picker spindle lubricants
Triglyceride/olefin, inactive	Gear lubricants, hydraulic fluids, greases for bearing lubrication, chassis lubricants

TABLE 9.5
Synergistic Effect of ZnDTP on Copper Corrosion (ASTM DISO)

Type	Total Sulfur	Active Sulfur	Treatment Level (%)	Cu Corrosion 3 h at 100°C	Cu Corrosion (+1.5% ZnDTP ^a) 3 h at 100°C
Triglyceride	18	10.5	5	4c	3b
Ester	17	8.5	5	3b	1b
Triglyceride	15	5	5	3a	1b

^a Thermally stabilized zinc dialkyldithiophosphate based on 2-ethylhexyl alcohol.

olefins in particular are known to reduce friction efficiently in engines. They provide not only AW and antifriction but also antioxidation properties. However, they cannot substitute the multifunctional zinc dialkyldithiophosphates in this application.

Besides crankcase applications, the use of sulfurized products in automotive gear lubricants is far more important. Since the middle of the twentieth century, almost every gear lubricant for automotive applications has been formulated with SIB.

The advantages of SIB are its high sulfur content, oxidation stability, and low corrosivity, but the very distinct odor and the low lubricity are its disadvantages.

Sulfurized esters and triglycerides are used in special transmission fluids to adjust the stick-slip properties. These sulfur carriers are also used in other lubricants in the automotive area such as wheel bearing or CVJ grease.

9.5.4 SYNERGIES/COMPATIBILITY WITH OTHER ADDITIVES

Sulfurized products are compatible with most of the additives used in lubricants. Only strong acids and bases must be avoided in combination with sulfur carriers.

9.5.4.1 Zinc Dialkyldithiophosphates

ZnDTPs are used in combination with sulfurized products in various applications. Besides their primary functions as AW and AOs, there is a well-known synergistic effect in regard to stabilization and improvement of copper corrosion of sulfur carriers. This behavior is demonstrated in the ASTM D-130 copper corrosion test (Table 9.5).

In addition, ZnDTP can have a very positive effect on the odor of sulfur carriers.

9.5.4.2 Basic Alkali Metal Salts

Sulfurized products show a very strong synergistic effect in combination with basic alkali metal salts [43], often referred to as overbased sulfonates or carboxylates. Particularly, active sulfur in combination with overbased calcium or sodium sulfonates exhibits advantageous performance with regard to improved load-carrying and AW properties. These additive combinations are used in lubricants for severe metalworking operations.

It is disclosed in International Patent WO 87/06256 [41] that the load-bearing characteristics of a grease composition and gear lubricant may be unexpectedly improved by formulating these compositions with an additive mixture comprising overbased salts of alkaline earth metals or alkali metals and at least one sulfurized organic compound. From today's point of view, the overbased products/sulfur combination has its advantages in some stainless steel cutting and forming operations. But the high alkalinity of such formulations shows big compatibility problems when in contact with lubricity esters and other types of acidic additives. Alkaline washing baths get used up quickly and need much more frequent changes as calcium soaps built up. Welding without cleaning the metal surface is also impossible as the high TBN sulfonates are generating high amounts of oxide ash.

9.5.4.3 Antioxidants

Inactive sulfur carriers show a synergism with aminic AOs. This effect is very distinct in low or even sulfur-free base fluids. Active sulfurized products do not show this synergy. On the contrary, the active types deteriorate the oxidation stability. Table 9.6 demonstrates the oxidation stability (ASTM D-2270, RPVOT Test) of active and inactive sulfur carriers based on the same raw materials.

The inactive product improves the oxidation stability (250 min) twice as much as the active type (120 min). In combination with the aminic AOs, the synergistic effect is obvious. Although the inactive sulfur carrier improves the AO properties of the aminic AO, the active type has a detrimental effect and reduces the oxidation stability.

9.5.4.4 Esters/Triglycerides

Esters are used either as base fluids or as additives. It is important to coordinate ester type and sulfur chemistry to achieve optimum performance. Unsaturated esters show strong synergistic effects with active sulfur, whereas inactive sulfur shows distinct synergies with saturated esters. The performance of sulfur carriers in saturated esters is similar to their performance in mineral oil. These synergies are widely used in the formulation of lubricants.

Combinations of active sulfur and unsaturated esters or triglycerides (mainly vegetable or animal oils such as canola, rapeseed, tall, sunflower oil, and esters thereof) are very common in all types of metalworking fluids, in oils, as well as in water-based systems. The combination of these products shows better EP and AW properties than the single components. This performance is illustrated in the four-ball test (see Table 9.7).

TABLE 9.6
Synergistic Effect of ZnDTP on Copper Corrosion

Base Oil	1.0% Inactive	1.0% Active
Hydrocracked, Dewaxed, No Sulfur (min)	Olefin, 20% S, 5% active S (min)	Olefin, 39% S, 30% active S (min)
Base oil	40	250
0.2% Aminic AO (alkylated diphenylamine)	400	135

TABLE 9.7
Esters, Synergistic Effect on EP and AW

Sulfurized Olefin 40% S, 36% active	TMP Oleate	Four-Ball Weld Load DIN 51350 Part 2 (N)	Four-Ball Wear Scar DIN 51350 Part 3 (mm)
1.5%	—	2800	0.8
—	5.0%	800	0.6
1.5%	3.5%	3200	0.55

Other applications for the combination of active sulfur and unsaturated ester are heavy-duty gear oils in agricultural applications and environmentally-friendly chain saw and bar saw lubricants (see Section 9.5.3.5).

If Cu corrosion presents a problem, the use of medium active sulfurized products in combination with unsaturated esters is of advantage. Some of these sulfur carriers are active enough to create the synergistic effects, but their Cu corrosion can be controlled with suitable yellow metal inhibitors.

Besides the improvement of EP and AW performance, inactive sulfur carriers can boost the AO properties.

Saturated esters are used where good oxidation stability is required. The performance of sulfurized products in saturated esters is comparable to the performance in mineral oil. Inactive sulfurized olefins and sulfurized triglycerides, and mixtures thereof, are typically used as additives in lubricants based on saturated esters.

9.5.5 COST-EFFECTIVENESS

Sulfurized products cover the whole range from relative cheap commodity to high-price specialty. Depending on the type and treatment level, sulfurized products can be a major cost factor in lubricants. However, the use of sulfur carriers enables us to run processes and to overcome lubrication problems that cannot be solved in a cost-efficient way with other additives. For example, it is possible to increase machine speeds and thus productivity while using appropriate sulfur carriers instead of esters or chlorinated paraffins. Depending on the type of sulfur carrier, other commonly used additives in a formulation, for example, esters or yellow metal deactivators, can be saved. In comparison with heavy-metal- or chlorine-containing lubricants, the disposal costs for the used lubricant can be much lower.

Besides direct cost savings, respectively, cost efficiency due to higher productivity and lower disposal costs, there are secondary cost factors. In comparison with some traditionally used EP additives such as chlorinated paraffins (HCl-formation > rust), overbased sulfonates (difficult degreasability, incompatibility with other additives), or heavy-metal-containing additives (residue formation), sulfurized products show, in general, lower cost-effective side effects.

9.6 MANUFACTURE AND MARKETING ECONOMICS

9.6.1 MANUFACTURERS

- Afton, United States
- Arkema, France
- DAI Nippon Inc., Japan
- DOG-Chemie, Germany
- Dover Chemical Corp., United States
- Elco, United States
- Harrison Manufacturing Company, Australia
- Hornett, United Kingdom

Lubrizol, United States
Miracema Nuodex, Brasil
PCAS, France
Rhein Chemie, Germany

Additionally, there are some lubricant manufacturers who still sulfurize dark-colored products for their own use, and some local sulfurization plants also sulfurize commodity-type products.

9.6.2 MARKETERS

In general, the manufacturers are also marketing the products. Some local manufacturers buy sulfurized products, blend them with esters, mineral oil, etc., and sell them under their own brand name. Sulfur carriers are intermediate and not consumer products.

9.6.3 ECONOMICS

Market prices vary depending on the raw materials, the production process, and the performance level of the products. Low-quality, dark sulfurized fats with distinct odor and limited stability sell for less than U.S.D 1.6/kg. High-performance, top-quality, low-odor, light-color products achieve prices of more than U.S.D 4.0/kg. Not only the raw materials, but much more the production process, determine the price for a sulfurized product. For example, the sulfurization of a typical gear oil sulfur carrier with di-sulfur-di-chloride and the necessary subsequent washing steps are more costly than the sulfurization of a fat with flower of sulfur.

9.6.4 GOVERNMENT REGULATIONS

9.6.4.1 Competitive Pressures

There are no government regulations concerning the use of sulfurized products, but depending on the location of the manufacturing plant, very stringent regulations and conditions concerning emission standards can apply. Therefore, there is a competitive distortion in production between more and less environmentally aware countries. Production technology and in particular low-emission production are key cost factors.

9.6.4.2 Product Differentiation

Apart from some commodities, there is a clear product differentiation mainly derived from quality and performance. A first criterion for differentiation is color, followed by sulfur content, raw materials, and odor. A classification is hardly possible because many of the products are tailor-made either to cover a specific performance profile or to meet specifications in various applications. A simple categorization by sulfur content or raw material bases would be too coarse and would not take performance into account. Even products based on the same raw materials but manufactured with a different process can be completely different in performance.

Modern, light-colored, high-performance products with low odor are sulfurized using H_2S or mercaptans. Even the appearance distinguishes these products from conventionally sulfurized dark-colored, smelly products.

9.7 OUTLOOK

9.7.1 CRANKCASE/AUTOMOTIVE APPLICATIONS

Steady demands on the reduction of phosphorus levels in motor oils as well as requirements for increased fuel efficiency, that is, friction reduction will open new opportunities for sulfur chemistry. Sulfurized products are already used in this type of application (see Section 9.5.3.6).

9.7.2 INDUSTRIAL APPLICATIONS

Multifunctional and multipurpose lubricants are on the wish list of many end users. The development for sulfurized products that can be used in these types of lubricants is in full progress, and the products have already been commercialized. Mainly light-colored products based on mixed, well-balanced raw materials to ensure a broad performance range are used for multipurpose applications.

Replacement of heavy metals and chlorinated paraffins in almost all industrial lubricants is also an ongoing project that is widely found in the lubricants industry. Sulfur carriers are playing a predominant role as substitutes for these products.

Increasing demands for environmentally more acceptable lubricants has led many formulators into the development of lubricants based on natural triglycerides such as canola oil, soybean oil, tall oil, or esters. Biodegradable sulfur carriers are used as EP and AW additives as well as secondary AOs in these applications.

9.8 TRENDS

9.8.1 CURRENT EQUIPMENT/SPECIFICATION

Sulfurized products are single components and not complete performance packages such as hydraulic or crankcase packages. Therefore, sulfur carriers are used in the whole variety of lubricants rather than in a specific equipment. Also, no national or international specification standards exist for these products. The manufacturer sets the specification in agreement with the user.

9.8.1.1 Types of Equipment

As already mentioned, the biggest use of sulfurized products (excluding SIB) is in industrial applications. Metalworking and grease applications followed by industrial gear oils are formulated with sulfur carriers. A lot of old equipment is still in use. Many mid-size and small companies have not modernized their metalworking machines for more than three decades. This older, robust equipment is very often running at low machining speeds and nonoptimized machining parameters. Modern machining equipment requires thermally stable fluids, based on highly refined or synthetic base fluids. Improved solubility in nonpolar oils and thermal stability of sulfurized products gain importance.

9.8.1.2 Additives in Use

Today's additive usage depends very much on regional technological requirements and local legislation. In countries with low, old or standard technology and little environmental concerns, additives such as chlorinated paraffins or heavy metals are used for the formulation of lubricants, often in combination with sulfurized products. In countries where legislation has put some pressure onto the formulators and users of lubricants (higher disposal costs for chlorine-containing lubricants, limits on heavy metals in waste water, etc.), sulfurized compounds play an even more important role. They are the main EP additives, very often combined with sulfonates, salicylates, phosphoric acid esters, dialkyldithiophosphates, or carboxylic esters to complement AW and lubricity performance.

9.8.1.3 Deficiencies in Current Additives

All available sulfur carriers are limited in their thermal stability. This is a desired feature, because reactive sulfur will only be released when the molecule breaks down. However, there are applications running at a high temperature, where a fast decomposition of the EP product is not desired. Corrosion toward yellow metals is another deficiency of sulfurized compounds. In high-temperature applications, the active sulfur will react with copper to form copper sulfide.

9.9 MEDIUM-TERM TRENDS

In general, there is a trend toward higher economy and ecologically and toxicologically safe lubricants.

9.9.1 METALWORKING

Increased lubricant temperatures are a consequence of higher machine speeds, completely encapsulated machines, and reduced process steps. In the future, the thermal stability of metalworking lubricants and their toxicological safety will be on the focus. Owing to integrated applications (e.g., one lubricant for process and machine lubrication), the additives need to cover wide temperature ranges. The trend to replace multiple cutting steps with forming operations exists. Therefore, the type of additives will also change.

Minimum amount lubrication requires new lubricant concepts in regard of performance and marketing. Maintenance of lubricants will further be reduced. Again this trend calls for increased stability of additives.

Sulfurized products for metalworking application will need improved thermal stability in combination with good solubility in high paraffinic or even synthetic base fluids. Ecological and toxicological safety will be the basic requirements. Improved lubricity and excellent compatibility with process materials such as cleaners and paints will be essential for the formulation of modern lubricants for deformation processes (e.g., cold forging and deep drawing).

9.9.2 INDUSTRIAL OILS

Synthetic fluids such as PAOs, polyalkyleneglycols (PAGs), extra high VI mineral oils (XHVI), or synthetic esters are being used in increasing volumes for the formulation of high-performance industrial lubricants. Smaller lubricant sumps, reduced sizes of components, and increased performance will place high demands on the lubricants. Especially in mobile equipment (e.g., excavator and lawn mower), ecologically and toxicologically harmless lubricants will become a demand. Reduced maintenance and longer lubricant change intervals require high lubricant stability.

Improved thermal stability, low copper corrosion, and excellent solubility in synthetic fluids are demands on sulfurized products for the new generation of industrial lubricants.

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Part 4

Viscosity Control Additives

10 Olefin Copolymer Viscosity Modifiers

Michael J. Covitch

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10.1 INTRODUCTION

Olefin copolymer (OCP) viscosity modifiers are oil-soluble copolymers comprising ethylene and propylene and may contain a third monomer, a nonconjugated diene, as well. By virtue of their high thickening efficiency and relatively low cost, they enjoy a dominant share of the engine oil viscosity modifier market [1]. First introduced as a lubricant additive by Exxon in the late 1960s, the chemical

and physical properties of OCPs continue to evolve to achieve improvements in low-temperature rheology, thickening efficiency, and bulk handling characteristics.

Several excellent reviews of OCP viscosity modifiers have been published [1–3]. This chapter serves as an update and current compilation of information relating to the chemistry, properties, and performance characteristics of this important class of lubricant additives.

10.2 CLASSES OF OLEFIN COPOLYMERS

There are many ways to classify OCP viscosity modifiers. From a user's perspective, OCPs are marketed as either solids or liquid concentrates. The physical state of the solids depends on several factors, primarily on the ethylene/propylene (E/P) mass ratio. When E/P is in the 45/55–55/45 range, the material is amorphous and cold flows at room temperature. Thus, OCPs of this composition are most commonly sold as bales, packaged in rigid boxes to maintain bale shape. When E/P is higher than 60/40, the copolymer becomes semicrystalline in nature and does not cold flow under ambient conditions. Thus, both bales and pellets can be produced.

Liquid concentrates of OCP in mineral oil contain enough rubber to raise the kinematic viscosity (KV) to 500–1500 cSt (mPa s) range at 100°C. A typical viscosity/concentration relationship is shown in Figure 10.1.

From the preceding discussion, OCPs can also be classified according to crystallinity, which is measured by x-ray diffraction or differential scanning calorimetry. The influence of crystallinity on rheological performance will be discussed in Section 10.5.

Shear stability is another parameter by which OCP viscosity modifiers are categorized. The higher the molecular weight of a polymer, the more prone it is to mechanical degradation when elongational forces are imposed by the fluid flow field. This subject is dealt with in detail in Section 10.5.2.2.3.

Finally, chemical functional groups can be grafted to the OCP backbone, providing added dispersancy, antioxidant activity, and low-temperature viscosity enhancement. A number of chemical routes for functionalizing OCPs are described in Section 10.3.3.

10.3 CHEMISTRY

10.3.1 SYNTHESIS BY ZIEGLER–NATTA POLYMERIZATION

Although methods for synthesizing high-molecular-weight polymers of ethylene were commercialized in the 1930s (the Imperial Chemical Industries (ICI) PLC, currently a division of AkzoNobel high-pressure process), the polymers contained a significant number of short- and long-chain

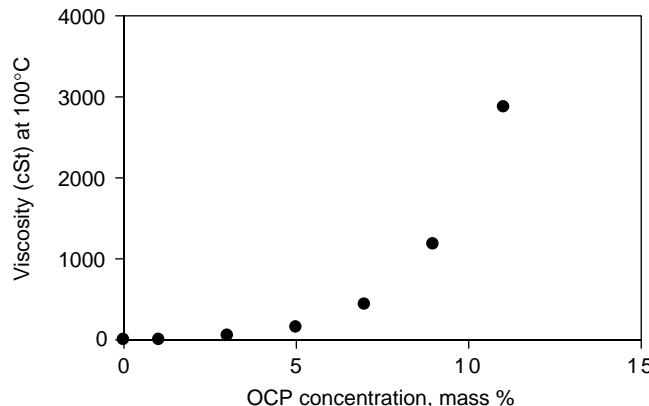


FIGURE 10.1 Kinematic viscosity of 50 permanent shear stability index (PSSI) amorphous OCP dissolved in 100N mineral oil. (Minick, J., A. Moet, A. Hiltner, E. Baer and S.P. Chum, *J. Appl. Poly. Sci.*, 58, 1371–1384, 1995. Reprinted with permission of John Wiley & Sons, Inc.)

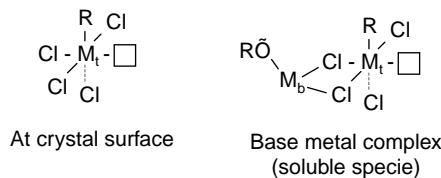


FIGURE 10.2 Active center in Ziegler–Natta catalysts. M_t = transition metal (such as Ti); M_b = base metal (such as Al). (Adapted from Boor, J., Jr., *Ziegler-Natta Catalysts and Polymerizations*, Academic Press, New York, 1979.)

branches that limited the ability to produce high-density polyethylene. The first commercially viable synthesis of linear polyethylene at low monomer pressure was pioneered by Ziegler in 1953, and the stereoregular polymerization of α -olefins was demonstrated by Natta the following year [4]. The secret to their success was the discovery of catalysts (called Ziegler or Ziegler–Natta catalysts), which are molecular complexes between halides and other derivatives of group IV–VIII transition metals (Ti, V, Co, Zr, and Hf) and alkyls of group I–III base metals. A typical catalyst of this type comprises an aluminum alkyl and a titanium or vanadium halide having the general structure shown in Figure 10.2. Electron donors, such as organic amines, esters, phosphines, and ketones, may be used to enhance reaction kinetics. Finally, molecular weight control is often aided by the use of chain transfer agents such as molecular hydrogen or zinc alkyls [5], which are effective in terminating chain growth without poisoning the active metal center.

Ziegler–Natta polymerization is probably the best-known example of insertion, coordination, stereoregular, or stereospecific polymerization. This nomenclature has been adopted to describe the mechanism(s) by which olefin monomers insert into the growing polymer chain, as directed by both steric and electronic features of the coordination catalyst. A commonly accepted chain propagation mechanism involves monomer insertion at the transition metal–carbon bond [4]. The main purpose of the base metal alkyl is to alkylate the transition metal salt, thus stabilizing it against decomposition. As pointed out by Boor [4], Ziegler–Natta catalysts may be modified to produce copolymers with varying degrees of randomness or, from a different perspective, blockiness of one or both comonomers. Owing to the higher reactivity ratio of ethylene to that of propylene [4–7], the formation of long runs of ethylene is more favored than long sequences of propylene. This is substantiated by ^{13}C NMR spectroscopy [8–13].

Ziegler–Natta catalysts are available in two forms—heterogeneous and homogeneous. Heterogeneous catalysts are insoluble in the reaction medium and are suspended in a fluidized-bed configuration. Reaction takes place at the exposed faces of the metal complex surface. Since each crystal plane has a slightly different atomic arrangement, each will produce slightly different polymer chains in terms of statistical monomer insertion and molecular weight distribution. Thus, they are often called multisite catalysts. Homogeneous Ziegler–Natta catalysts are soluble in the reaction solvent and, therefore, function more efficiently since all molecules serve as potential reaction sites. Since the catalyst is not restrained in a crystalline matrix, it tends to be more “single-site” in nature than heterogeneous catalysts. Polymers made by homogeneous polymerization generally are more uniform in microstructure and molecular weight distribution and, therefore, are favored for use as viscosity modifiers [1,4].

Nonconjugated dienes are often used in the manufacture of ethylene–propylene copolymers (known as EPDMs–Ethylene Propylene Diene Monomer) to provide a site for cross-linking (in non-lubricant applications) or to reduce the tackiness of the rubber for ease of manufacture and handling. Certain dienes promote long-chain branching [2,5,14,15] that, in turn, increases the modulus in the rubber plateau region. The terpolymer is then easier to handle as it is dried and packaged [1]. A disadvantage of long-chain branching is that it reduces the lubricating oil thickening efficiency relative to a simple copolymer of similar molecular weight and copolymer composition, although low levels of vinyl norbornene or norbornadiene are claimed [15] to improve cold flow without loss in thickening efficiency or shear stability.

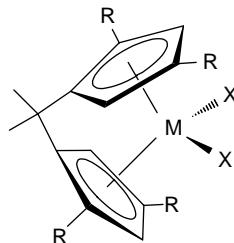


FIGURE 10.3 Chemical structure of generalized bridged bis-cyclopentadienyl metallocene catalyst. M is a group IVB transition metal; X is a halogen or alkyl radical. (Rubin, I.D. and A. Sen, *J. Appl. Polym. Sci.*, 40, 523–530, 1990. Reprinted with permission of John Wiley & Sons, Inc.)

10.3.2 SYNTHESIS BY METALLOCENE POLYMERIZATION

The desire to achieve higher levels of control over stereoregularity, composition, and molecular weight distribution led to the development of activated metallocene catalysts. Although known to Zieger and Natta, the technology was rediscovered by Kaminsky and Sinn in 1980 and further developed by workers such as Brintzinger, Chien, Jordan, and others [16–20]. Metallocene catalysts consist of compounds of transition metals (usually group IVB: Ti, Zr, and Hf) with one or two cyclopentadienyl rings attached to the metal. The most common activator is methylaluminoxane (MAO). A large number of variants have been reported, but the highest levels of stereospecificity have been achieved with bridged, substituted bis-cyclopentadienyl metallocenes (Figure 10.3) [21]. One of the major advantages of metallocenes over Ziegler–Natta catalysts is the ability to incorporate higher α -olefins and other monomers into the ethylene chain.

The first commercial use of metallocene single-site catalysts to manufacture EPDM elastomers was DuPont Dow Elastomers' Plaquemine, LA facility, which began operation in 1996 using Dow's Insite® constrained geometry catalyst [22,23]. The catalyst is described as “monocyclopentadienyl Group 4 complex with a covalently attached donor ligand ... requiring activation by strong Lewis acid systems [such as] MAO...” Several advantages of this technology over conventional Ziegler–Natta processes were reported. Since the catalyst is highly efficient, less is needed; therefore, the process does not require a metal removal or de-ashing step. In addition, the copolymers produced by this chemistry are reported to have narrow molecular weight distributions for good thickening efficiency and shear stability as well as good control over copolymer microstructure. Metallocene-catalyzed polyolefins also differ from Ziegler–Natta polymers in that the former contains a predominance of unsaturated ethyldene end groups [24].

10.3.3 FUNCTIONALIZATION CHEMISTRY

Traditionally, OCPs are added to lubricating oil to reduce the degree to which viscosity decreases with temperature, that is, to function solely as a rheology control agent. Other lubricant additives—such as ashless succinimide dispersants, a variety of antioxidants, detergents, antiwear agents, foam inhibitors, friction modifiers, and anticorrosion chemicals—provide other important functions (dispersing contaminants, keeping engines clean, maintaining piston ring performance, preventing wear, etc.). It has been recognized for many years that it is possible to combine some of these performance and rheology control features on the same molecule. Some report that “both dispersant and antioxidant functionality may exhibit more potent activity when attached to the polymer backbone than in their monomeric form” [25]. Three hybrids have been commercialized, although many more have been disclosed in the patent literature.

They include dispersant OCPs (DOCPs), dispersant antioxidant OCPs (DAOCPs), and grafted OCPs (gOCPs). The addition of antiwear functionality has also been reported [25,26].

Although many grafting reactions have been described in the literature, two general classes have received the most attention. Free radical grafting of nitrogen-containing monomers or alkylmethacrylates onto the OCP molecule is one class. Nitrogen-containing monomers such as vinyl pyridines, vinylpyrrolidinones, and vinylimidazoles are often cited in the patent literature [28–33]. Free radical grafting with phenothiazine is claimed [28–33] to provide antioxidant functionality as well. The grafting reaction may be conducted with the OCP molecule dissolved in mineral oil or another suitable solvent [77,86,130,131]; alternately, solvent-free processes have been disclosed [28–33] in which the reaction is conducted in an extruder.

Mixtures of alkylmethacrylate monomers, which are typical of those found in poly(alkyl methacrylate) (PMA) viscosity modifiers, may be grafted to OCPs [34] to provide improved low-temperature properties. Adding nitrogen-containing monomers to the alkylmethacrylate mixture provides dispersancy characteristics as well. A common side reaction is homopolymerization, which can be minimized by process optimization. Homopolymers of nitrogen-containing monomers are usually not very soluble in mineral oils and often lead to hazy products and can attack fluoroelastomer seals. Homopolymers of alkylmethacrylates are fully soluble in oil, however. Thus, optimizing the grafting process is much more critical when working with nitrogen-containing monomers.

A second class of grafting reactions involves two steps [25,35–47]. In the first step, maleic anhydride or a similar diacyl compound is grafted onto the OCP chain, assisted by free radical initiators, oxygen, and heat [54,77,86,130,131]. In the second step, amines and alcohols are contacted with the anhydride intermediate to create imide, amide, or ester bonds. In many respects, this chemistry is very similar to that used to create ashless succinimide dispersants. An advantage of this approach over free radical monomer grafting is that homopolymerization is avoided. The patent literature describes a related functionalization process in which free primary or secondary nitrogens of highly basic succinimide dispersants may be used to couple preformed dispersants to the maleic anhydride-grafted OCP molecule [49–52]. Amine derivatives of thiadiazole, phenolic [25], and amino-aromatic polyamine [53,54] compounds have been reacted with maleic anhydride-grafted OCP to provide enhanced antioxidant character to the additive [25].

Although maleic anhydride is the most common chemical “hook” for attaching functional groups to OCP polymers, a number of other approaches have been reported [55–61]. Further elaboration is beyond the scope of this chapter.

Another approach for attaching functionality to the OCP chain is through the nonconjugated diene in the terpolymer [26,62]. For example, 2-mercaptop-1,3,4-thiadiazole is attached to the ethylenenorbornene site on an EPDM polymer through addition of the thio group across the ethylenedene double bond. The thiadiazole group is claimed to provide antiwear, antifatigue characteristics to lubricants containing the grafted OCP.

10.4 MANUFACTURING PROCESSES

Two polymerization processes have been used for the manufacture of E/P copolymer viscosity modifiers: solution and slurry. In the solution process, the gaseous monomers are added under pressure to an organic solvent such as hexane, and the polymer stays in solution as it forms. By contrast, the slurry or suspension process utilizes a solvent such as liquid propylene in which the resultant copolymer is not soluble. It is reported [63] that removing the catalyst residue from the polymer is more difficult in the slurry process, although some contend [27] that the levels of catalyst are so low that catalyst removal is not necessary.

Ethylene-propylene rubber was reported [64] to have been successfully manufactured in a fluidized-bed gas-phase reactor. However, the use of fluidization aids such as carbon black is necessary to process low-molecular-weight grades that are typical of lubricating oil viscosity modifiers. Thus, the gas-phase process is not appropriate for manufacturing OCP viscosity modifiers.

10.4.1 SOLUTION PROCESS

The most common method for manufacturing OCP viscosity modifiers is the solution process as described in Figure 10.4 [65]. It is made up of four sections—polymerization, polymer isolation, distillation, and packaging. In the polymerization section, monomers, an organic solvent such as hexane, and a soluble catalyst are introduced into a continuously stirred polymerization reactor. During polymerization, the polymer remains in solution and causes the bulk viscosity of the reaction medium to increase. To maintain good agitation, monomer diffusion, and thermal control, polymer concentration in the polymerization reactor is typically limited to 5–6 wt% [27]. Up to five reactors arranged in series have been reported in the literature [66]. The effluent from the last reactor is contacted with an aqueous shortstop solution to terminate polymerization and wash away the catalyst, although this step is often omitted when using metallocene catalysts due to their high reactivity and, therefore, low concentration [22]. While the copolymer is still in solution, extender oils or antioxidants can be added.

In the isolation section, three techniques have been described in the literature. In the most common method (shown in Figure 10.4), the polymer is flocculated with steam, and the solvent and unreacted monomers are recovered, purified, and recycled. The aqueous polymer slurry is mechanically dewatered, granulated, and air-dried. A second nonaqueous method for isolating the polymer has been described in which the polymer is concentrated in a series of solvent removal steps [67,68]. The final step may be conducted in a devolatilizing extruder. A third technique does not isolate the polymer as a solid; rather, it mixes the polymer solution into mineral oil and distills off the solvent, producing a finished liquid OCP product [2].

Another type of solution polymerization process that has received a great deal of attention has been Exxon's tubular reactor technology. Its purpose is to generate a polymer with long blocks differing in monomer composition for improved performance as a viscosity-improving polymer [3,69–71]. A schematic of this process is shown in Figure 10.5. Monomers and solvent are premixed

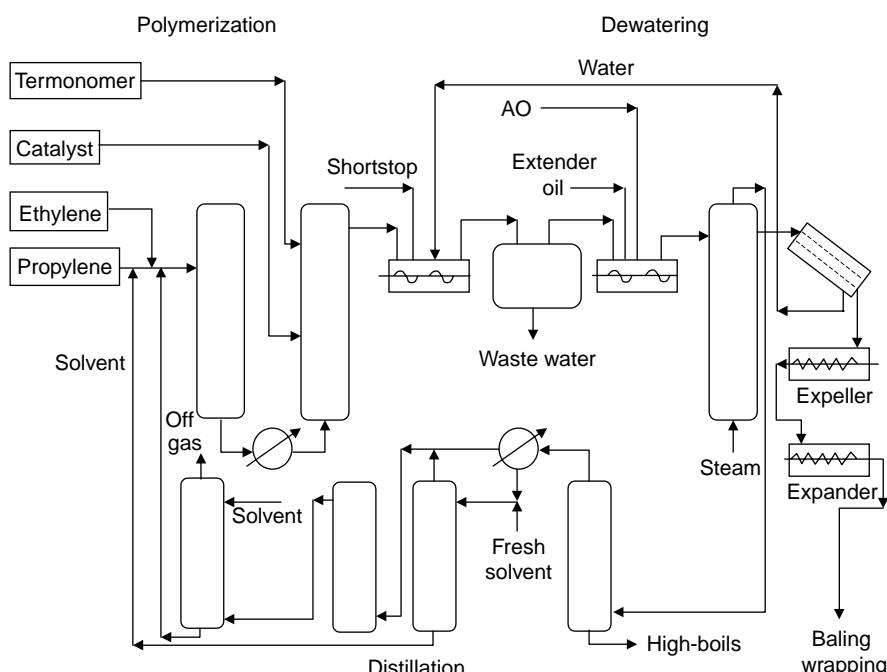


FIGURE 10.4. Solution process for manufacturing EPDM. (Adapted from *Hydrocarbon Processing*, 164, November 1981.)

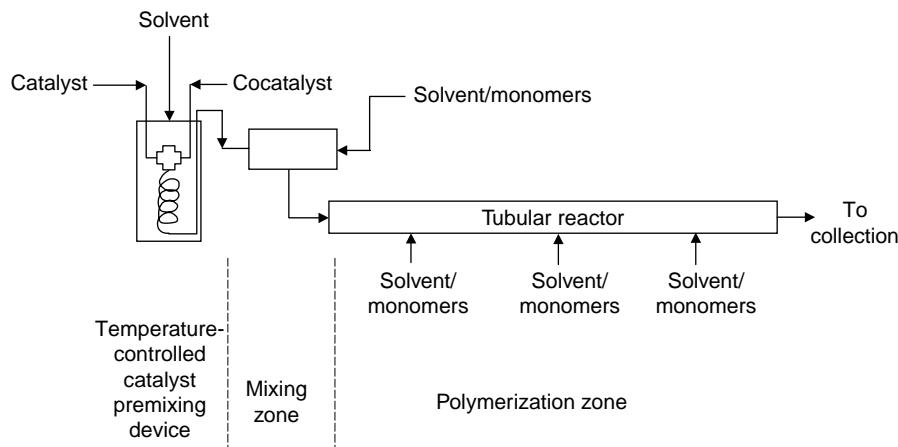


FIGURE 10.5 Tubular reactor process for preparation of multiblock ethylene–propylene copolymers. (U.S. Patent 4874820, 1989; U.S. Patent 4804794, 1989; U.S. Patent 5798420, 1998.)

with a highly active Ziegler–Natta polymerization catalyst and metered into a plug flow reactor under conditions that minimize chain transfer and termination reactions. Ethylene or propylene is injected into the tube at different points to adjust the local monomer concentration and, thereby, the monomer composition along the growing polymer chain. In comparing the rheological properties of different A-B-A type block compositions, Ver Strate and Struglinski reported [12] that “chains with high ethylene section in the center of the chain … associate at low temperature with little intermolecular connectivity.” When the high ethylene (crystallizable) segments are at the ends, polymer networks can form at low temperatures, which can impart a gelatinous texture to the solution.

10.4.2 SUSPENSION PROCESS

Ethylene and a nonconjugated diene, if desired, are contacted with liquid propylene, which acts both as a monomer and a reaction medium [27,72]. In the presence of a suitable catalyst, polymerization takes place rapidly, producing a suspension of copolymer granules that are insoluble in the reaction medium. The heat liberated during the polymerization reaction is dissipated by propylene evaporation, thus providing a convenient mechanism for temperature control. In addition, since the polymer is not soluble in the reaction medium, viscosity remains low. Thus, relative to typical solution processes, the polymer concentration in a suspension reactor can be five to six times higher. Upon exiting the polymerization reactor, the polymer suspension is contacted with steam to strip off unreacted propylene that is then recycled. According to Corbelli and Milani [72], the Dutral® process does not include a catalyst washing step. The copolymer product, in aqueous suspension, is dewatered, dried, and packaged in a similar fashion to polymer made by the solution process.

10.4.3 POSTPOLYMERIZATION PROCESSES

There are two main types of packaging processes in practice today [64]. In one, the isolated polymer is mechanically compressed into rectangular bales. The bales are often wrapped in a polyolefin packaging film to prevent the bales from adhering to one another during storage and foreign matter from sticking to the tacky rubber surface. Typical types of polyolefins films include poly(ethylene-co-vinyl acetate), low-density polyethylene, and ethylene/α-Olefin Copolymers (OCP). Another method for packaging solid OCP rubber is to extrude the polymer, pass the melt stream into a water-cooled pelletizer, and dry the final product. The pellets may be packaged in bags or boxes or may be compressed into rectangular bales.

The mechanical properties of the rubber often dictate what type of isolation and packaging processes are the most appropriate. Amorphous Ethylene propylene (EP) copolymers are often too sticky to successfully traverse the conventional flocculation/drying/baling process. One way to modify these compositions to improve their handling characteristics is by introducing long-chain branching [5,48,73] through the use of low concentrations of nonconjugated dienes or other branching agents. For nonfunctionalized OCPs, this is the main reason that some commercial viscosity modifiers contain dienes [2]. Copolymer compositions higher in ethylene content (>60 wt% [5]) are often semicrystalline and may be amenable to packaging in pellet form. In some cases, the pellets may contain an anticaking or antiblocking agent to prevent agglomeration.

Another type of manufacturing process has been used to manufacture low-molecular-weight OCP viscosity modifiers that are difficult to isolate and package in conventional equipment. A higher-molecular-weight feedstock of the appropriate composition may be fed into a masticating extruder or Banbury mixer to break down the polymer chain to lower-molecular-weight fragments using a combination of heat and mechanical energy [74–81]. Several patents describe the use of oxygen [82–85] or free radical initiators [86,87] to enable this process.

10.4.4 MAKING THE OCP LIQUID CONCENTRATE

After the solid OCP viscosity modifier has been manufactured, it must be dissolved in oil before it can be efficiently blended with base stocks and other additives. The first stage entails feeding the rubber bale into a mechanical grinder [2] and then conveying the polymer crumb into a high-quality diluent oil that is heated to 100–130°C with good agitation. The rubber slowly dissolves, raising the viscosity of the oil as shown in Figure 10.1. Certain high-intensity homogenizers can also be used in which the entire rubber bale is fed directly into a highly turbulent diluent oil tank at high temperature; this bypasses the pregrinding step.

When the solid polymer is supplied in pellet form, the rubber can be fed directly into hot oil, or, if it is slightly agglomerated, it may first be passed through a low-energy mechanical grinder.

10.5 PROPERTIES AND PERFORMANCE CHARACTERISTICS

10.5.1 EFFECT OF ETHYLENE/PROPYLENE RATIO ON PHYSICAL PROPERTIES OF THE SOLID

The comonomer composition of E/P copolymers has a profound influence on the physical properties of the rubber. These properties, in turn, dictate the type of containers in which the product can be stored and how it is handled during distribution and use.

^{13}C NMR has been used extensively to characterize the sequence distribution of EP copolymers [88–93]. As the ratio of E/P increases, the fraction of ethylene–ethylene (EE) sequences (dyads) rises, as demonstrated by the data in Figure 10.6. Concurrently, the total fraction of E/P dyads decreases (forward and reverse propylene insertion are designated as p and p^* , respectively). Thus, the average length of contiguous ethylene increases with ethylene content. Above ~60 wt% ethylene, these sequences become long enough to crystallize, as measured by differential scanning calorimetry (Figure 10.7) or x-ray diffraction.

When the degree of crystallinity exceeds ~25%, EP copolymers become unsuitable as viscosity modifiers due to limited solubility in most mineral oils. As the propylene content approaches zero, the copolymer takes on the physical characteristics of high-density polyethylene, which, due to its inertness to oil, is used as the packaging material of choice for engine oils and other automotive fluids. Microstructural investigations of metallocene ethylene/ α -OCPs by Minick et al. [94] concluded that the relatively short ethylene sequences of low-crystallinity (<25%) samples are capable of crystallizing into fringed micelle or short-bundled structures (Figure 10.8). Higher-order morphologies such as lamellae or spherulites are not observed. Therefore, the physical properties of semicrystalline OCPs fall in between those of polyethylene and amorphous EP rubber.

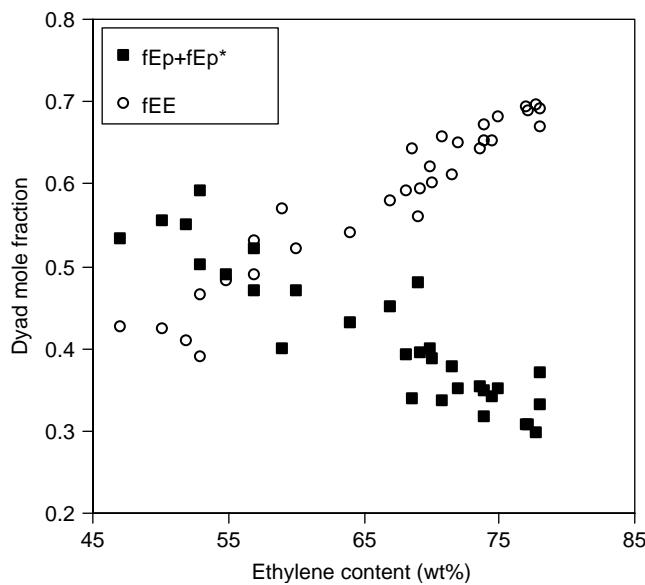


FIGURE 10.6 The effect of ethylene content (wt% as measured by NMR) on ethylene–ethylene (EE) and ethylene–propylene (EP) dyad concentration.

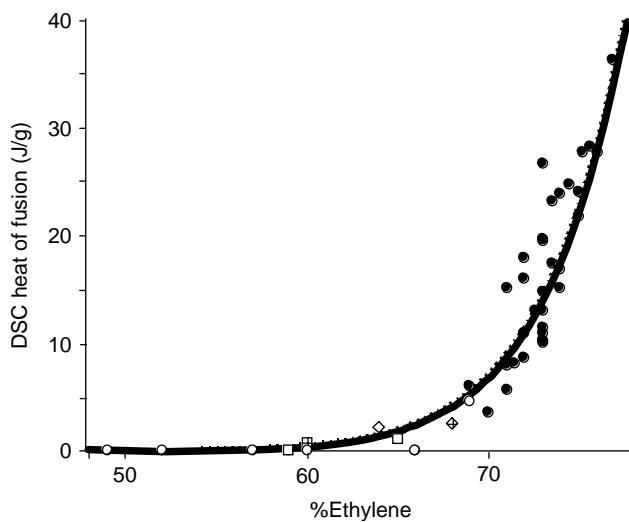


FIGURE 10.7 The effect of ethylene content (wt%) on crystallinity as measured by differential scanning calorimetry (DSC) for a range of experimental EPDM copolymers.

Polyethylene is a rigid, high-modulus solid at room temperature. Amorphous E/P rubber is a relatively soft material under ambient conditions, which, cold, flows and exhibits a tacky feel. The degree of tack is inversely proportional to its molecular weight and can be reduced by the incorporation of long-chain branching. Solid bales of this type of rubber are easily compressed and further densify during storage. Semicrystalline OCPs hold their shape during storage but are slightly tacky to the touch. Higher compression pressures, longer compression times, and higher finishing temperatures are required to successfully produce dense bales. Typical physical properties of E/P copolymers are summarized in Table 10.1.

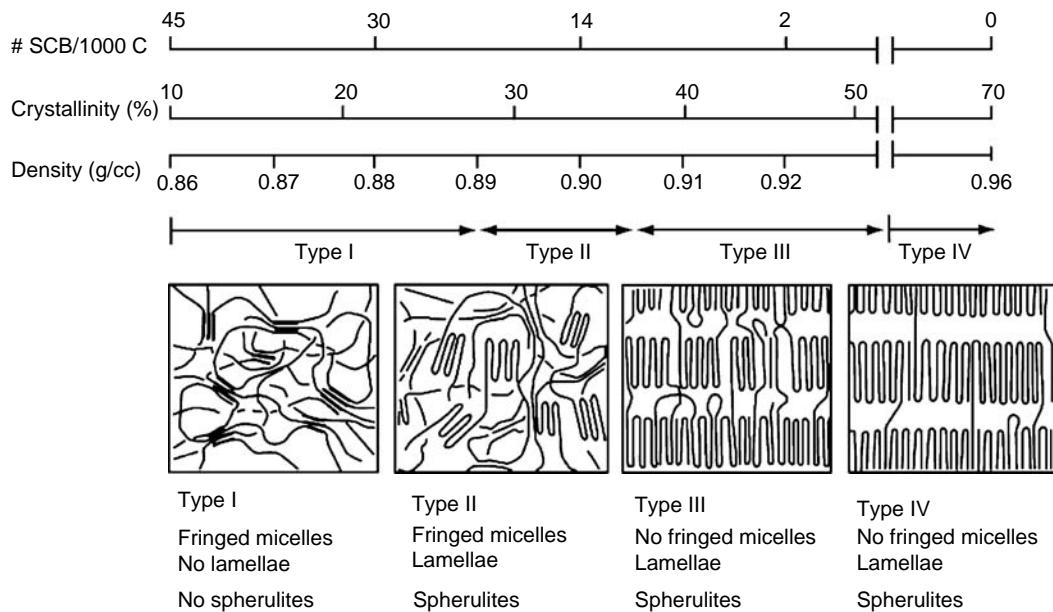


FIGURE 10.8 Schematic illustration of solid-state morphologies of four types of poly(ethylene-co-octene) copolymers. # SCB/1000 C is defined as the number of side chain branches per 1000 backbone carbon atoms. (Minick, J., Moet, A., Hiltner, A., Baer, E., and Chum, S.P., *J. Appl. Poly. Sci.*, 58, 1371–1384, 1995. Reprinted with permission of John Wiley & Sons, Inc.)

TABLE 10.1
Typical Physical Properties of Ethylene–Propylene Copolymers

Property	Typical Value
Density (kg/m ³)	860
Heat capacity (cal/g °C)	0.52
Thermal conductivity (cal/cm s °C)	8.5 × 10–4
Thermal diffusivity, (cm ² /s)	9.2 × 10–4
Thermal coefficient of linear expansion (per °C)	2.2 × 10–4

Source: Adapted from Corbelli, L., *Dev. Rubber Tech.*, 2, 87–129, 1981.

10.5.2 EFFECT OF COPOLYMER COMPOSITION ON RHEOLOGICAL PROPERTIES IN SOLUTION

10.5.2.1 Low-Temperature Rheology

Rubin et al. [95–101] and others [102] measured the intrinsic viscosity [η] of EP copolymers as a function of temperature in various solvents (Figure 10.9). Intrinsic viscosity, a measure of polymer coil size in dilute solution, is fairly insensitive to temperature for noncrystalline OCPs. Semicrystalline copolymers undergo a precipitous drop in [η] as temperature drops below ~10°C. In this region, the polymer begins to crystallize, forming intermolecular associations that effectively cause the molecule to shrink in on itself, yet remain sufficiently solvated to remain suspended in oil solution.

The viscosity of a dilute polymer solution often follows the Huggins equation [103]

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

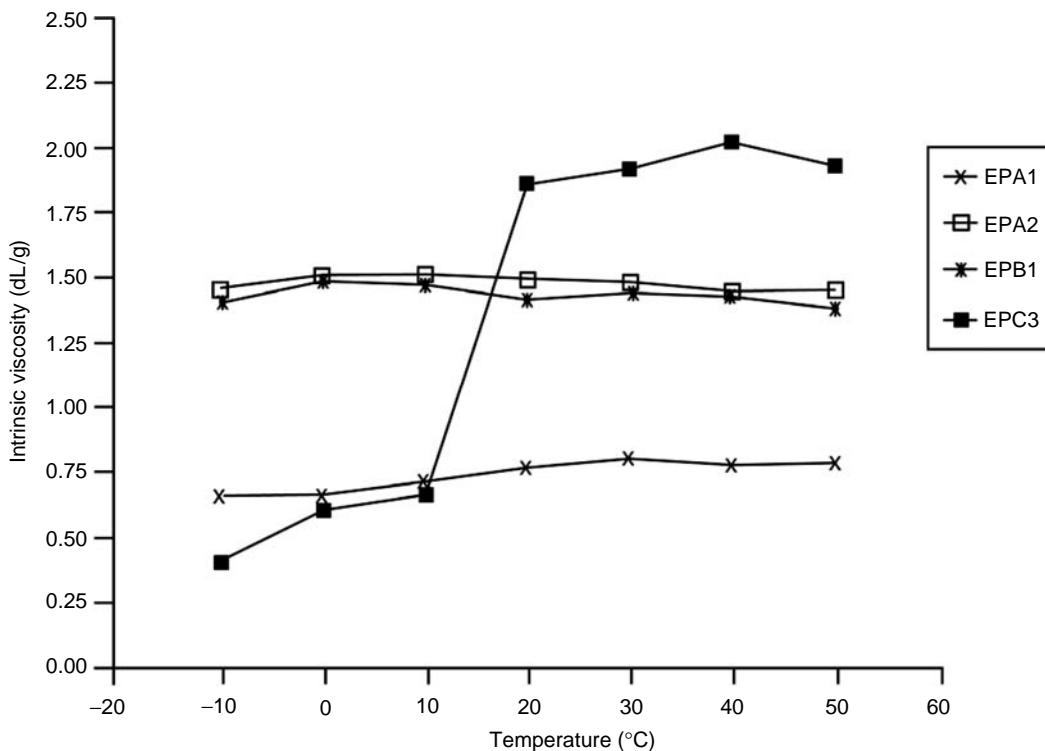


FIGURE 10.9 Intrinsic viscosities of EP copolymers in SNO-100 base oil at various temperatures. EPC3, EPB1, EPA2, and EPA1 have 73, 61, 50, and 50 wt% ethylene, respectively. Differences in intrinsic viscosity above 20°C are attributable to differences in molecular weight. (Rubin, I.D. and Sen, A., *J. Appl. Poly. Sci.*, 40, 523–530, 1990. Reprinted with permission of John Wiley & Sons, Inc.)

where

c = polymer concentration (g/dL)

η_{sp} = specific viscosity $(\eta - \eta_0)/\eta_0$

η = solution viscosity

η_0 = solvent viscosity

k' = constant

Thus, for a specific lubricant composition, c and η_0 are fixed, and the temperature dependence of the solution viscosity is directly related to that of the intrinsic viscosity.

Low-temperature viscosity is an important rheological feature of automotive lubricants. For the vehicle to start in cold weather, the lubricant viscosity in the bearings should be below a critical value as determined by low-temperature engine startability experiments [7] and defined within SAE J300 [104] for all “W” grades. The cold cranking simulator (CCS) test, ASTM D5293, is a high-shear rate rheometer operating at fixed subambient temperatures, designed to simulate oil flow in automotive bearings during start-up. After the engine starts, the lubricant must also be able to freely flow into the oil pump and throughout the internal oil distribution channels of the engine. This is the other half of the low-temperature viscosity specification for motor oils [104]. The mini-rotary viscometer (MRV), ASTM D4684, is a low-shear rate rheometer designed to simulate pumpability characteristics of a multigrade oil in a vehicle that was sitting idle for about 2 days in cold weather. SAE J300 also contains upper viscosity limits for MRV viscosity and yield stress for all W grades.

Thus, the mechanism of intermolecular crystallization, which leads to molecular size contraction in solution, affords high ethylene OCP viscosity modifiers the opportunity to contribute less to

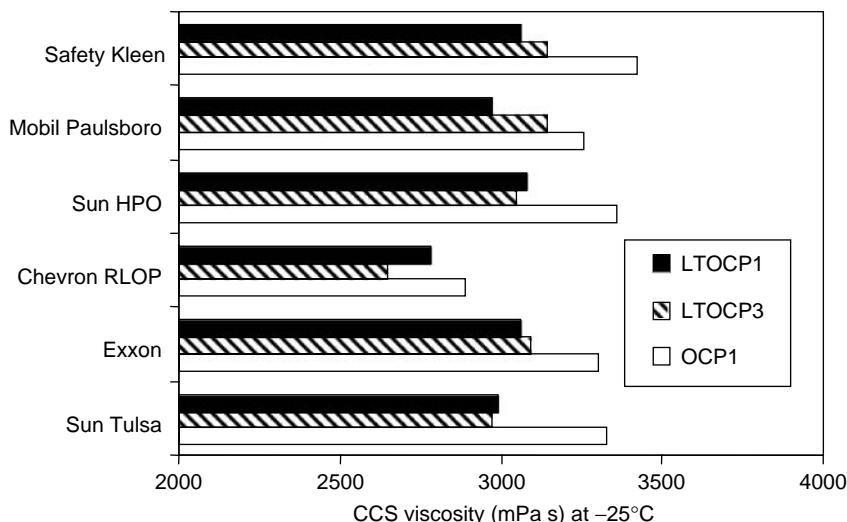


FIGURE 10.10 Cold cranking simulator (CCS) viscosity for six SAE 5W-30 lubricant formulations, each blended with one of three viscosity modifiers: LTOCP1, LTOCP3, or OCP1. Within each base oil type, the ratio of high and low-viscosity base oils was kept constant.

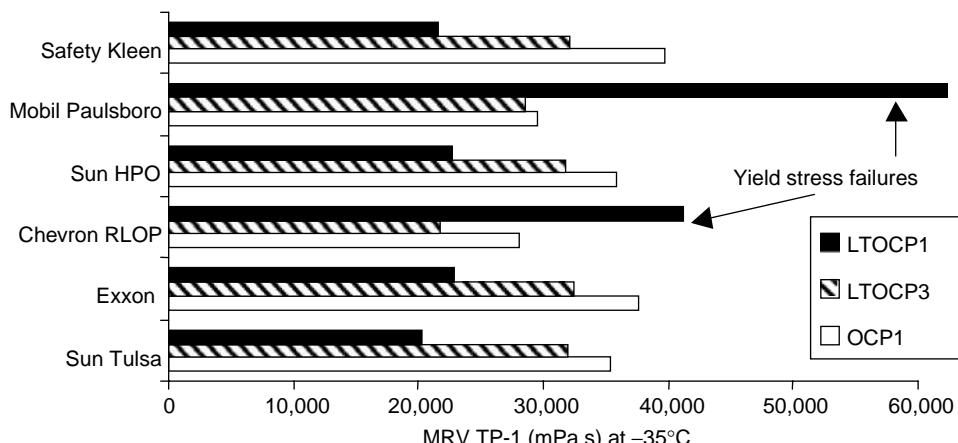


FIGURE 10.11 Mini-rotary viscosity results for six SAE 5W-30 lubricant formulations, each blended with one of three viscosity modifiers: LTOCP1, LTOCP3, or OCP1. Within each base oil type, the ratio of high and low-viscosity base oils and the type and concentration of pour point depressant were held constant.

viscosity at low temperatures than noncrystalline or amorphous copolymers of similar molecular weight. For this reason, the class of EP copolymers having ethylene content greater than ~60 wt% are often called low-temperature OCPs or LTOCPs. A rheological comparison of two LTOCPs and one conventional OCP viscosity modifier in several SAE 5W-30 oil formulations is seen in Figures 10.10 and 10.11. These data illustrate the low-temperature rheological benefits of LTOCPs.

A number of workers have cautioned, however, that the long ethylene sequences of LTOCPs are similar in structure to paraffin wax and can interact with waxy base oil components at low temperatures. In many cases, they require specially designed pour point depressants (PPDs) to function properly in certain base stocks. Thus, LTOCP viscosity modifiers have been implicated in problems such as MRV failures in comingled fresh oils [105] and used passenger car lubricants [106,107].

10.5.2.2 High-Temperature Rheology

Copolymer composition has less influence on high-temperature rheological behavior than it has at low temperatures, partly because lightly crystalline OCPs have melting points well below 100°C [97]. Since both high-temperature KV and high-temperature high-shear rate viscosity (HTHS) are used to classify multigrade engine oils [104], it is important to understand how copolymer composition and molecular weight influence these key parameters.

10.5.2.2.1 Kinematic Viscosity

For both economic and performance reasons, it is desirable to limit the amount of polymer needed to achieve a given set of rheological targets. Therefore, it is important to quantify the effects of molecular weight, molecular weight distribution, and branching on thickening efficiency. Thickening efficiency has been defined in many ways, but the most common definitions are (1) the amount of polymer necessary to increase the KV of a reference oil to a certain value or (2) the KV or specific viscosity (see Section 10.5.2.1) of a given polymer concentration in a reference oil. For polymers of equal molecular weight, thickening efficiency increases with ethylene content and is highest for copolymers with narrow molecular weight distributions [1,2]. In Figure 10.12, a plot of intrinsic viscosity versus weight average molecular weight (M) demonstrates the familiar Mark–Houwink power law relationship:

$$[\eta] = K'M^a$$

where K' and a are constants.

Assuming a single value for the power law constant $a = 0.74$, Crespi et al. [5] published a table of K' values as a function of ethylene content, which is reproduced in Table 10.2. This clearly shows that thickening efficiency can be improved by increasing ethylene concentration.

This is further illustrated by plotting data from Kapuscinski et al. [98] in Figure 10.13. The 80 mol% ethylene copolymer requires less polymer to achieve a target viscosity than a 60 mol% copolymer; therefore the former has a higher thickening efficiency than the latter.

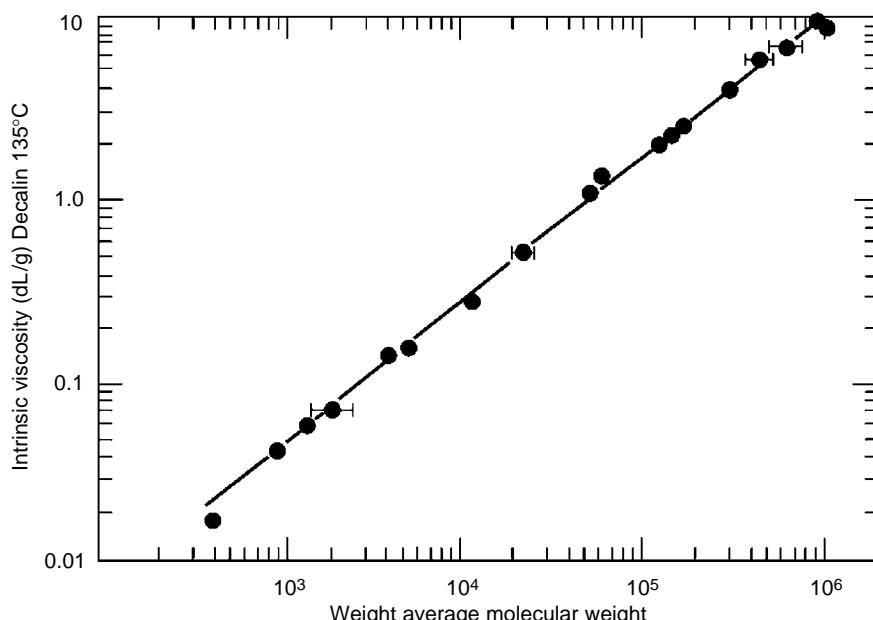


FIGURE 10.12 Intrinsic viscosity as a function of weight average molecular weight for EP copolymers of narrow polydispersity ($M_w/M_n \sim 2$). (Spiess, G.T., Johnston, J.E., and VerStrate, G., *Addit. Schmierst. Arbeitsflüssigkeiten*, Int. Kolloq., 5th, 2, 8.10-1, Tech. Akad. Esslingen, 1986. Reproduced with permission of ExxonMobil Chemical Company.)

TABLE 10.2
Mark-Houwink K' Constants for E/P Copolymers Containing Different Mole Percentages of Ethylene ($a = 0.74$)

Mol% ethylene	$K' \times 10^4$	Mol% ethylene	$K' \times 10^4$
5	2.020	55	3.020
10	2.115	60	3.140
15	2.205	65	3.260
20	2.295	70	3.385
25	2.390	75	3.515
30	2.485	80	3.645
35	2.585	85	3.790
40	2.690	90	3.940
45	2.795	95	4.240
50	2.910	—	—

Source: Adapted from Crespi, G., Valvassori, A., and Flisi, U., *Stereo Rubbers*, W.M. Saltman, ed., Wiley-Interscience, New York, NY, 365–431, 1977.

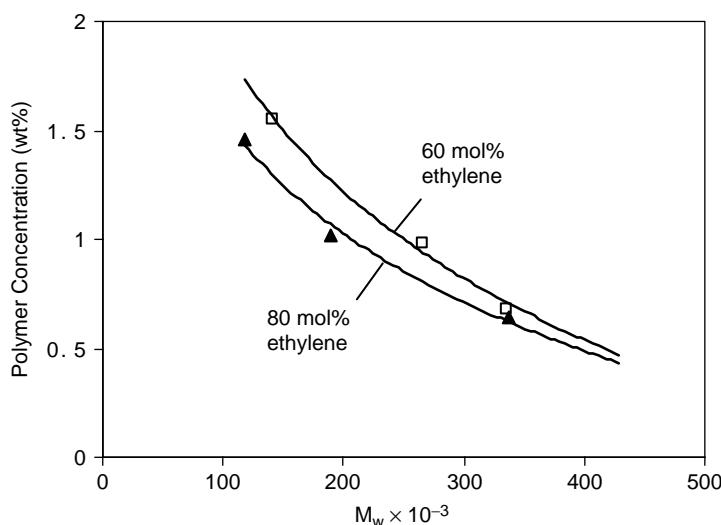


FIGURE 10.13 Polymer concentration needed to raise the kinematic viscosity of a 130N base oil to 11.5 cSt. (Data from Kapuscinski M.M., Sen, A., and Rubin, I.D., Soc. Automot. Eng. Tech. Paper Ser. No. 892152, 1989.)

Long-chain branching has a directionally detrimental effect on thickening efficiency for polymers of equal molecular weight. This is not surprising, since the average chain end-to-end distance of a random coil in solution is controlled, in large part, by the length of the main chain. Branching essentially shortens the chain and lowers its hydrodynamic radius. For example, Table 10.3 contains thickening efficiency data for two sets of noncrystalline OCP viscosity modifiers, one linear and the other containing 2% branching agent, each set differing only in molecular weight.

10.5.2.2.2 High-Temperature, High-Shear Rate Viscosity

Since concentric journal bearings operate in the hydrodynamic or elastohydrodynamic lubrication regimes, oil film thickness is a critical factor influencing wear [108,109]. For this reason, SAE J300 specifies a minimum HTHS viscosity for each viscosity grade [104]. HTHS viscosity is measured at very high shear rates and temperatures (10^6 s⁻¹ and 150°C, respectively), which is similar to the

TABLE 10.3
Thickening Efficiency of Linear and Branched
OCP Viscosity Modifiers

M_w	Linear	Branched
230,000	13.50	12.03
180,000	11.17	10.87

Note: Thickening efficiency is defined as the kinematic viscosity (at 100°C) of a 1.0 wt% polymer solution in 6.05 cSt mineral oil.

TABLE 10.4
Rheological Comparison of Lubricants Containing OCP Viscosity Modifiers Differing in Molecular Weight

Viscosity Modifier	Weight Average Molecular Weight	PSSI	Capillary Viscosity (cP) at 150°C	HTHS (cP) at 150°C	% TVL
OCP1	160,000	45	5.33	3.43	36
OCP2	80,000	30	5.33	3.77	29
OCP3	50,000	22	5.33	3.88	27

Source: Adapted from Spiess, G.T., Johnston, J.E., and VerStrate, G., *Addit. Schmierst. Arbeitsfluessigkeiten*, Int. Kolloq., 5th, 2, 8.10-1, Tech. Akad. Esslingen, 1986.

flow environment in an operating crankshaft bearing at steady state. At these rates of deformation, most high-molecular-weight polymers will align with the flow field [110], and a temporary reduction in viscosity is measured. The difference between low-shear rate viscosity and HTHS at 150°C is termed temporary viscosity loss (TVL) or percent temporary viscosity loss (relative to the low-shear rate KV). As is true for most polymers [110], TVL is proportional to molecular weight [1] as seen in Table 10.4. For polymers of equal weight average molecular weight, those with narrow molecular weight distributions undergo less TVL than those with broad M_w/M_n values [1].

HTHS viscosity can be adjusted by increasing the viscosity of the base oil or by increasing the viscosity modifier concentration, as shown in Figure 10.14. Since the formulation also has to meet KV and CCS viscosity limits, there is often only limited flexibility to adjust HTHS viscosity within the bounds of a given set of base oils and additives.

10.5.2.2.3 Permanent Shear Stability

The tendency of an OCP molecule to undergo chain scission when subjected to mechanical forces is dictated by its molecular weight, molecular weight distribution, ethylene content, and degree of long-chain branching. Mechanical forces that break polymer chains into lower-molecular-weight fragments are elongational in nature, causing the molecule to stretch until it can no longer bear the load. This loss in polymer chain length leads to a permanent degradation of lubricant viscosity at all temperatures. In contrast to temporary shear loss, permanent viscosity loss (PVL) represents an irreversible degradation of the lubricant and must be taken into account when designing engine oil for commercial use.

PVL is similar to TVL, except that the viscosity loss is measured by KV before and after shear. Permanent shear stability is more commonly defined by the permanent shear stability index (PSSI) or simply SSI, according to ASTM D6022 as follows:

$$\text{PSSI} = \text{SSI} = 100 \times (V_0 - V_s) / (V_0 - V_b)$$

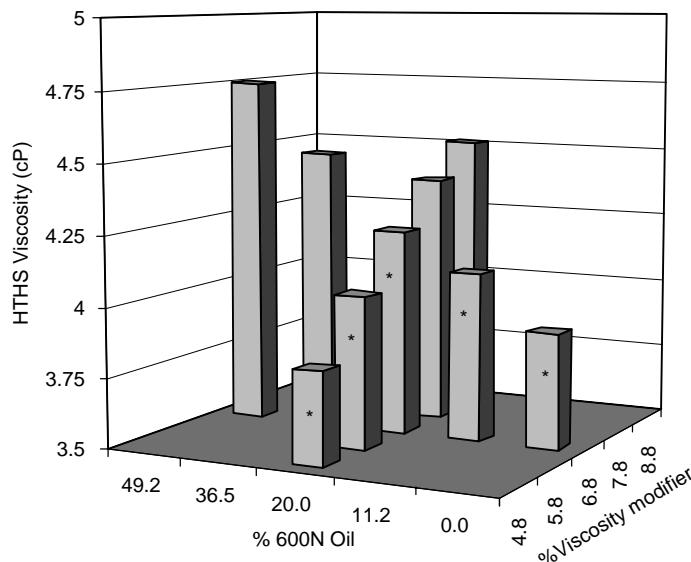


FIGURE 10.14 The effects of base oil composition and viscosity modifier concentration on HTHS viscosity. SAE 15W-40 engine oil consisting of European API Group I base oils (150N + 600N), an ACEA A3-98/B3-98 quality performance additive, an oil diluted amorphous OCP viscosity modifier, and a pour point depressant. Bars marked with an asterisk comply with ASTM D445 and D5293 limits for SAE 15W-40 oils.

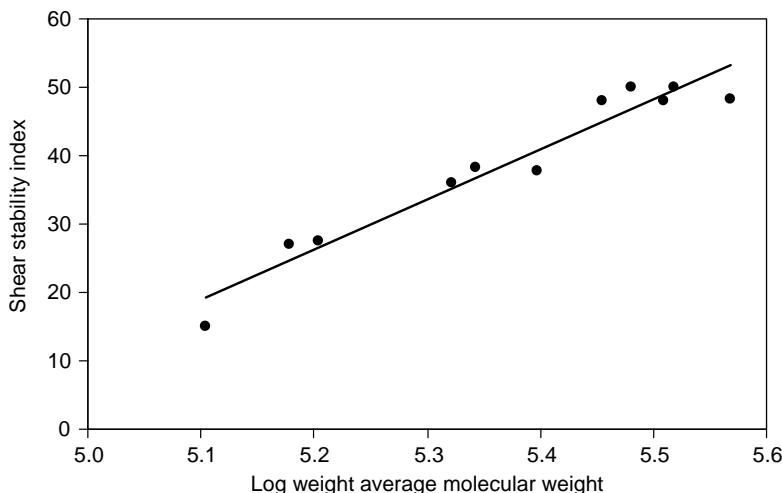


FIGURE 10.15 Relationship between weight average molecular weight and SSI (ASTM D3945) for a series of OCP viscosity modifiers.

where

V_o = viscosity of unsheared oil

V_s = viscosity of sheared oil

V_b = viscosity of the base fluid (without polymer)

SSI represents the fraction of viscosity contributed by the viscosity modifier that is lost during shear. SSI is proportional to \log_{10} molecular weight (M_w), as shown in Figure 10.15. Commercial OCP viscosity modifiers have SSI values in the range of 23–55.

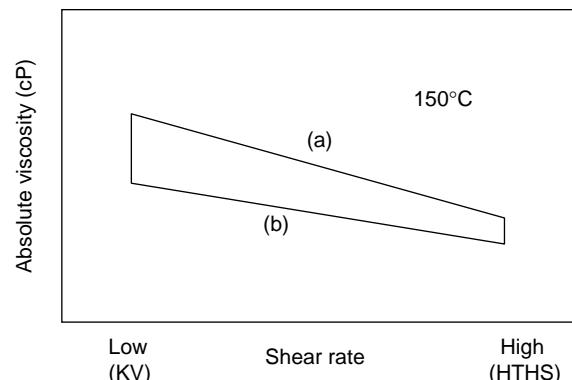


FIGURE 10.16 Viscosity loss trapezoid, per Selby: (a) Fresh oil viscosities and (b) oil viscosities after permanent shear. (Selby, T.W., Soc. Automot. Eng. Tech. Paper Ser. No. 932836, 1993.)

Although ASTM D6022 provides a definition for SSI, it is important to recognize that the only component that is responsible for viscosity loss during shear is the high-molecular-weight polymer. If the additive for which SSI is calculated happens to be a concentrated polymer solution in oil, according to the strict definition of ASTM D6022, the composition of the *base fluid* does not include the viscosity modifier (VM) diluent oil. Since the diluent oil viscosity is usually lower than the base blend viscosity for most viscosity grades, V_b is higher than it would be if the VM diluent oil viscosity was factored into V_b . For example, take an SAE 15W-40 engine oil formulated with a liquid OCP concentrate containing 10 wt% polymer in a 5.1 cSt mineral oil. V_0 and V_s are 15.2 and 12.8 cSt, respectively. The base blend viscosity (when the VM component is a liquid) is 9.4 cSt. When the VM component is defined as the solid polymer, V_b is 9.15 cSt. Calculated shear stability index values are 41.4 and 39.7, respectively. Thus, the numerical value of SSI is dependent on the definition of the polymeric additive in question.

The concept of “stay-in-grade” is generally used to refer to a lubricating oil, when tested in vehicles or laboratory shearing devices, which maintains its KV within the limits of its original SAE viscosity grade. The problem with viscosity measurements of engine drain oils is that many factors other than permanent polymer shear influence viscosity—such as fuel dilution, oxidation, and soot accumulation. Therefore, it is customary to measure PVL after shear in a laboratory rig, the most common being the Kurt Orbahn test, ASTM D6278. Several reviews of methods for determining the shear stability of polymer-containing lubricating oils have been published [111–113].

Selby devised a pictorial scheme for mapping the effects of shear rate and PVL on high-temperature viscosity, the viscosity loss trapezoid (VLT) [114], shown in Figure 10.16. The corners of the *trapezoid* are defined by viscosity data, and the points are connected by straight lines. Note that the straight lines do not imply that there is a linear relationship between viscosity and shear rate. The VLT is a convenient graphical representation of the temporary and permanent shear loss characteristics of polymer-containing oils. Molecular weight degradation causes a permanent loss in both KV and HTHS, but the magnitude of the former is always larger than the latter. The shape of the VLT is the characteristic of polymer chemistry and molecular weight.

It is experimentally observed [115] that the Kurt Orbahn shear test breaks molecules above a threshold molecular size; molecules smaller than the threshold value are resistant to degradation. Selby [114] uses this observation to derive certain qualitative conclusions of the polymer molecular weight distribution from the shape of the VLT.

10.5.3 EFFECT OF DIENE ON THERMAL/OXIDATIVE STABILITY

There has been little solid scientific data published in the literature to compare the relative thermal/oxidative stability of oil solutions containing E/P copolymers versus EPDM terpolymers. Marsden [2]

states that “introduction of a termonomer … can … detrimentally affect shear and oxidation stability, dependent on the monomer,” but he offers no data. Others [5,27] cite high-temperature aging experiments on solid rubber specimens, which demonstrate that EP copolymers are more stable (in terms of tensile properties) than EPDM terpolymers of similar E/P ratio. Copolymers containing higher levels of ethylene are claimed to have better thermal/oxidative stability than more propylene-rich copolymers, presumably due to the lower concentration of oxidatively labile tertiary protons contributed by the propylene monomer. High thermal stresses are sufficient to promote hydrogen abstraction by a free radical mechanism. The relative susceptibility of protons to hydrogen abstraction follows the classical order tertiary > secondary > primary. In the presence of oxygen, peroxy radicals are formed, which can accelerate the degradation process.

Despite these suggestions that diene-containing E/P copolymers may be less thermally stable than EP copolymers, the author is not aware of any definitive studies that have shown that EPDM viscosity modifiers are more likely to degrade in service than EP copolymers. Indeed, engine oils formulated with both types have been on the market for years.

10.5.4 COMPARATIVE RHEOLOGICAL PERFORMANCE IN ENGINE OILS

The most influential factors governing the rheological performance of OCPs in engine oils are molecular weight and monomer composition. The effects of molecular weight and molecular weight distribution were discussed in Section 10.5.2.3, and the influence of E/P ratio on low-temperature rheology was covered in Section 10.5.2.1. In this section, two comparative rheological studies are presented to further illustrate the links between OCP structure and rheological performance.

10.5.4.1 Comparative Study of OCP Viscosity Modifiers in a Fixed SAE 5W-30 Engine Oil Formulation

There are two ways to compare the relative performance of several viscosity modifiers. One is to choose a fixed engine oil formulation where the base oil composition and additive concentrations are held constant, and the VM level is adjusted to achieve a certain 100°C KV target. The other is to adjust both base oil composition and VM concentration to achieve predetermined KV and CCS viscosity targets. Section 10.5.4.1 offers an example of the first approach and Section 10.5.4.2 illustrates the second approach.

Four OCP viscosity modifiers were blended into an SAE 5W-30 engine oil composition consisting of a 95/5 w/w blend of Canadian 100N/250N mineral base stocks, an ILSAC GF-2 quality performance additive, and a polyalkylmethacrylate PPD. The viscosity modifiers are described in Table 10.5. OCP1 and OCP2 are high SSI polymers differing in both E/P ratio and diene content. OCP3 and OCP4 are progressively more shear stable and have essentially 0% crystallinity.

Rheological data are summarized in Table 10.6. Comparing OCP1 and OCP2, the former is a more efficient thickener because it contains no long-chain branching (no diene monomer) and it has

TABLE 10.5
Properties of OCP Viscosity Modifiers Used in Table 10.6

Viscosity Modifier Code	Shear Stability Index (ASTM D6278)	Copolymer Type
OCP1	55	EP, LTOCP
OCP2	50	EPDM, amorphous
OCP3	37	EP, amorphous
OCP4	25	EP, amorphous

TABLE 10.6
Rheological Properties of SAE 5W-30 Engine Oils Containing Different OCP Viscosity Modifiers

	OCP1	OCP2	OCP3	OCP4
Polymer content (wt%)	0.58	0.71	0.73	1.05
Kinematic viscosity (cSt) at 100°C	10.17	10.09	9.99	10.10
Viscosity index	156	160	160	158
CCS viscosity (cP) at -25°C	3080	3280	3510	3760
MRV viscosity (cP) at -30°C	13,900	26,500	26,700	28,100
MRV viscosity (cP) at -35°C	40,100	Yield stress	Yield stress	Yield stress
HTHS (cP)	2.95	2.88	2.96	3.07

TABLE 10.7
OCP Viscosity Modifiers Used in Rheological Study in Table 10.8

Viscosity Modifier Code	Copolymer Type
OCP7	EPDM, amorphous
OCP3	EP, amorphous
OCP8	EPDM, LTOCP
OCP9	EP, LTOCP

a higher ethylene content (see Figure 10.13). The latter property also manifests itself in lower CCS viscosity. The MRV viscosity is also lower for OCP1 relative to the other amorphous OCPs, but this is highly dependent on the particular PPD that was chosen for this study. The fact that most of the oils displayed yield stress failures at -35°C shows that the PPD was not optimized for this particular set of components.

As SSI decreases from OCP1 to OCP4, the polymer concentration needed to reach a KV target of 10 cSt increases. In other words, polymer thickening efficiency is proportional to shear stability index. Among the noncrystalline OCPs, increasing polymer level causes the CCS viscosity to increase. Since all oils were formulated with the same base oil composition, high-temperature HTHS is relatively constant, independent of OCP type. OCP4, the lowest molecular weight polymer, should have the lowest degree of TVL, and it indeed has the highest HTHS viscosity of the group.

10.5.4.2 Comparative Study of 37 SSI OCP Viscosity Modifiers in an SAE 15W-40 Engine Oil Formulation

In this example, the base oil ratio and polymer concentration were adjusted to achieve the following targets: KV = 15.0 cSt and CCS = 3000 cP at -15°C. The base stocks were American Petroleum Institute (API) Group I North American mineral oils, the additive package was of API CH-4 quality level, and the PPD was a styrene ester type that was optimized for these base oils. All viscosity modifiers (see Table 10.7) were nominally 37 SSI according to ASTM D6278. Rheological results are summarized in Table 10.8.

OCP3 is the same polymer as in Table 10.5. Although OCP8 and OCP9 are semicrystalline LTOCPs, they represent different manufacturing technologies, broadly described in Figures 10.4 and 10.5, respectively. Incidentally, OCP1 in Table 10.5 was also manufactured by the tubular reactor technology described in Figure 10.5.

TABLE 10.8
Rheological Properties of SAE 15W-40 Engine Oils Containing Different OCP Viscosity Modifiers

	OCP7	OCP3	OCP8	OCP9
Polymer content (wt%)	0.95	0.85	0.85	0.64
150N base oil percentage	76	76	70	70
600N base oil percentage	24	24	30	30
Kinematic viscosity (cSt) at 100°C	15.04	14.97	15.25	15.12
Viscosity index	141	140	140	135
CCS viscosity (cP) at -15°C	3,080	3,040	3,070	3,010
MRV viscosity (cP) at -20°C	10,000	9,900	8,800	Solid
MRV viscosity (cP) at -25°C	20,500	18,600	18,300	Solid
HTHS (cP)	4.17	4.38	4.25	4.42

The rheological data in Table 10.8 further illustrate several features of LTOCPs mentioned earlier. Their inherently lower CCS viscosity contributions permit the greater use of higher-viscosity base oils, which can be beneficial in meeting volatility requirements. The low-temperature MRV performance of OCP9 was far inferior to that of the other copolymers, indicating that the PPD chosen for this particular study was not optimized for OCP9 in these base stocks.

Another polyalkymethacrylate PPD was found to bring the MRV viscosity of the OCP9 formulation down to 7,900 and 18,000 cP at -20 and -25°C, respectively. More about interaction with PPDs is discussed in Section 10.5.5.

Again, the higher thickening efficiency of EP copolymers versus EPDMs of similar molecular weight (shear stability) is clearly demonstrated in Table 10.8. Another feature worth noting is that increasing base oil viscosity can nudge HTHS viscosity upward (compare OCP7 with OCP8 or OCP3 with OCP9).

10.5.5 INTERACTION WITH POUR POINT DEPRESSANTS

Although base oil and VM play a role in determining low-temperature oil pumpability, the PPD provides the primary control in this area. SAE J300 [104] specifies the MRV test (ASTM D4684) as the sole guardian of pumpability protection, although it acknowledges that other tests may also be useful in the development of lubricants from new components. The Scanning Brookfield test (ASTM D5133) and Pour Point (ASTM D5873), although not required within SAE J300, are often contained in other standards established by original equipment manufacturers, oil marketers, and governmental agencies and, therefore, must also be considered in the development of modern engine oils.

Advances in base oil technology have led, in recent years, to a wide range of mineral and synthetic lubricant base stocks [116], classified as API Group I, II, III, IV, and V stocks. The API system classifies oils according to viscosity index (VI), saturates content, and sulfur level. Group I mineral oils are defined as having <90% saturates, VI >80 and more than 0.03% sulfur. Groups II and III oils have <0.03% sulfur and >90% saturates, but they differ mainly in VI. Group II oils have VI >80, whereas Group III stocks have VI values in excess of 120.

Formulating these conventional and highly refined oils to meet all the rheological requirements of SAE J300 is not always straightforward. An important aspect of base oil technology that is not embodied within the API Group numbering scheme is the type of de-waxing process or processes employed. It is well known [117–123] that the low-temperature oil pumpability performance of engine oils is often impeded by nucleation and growth of wax crystals, which can coalesce and restrict the flow of oil at low temperatures. The type and amount of wax that forms dictates the

type and concentration of PPD that will be effective in keeping wax crystals small so that they do not form network structures and lead to high viscosity and yield stress. Both the feedstocks and dewaxing steps used in the manufacture of a given base oil determine wax composition and, in turn, PPD response.

Certain types of viscosity modifiers can interact with base oils and PPDs at low temperatures and can lead to excessively high MRV viscosities in some situations (see, for example, OCP9 in Table 10.8). Formulating with amorphous OCPs has not, in the author's experience, posed many difficulties. Conversely, LTOCPs possess longer ethylene sequences that have the potential to interact with wax crystals at low temperatures. Several reports in the literature [66,76] suggest that high-ethylene OCPs can, under certain circumstances, interact negatively on MRV viscosity and yield stress and may be more sensitive to the type of PPDs that will be effective in some formulating systems.

A previously unpublished study of low-temperature interactions among base oils, OCP viscosity modifiers, and PPDs was carried out in the author's laboratory using components listed in Tables 10.9 through 10.11.

Fully formulated SAE 5W-30 and 15W-40 engine oils were blended using performance additive packages DI-1 (at 11 wt%) and DI-2 (at 13 wt%); API SJ quality and CH-4 quality, respectively; and all combinations of base oil, VM, and PPD.

TABLE 10.9
Base Oils Used in Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

Base Oil Code (API Group)	Saturates (wt%)	Kinematic Viscosity (cSt) at 100°C	Sulfur (wt%)	Viscosity Index	CCS Viscosity (cP) at -25°C
B1-L (I)	73.6	3.88	0.276	104	1170
B1-M (I)	71.8	5.15	0.553	102	4060
B1-H (I)	61.8	12.10	0.381	97	—
B2-L (I)	75.2	4.18	0.193	105	1510
B2-M (I)	75.0	4.91	0.544	106	3060
B2-H (I)	72.3	12.73	0.412	99	—
B3-L (II)	100	4.20	0.006	100	1570
B3-M (II)	100	5.49	0.011	117	2430
B3-H (II)	100	10.72	0.016	98	—
B4-L (III)	100	4.50	0.007	123	1120
B4-H (III)	100	6.49	0.006	131	2710

TABLE 10.10
Viscosity Modifiers Used In Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

VM Code	OCP Type	SSI (ASTM D6278)
VM-1	Amorphous	37
VM-2	LTOCP	35
VM-3	LTOCP	37

TABLE 10.11
Pour Point Depressants Used In Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

Pour Point Depressant Code	Chemistry
PPD-1	Poly(styrene-maleate ester)
PPD-2	Poly(alkylmethacrylate)
PPD-3	Poly(styrene-maleate ester)
PPD-4	Poly(alkylmethacrylate)

Figures 10.17 through 10.20 summarize VM/PPD effects on MRV viscosity for each base oil type. In these graphs, the letter Y adjacent to a vertical bar denotes a yield stress failure. For the API Group I base oil B1 (SAE 5W-30, Figure 10.17), only PPD-3 is effective with all three viscosity modifiers. Both VM-1 and VM-3 suffer yield stress failures with at least one PPD. In the 15W-40 formulation, VM-3 exhibits yield stress behavior with all four PPDs, even in one case in which the MRV viscosity is quite low (PPD-1). In the author's experience, it is quite unusual to observe yield stress failures in the MRV test when viscosity is below ~40,000 cP.

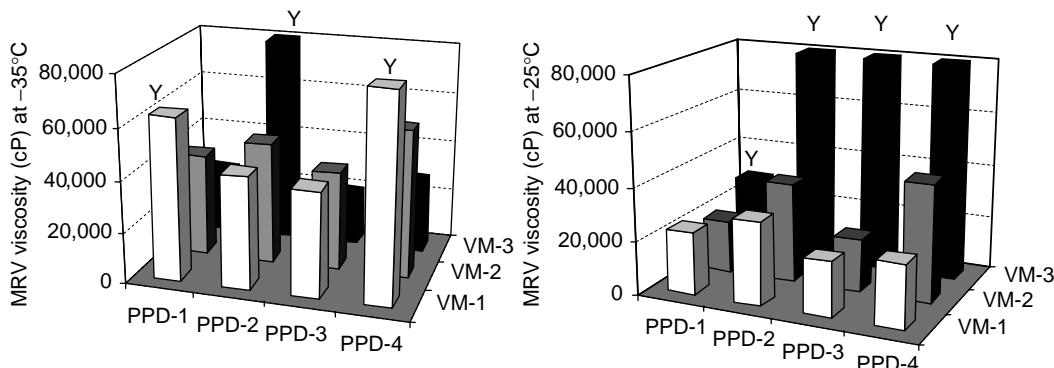


FIGURE 10.17 Rheological results for oil B1. SAE 5W-30 (left) and SAE 15W-40 (right).

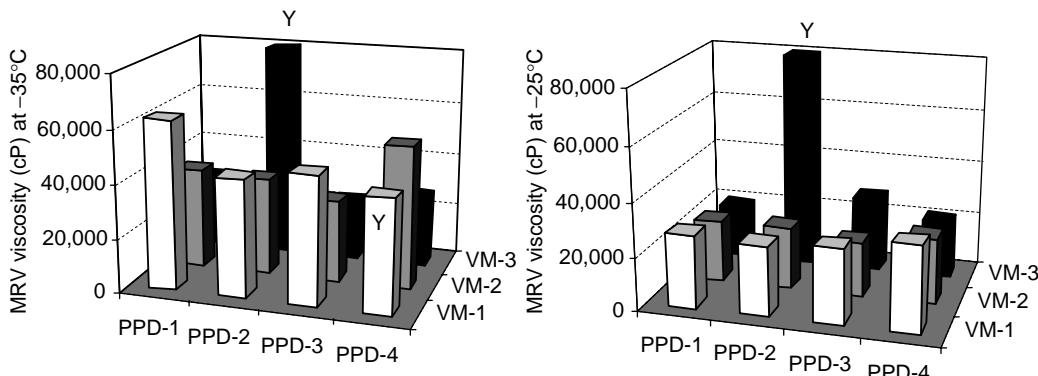


FIGURE 10.18 Rheological results for oil B2. SAE 5W-30 (left) and SAE 15W-40 (right).

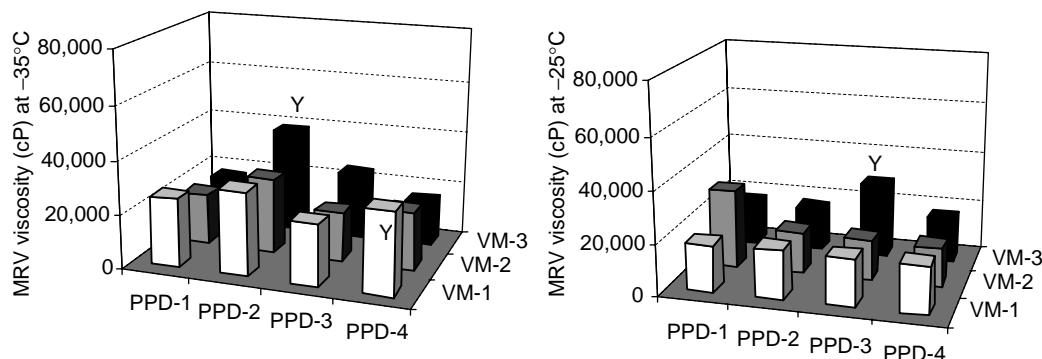


FIGURE 10.19 Rheological results for oil B3. SAE 5W-30 (left) and SAE 15W-40 (right).

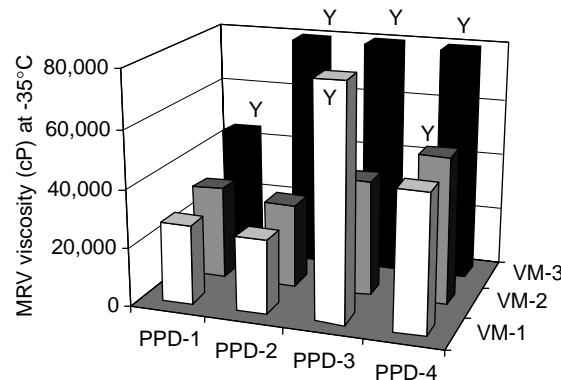


FIGURE 10.20 Rheological results for oil B4. SAE 5W-30.

TABLE 10.12
Number of MRV Failures due to Yield Stress in Low-Temperature Viscosity Modifier/Pour Point Depressant Interaction Study

VM	PPD-1	PPD-2	PPD-3	PPD-4	Total
VM-1	1		1	3	5
VM-2				1	1
VM-3	2	6	3	2	13
Total	3	6	4	6	19

The other API group I blended oils, B2 (Figure 10.18), respond to PPDs in a similar manner to B1, but only in the SAE 5W-30 formulation. In the 15W-40 case, VM-3 is the only VM to experience yield stress failure, but only in the presence of PPD-2; all other combinations demonstrate acceptable pumpability performance.

Figure 10.19 describes the MRV map of B3, the API Group II oil. Overall, low-temperature viscosities are all quite low for all VM/PPD combinations, although VM-3 again experiences one yield stress failure in each viscosity grade. VM-1 fails the yield stress criterion once.

Finally, the API Group III SAE 5W-30 formulation (Figure 10.20) was the most difficult to pour depress. All four oils blended with VM-3 were yield stress failures, and each of the other two VMs showed significant yield stresses for one PPD each.

In summary, the number of MRV failures due to yield stress is given in Table 10.12. Clearly, one of the LTOCP viscosity modifiers, VM-3, is substantially more sensitive to PPDs than the other two polymers. It is especially incompatible with PPD-2. The other LTOCP in this study, VM-2, and the amorphous VM-1 were found to be far more tolerant of PPD type. Similar to the discussion in Section 10.5.4.2, one of the major differences between VM-3 and VM-2 is that they were manufactured by different technologies, broadly described in Figures 10.5 and 10.4, respectively.

10.5.6 FIELD PERFORMANCE DATA

Multigrade lubricants containing EP viscosity modifiers have been tested in passenger car and heavy-duty truck engines for over three decades, but very few studies devoted to VM effects on engine cleanliness and wear have been published. It is generally believed that adding a polymer to the engine lubricant will have a detrimental effect on engine varnish, sludge, and piston ring-pack

TABLE 10.13
120 h Caterpillar 1H2 Piston Deposit Ratings of SAE
10W-40 Oils Formulated with N-Vinyl Pyrrolidone-
Grafted OCPs

Sample	Nitrogen (wt%)	TGF	WTD
OCP	0	—	>800
MFOCP5	0.3	46	244
MFOCP6	0.5	39	173
MFOCP7	0.7	47	149
MFOCP6 ^a	0.26	28	156
MFOCP2 ^a	0.28	11	139

Note: TGF, top groove fill rating; WTD, weighted total (piston) demerits rating.

^a OCP grafted with maleic anhydride and subsequently reacted with amines.

Source: Adapted from Spiess, G.T., Johnston, J.E., and VerStrate, G., *Addit. Schmierst. Arbeitsflüssigkeiten*, Int. Kolloq., 5th, 2, 8.10-1, Tech. Akad. Esslingen, 1986.

deposits [1,2], but the performance additive can be formulated to compensate for these effects. Kleiser et al. [124] ran a taxicab fleet test designed to compare the performance of a nonfunctionalized OCP viscosity modifier with a highly dispersant-functionalized OCP (HDOCP) as well as to test other oil formulation effects. They were surprised to find that SAE 5W-30 oil containing a higher concentration of non-DOCP showed statistically better engine deposit control when compared to a similar SAE 15W-40 oil with lower polymer content. They also observed significant improvements in sludge and varnish ratings attributed to the use of HDOCP. Others have also reported that DOCPs can be beneficial in preventing buildup of deposits in laboratory engines such as the Sequence VE [125], VD [1], and Caterpillar 1H2/1G2 [1] tests. These authors found that engine oils containing certain DOCPs need less ashless dispersant to achieve an acceptable level of engine cleanliness than NOCPs. The actual level of deposit prevention is highly influenced by the functionalization chemistry as well as the number of substituents per 1000 backbone carbon atoms, as shown in Table 10.13 (MFOCP = Multi-functional OCP).

10.6 MANUFACTURERS, MARKETERS, AND OTHER ISSUES

10.6.1 EP/EPDM MANUFACTURERS

EP copolymers and EPDM terpolymers are manufactured by a number of companies around the globe. Table 10.14 [126] contains a listing of those with production capacity >30,000 metric tons/year (£65 million per annum). Not all are necessarily supplying rubber into the viscosity modifier market. The vast majority of the capacity goes into other applications such as automotive (sealing systems, radiator hoses, injection molded parts), construction (window gaskets, roofing/sheeting, cable insulation, cable filler), and plastics modification.

Various grades are often classified by melt viscosity, EP ratio, diene type and content, and physical form and filler type and level (carbon black, pigments, or extender oils). Melt viscosity is measured by two main techniques—Mooney viscosity (ASTM D1646 or ISO 289) and melt index (ASTM D1238 or ISO 1133-1991, also called melt-mass flow rate). Mooney viscosity is directly proportional to molecular weight, whereas melt index is inversely proportional to molecular weight.

TABLE 10.14
Manufacturers with Production Capacity Greater than 30,000 Metric Tons/Year

Company	Manufacturing Location(s)	Capacity (Metric tons/Year)	Technology	Trade Name	Comments
Dow Chemical	Plaquemine, Louisiana Seadrift, Texas	230,000	Metallocene, solution and gas-phase processes	Nordel IP Nordel MG	EPDM
DSM Elastomers	Geleen, The Netherlands; Triunfo, Brazil	185,000	Ziegler–Natta, solution process	Keltan	EP and EPDM
ExxonMobil Chemical	Baton Rouge, Louisiana, United States; Notre Dame de Gravenchon, France; Kumbo Polychem, South Korea (JV)	272,500	Ziegler–Natta and metallocene, solution process	Vistalon	EP and EPDM
JSR Corporation (Japan Synthetic Rubber)	Yokkaichi and Kashima, Japan	87,500	Ziegler–Natta, solution process	Esprene	EPDM
Lanxess	Orange, Texas Marl, Germany	110,000	Ziegler–Natta, suspension and solution processes	Buna EP T Buna EP G	EP and EPDM
Lion Copolymer	Geismar, Louisiana, United States	93,000	Ziegler–Natta, solution process	Royalene, Trilene	EP and EPDM
Mitsui	Chiba, Japan	120,000 ^a	Ziegler–Natta and metallocene, solution process	Mitsui EPT	EP and EPDM
Polimeri Europa	Ferrara, Italy	85,000	Ziegler–Natta, suspension process	Dutral	EP and EPDM
Sumitomo	Japan	45,000	Ziegler–Natta, solution process	Esprene	EPDM

^a Includes 75,000 metric tons/year metallocene plant to begin operation in 2007.

10.6.2 OLEFIN COPOLYMER VM MARKETERS

Companies which provide EP copolymers and EPDM terpolymers to the viscosity modifier market are listed in Table 10.15. A wide variety of products, varying in shear stability and level of crystallinity, are available in both solid and liquid forms. Functionalized polymers that provide added dispersancy and antioxidantancy are available from several suppliers. The reader is advised to update this information periodically, since each company's product lines change over time.

Mergers and acquisitions have also contributed to significant flux in the OCP market. For example, the Paratone® product line was originally developed and marketed by the Paramins Division of Exxon Chemical Company. When Exxon and Shell combined their lubricant additives businesses to form Infineum in 1998, the Paratone business was sold to Oronite, the lubricant additives division of Chevron Chemical Company. Ethyl's purchase of Amoco and Texaco OCP product technology in the 1990s resulted in rebranding of Texaco's TLA-XXXX products to Ethyl's Hitec® product line. Ethyl Additives changed its name to Afton Chemical Company in 2004. Dupont originally marketed EPDM—manufactured at its Freeport, Texas, facility—into the viscosity modifier market under the Ortholeum® trademark until it was sold to Octel in 1995. Thereafter, DuPont adopted

TABLE 10.15
Marketers of E/P Copolymers and EPDM Terpolymers as Engine Lubricating Oil Viscosity Modifiers

Company	Headquarters	Trade Name	Product Classes	Product Form
Afton	Richmond, Virginia	Hitec 5700 series	NDOCP, DOCP, DAOCP	Liquid concentrates
Chevron Oronite	Richmond, California	Paratone	NDOCP, DOCP	Pellet, bales, and liquid concentrates
Dow Chemical	Midland, Michigan	Nordel IP	NDOCP	Bales and pellets
Infineum	Linden, New Jersey	Infineum V8000 series	NDOCP	Pellets and liquid concentrates
Lubrizol	Wickliffe, Ohio	Lubrizol 7000 series	NDOCP, DOCP	Bales and liquid concentrates
RohMax (Degussa AG)	Darmstadt, Germany	Viscoplex	NDOCP, mixed PMA/OCP	Liquid concentrates

Note: DAOCP = olefin copolymer with dispersant and antioxidant functionality; DOCP = dispersant-functionalized olefin copolymer; NDOCP = nonfunctionalized olefin copolymer; PMA = poly(alkyl methacrylate).

the NDR brand name. DuPont and Dow Chemical Company formed a 50/50 joint venture in 1995, merging their elastomer businesses. Shortly following the successful start-up of their metallocene plant in Plaquemine, Louisiana, 2 years later, the Freeport facility was closed. Dow Chemical Company acquired control of the EPDM product line, marketed under the Nordel® IP trade name, in 2005. Bayer transferred its EPDM business to a new company named LANXESS in 2004. Although primarily a poly(alkylmethacrylate) company, Rohm GmbH of Darmstadt, Germany, developed several OCP-based viscosity modifiers under the Viscoplex® trade name, currently owned and marketed by RohMax Additives, a Degussa company. In mid-2007, Crompton sold its EPDM business to Lion Copolymer.

10.6.3 READ ACROSS GUIDELINES

Various lubrication industry associations have published highly detailed guidelines [127–129] for defining conditions under which certain additive and base oil changes to a fully or partially qualified engine oil formulation may be permitted without requiring complete engine testing data to support the changes. The purpose of these standards is to minimize test costs while ensuring that commercial engine oils meet the performance requirements established by industry standards, certification systems, and original equipment manufacturers (OEMs). From a viscosity modifier perspective, changes are often driven by one or more of the following needs:

1. To optimize viscometrics within a given viscosity grade
2. To improve the shear stability of the formulation
3. To interchange one polymer for another (cost, security of supply, customer choice)

There are similarities and differences among codes of practice adopted by the American Chemistry Council (ACC) and the two European agencies, ATC (Technical Committee of Petroleum Additive Manufacturers of Europe) and ATIEL (Technical Association of the European Lubricants Industry). All permit minor changes in VM concentration (no more than 15% relative on a mass basis) to accomplish the first need mentioned earlier. The European codes explicitly allow the interchange of one VM for another (if both are from the same supplier) if the VM supplier deems them to be “equivalent and interchangeable.” VMs from different suppliers, or those from the same supplier that are not judged to be “equivalent,” must undergo a rigorous engine testing program such as that outlined in Table 10.16.

TABLE 10.16
Engine Test Requirements for Interchanging Viscosity Modifiers within the ATIEL Code of Practice

Performance Category	NDVM to NDVM (1, 2, 3, 4)	DVM to DVM or NDVM to DVM (1, 2, 3, 4)
Gasoline	TU572 (8) M111 or VG (9) M111FE	TU572 (8) M111 or VG (9) M111FE
Light-duty diesel	VWICTD (9) VW DI M111FE	OM602A VWICTD (9) XUD11 (12) VW DI M111FE
Gasoline/light-duty diesel	TU572 (8) M111 or VG (9) VWICTD (9) VW DI M111FE	TU572 (8) M111 or VG (9) OM602A VWICTD (9) XUD11 (12) VW DI M111FE
Gasoline/light-duty diesel with after treatment devices	TU572 (8) M111 or VG (9) VW DI M111FE	TU572 (8) M111 or VG (9) OM602A XUD11 (12) VW DI M111FE
Heavy-duty diesel	OM364LA (10) Mack T8 (6) Mack T8E (7) OM 441 LA M11 (5) (11)	OM364LA (10) OM602A Mack T8 Mack T8E OM 441 LA M11 (5) (11)

Note:

1. Full testing required for any other viscosity modifier interchange (VMI) not listed above.
2. Physical mixes of non-dispersant viscosity modifier (NDVM) and DVM are treated as DVM.
3. Only the tests included in the ACEA sequence for which read across is required have to be run.
4. Where alternative tests are listed, for example, “M111 or VG,” the alternative test cannot be run to document read across if a failing result has already been obtained on the other test.
5. Not required if the new oil formulation has the same or greater HTHS value compared with the original tested formulation.
6. The Mack T8 requirement is waived, if the replacement NDVM has the same or poorer shear stability as determined on candidate test oil formulated to similar viscosity as the original NDVM tested formulation and measured by CEC-14-A-93 (ASTM D 6278-98), and if the requirements of note 7 are also met.
7. The T8 or T8E requirement is waived, if the replacement NDVM is within the same chemical type as the tested NDVM (“chemical type” means chemical family such as, but not limited to, styrene ester, polymethacrylate, styrene butadiene, styrene isoprene, polyisoprene, olefin copolymer, and polyisobutylene).
8. TU3MH results can be used in support of A2-96 issue 3 provided the results are passing for A2-96 issue 2.
9. The VWICTD may be replaced by the VWDI (with B4 performance limit).
10. The OM364LA requirement may be met by a passing OM441LA at E5 level.
11. The M11EGR test may be used in place of the M11.
12. The XUD 11 test can be replaced by the DV4 test.

Source: *Code of Practice for Developing Engine Oils Meeting the Requirements of the ACEA Oil Sequences*, ATIEL, Technical Association of the European Lubricants Industry, Issue No. 13, Appendix C, Brussels, Belgium, November 28, 2005.

TABLE 10.17
CAS Index of EP and EPDM Copolymers

EP/EPDM	CAS Index
EP	9010-79-1
EPDM (ENB termonomer)	25038-36-2
EPDM (DCPD termonomer)	25034-71-3
EPDM (1,4-hexadiene termonomer)	25038-37-3

The ACC guidelines impose two levels of data needed to support viscosity modifier interchange. Level 1 support is defined as analytical and rheological test data. Level 2 support includes both level 1 data and full-length valid ASTM engine tests, intended to demonstrate that the proposed VM interchange presents no harm in terms of lubricant performance. There are three categories of engine tests that can be used to satisfy the ACC level 2 criterion: (1) statistically designed engine test matrices, (2) complete programs, or (3) partial data sets from the same technology family. This broad definition of additive interchange testing is more open for interpretation than the ATIEL guidelines as represented in Table 10.16. Minor formulation modifications needing only level 1 data do not permit changes in VM type, defined as polymers of a “specific molecular architecture with a specific shear stability characterized by a specific trade name, stock or code number.” When a change in shear stability is required, level 2 support is sufficient for polymers of the same chemical family (e.g., OCPs) and from the same manufacturer. Otherwise, a full engine testing program is needed. The ACC guidelines also specify that if a dispersant viscosity modifier (DVM) is used in a core multigrade formulation, the additional dispersant needed to read across to a monograde or other multigrades with lower VM concentration requires a Sequence VG test and level 2 support in other tests.

10.6.4 SAFETY AND HEALTH

E/P copolymers as well as EPDMs are classified as “nonhazardous” substances by OSHA (1910.1200) and the European Economic Community (EEC). They are generally considered to be not acutely toxic, similar to other high-molecular-weight polymers. Material that is heated to the molten state can emit fumes, which can be harmful and irritating to the eyes, skin, mucous membranes, and respiratory tract, especially copolymers containing nonconjugated diene termonomers. Proper ventilation and respiratory protection are recommended when handling EP and EPDM copolymers under these conditions. Appropriate personal protective equipment is also advised to guard against thermal burns.

EP/EPDM grades are indexed by the Chemical Abstract Service in Table 10.17.

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11 Polymethacrylate Viscosity Modifiers and Pour Point Depressants

Bernard C. Kinker

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11.1 HISTORICAL DEVELOPMENT

11.1.1 FIRST SYNTHESIS

The first synthesis of a polymethacrylate (PMA) intended for potential use in the field of lubricant additives took place in the mid-1930s. The original work was conducted under the supervision of Herman Bruson, who was in the employ of the Rohm and Haas Company (a parent of RohMax), and

it was conducted in Rohm and Haas' Philadelphia Research Laboratories. Bruson was exploring the synthesis and possible applications of longer alkyl side chain methacrylates [1]. He had proposed poly lauryl methacrylate as a product that might serve as a potential thickener or *viscosity index improver* (VII) for mineral oils. The result of the work was the 1937 issuance of two U.S. patents, for "Composition of matter and process" [2] and for "Process for preparation of esters and products" [3].

11.1.2 FIRST APPLICATION

Bruson's invention did indeed thicken mineral oils, and it was effective in increasing viscosity at higher temperatures more so than at lower, colder temperatures. Since this behavior influences the viscosity-temperature properties or VI of a fluid, these materials eventually became known as viscosity index improvers (VIIs). Although PMAs successfully thickened oils, there were other competitive thickeners of that time, which increased the viscosity of mineral oils; these were based on poly isobutylene and alkylated polystyrene. The commercial success of PMA was not at all assured. The driving force behind PMA eventually eclipsing the other commercial thickeners of the era was PMA's value as a VII rather than as a simple thickener of oils. In other words, PMAs have the ability to contribute relatively little viscosity at colder temperatures such as those that might be encountered at equipment start-up, but have a much higher contribution to viscosity at hotter temperatures at which equipment tends to operate. This desirable behavior enabled oil formulators to prepare multigrade oils that could meet a broader range of operating-temperature requirements. The positive enhancement of VI ensured the future success of PMAs.

11.1.3 FIRST MANUFACTURE AND LARGE-SCALE APPLICATION

The commercial development of PMAs as VIIs lagged until the beginning of World War II, when the U.S. government board *rediscovered* Bruson's VII invention. The board was charged with searching the scientific literature for useful inventions that might aid the war effort. When considering potential utility, they hypothesized about a PMA VII providing more uniform viscosity properties over a very broad range of temperatures, particularly in aircraft hydraulic fluids. The fluids of that era were judged to be deficient particularly in fighter aircraft because of the exaggerated temperature/time cycles experienced. On the ground, the fluids could experience high-temperature ambient conditions and engine waste heat; and then after a rapid climb to high, very cold altitudes, the fluid might experience temperatures below -40°C . After successful trials of the multigrade aircraft hydraulic fluid concept, Rohm and Haas, in cooperation with the National Research Defense Committee, rapidly proceeded to commercialize PMA VIIs and delivered the first product, Acryloid HF, in 1942. These multigraded hydraulic fluids were quickly adopted by the U.S. Army Air Corps and were followed by other multigraded hydraulic fluids and lubricants in ground vehicles that incorporated VIIs.

After the war, Rohm and Haas introduced PMA VIIs to general industrial and automotive applications. Early passenger car engine oil VIIs were first introduced to the market in 1946. The adoption of "all season" oils in the commercial market was greatly influenced by two events. First, the automotive manufacturers' viscosity specification introduction of the new designation "W" (for winter grades); and then by Van Horne's publication [4] pointing to the possibility of making and marketing cross-graded oils such as the now well-known "10W-30" as well as other cross-grades. By the early 1950s, use of multigrade passenger car oils became widespread in the consumer market. Methacrylates played a major role in enabling the formulation of that era's multigrade engine oils. The use of PMA VIIs has since been extended to gear oils, transmission fluids, and a broad array of industrial and mobile hydraulic fluids in addition to the early usage in aircraft hydraulic fluids.

11.1.4 DEVELOPMENT OF OTHER APPLICATIONS

Another important application area for PMA chemistry is in the field of *pour point depressants* (PPDs). When a methacrylate polymer includes at least some longer alkyl side chains, relatively similar to the chain length of waxes normally present in mineral oil, it can interact with growing wax crystals at sufficiently low temperatures. Wax-like side chains can be incorporated into a growing wax crystal and disrupt its growth. The net effect is to prevent congealing of wax in the oil at the temperature where it would have occurred in the absence of a PPD. Early PMA PPDs were used first by the military and later by civilian industry when Rohm and Haas offered such products to the industrial and automotive markets in 1946. Although PMAs were not the first materials used as PPDs (alkylated naphthalenes were), PMAs are probably the predominant products in this particular application now.

Another use of wax-interactive PMAs is as refinery *dewaxing aids*. The process of dewaxing is carried out primarily to remove wax from paraffinic raffinates to lower the pour point of the resulting lube oil base stocks. PMA dewaxing aids are extremely interactive with waxes found in raffinates and thus function as nucleation agents to seed wax crystallization and promote the growth of relatively large crystals. The larger crystals are more easily filtered from the remaining liquid so that lube oil throughputs and yields are improved, whereas pour points are lowered by virtue of lower wax concentrations.

Incorporating monomers more polar than alkyl methacrylates into a PMA provides products useful as ashless *dispersants* or *dispersant VIIIs*. The polar monomer typically contains nitrogen and oxygen (other than the oxygen present in the ester group), and its inclusion in sufficient concentration creates hydrophilic zones along the otherwise oleophilic polymer chain. The resulting dispersant PMAs (d-PMAs) are useful in lubricants since they can suspend in solution what might otherwise be harmful materials ranging from highly oxidized small molecules to soot particles.

PMAs have also been used in a number of other petroleum-based applications albeit in relatively minor volumes. An abbreviated list would include asphalt modifiers, grease thickeners, demulsifiers, emulsifiers, antifoamants, and crude oil flow improvers. PMAs have been present in lubricants for about 65 years now, and their longevity stems from the flexibility of PMA chemistry in terms of composition and process. Evolution of the original lauryl methacrylate composition to include various alkyl methacrylates and nonmethacrylates has brought additional functionality and an expanded list of applications. Process chemistry has also evolved such that it can produce polymers of almost any desired molecular weights (shear stability) or allow the synthesis of complex polymer architectures. The evolution of efficient processes for controlled radical polymerization in the 1990s has led to the development of taper and block copolymers and has permitted the development of products with narrower molecular weight distribution.

11.2 CHEMISTRY

11.2.1 GENERAL PRODUCT STRUCTURE

Typically, a methacrylate VII is a linear polymer constructed from three classes (three distinct lengths) of hydrocarbon side chains. These would be short, intermediate, and long-chain lengths. A more extensive discussion is given in Section 11.3, but an abbreviated description is given here to better understand the synthesis and chemistry of methacrylate monomers and polymers.

The first class is short-chain alkyl methacrylate of one to seven carbons in length. The inclusion of such short-chain materials influences polymer coil size particularly at colder temperatures and thus influences the viscosity index of the polymer in oil solutions. The intermediate class contains 8–13 carbons, and these serve to give the polymer its solubility in hydrocarbon solutions. The long-chain class contains 14 or more carbons and is included to interact with wax during its crystallization and thus provide pour point depressing properties.

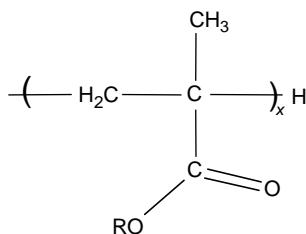


FIGURE 11.1 Generalized structure of polyalkylmethacrylate.

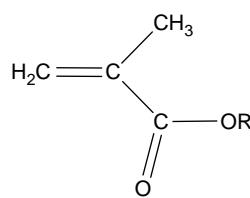


FIGURE 11.2 Alkyl methacrylate monomer.

The structure of PMAs used as PPDs differs from that of a VII by virtue of normally containing only two of these sets of components. These are the long-chain, wax crystallization interactive materials, and intermediate chain lengths.

The selected monomers are mixed together in a specific ratio to provide an overall balance of the aforementioned properties. This mixture is then polymerized to provide a copolymer structure in which R represents different alkyl groups and x indicates various degrees of polymerization. The simplified structure is shown in Figure 11.1.

11.2.2 MONOMER CHEMISTRY

Before discussing lubricant additives based on PMA, it is necessary to give an introduction to the chemistry of their parent monomers. The basic structure of a methacrylate monomer is shown in Figure 11.2.

The four salient features of this vinyl compound are as follow:

1. The carbon–carbon double bond that is the reactive site in addition polymerization reactions.
2. The ester functionality adjacent to the double bond, which polarizes and thus activates the double bond in polymerization reactions.
3. The pendent side chain attached to the ester (designated as R). These chains may range from an all-hydrocarbon chain to a more complex structure containing heteroatoms. A significant portion of the beneficial properties of PMAs is derived from the pendant side chain.
4. The pendant methyl group adjacent to the double bond, which serves to shield the ester group from chemical attack, particularly as it relates to hydrolytic stability.

As mentioned earlier, various methacrylate monomers, differing by length of the pendant side chains, are normally used to construct PMA additives. The synthesis chemistry of these monomers falls into two categories: shorter chains with four or fewer carbons and longer chains with five or more carbons. The commercial processes used to prepare each type are quite different.

The short-chain monomers are often mass produced because of their usefulness in applications other than lubricant additives. For instance, methyl methacrylate is produced in large volumes and used primarily in the production of Plexiglas® acrylic plastic sheet and as a component in emulsion paints and adhesives. It is also used in PMA lubricant additives, but the volumes in this application pale in comparison with its use in other product areas. Methyl methacrylate is generally produced by either of two synthetic routes. The more prevalent starts with acetone, then proceeds through its conversion to acetone cyanohydrin, followed by its hydrolysis and esterification. The other route is oxidation of butylenes followed by subsequent hydrolysis and esterification. Recently, additional processes for methyl methacrylate have been introduced based on propylene and propyne chemistry, but their use remains comparatively small.

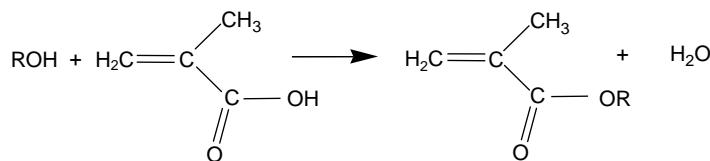


FIGURE 11.3 Direct esterification of methacrylic acid and alcohol.

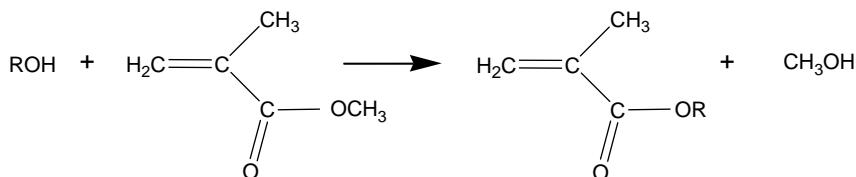


FIGURE 11.4 Transesterification of methyl methacrylate and alcohol.

The long-chain monomers are typically but not exclusively used in lubricant additives and can be produced by either of two commercial processes. The first is direct esterification of an appropriate alcohol with methacrylic acid. This well-known reaction is often used as a laboratory model of chemical strategies used to efficiently drive a reaction to high yield. These strategies involve a catalyst, usually an acid; an excess of one reagent to shift the equilibrium to product; and removal of at least one of the products, typically water of esterification, again to shift the equilibrium. The relevant chemical equation is given in Figure 11.3.

A second commercial route to longer-side-chain methacrylate monomers is transesterification of methyl methacrylate with an appropriate alcohol. The reaction employs a basic compound or a Lewis base as a catalyst. The equilibrium is shifted to product by use of an excess of methyl methacrylate and by removal of a reaction product, that is, methanol (if methyl methacrylate is used as a reactant). Figure 11.4 shows the reaction equation.

11.2.3 TRADITIONAL POLYMER CHEMISTRY

A combination of alkyl methacrylate monomers chosen for a given product is mixed together in specific ratios and then polymerized by a solution, free radical-initiated addition polymerization process that produces a random copolymer. The reaction follows the classic pathways and techniques of addition polymerization to produce commercial materials [5].

Commercial polymers are currently synthesized through the use of free radical initiators. The initiator may be from either oxygen or nitrogen-based families of thermally unstable compounds that decompose to yield two free radicals. The oxygen-based initiators, that is, peroxides, hydroperoxides, peresters, or other compounds containing an oxygen–oxygen covalent bond, thermally decompose through homolytic cleavage to form two oxygen-centered free radicals. Nitrogen-based initiators also thermally decompose to form two free radicals, but these materials quickly evolve a mole of nitrogen gas and thus form carbon-centered radicals. In any event, the free radicals attack the less hindered, relatively positive side of the methacrylate vinyl double bond. These two reactions are the classic initiation and propagation steps of free radical addition polymerization and are shown in Figures 11.5 and 11.6.

The reaction temperature is chosen in concert with the initiator's half-life and may range from 60 to 140°C. Generally, a temperature–initiator combination would be selected to provide an economic, facile conversion of monomer to polymer and avoid potential side reactions. Other temperature-dependent factors are taken into consideration. Chief among these might be a need to maintain a reasonable viscosity of the polymer in the reactor as it is being synthesized. Obviously,

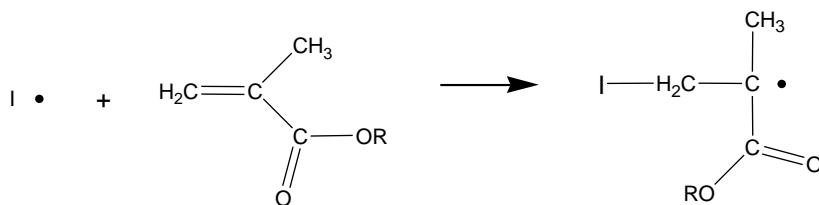


FIGURE 11.5 Free radical initiation of methacrylate polymerization.

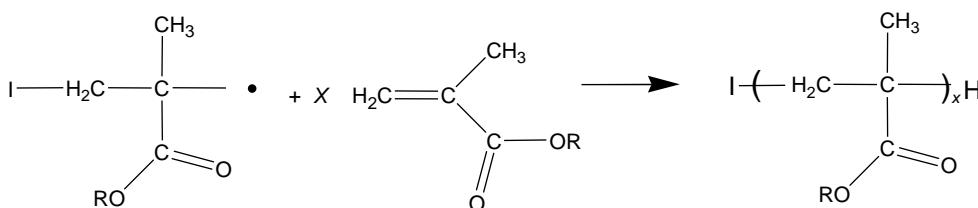


FIGURE 11.6 Monomer addition—propagation step.

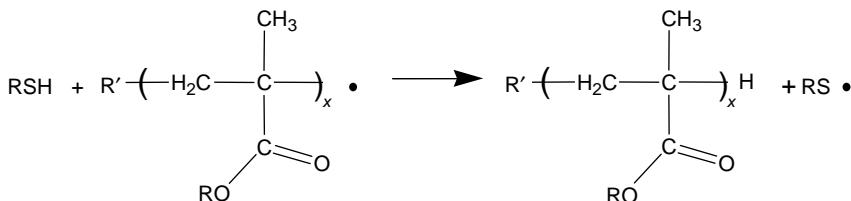


FIGURE 11.7 Termination by chain transfer.

the temperature can be utilized (as well as solvent) to maintain viscosity at a level appropriate for the mechanical agitation and pumping systems within a production unit. Excessive temperatures must be avoided to avoid the ceiling temperature of the polymerization, which is the temperature where the depolymerization reaction commences (see Section 11.3.1.2).

Normally, a mixture of alkyl methacrylate monomers is used to produce a random copolymer. No special reaction techniques are needed to avoid composition drift over the course of the reaction since reactivity ratios of alkyl methacrylates are quite similar [6].

The most important concern during a synthesis reaction is to provide polymer at a given molecular weight so as to produce commercial product of suitable shear stability. As normal for vinyl addition polymerizations, methacrylates can undergo the usual termination reactions: combination, disproportionation, and chain transfer. Chain transfer agents (CTA), often mercaptans, are the most commonly chosen strategy to control molecular weight. Selection of the type and amount of CTA must be done carefully and with an understanding that many other factors influence molecular weight. Numerous factors can impact the degree of polymerization: initiator concentration, radical flux, solvent concentration, and opportunistic chain transfer with compounds other than the CTA. An undesirable opportunistic chain transfer possibility is hydrogen abstraction at random sites along the polymer chain leading to branched polymers that are less efficient thickeners than strictly linear chains. The mercaptan chain transfer reaction is shown in Figure 11.7. In addition to chain transfer, the other usual termination reactions of chain combination or disproportionation can occur with methacrylates.

Commercial products cover a broad range of polymer molecular weights ranging from ~20,000 to ~750,000 Da. Molecular weight is carefully controlled and targeted to produce products that achieve suitable shear stability for a given application.

Higher-molecular-weight PMAs are rather difficult to handle as neat polymers; hence, it is necessary in almost all commercial cases to use a solvent to reduce viscosity to levels consistent with reasonable handling properties. Additionally, it is important to maintain reasonable viscosity during the polymerization reaction (although it always increases as monomer to polymer conversion increases), so that sufficient agitation can be maintained. Thus, solvents are almost invariably employed. An appropriate solvent would (1) be nonreactive, (2) be nonvolatile (at least at the reaction temperature), (3) avoid chain transfer reactions, and (4) be consistent with the intended application of the resulting product. It turns out that mineral oil meets the aforementioned criteria reasonably well, so that a solvent choice can be made from higher-quality, lower-viscosity-grade mineral oils. Nonreactivity demands relatively higher saturate contents; hence, better quality American Petroleum Institute (API) Group I (or higher API group) mineral oil can be used. Choice of solvent viscosity primarily depends on the end application; choices range from very-low-viscosity oils of 35 SUS to light neutrals typically up to 150N. Alternatively, one can use a nonreactive but volatile solvent when mineral oil might interfere with a sensitive polymerization and then do a solvent exchange into a more suitable carrier oil. The amount of solvent added to commercial PMA VIIIs is sufficient to reduce viscosity to levels consistent with reasonable handling or container pump out properties. This amount is dictated by polymer molecular weight, as this also heavily influences product viscosity. Generally, a higher-molecular-weight polymer requires more solvent. Commercial products may thus contain polymer concentrations over a very broad range of ~30 to 80 wt%.

d-PMAs were first described by Catlin in a 1956 patent [7]. The patent claims the incorporation of diethylaminoethyl methacrylate as a way of enhancing the dispersancy of VIIIs and thus providing improved deposit performance in engine tests of that era. The original dispersant methacrylate polymers utilized monomers that copolymerized readily with alkyl methacrylates and did not require different polymerization chemistry. Beyond these original random polymerizations, grafting is also an important synthetic route to incorporate desirable polar monomers onto methacrylate polymers. Stambaugh [8] identified grafting of *N*-vinylpyrrolidinone onto a PMA substrate as a route to improved dispersancy of VIIIs. Another approach is to graft both *N*-vinylpyrrolidinone and *N*-vinyl imidazole [9]. An obvious benefit of grafting is an ability to incorporate polar monomers that do not readily copolymerize with methacrylates due to significant differences in reactivity ratios. Grafting reactions are carried out after achieving high conversion of the alkyl methacrylates to polymer. Bauer [10] identified an alternate synthetic route to incorporate dispersant functionality by providing reactive sites in the base polymer and then carry out a postpolymerization reaction. For example, maleic anhydride copolymerized into or grafted onto the polymer backbone can be reacted with compounds containing desirable chemical functionality such as amines. This strategy is a route to incorporate compounds that are otherwise not susceptible to addition polymerization because they lack a reactive double bond.

This discussion characterizes most of the chemistry used to prepare the great majority of commercial PMA products. Additional chemical strategies as well as some novel processes and polymer blend strategies are reviewed in the literature and in the patent section below.

11.2.4 PATENT REVIEW

A review of pertinent literature and patents shows PMAs to have been the subject of numerous investigations over the course of years. A huge body of PMA patent literature exists, and a large subset of it is related to lubricant additives. A summary from the additive-related patents suggests five major areas of investigation, which can be categorized as variation of polymer composition; incorporation of functionality to enhance properties other than rheology, that is, dispersancy; improved processes to improve economics or enhance a performance property; polymer blends to provide unique properties; and finally, polymer architecture. A brief discussion of only a few of the more important patents within the five categories ensues.

Since the first PMA patents [2,3], there has been a continuing search for *composition modifications* to methacrylate polymers to improve some aspects of rheological performance. As expected, much of the earlier work explored uses of various alkyl methacrylate monomers and examined the ratios of one to another; this work is part of the well-established art. But, even more modern patent literature includes teachings about PMA compositions. For instance, highly polar PMA compositions made with high concentrations of short-chain alkyl methacrylates are useful in polar synthetic fluids such as phosphate esters to impart rheological advantages [11]. There are numerous examples of incorporating nonmethacrylates into polymers; a good example is the use of styrene [12] as a comonomer to impart improved shear stability. However, styrenic monomers have different reactivity ratios than methacrylates, and the usual processes lead to relatively low conversions of styrene. This can be overcome by a process utilizing additional amounts of methacrylate monomers near the end of the process to drive the styrene to high conversion [13].

Incorporation of *functional monomers* to make dispersant versions of PMA has been discussed in the preceding section on chemistry. Despite the well-known nature of d-PMA, it remains an area of active research as exemplified in Ref. 14, which describes a dispersant for modern diesel engine oil soot. Although nitrogen-based dispersants are the focus of much research, oxygen-based dispersants such as hydroxyethyl methacrylate [15] and ether-containing methacrylates [16] have also been claimed. In addition to incorporating dispersant functionality, significant efforts to incorporate other types of chemical functionality such as antioxidant moieties [17] have been made.

Novel processes have been developed to improve either economics or product properties. Tight control of molecular-weight distribution and degree of polymerization can be achieved through constant feedback of conversion information to a computer control system that adjusts monomer and initiator feeds as well as temperature [18]. Coordinated polymerizations are useful in preparing alternating copolymers of methacrylates with other vinyl monomers [19]. A process has been described to prepare continuously variable compositions, which can obviate the need to physically blend polymers [20].

Polymer blends of PMA and olefin copolymer (OCP) VIIIs provide properties intermediate to the individual products with OCP imparting efficient thickening (and economics) and PMA imparting good low-temperature rheology. However, a physical mixture of the two VIIIs in concentrated form is incompatible. This problem is overcome by using a compatibilizer, actually a graft polymer of PMA to OCP, to make an ~70% PMA and ~30% OCP mixture compatible [21]. Very-high-polymer content products can be prepared by emulsifying the mixture, so that the PMA phase is continuous in a slightly polar solvent, whereas the normally very viscous OCP phase is in micelles [22,23]. Blends of PMAs can provide synergistic thickening and pour depressing properties [24].

PMA polymer architecture is being very actively investigated today. Preparations of PMA blocks, stars, combs, and narrow MWD polymers are all the subject of relatively recent patents or patent applications. For instance, the newer polymerization technique of controlled radical polymerization (CRP), specifically atom transfer radical polymerization (ATRP), has been used to prepare PMAs of very narrow molecular weight distribution to improve the thickening efficiency/shear stability balance of the resulting product [25]. Similarly, a CRP nitroxide-mediated polymerization (NMP) has been described [26] as providing products with similar improved properties. The ATRP technique has been used to prepare PMAs with functional (polar) monomers in blocks to enhance physical attraction to metal surfaces and thus improve frictional properties under low-speed conditions [27,28]. Star-shaped PMAs made through CRP processes including reversible addition–fragmentation chain transfer (RAFT) polymerization, NMP, and ATRP have been described as providing improved solution properties [29]. Star shapes and other polymer architectures through various CRP processes are described [30,31] as having enhanced thickening efficiency/shear stability and VI contribution relative to the more traditional linear polymers. Another new polymer architecture of interest is comb polymers with polyolefin and PMA elements as described in Ref. 32; the same enhancement of properties as mentioned previously applies to these structures.

11.3 PROPERTIES AND PERFORMANCE CHARACTERISTICS

11.3.1 CHEMICAL PROPERTIES

PMAs are rather stable materials and do not normally undergo chemical reactions under moderate to even relatively severe conditions. The chemical design of any VII or PPD clearly entails avoiding reactive sites in their structure to provide as high a degree of stability as possible in the harsh environments to which lubricants are exposed. It is expected that these PMA additives are not chemically active, as they are added to alter only physical properties, that is, viscosity and wax crystallization phenomena. When considering d-PMAs, which include chemistry other than alkyl methacrylate, even these have essentially the same fundamental stability as the nondispersant polyalkylmethacrylates. The most notable reaction of any VII, including PMA, is polymer shearing brought about by mechanical mastication.

11.3.1.1 Hydrolysis

PMAs are not very susceptible to hydrolysis reactions; however, the question of hydrolytic stability is often posed because of the presence of the ester group. In the polymeric form, methacrylate ester groups are quite stable since they are well shielded by the surrounding polymer as well as the pendant side chains. The immediate chemical environment surrounding the ester is definitely hydrophobic and not compatible with compounds that participate in or catalyze hydrolytic reactions. Extraordinary measures can be used to induce hydrolysis; for instance, lithium aluminum hydride hydrolyzes PMAs to yield the alcohols from the side chain. Nevertheless, there is no evidence that PMA hydrolysis is of any significant consequence in lubricant applications.

11.3.1.2 Thermal Reactions: Unzipping and Ester Pyrolysis

These reactions are known to occur with PMAs, but very vigorous conditions are needed. Thus, there appears to be no important consequences in lubricant applications since bulk oil temperatures are usually lower than the onset temperatures of these reactions [33].

A purely thermal reaction of PMA is simple depolymerization (unzipping of polymer chains). PMA chains at sufficiently high enough temperatures unzip to produce high yields of the original monomers; the unzipping reaction is merely the reverse of the polymerization reaction. One consequence of unzipping is that care must be taken to avoid depolymerization during polymer synthesis by simply avoiding excessive temperatures. Thus, synthesis temperatures are designed to be well below the *ceiling temperature* of the polymerization/depolymerization equilibrium. Onset temperatures for unzipping of PMAs are on the order of 235°C—the temperature listed in the literature for polymethylmethacrylate depolymerization [34]. There may be a minor dependence on detailed side chain structure, but relatively little investigation has been done on longer-side-chain alkyl methacrylate polymers useful in lubricants. It is also thought that terminal double bonds on the polymer chain are the point where unzipping most readily starts. When terminal double bonds are present in the structure, they are most likely the product of termination by disproportionation.

Another potential reaction is the thermal decomposition of individual ester units within the polymer chain. This reaction, usually termed *beta ester pyrolysis*, degrades polymer side chains to yield an alpha olefin from the pendant side chain. The olefin is of the same length as the carbon skeleton of the side chain (as long as the original alcohol is used to make the monomer). The other reaction product is an acid that presumably remains in the polymer chain. The acid may react with an adjacent ester to yield alcohol and a cyclic anhydride. Another possibility is the reaction of two adjacent acid groups to form a cyclic anhydride with the elimination of a molecule of water. The pathway for the pyrolysis reaction proceeds through the formation of a six-membered intermediate ring formed from a hydrogen bond of side chain beta carbon hydrogen to the ester carbonyl oxygen.

TABLE 11.1
Pyrolysis of PMA

Percentage Weight Loss After	Pyrolysis Temperature (°C)	
	290	315
2 min	—	18.7
3 min	93.2	
5 min	93.1	94.6
10 min	94.9	96.1
15 min	96.3	97.7

The intermediate ring decomposes to alpha olefin and acid products [35]. Temperatures on the order of 250°C are needed to initiate this reaction.

Ester pyrolysis produces volatile alpha olefins as well as acids or anhydrides along the polymer backbone or perhaps monomeric acids or anhydrides should the reaction occur after depolymerization. The fate of acid or anhydride in the polymeric backbone would still be depolymerization under the vigorous thermal conditions present. The ultimate products are volatile under the conditions needed to initiate the reaction.

Consequences of either thermal reaction are loss of activity as a VII or PPD and the generation of volatile small molecules. The products distill from the high-temperature reaction zone and thus offer no further opportunity for the chemical reaction. The data in Table 11.1 indicate the very high volatility of a PMA VII that has been exposed to extreme temperatures in air. There is no evidence that unzipping or ester pyrolysis is important in normal lubricant applications. Most applications generate temperatures less than reaction onset temperatures; thus, these reactions do not appear to be an issue. A limited potential might exist in a microenvironment, such as if VII were trapped in a piston deposit where temperatures near the combustion chamber exceed the onset temperature [6].

11.3.1.3 Oxidative Scissioning

Like any hydrocarbon when exposed to severe oxidative conditions, PMAs can be subject to classic oxidation reactions resulting in polymer scissioning [33]. The scissioning reaction yields two fragments of various lengths each of which is obviously of lower molecular weight than the parent chain, and consequently, there is some loss of viscosity contribution. The reaction takes place at random sites along the backbone since oxidative or free radical attack may occur anywhere along the polymer chain. Allylic, benzylic, or tertiary hydrogen are most susceptible to oxidative or free radical attack. Methacrylates do not normally contain those structural elements; thus, the reaction is not normally an important consideration. The pyrolysis data in Table 11.1 would seem to support this conclusion, as scission fragments would by and large not be volatile under the conditions of the experiment.

Proof of PMA oxidative stability and continued effectiveness has been demonstrated by comparing viscosities of used oils exposed to the very severe Sequence IIIG oxidative engine procedure. One oil contained a PMA PPD. The other had all the same components but had no PPD; after the engine-aging procedure, this oil was treated with exactly the same PPD in the same concentration as the PPD-containing oil. The resulting viscosities were essentially the same, and of particular note, the low temperature, low shear rate viscosities did not differ in any significant way, indicating that the PMA PPD was not degraded in the severe environment of a Sequence IIIG [36].

On the whole, PMAs are not prone to thermal or oxidation reactions under normal conditions of use, and there is little evidence that these reactions are important in the vast majority of PMA-based lubricant applications.

11.3.1.4 Mechanical Shearing and Free Radical Generation

A well-known, very important degradation reaction of any VII including PMAs is mechanical shearing. Although polymer shearing begins as a physical process, it does generate free radicals. For each polymer chain rupture, two transitory carbon-centered free radicals are generated. In lubricants, the free radicals are apparently quickly quenched, presumably by abstracting hydrogen from the surrounding hydrocarbon solvent or perhaps by the antioxidants in formulated lubricants. Overall, there appear to be few if any further chemical consequences. However, there are important viscometric consequences since the rupture leads to two lower-molecular-weight fragments that provide a reduced viscosity contribution. The shearing process is initiated through the concentration of sufficient energy within the polymer chain to induce homolytic cleavage of a carbon–carbon bond in the backbone of the polymer. The susceptibility of the polymer to mechanical shearing is not related to its chemical structure; rather it is very clearly a function of polymer molecular weight or even more appropriately to the end-to-end distance of the polymer chain [37]. Overall, VII shear stability, although an important physical process, does not appear to carry any appreciable chemical consequences. Further discussion of shearing can be found in the section on the effect of structure on physical properties.

11.3.2 PHYSICAL PROPERTIES

The paramount properties of PMAs are those associated with their use in solution as PPDs, VIIIs, or dispersants. The dispersants may also be utilized for their VI improving or thickening properties, but in some cases, thickening properties are not needed, and the molecules are used solely as dispersants. The useful properties of PMAs are related to both their physical (primarily molecular weight) and chemical nature (primarily side chain structure).

11.3.2.1 Pour Point Depressants

PPDs are used to modify and control wax crystallization phenomena in paraffinic mineral oils. As temperature decreases, waxy components begin to form small, plate-like crystals. The plates eventually grow together to form an interlocking network that effectively traps the remaining liquid. Flow ceases unless a force strong enough to break the relatively weak wax gel matrix structure is applied. Control of wax crystallization in lubricants is often described as pour point depressancy since one of the quantifiable effects is to reduce the ASTM D 97 pour point. The pour point test is fairly archaic as it utilizes a very rapid cool down to measure only flow versus no-flow conditions. PPDs also control wax crystallization during various slower, more realistic cooling conditions that better favor crystal growth. PPDs are used to maintain fluidity of lubricants under various cooling conditions to expand the operating temperature window into colder regimes. How much the operating window can be expanded is a complex function of wax chemistry, its concentration in base oil, the presence or absence of other waxy additives, the cooling conditions, the final cold temperature, and, of course, PPD chemistry and concentration [38].

PPDs do not affect either the temperature at which wax crystallizes from solution or the amount of wax precipitate. PPDs cocrystallize on the edges of the growing wax plates by virtue of their longer alkyl side chains. Thus, the growing wax crystal is attached to the polymer, and then, because of the presence of the molecularly large polymer backbone, crystal growth is sterically hindered in-plane. Further growth is redirected in a perpendicular direction, resulting in the formation of more needle-like crystals. Thus, the usual tendency to form a three-dimensional structure based on

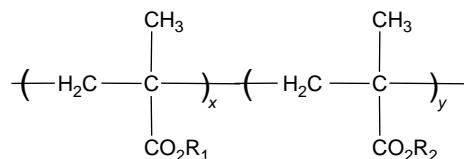


FIGURE 11.8 PMA pour point depressant.

plate-like crystals is disrupted, and wax gel matrices are prevented at least temporarily. At exceedingly low temperatures, oils may eventually become so viscous as to appear to cease flowing, but this is irrespective of wax issues [39].

PMAs were the first polymeric PPDs and were commercialized in the 1940s by Rohm and Hass Company. Today, they are the predominant chemistry in this application enjoying a majority of the worldwide market. The reason for this success is related to the molecular structure, as shown in Figure 11.8, and its inherent chemical flexibility in terms of polymer chain length but more importantly its ability to include various side chain lengths and at appropriate concentrations.

In Figure 11.8, R_1 and R_2 represent two different lengths of alkyl side chains; one is wax-interactive and the other is “neutral,” or noninteractive with wax. But, the side chains are actually complex mixtures of alkyl groups, which may be anywhere from 1 to more than 20 carbons. The longer carbon side chains are intended to interact with wax; to do so, they should be linear and typically be at least 14 carbon atoms in length. The interaction of a waxy alkyl side chain with wax intensifies as its length increases. However, shorter chains are added to serve as inert diluents, thereby ensuring a controlled degree of wax interaction or to act as *spacers* between the longer side chains so as to better fit into crystal lattice structures.

Pour point depressancy is largely independent of molecular weight over a broad range and degree of polymerization, which may vary from ~200 to ~3000. But it is important to achieve a minimum degree of polymer backbone size to provide enough steric hindrance to crystal growth as described earlier.

The optimum positive interaction with wax requires a careful balance of the waxy alkyl groups in terms of both type and concentration. This thought is sometimes expressed as a function known as the *wax interaction factor* (WIF) that takes into account the amount of each alkyl group that interacts with wax and the strength of the interaction. Since mineral oils contain a distribution of wax chain lengths, PPDs often contain a distribution of waxy side chains to best interact with wax in a specific situation. As the wax structure and content change because of different base stocks and additives, a different PPD with a different WIF may be the optimum. This effect is shown in Table 11.2 where different base stocks with different wax chemistries and concentrations respond differently to PPDs with different WIF.

Finished lubricant formulations often respond differently to PPDs than do the base oils used to make the fully formulated oils. For example, in the MRV TP-1 measurement, two different 150N base stocks respond to PPD 3: base stock A with some yield stress and base stock B with no yield stress; however, when these base stocks are additized each with the same DI and VII, they respond in an opposite way. The SAE 10W-40 based on oil A has passing rheology, whereas the SAE 10W-40 based on oil B is a clear failure. PPD 4 with different WIF does provide passing results with the formulation based on oil B. These data are shown in Table 11.3.

Previously (Section 11.3.1.3), the oxidative and thermal stability of PMA had been discussed and a conclusion was reached that PMA PPDs remain effective even after exposure to a severe oxidative environment. The background for the experimentation is a new low-temperature pumpability requirement for used gasoline engine oils appearing in the International Lubricants Standardization and Acceptance Committee (ILSAC) GF-4 standard for passenger car engine oils [40]. Pumpability is measured by ASTM D 4684 on an oil after undergoing a Sequence IIIG engine-aging procedure

TABLE 11.2
PPD Response^a in Different Base Oils

Wt%	Base Stock 1		Base Stock 2	
	PPD 1 Low WIF	PPD 2 High WIF	PPD 1 Low WIF	PPD 2 High WIF
None		-18		-12
0.05	-24	-21	-18	-18
0.10	-33	-30	-21	-27
0.20	-36	-30	-27	-33

^a ASTM D 97 pour point (°C).

TABLE 11.3
Comparison of PPD Response^a in Base Stocks versus Fully Formulated Fluids

PPD Treat Rate	Base Stock A	Base Stock A + DI and VII	Base Stock B	Base Stock B + DI and VII
0.1 wt%	150N	SAE 10W-40	150N	SAE 10W-40
PPD 3	31,100/35	39,700/<35	26,500/<35	62,000/70
PPD 4	—	—	28,100/<35	35,800/<35

^a ASTM D 4684 TP-1 MRV at -30°C, viscosity (cP)/yield stress (Pa).

(ASTM D 7320), which is a severe oxidative and volatilization environment. One normally associates low-temperature pumpability with wax-related phenomena and ultimately with PPD activity; however, the used oil pumpability requirement was added to address original equipment manufacturer (OEM) concerns of oil degradation in the field, which could be identified by low-temperature viscosity measurements and not necessarily by the usual higher-temperature kinematic viscosity determinations [41]. The need for a low-temperature measurement is because of severe oxidation, which may lead to the formation of polar molecular species that associate to form gel-like structures at relatively cold temperatures but not necessarily at warmer temperatures.

11.3.2.2 Viscosity Index Improvers

VIIIs are used to achieve the advantages of multigrade lubricating oils in numerous applications including crankcase engine oils, automatic-transmission fluids, high VI hydraulic fluids, gear oils, and other lubricants used primarily (but not necessarily) outdoors. VIIIs, also known as viscosity modifiers, are high-molecular-weight, oil-soluble polymers, which ideally provide increased viscosity at higher temperatures and minimal viscosity contribution at lower temperatures [42]. Current commercial chemistries are based on either of two chemical families: hydrocarbons such as ethylene-propylene copolymers or ester-containing materials such as PMAs. There are other examples of each chemical family. PMA chemistry dominates applications where high viscosity index and superior low-temperature properties are required [36]. These benefits can usually be observed in typical lubricant industry low-temperature, low-shear-rate rheology tests such as ASTM D 4684 mini rotary viscometer (MRV TP-1), Scanning Brookfield, and ASTM D 2983 Brookfield as well as numerous others. Polymer molecular size influences thickening at all temperatures, and the larger

the coil size, the higher the thickening power. Conversely, with smaller coil size, less thickening occurs. PMA VII's thicken oils well at higher temperatures but contribute relatively little low-temperature viscosity. This desirable viscosity–temperature behavior stems from PMA ester functionality imparting polarity to the polymer in the nonpolar hydrocarbon solvent, mineral oil, leading to a relatively small molecular coil size at low temperature. The ester polarity can be accentuated by the use of short pendant side chain monomers.

Thickening properties for any chemical class of VII's or viscosity modifier are related to their immensely greater molecular size compared to that of the solvent in which they are dissolved. The long polymeric strand, the backbone of the polymer, is configured in a random coil shape. The size of the coil, or more appropriately its hydrodynamic volume, is proportional to polymer molecular weight as a first approximation; but more precisely, it is proportional to the cube of the root mean square end-to-end distance of the polymer. In the lattice theory of viscous flow, segments of polymer molecules fill holes in the lattice (constructed of all surrounding molecules) and thereby limit the ability of smaller molecules to participate in movement through the lattice [38]. The increase in degree of viscosity depends on coil size; thus, higher-molecular-weight polymers provide more thickening. The overall viscosity of a polymer-thickened solution is related to polymer concentration and molecular weight through the following equation developed by Stambaugh [6].

$$\ln \eta = KM_v^a c - k''(M_v^a)^2 c^2 + \ln \eta_0 \quad (11.1)$$

where

M_v = VII viscosity average molecular weight

c = VII (or thickener) concentration

η_0 = solvent viscosity

exponent a relates to solubility of the specific polymer chemistry, solvent, and temperature

For a PMA VII in solution, the coil size expands and contracts with temperature [43]. At lower temperatures, PMA is, on a relative basis, poorly soluble in oil. This is *not* meant to say that PMA precipitates from solution, but the relatively poor solubility results in a contracted, smaller-volume polymer coil, which has a relatively low viscosity contribution. As temperature increases, solubility improves and polymer coils eventually expand to some maximum size and in doing so donate more and more viscosity. The process of coil expansion is entirely reversible. The polymer coil will continue to expand or contract with temperature changes irrespective of the aging history of the solution (see Figure 11.9). In contrast, nonpolar polymeric thickeners are well solvated by oils at all temperatures and experience far less change to coil size with temperature [44]. For any VII or VM chemistry, these solubility factors relate to the value of the exponent a in Equation 11.1 and, specifically for

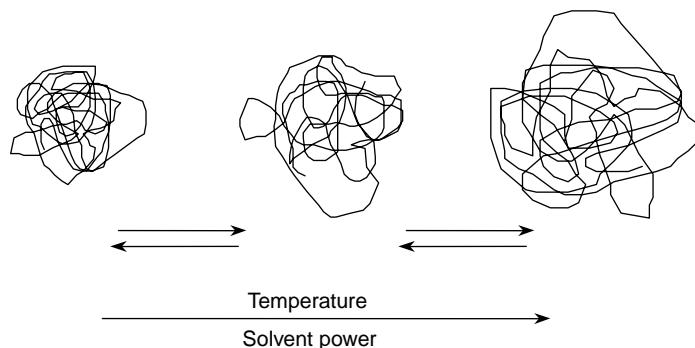


FIGURE 11.9 PMA coil expansion.

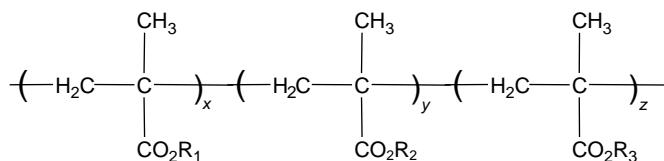


FIGURE 11.10 PMA VII structure.

PMA, are a function of the average length side chain chemistry: short, intermediate, and long alkyl chains. This structural concept of three distinct chain lengths is represented in Figure 11.10.

A typical average side chain length of about eight carbons will provide PMA solubility in oil, even down to extremely low temperatures. Thus, an intermediate-chain length monomer is used to provide overall oil solubility and is normally selected from linear or branched chains composed of 8–14 carbons. The longer chains consisting of more than 14 carbons may be incorporated to provide wax crystallization interactions as described earlier in the section on PPDs. Very short chains, usually C1 or C4, are used to balance the composition and make the average chain length at least eight carbons for paraffinic mineral oil solubility. To a very good first approximation, the average side chain length will determine viscosity–temperature properties rather than the detailed nature of the side chain structures.

Building pour point depressancy into PMA VIIIs by including longer-side-chain monomers may involve compromises. An optimized wax interaction provided by the VII may not be possible because of the many different base stocks (with different wax types and contents) in which the VII might be used. However, VII treat rates are relatively high compared to PPDs, and the high polymer concentration may simply overwhelm wax crystallization as it occurs and thereby prevent wax gel matrix consequences (see Section 11.3.2.1).

Commercial PMA VIIIs are available in various chemical compositions and molecular weights ranging from ~20,000 to 740,000 Da. The higher-molecular-weight materials are not only the most efficient thickeners and provide the greatest VI lift but also the most susceptible to shearing effects. Selection of a suitable VII for a given application should focus on shear stability, thickening efficiency, and VI lift.

Shearing effects, either temporary or permanent, are related to polymer backbone molecular weight. High-molecular-weight polymers are subject to both temporary viscosity loss through shear thinning and permanent viscosity loss when polymer chains are broken in mechanical mastication, both of which result in loss of thickening.

Temporary viscosity loss occurs when polymer molecules become oriented along the axis of flow at sufficiently high shear rates. This phenomenon, known as shear thinning, occurs at a minimum, nominal value on the order of 10^4 s^{-1} . Shapes of individual polymer coils change from a spherical to an elongated configuration that occupies a smaller hydrodynamic volume and thus contribute less viscosity. With further increases of shear rate, molecules increasingly deform leading to a corresponding greater loss of viscosity contribution until maximum distortion is reached. Within the lubricant community, non-Newtonian, shear-thinning behavior is better known as “temporary loss of viscosity” since the process is reversible upon removal of high shear rates. Distorted polymer molecules resume random coil shapes, reoccupy original hydrodynamic volumes, and contribute viscosity just as before the application of a higher shear rate. The degree of temporary viscosity loss depends on the level of shear stress and the molecular weight (size) of the polymer. Because of their small coil sizes, low-molecular-weight polymers are less susceptible to shear thinning.

The temporary viscosity loss of PMAs is directly related to molecular weight, or even more appropriately, to backbone molecular weight. PMAs are not associative thickeners and do not experience viscosity losses through the loss of molecular associations in high shear stress fields. Any loss of viscosity is related merely to at-rest molecular size and subsequent molecular shape

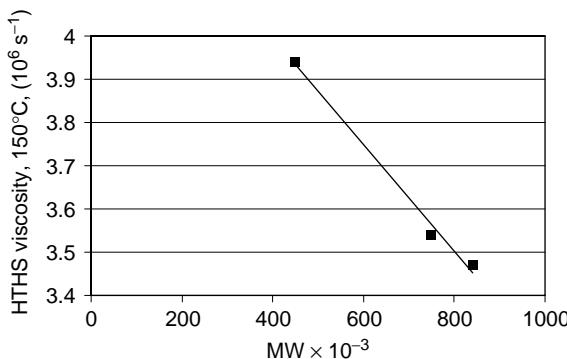


FIGURE 11.11 Relationship of PMA VII molecular weight to temporary shear stability. (SAE 10W-40 oils blended to 14.5 mm²/s at 100°C.)

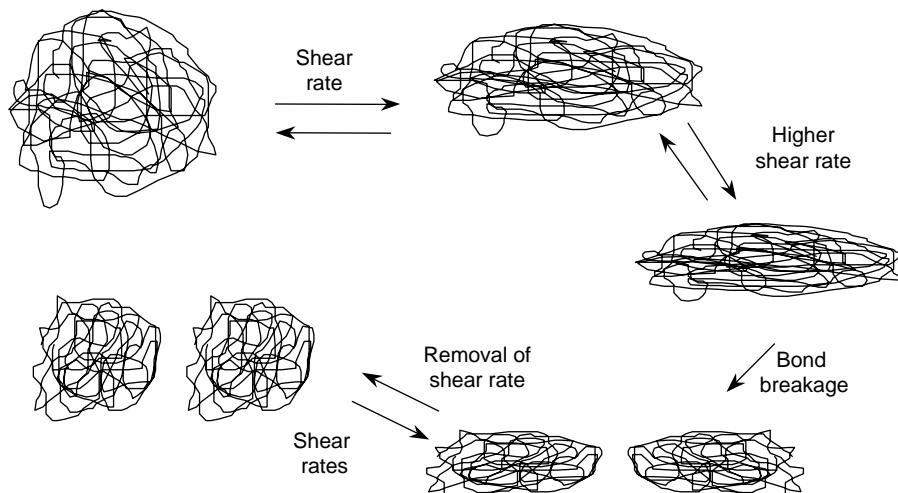


FIGURE 11.12 Temporary and permanent shearing of polymer.

distortion leading to lower hydrodynamic volume. Figure 11.11 is compiled with data taken from a set of SAE 10W-40 oils blended to constant kinematic viscosity (14.5 mm²/s) and constant cold cranking simulator (CCS) viscosity with the same compounding materials, except for the VII. Three chemically equivalent d-PMA VIIIs, differing only in molecular weight, were used in the formulations. The resulting high-temperature, high-shear-rate (HTHS) viscosities are clearly a function of polymer molecular weight, showing essentially an inverse linear relationship with polymer molecular weight.

Permanent viscosity loss through mechanical degradation occurs when very high shear stresses, perhaps coupled with turbulent flow, lead to extreme polymer coil distortion and concentrate enough vibrational energy to cause polymer chain rupture. Cavitation probably also plays an important role by producing intense velocity gradients. Polymer chain rupture occurs through homolytic cleavage of a carbon–carbon bond, statistically near the middle of the polymer chain. The cleavage produces two molecules each having approximately half the molecular weight of the original molecule; Figure 11.12 represents molecular elongation and rupture concepts. The total hydrodynamic volume of the two smaller molecules is less than that of the single parent molecule, resulting in lower viscosity contribution. Since the bond scission is not reversible, the viscosity loss is permanent.

Higher-molecular-weight polymers are more susceptible to distortion and mechanical degradation, whereas polymers of sufficiently low molecular weight may not even undergo permanent shearing. The sheared polymer molecules are typically of sufficiently lower molecular weight that are not normally susceptible to further degradation. Thus, the degradation process is self-limiting under any given intensity of shearing.

As with shear-thinning phenomenon, PMAs of sufficient molecular weight are subject to mechanically induced permanent loss of viscosity, again, the amount of viscosity loss for linear PMA is a reasonably straightforward function of molecular weight. Molecular weight distribution plays a secondary role. If the molecular weight distribution were skewed to larger fractions of high molecular weight polymer, then the loss of viscosity would be greater than that of a polymer of similar average molecular weight but with a Gaussian distribution. It should also be noted that different applications can create very different shear stresses, and because of this, viscosity losses of polymers of a given molecular weight may vary by application. The net result is that viscosity loss to a first approximation is directly related to molecular weight and the amount of shearing force in a given application or laboratory bench test. The relationship of shear stability index to polymer molecular weight and shearing severity by application are shown in Figure 11.13 for a set of PMA VII's [45].

Dispersant functionality may be incorporated into PMA chemistry by using a monomer that contains a heteroatom, which will create polar zones along the otherwise oleophilic polymer chain. Typically, the heteroatom is nitrogen incorporated in an amine, amide, or lactam, but oxygen-containing monomers are sometimes used. As previously discussed, incorporation can be achieved through monomer copolymerization, grafting a monomer onto the preformed polymer chain, or incorporating a reactive chemical site on the polymer and then postreacting with an appropriate chemical species, for instance, incorporating an anhydride, such as maleic anhydride, as the reactive chemical site, then after the polymerization reacting with an amine, thus creating succinimide sites along the polymer chain. The resulting polar region(s) serves to attract and peptize small polar molecules or particles, that is, oxidized oil, oxidized fuel, or even soot. These undesirable materials are often unintentional by-products of combustion or oxidation of the lubricant. Left undispersed,

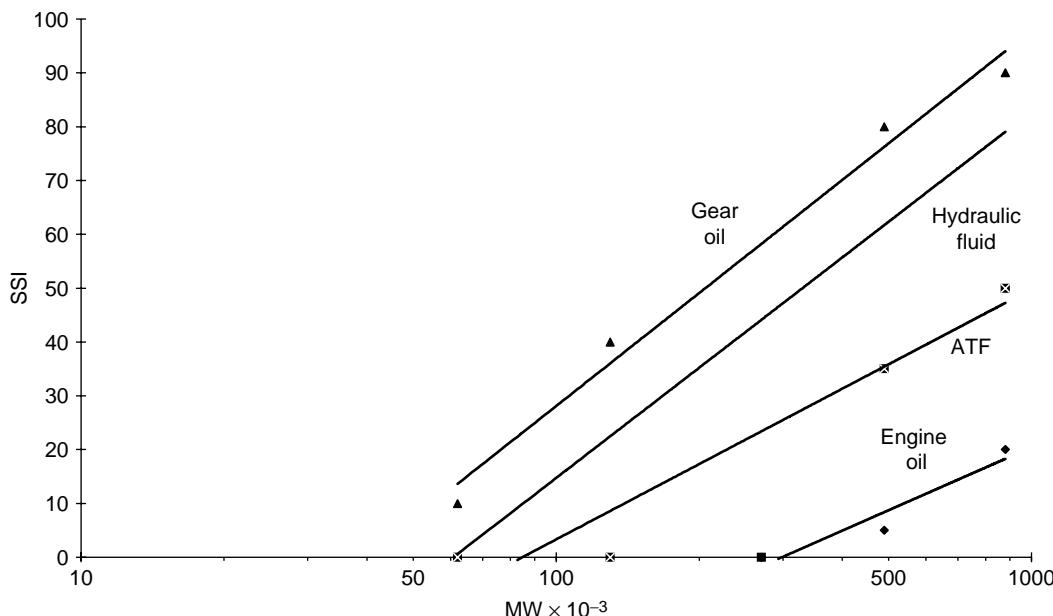


FIGURE 11.13 Relationship of shear stability index to PMA VII molecular weight and shear severity by application.

TABLE 11.4
Engine Performance^a Dispersant PMA versus Nondispersant PMA
in SAE 5W-30 API SG Oils

PMA VII ^s (45 SSI)	Average Sludge	Average Varnish	Average Cam Wear
Dispersant	9.23	6.25	1.5
Nondispersant	4.55	4.56	5.8

^a Sequence VE test—summary data (average from six tests of each formulation).

the small molecules may undergo further reactions, resulting in the formation of harmful deposits, whereas particulate matter may become a source of abrasive wear.

d-PMAs are used as stand-alone dispersant products in a few applications but more typically as dispersant VII^s, which augment the dispersancy provided by classic ashless dispersant molecules found in DI packages. An example of a stand-alone d-PMA is its use in Society of Automotive Engineer (SAE) specification J1899 piston aircraft engine oils. PMA dispersants can also be employed to boost the overall dispersancy of a formulation. These materials have been used in engine oils either to supplant some of the traditional ashless dispersants or simply to enhance dispersancy as well as imparting the usual rheological properties. Table 11.4 contains data from Sequence VE engine testing of a SAE 5W-30 API SG oil made from d-PMA VII (45 Bosch SSI) and another SAE 5W-30 oil containing all the same compounding materials but with a *nondispersant* PMA VII (also 45 Bosch SSI). The results in each case are the average of six engine tests. Clearly, the dispersant VII provides enhanced dispersancy relative to its nondispersant analog.

11.4 MANUFACTURERS, MARKETERS, AND ECONOMICS

11.4.1 MANUFACTURERS AND MARKETERS

The following companies offer commercial quantities of PMA additives:

Afton Petroleum Additives, Inc.
 330 South Fourth Street
 P.O. Box 2189
 Richmond, VA, 23219

Chevron Oronite
 6001 Bollinger Canyon Road
 San Ramon, CA 94583

CIBA Specialty Chemicals Corporation
 540 White Plains Road
 Tarrytown, NY 1059

Infineum UK Limited
 P.O. Box 1 Milton Hill
 Abingdon Oxfordshire
 OX 13 6BB, United Kingdom

Nippon NSC Ltd.
 Specialty Synthetic Polymers Ginza Wall Bldg. 6-13-16, Ginza, Chuo-ku
 Tokyo 104-0061, Japan

The Lubrizol Corporation
29400 Lakeland Boulevard
Wickliffe, OH 44092-2298

RohMax Additives GmbH
Kirschenallee D-64293
Darmstadt, Germany

Sanyo Chemical Industries, Ltd.
11-1, Ikkyo Nomoto-Cho, Higashiyama-Ku
Kyoto 605-0995, Japan

Toho Chemical Industry Co. Ltd.
6-4, Akashi-Cho, Chuo-Ku
Tokyo 104-0044, Japan

Within the realm of lubricant additives, NSC primarily offers PMA VIIIs and PPDs. RohMax, Sanyo Kasei, and Toho, although focused on PMAs, do offer other product types to the lubricant and oil-refining industries. CIBA offers additives other than methacrylates most notably antioxidants and other ashless components. Afton, Chevron Oronite, Infineum, and Lubrizol offer PMAs as well as numerous other additive types and additive packages for lubricants.

11.4.2 ECONOMICS AND COST-EFFECTIVENESS

Current list prices for a few PMA VII products intended for different applications and PMA PPDs are given in Table 11.5. The PPD price range covers products of varying complexity from the least to the most expensive.

Of course, one must know an additive's treat rate to do a meaningful economic study. Although this is true for any additive, it is particularly true for VIIIs as their treat rates may vary widely depending on their chemical nature, base oil viscosities, as well as by the desired viscosity grade of the treated oil. The cost-effectiveness of PMA VIIIs varies widely by application. When enhanced low-temperature performance, high viscosity index, and excellent shear stability are the requirements, then PMAs often enjoy excellent cost-competitiveness. Examples of these applications are

TABLE 11.5
List Price of PMA Products

Product Description	Application	U.S. Dollars per Pound
VII—45 SSI	Engine oil	1.22
Dispersant VII—45 SSI	Engine oil	1.60
Dispersant VII—25 SSI	Engine oil	1.91
VII—15 SSI	Hydraulic fluid	2.29
VII—30 SSI	Hydraulic fluid	1.99
PPDs	Various	2.03–2.72

Note: SSI values for engine oil application are for ASTM D 6278 (30 Pass Bosch Diesel injector). SSI values for hydraulic fluid applications are from ASTM D 5621 (40 min sonic shear).

Source: Courtesy of RohMax USA, LLC.

automatic transmission fluids (ATF), multigrade hydraulics, and the lower SAE W grade gear oil grades. In these situations, it may often be impractical to employ other VII chemistries because of some technical deficiency related to the aforementioned properties.

In engine oils where these technical criteria are not as stringent, PMA VIIIs are often at a cost disadvantage. Fundamentally, PMAs are less-efficient thickeners than many competitive hydrocarbon VIIIs such as ethylene-propylene copolymers or isoprene-based polymers as described earlier. VII thickening is a function of polymer backbone molecular weight (actually the unperturbed root mean-square end-to-end distance), but only a minor portion (~15%) of a typical PMA's molecular weight is in the backbone compared to an olefin polymer with ~80 to 90% backbone molecular weight. Recall that a large majority of the molecular weight of a PMA is found in the pendant side chain simply to provide oil solubility. Therefore, when comparing a PMA to a polyolefin of similar molecular weight, the PMA clearly has a shorter end-to-end distance and is clearly a less efficient thickener. In situations where a PMA may bring some unique value to the formulation such as additional dispersancy (i.e., soot control in Heavy Duty Diesel Engine Oil) or superior low-temperature properties, these technical advantages may make PMA more economic.

For PPDs, it is again difficult to assign a typical treat rate. PPD concentrations may vary widely due to numerous factors including the types of base stocks employed, the impact of other additives on desired properties, and even the types of cold-temperature tests used for a given application.

11.4.3 OTHER INCENTIVES

In addition, if the VII brings value-added features such as pour point depressancy or dispersancy, then the economic credit for these features must be accounted for in the net treat cost.

PPDs economics also involve the commercial reality that as few PPD products as possible, more likely a single PPD, would be favored at a blend plant. Thus, performance robustness in various formulations is highly leveraged. Methacrylates with their inherent flexible chemistry can be well tuned to meet this objective and thus often provide a further degree of cost-effectiveness. Overall, it is difficult to quantify cost-effectiveness in a simple way; however, PMA PPDs are believed to be the most widely used chemistry in this application and command over 50% of the world market.

11.5 OUTLOOK AND TRENDS

11.5.1 CURRENT AND NEAR-TERM OUTLOOK

The commercial presence of PMAs over so many decades is a compliment to adaptability and the innovative effort to evolve the chemistry to meet more and more demanding rheological requirements. Competitive pressures from other chemistries will always remain high in the modern, global economy, thus the continued use of PMAs depends on the market's continuing and evolving needs for higher rheological performance. Given this, PMA compositions will almost assuredly evolve, as well. At the same time, raw materials and processes will be under constant investigation to create more cost-effective materials. Finally, advanced polymer processes are being developed to provide unique polymer architectures that provide enhanced rheological properties.

The outlook for PMA VIIIs is, to a large degree, tied to transportation and industrial multigrade fluid viscosity requirements that are driven by equipment and operating condition needs. Both equipment and operating conditions are in a time of flux. The evolution of automatic transmission equipment offers a pronounced example of such change with a concomitant change to ATF requirements. This has created need in ATFs for more stringent, low-temperature viscometrics (cold temperature operation), lower high-temperature viscosity and higher VIs (improved fuel economy contribution), better shear stability performance (long fluid life), while maintaining the traditional properties of fluid film strength and thermal/oxidative stability. PMAs offer the best commercial route to low-temperature viscometric performance and high VI contribution at the same time as being entirely

adaptable relative to shear stability needs. Obviously, the evolution of ATFs has favored the continuing use of PMA VII.

Fluid requirements may often appear to be contradictory. For instance, modern ATFs frequently require low overall viscosity but high VI for fuel economy reasons. Another example is the constant push to better low-temperature viscometric performance at the same time as improved shear stability; typically, better shear stability implies higher polymer treat rates, which imply higher low-temperature viscosity. In so much as these contrasting requirements emphasize one or more of the desirable properties of PMAs, these factors further reinforce PMA.

Transmission oils satisfying lubricant needs for more complex step transmissions, continuously variable transmissions, and double clutch transmissions are not the only multigrade fluids undergoing change. Transportation gear oils will evolve to better meet fuel economy expectations and more thermally demanding environments. In industrial and tractor hydraulics, higher-pressure hydraulic pumps and the ubiquitous desire for fuel economy improvement will drive fluid change. In so much as these changes involve higher VI, better low-temperature viscometrics, and enhanced shear stability, PMA VII will be involved.

It seems quite probable that such equipment trends and usually more severe operating environments will continue to evolve over the near and mid-term future and thus require further enhancement of fluid viscometric properties. In those applications where PMA VIIIs provide valued advantages, this should not only reinforce their use but also spur further innovation. In lubricants such as engine oils where PMA VIIIs are not necessarily needed for value-added features and are not cost-competitive, it is not easy to foresee significant future use unless requirements change appreciably.

The outlook for PMA PPDs is obviously tied to low-temperature rheology specifications as well as to the wax characteristics of lubricant fluids. Certainly, low-temperature specifications have trended to become more restrictive for many lubricants in addition to the ATF situation discussed earlier. North American engine oil specifications have now added used oil low-temperature requirements to deal with oxidative thickening (light-duty engines) and soot-related thickening (heavy-duty engines). The existence of these requirements adds a new dimension to PPD evaluations since used oils must now be evaluated. The latter point on wax characteristics of lubricant fluids deals with wax chemistry and wax concentration in base stocks as these factors will continue to be of paramount importance to the future use of PPDs. As base oil processing moves forward to provide more advanced oils, these will likely contain different combinations of wax structures than past base oils. PPDs will need to be developed to control the resulting different wax crystallization phenomena. In addition, the interaction of base stock wax with other additives that contribute waxlike character (i.e., detergents) provides a complex overlay that often impacts the choice of PPD chemistry. PMA PPD structure can be modified to provide appropriate crystallization interaction with the various types and levels of wax in any fluid. Given the ability of PMA to meet both current and future wax-related needs, their future as PPDs seems assured.

For PMA *dispersant VIIIs* (disregarding thickening effects), the outlook is not as clear. In those applications where these materials are currently employed, their use will probably continue for the foreseeable future with little change in terms of chemistry or commercial volumes. There are potentially important commercial possibilities if industry needs for dispersancy reach higher levels. An example is enhanced soot dispersancy in future diesel engine; however, the advent of diesel particulate filters would seem to reduce the possibility of this need.

11.5.2 LONG-TERM OUTLOOK

Just as for many other additives and base stocks, the future of PMAs depends on the rheological appetites of future equipment. In the absence of revolutionary equipment development, longer-term lubricant trends will continue to be driven by the concerns mentioned earlier: emissions control, fuel efficiency, and longer fluid life times. These three concerns certainly apply in varying degrees to all multigrades and will cause fluid requirements to continue their migration to enhanced rheological

properties. This should solidify the case for PMA in those applications where it holds prominent technical advantages. At the same time, PMAs will also continue to evolve to better provide improvements in shear stability, low-temperature viscometrics, wax interaction, VI, and perhaps, dispersancy. Current polymer architecture research noted in Section 11.2.4 certainly points in this direction.

Another important factor for future use of PMAs depends intimately on future base stocks. For instance, should entirely synthetic polyalphaolefin (PAO) base stocks be the choice of the future to provide enhanced properties, then this would obviate the use of any PPDs, as these base stocks are wax free. However, additives such as PMA PPDs may be an enabling factor in the use of newer base stocks such as API group II or API group III base stocks in meeting performance goals that match or are quite similar to those of API group IV (PAO) base stocks.

For the case of revolutionary equipment changes such as ceramic engine parts or vehicles based on batteries, fuel cells, or even clean burn systems (e.g., hydrogen or natural gas), lubricant requirements will surely change and lubricants themselves will undergo a similar revolution. Most of these changes would radically alter the chemical and physical characteristics and volumes of lubricants since the interesting but hostile environment of an internal combustion engine would no longer dictate the complex chemistry of engine lubricants. If engine lubricant volumes decline because of radical new materials or power sources, then surely all PPDs and VIIIs would experience a proportional decline. However, in other applications, such as hydraulics, where PMA VIIIs are primarily employed, such radical equipment changes do not seem to be on the horizon.

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12 Pour Point Depressants

Joan Souchik

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12.1 INTRODUCTION

Pour point depressants (PPDs), also known as low-temperature flow improvers and wax crystal modifiers, are polymeric molecules that are added to mineral oil-based lubricants to improve their cold flow properties. Without the addition of a PPD, many lubricants at cold temperatures would be too viscous to flow easily, or might even be gelled, and the result would be little or no lubricant moving through the system or machine requiring lubrication. For various lubricant applications such as automatic transmission fluids (ATFs), engine oils, gear oils, and hydraulic fluids, paraffinic base stocks are the preferred lubricant. These paraffinic base stocks are typically derived from crude petroleum and are composed of nonaromatic saturated hydrocarbons. Paraffinic stocks, also called base oils, make excellent lubricants because they are chemically stable, resistant to oxidation, and have good viscosity index values. However, paraffinic stocks, by their very nature, contain molecular species that have linear carbon chains of 14 carbons or more. These species, recognized as waxy materials, can cause oil pumpability failures at low temperatures. In addition to the inherent waxy base stock components, other sources of waxy material are added to the lubricant as part of its product-specific formulation. These additional components include some viscosity index improvers (VII) and components of the detergent-inhibitor (DI) package.

12.2 FLUID MECHANICS AND POUR POINT DEPRESSANT MECHANISM OF ACTION

Mineral oils are commonly understood to be Newtonian fluids, meaning that they behave according to the following equation:

$$\text{Shear stress} = \text{shear rate} \times \text{viscosity}$$

Experiments show that this equation holds for mineral oils as long as the temperature is above the cloud point of that oil. The cloud point is the temperature at which some of the waxy components of a mineral oil start to crystallize and precipitate from solution, leading to a hazy appearance. This visual evidence of the onset of wax crystals can be tested using American Society for Testing and Materials (ASTM) D 2500 [1]. A plot of log–log viscosity versus log temperature is shown in Figure 12.1. Above the cloud point, denoted by the data point in Figure 12.1, the viscosity decreases proportionally with temperature. At temperatures below the cloud point, the viscosity increases steeply as the temperature decreases. Below the cloud point, it is not uncommon to observe one of the two non-Newtonian behaviors in these otherwise Newtonian fluids: Bingham fluid behavior or unpredictably high viscosity.

12.2.1 BINGHAM FLUID BEHAVIOR

Bingham fluid behavior is the failure of a fluid to move under low-shear conditions, that is, unless some energy is added to the system.

The following equation describes Bingham fluid behavior:

$$\text{Shear stress} = (\text{shear rate} - \text{yield stress}) \times \text{viscosity}$$

The relationship between shear stress and shear rate for a Bingham fluid is shown in Figure 12.2.

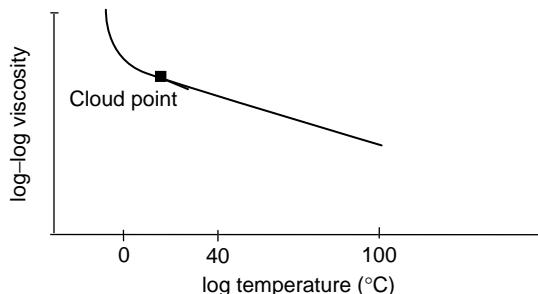


FIGURE 12.1 Relationship between viscosity and temperature for a mineral oil.

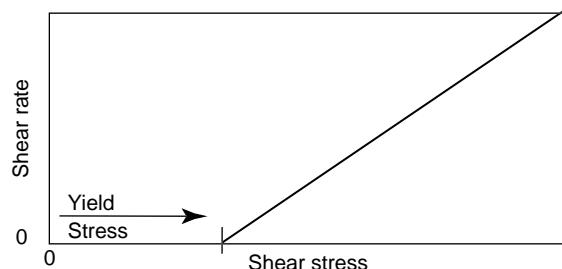


FIGURE 12.2 Bingham fluid behavior.

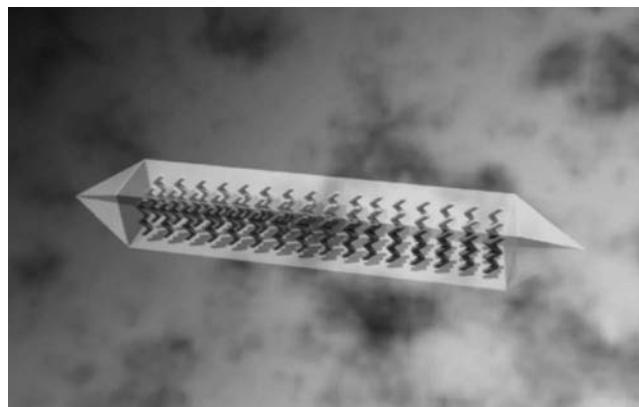


FIGURE 12.3 Three-dimensional needle-like structure of crystal platelets.



FIGURE 12.4 Gel network of needle-like structures.

This failure to flow is similar to the initial flow observed on opening a bottle of ketchup. When a bottle of ketchup is turned over, the ketchup does not flow out of the bottle due to weak associations among some molecular components of the ketchup. However, adding energy to the system by tapping the bottom of the bottle triggers the ketchup to move. Likewise, mineral oils at cold temperatures often do not flow because they contain molecules that have a crystalline nature at low temperatures. First, two-dimensional crystals (platelets) form and then ultimately three-dimensional needle-like structures form. The needle-like structure containing platelets is shown in Figure 12.3. The needle-like structures layer on one another, forming a network of crystals that trap the noncrystalline oil molecules within the gel network, which impedes the flow of the oil (see Figure 12.4). This process is known as gelation, and the source of the yield stress (YS) in the preceding equation is the wax–gel matrix in which the noncrystalline oil molecules are immobilized.

Bingham fluid behavior can be observed by running two widely recognized industry tests: ASTM D 4684 [2] and ASTM D 5133 [3]. A YS observation in the ASTM D 4684 test or a high gelation index (>12) measurement in the ASTM D 5133 test indicates the formation of a crystal network and quantifies the extent of it.

Air binding is an example of problematic Bingham fluid behavior that can occur in an automobile engine. When the engine is at rest, the oil drains and collects in the oil pan. At cold temperatures, the waxy materials crystallize in the oil creating a gel network. When the engine is started,

there is enough energy created by the oil pump to break apart the fragile gel structure just at the oil filter. A small bit of oil is pumped into the engine leaving an air gap at the filter. It is possible that the oil in the pan is of a viscosity that it could pump, but is locked in place by the wax crystal network that has formed. At this point, air is being pumped into the engine and as air is a very poor lubricant, this can lead to engine failure.

12.2.2 HIGH-VISCOSITY BEHAVIOR

The second non-Newtonian behavior often observed in a mineral oil at temperatures below its cloud point is unpredictably high viscosity. As waxy molecules in the oil crystallize, they cocrystallize but possibly do not form a strongly organized network. However, these cocrystals have enough hydrodynamic volume that they impede the flow of the noncrystalline oil molecules, greatly increasing the viscosity of the oil. In this situation, the oil is so viscous that it cannot be pumped at all into the engine, creating a serious situation where the engine runs with limited, if any, lubrication.

It is important to note that flow-limited behavior can occur in an oil for another reason, unrelated to wax crystal precipitation and growth. All fluids will become more viscous as the temperature decreases, eventually reaching a viscosity where the fluid cannot be pumped. The temperature at which the fluid no longer flows under gravity, not due to wax crystal growth, but simply due to the viscosity contribution of the other molecular species present, is called the viscous pour point. The addition of a PPD to a fluid will not change its viscous pour point.

12.2.3 POUR POINT DEPRESSANT MECHANISM OF ACTION

A PPD can resolve both gel structure and high-viscosity modes of failure. PPDs work by controlling the wax crystallization phenomenon in two principal ways: delaying the formation of wax–gel matrix to significantly lower temperatures than would normally occur or reducing the viscosity contribution of the crystal wax particles. PPDs act by interrupting the three-dimensional growth of wax crystals.

12.3 POUR POINT DEPRESSANT CHEMISTRY

Before the use of PPDs in the early 1930s, options were few for controlling wax crystallization. One method was to use heat. For example, fires were built under the oil reservoir of a vehicle. Another technique was to increase the solvency of the lubricant fluid portion by the addition of kerosene. The kerosene would then evaporate during use. A third alternative was the use of naturally occurring materials such as microcrystalline waxes or asphalt resin. Although these natural additives were somewhat effective, they were often specific to an application. This motivated the investigation of synthetic PPDs with structures based on the hydrocarbon structures of the naturally occurring PPDs. In 1931, small molecule chemistry efforts identified alkylated naphthalenes as one type of PPD, and in 1937, polymer chemistry studies by Rohm and Haas established polymethacrylates as the first polymeric PPD [4].

Since the early 1930s, other synthetic PPDs have been introduced. However, polymeric PPDs remain the most commercially viable option and include, but are not limited to, acrylates, alkylated styrenes, alpha olefins, ethylene/vinyl acetates, methacrylates, olefin/maleic anhydrides, styrene/acrylates, styrene/maleic anhydrides, and vinyl acetate/fumarates. All of these polymers work according to the same principles of operation.

The chemical structure of a PPD resembles a *comb polymer*, as shown in Figure 12.5. Long waxy side chains are added into the polymer side chains and interspersed with short neutral (non-wax interacting) side chains. The long waxy side chains interact with the wax in the oil in a manner that is proportional to the length of the side chain. These side chains can be linear or branched and should contain at least 14 carbon atoms for the PPD to interact with the wax in the oil. The short neutral side chains act as inert diluents and help to control the extent of wax interaction. Also, a

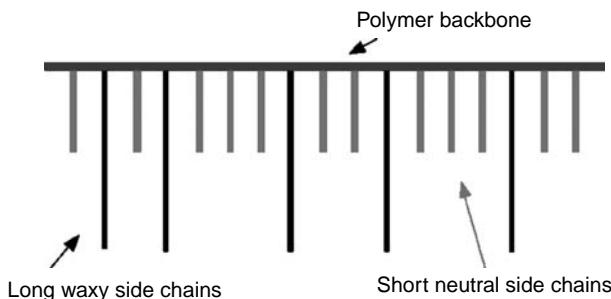


FIGURE 12.5 PPD comb polymer diagram.

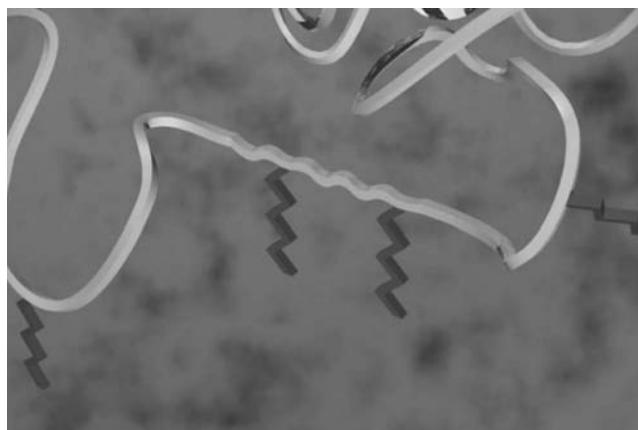


FIGURE 12.6 Three-dimensional representation of a PPD.

distribution of hydrocarbon side chain lengths can be utilized for best interaction with the wax in the oil because the wax contains a range of molecule chain lengths. The backbone molecular weight of a PPD, generally, can vary with little effect on performance; however, there is a minimum backbone size below which a PPD will become largely ineffective.

Figure 12.6 depicts the three-dimensional structure of a PPD. The long coil represents the backbone of the PPD, and the shorter zigzag pieces attached to the backbone represent the side chains. Figure 12.7 shows the side chains of the PPD crystallizing with the oil crystals on the edges of the platelets. This cocrystallization sterically inhibits the formation of the three-dimensional network (see Figure 12.8), thus preserving the wax as a distribution of tiny crystals and ensuring the complete fluidity of the oil.

The intensity of interaction between the wax and the alkyl side chains is a function of the types and amounts of side chains. This interaction can be expressed by a wax interaction factor (WIF). WIF is a method of ranking PPDs by their wax nature, accounting for the amount of waxy side chains in a PPD and their strength of interaction. A low-wax fluid usually responds best to a low-WIF PPD, and likewise, optimum performance per unit will be achieved in a more waxy fluid with a higher-WIF PPD. Because of the need to treat a vast variety of wax-related situations, a multitude of PPD products have been developed [5].

As described, the mode of operation for a PPD is physical interference. In selecting an optimum PPD, consideration needs to be given to the nature and amount of waxy molecules that may be present in a fluid. The waxy side chains present in the PPD need to be in balance with those waxy molecules found in the fluid. This balance is critical to blending oils with good low-temperature flow properties.

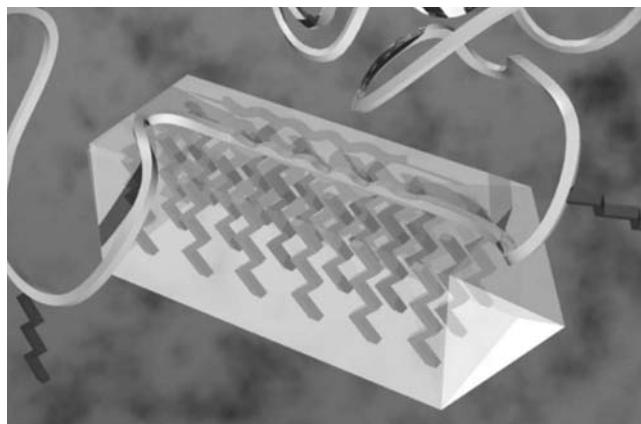


FIGURE 12.7 Crystallization of a PPD with a needle-like structure.

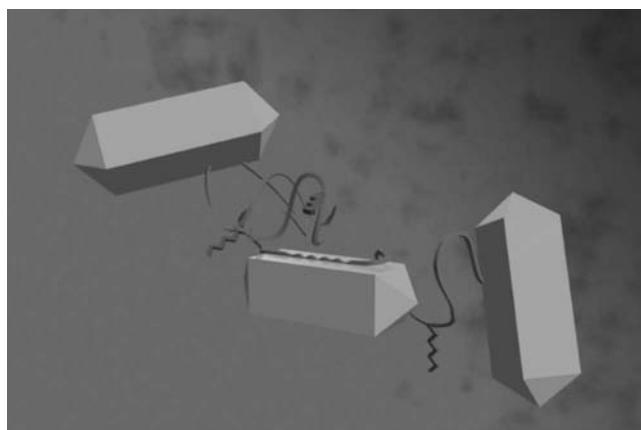


FIGURE 12.8 PPD prevention of gel network formation.

12.4 POUR POINT DEPRESSANT PERFORMANCE TESTING

Mineral oil is typically non-Newtonian at low temperatures; therefore, no single test can ensure that a lubricant blended with mineral oil will remain fluid over a wide range of conditions. Thermal history, including temperature cycling and cooling rates, can also affect the flow behavior of the oil. Various test methods have been developed over the years to evaluate oils under conditions that are experienced during operation.

A test, to be meaningful in predicting wax crystal growth, must incorporate three critical factors: a low-temperature end point, a defined cooling profile, and a low shear rate. Obviously, wax crystal growth is a low-temperature phenomenon, so a low-temperature end point is required. The low temperature finally achieved in a test needs to reflect the temperature requirements of the application. Not all waxy molecules in a fluid are crystalline at the same temperature, and changing the temperature point for a measurement will greatly impact the quantity of wax present as a crystal; hence, making an appropriate choice of a final test temperature is critical. The rate of cooling affects the competing factors of crystal growth and nucleation of new crystals, thus affecting the number of crystals formed and their relative sizes. The existence of temperature cycling within the cooling profile can further affect the number or size of wax crystals. Clearly,

TABLE 12.1
Comparison of Low-Temperature and Low-Shear Rate Tests

Test	Cooling Rate (°C)	Shear Rate (s ⁻¹)	Test Duration
ASTM D 97 (pour point)	0.6/min	0.1–0.2	2 h
Stable pour point	0 to –40 over 7 days	0.1–0.2	7 days
ASTM D 3829 (MRV)	2/h	17.5	16 h
ASTM D 4684 (MRV TP-1)	0.33/h	17.5	48 h
ASTM D 2983 (Brookfield viscosity)	Shock	0.1–12	16 h
ASTM D 5133 (scanning brookfield viscosity and gelation index)	1/h	0.25	35 h

Note: MRV = mini-rotary viscometer; MRV TP-1 = mini-rotary viscometer temperature profile 1.

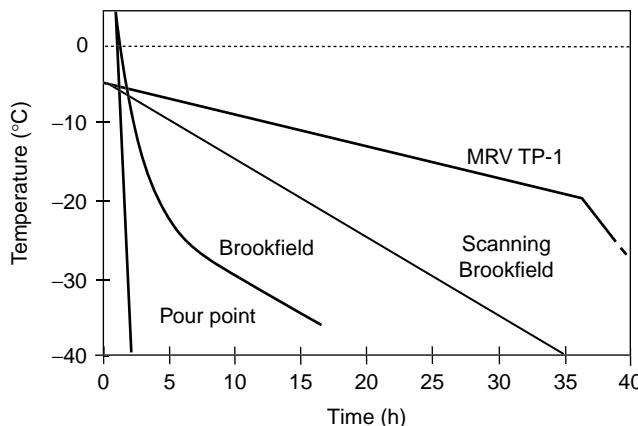


FIGURE 12.9 Cooling rates of pumpability bench tests. MRV TP-1 = mini-rotary viscometer temperature profile 1.

a defined cooling rate is critical in understanding wax crystal growth. Lastly, low shear rate is also a critical part of characterizing low-temperature behavior. Wax networks are fragile and easily disrupted under higher shear conditions. To understand whether wax crystal networks have formed, it is important to study the fluid under low shear conditions, allowing any network that formed to be preserved.

A comparison of the cooling and shear rates for the different low-shear test methods is given in Table 12.1. The ASTM D 97 [6] test for pour point employs a rapid and unrealistic cooling rate for wax crystal growth. Quick cooling does not allow the wax crystals that form to fully associate. However, this test has been used by the industry for many years, and its quickness certainly has benefit in quality control situations. The stable pour point [7] is more realistic than the ASTM D 97 pour point because of its longer cooling time. ASTM D 3829 [8] and ASTM D 4684 have comparable shear rates, but ASTM D 3829 employs a programmed cooling rate over a shorter time period, on average 2°C/h over 16 h, versus 0.33°C/h over ~48 h for ASTM D 4684. Figure 12.9 illustrates the cooling rates for several pumpability bench tests. Because of the differences in the tests, analysis of several test method results is critical to selecting the best PPD for a

TABLE 12.2
CCS Viscosity of SAE 5W-30 Oil with PPD

Percentage PPD	As is	0.15%	0.3%
Viscosity at -25°C (mPa s)	2900	2950	2850

lubricant formulation. A PPD that gives satisfactory performance at both rapid and slow cooling rates under low shear conditions is presumed to be better able to deliver performance over all foreseeable conditions than a PPD that already shows performance deficits under one of the limiting test conditions. In the end, it is impossible to test all conditions that might possibly arise.

The cold cranking simulator (CCS) test (ASTM D 5293 [9], which replaced ASTM D 2602 [10]) is a common oil testing method that is inappropriate for wax gel testing because it uses a rapid cooling rate and high shear rate. One set of results from ASTM D 2602 testing to determine whether PPD addition can affect the CCS viscosity of a Society of Automotive Engineers (SAE) 5W-30 oil is depicted in Table 12.2. As the PPD content was increased from 0 to 0.3%, virtually no change in the viscosity was observed. This result is contrary to what many hope for with the addition of a PPD and is explained by the high shear nature of the CCS test. PPDs are added to a fluid to control wax crystal growth. Wax crystal networks are fragile. Any wax network that formed would be broken up under the high shear conditions of the CCS test and as a result PPDs cannot improve the CCS viscosity of an oil.

12.5 PRINCIPLES OF POUR POINT DEPRESSANT SELECTION

12.5.1 TREAT RATE AND POUR POINT REVERSION

Using a PPD to improve the pour point means the addition of a waxy material to the lubricant. The treat rate, or concentration, of a PPD should be optimized so that the PPD itself does not cause crystallization. The effect of the PPD treat rate on the pour point of Group I 100N base oil is shown in Figure 12.10. The addition of a PPD at 0.2% by weight reduces the pour point from -15 to -33°C . Doubling the concentration to 0.4% produces only an incremental decrease of $\sim 3^\circ\text{C}$. An additional increase in the PPD content does not reduce the pour point any further. For this particular oil–PPD system, the optimum treat rate is $\sim 0.2\%$.

Continued increases in the PPD content result in a phenomenon known as pour point reversion. The addition of PPD beyond the optimum treat rate is in effect adding wax to the system and consequently reversing the benefit of the PPD by contributing to the formation of crystals or PPD polymer networks. An example of PPD overtreatment of the oil is shown in Figure 12.11. At a treat rate of 0.7; the pour point begins to increase at a treat rate of 0.7% from its minimum value at the treat rate of 0.3%. At the highest concentration tested, 1.2%, the pour point was similar to the untreated oil. Pour point reversion can also occur with improper selection of a PPD with a WIF that is too high for the oil being treated.

Figure 12.12 is a typical response curve demonstrating the effect of a PPD as a function of the WIF in one specific base oil. The lowest treat rate of 0.05% (top curve of Figure 12.12) indicates that a specific WIF is responsible for optimum performance. As the treat rate increases, the size of the response window increases. If a less-specific response is desired, then a higher treat rate can be used. Also, WIF and treat rate can, to some degree, be traded off, meaning that a nonoptimum WIF can be offset by a higher treat rate and vice versa. This flexibility can allow for one PPD to function well in multiple oils or across plant systems.

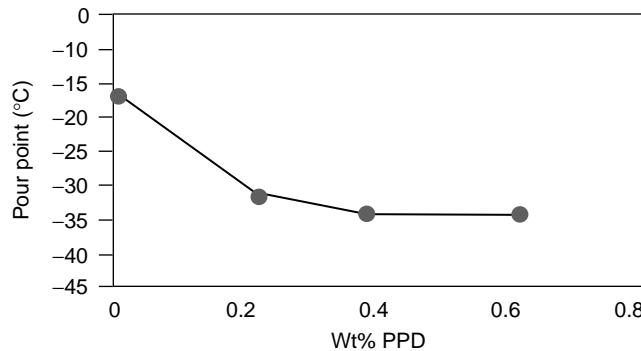


FIGURE 12.10 Effect of PPD treat rate on the pour point of Group I 100N base oil.

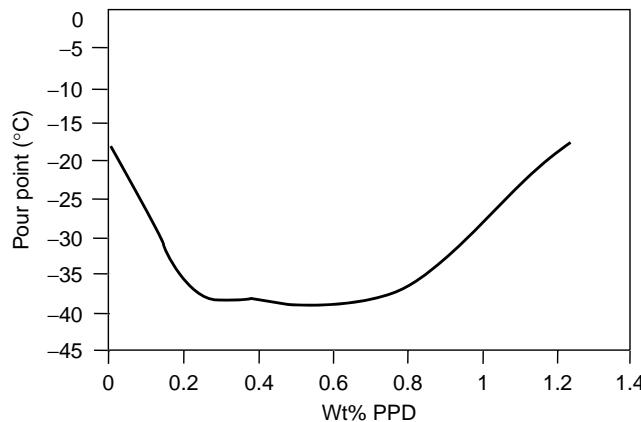


FIGURE 12.11 Pour point reversion.

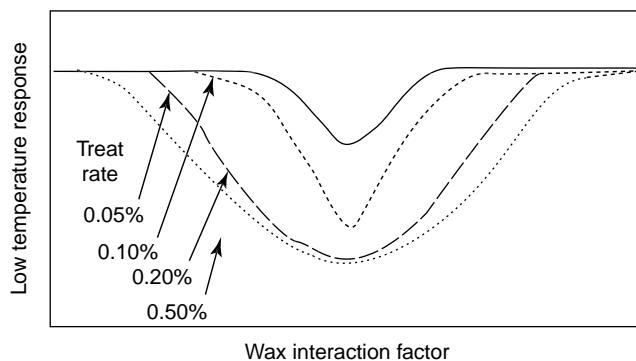


FIGURE 12.12 Low-temperature response of PPD as a function of the WIF.

12.5.2 EFFECT OF PERFORMANCE ADDITIVES

12.5.2.1 Base Oil Wax Chemistry and Content

The wax content of base oils from which lubricants are formulated varies with the source of the crude oil, the refining process used for the crude oil, the dewaxing process used for the refined oil, and the final viscosity grade of the base oil. The wax removal process is certainly a key determinant

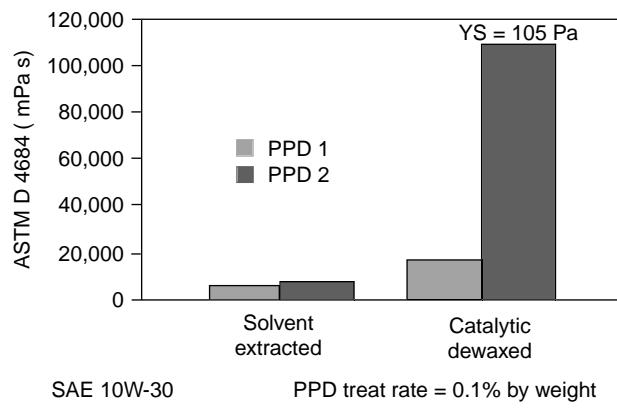


FIGURE 12.13 Solvent-extracted versus catalytically dewaxed oil.

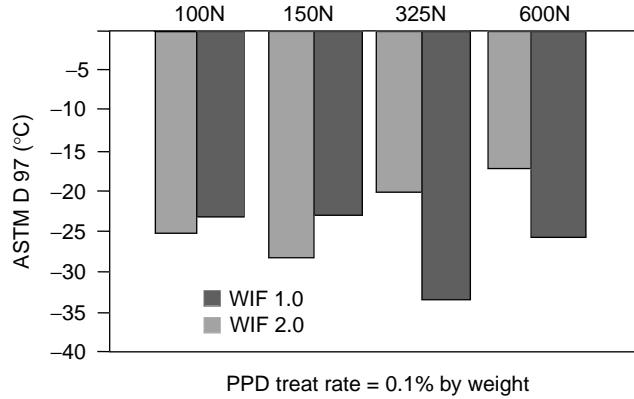


FIGURE 12.14 Viscosity grade effects of Group I base oils.

of the low-temperature low-shear (LTLS) behavior of an oil. Different types of hydrocarbons remain in the oil after refining, depending on the process. Dewaxing of the refined crude oil by solvent extraction removes the long-chain hydrocarbons. In contrast, catalytic dewaxing changes the structure of the hydrocarbons by either cracking them into smaller pieces or isomerizing them, rather than removing them. Lastly, the viscosity grade of the base oil is directly dependent on the wax content of the oil given that the higher-viscosity oils are produced by including longer-chain hydrocarbons.

The effect of two different PPDs on the viscosity of solvent-extracted and catalytically dewaxed SAE 10W-30 formulated oils is shown in Figure 12.13. ASTM D 4684 was used to determine the viscosity of the four PPD–oil formulations. Both oils had the same DI and VII, and PPD 1 had a lower WIF than PPD 2. For the solvent-extracted oil, the viscosity remained fairly low for both PPDs. However, the catalytically dewaxed oils had a higher viscosity with PPD 2 than with PPD 1 and extremely high YS of 105 Pa with PPD 2. To pass current North American engine oil specifications, YS must be less than 35 Pa. The higher WIF of PPD 2 most likely caused the increase in viscosity and YS in the catalytically dewaxed oil. One explanation for this is that the catalytically dewaxed stock contains fewer linear molecules of C14 or greater. The waxy side chains of the PPD, finding limited natural waxes to interact with, self-associate and built viscosity and structure through polymer-to-polymer interactions.

The effect of the WIF of a PPD on different viscosity grades of Group I base oils is shown in Figure 12.14. For the lower viscosity grades of 100N and 150N, increasing the WIF from 1 to 2 had

a small effect on decreasing the pour point temperature. For the higher viscosity grades of 325N and 600N, the result was reversed, and the higher WIF decreases the pour point temperature significantly. This result can be explained by the interaction of the PPD with the longer-chain hydrocarbons present in the higher viscosity grades.

12.5.2.2 Other Wax Sources

Other wax sources include DI packages and friction modifiers that may themselves contain waxy hydrocarbon chains. Also, VIIIs, which can typically contain long ethylene sequences, should be considered. These waxy components can affect the LTLS performance of the fully formulated oil, both positively and negatively, and therefore it is important to understand their contribution when selecting a PPD for a lubricant.

Detergent effects using two different PPDs in SAE 15W-40 are shown in Figure 12.15.

The viscosity of two oils was tested by ASTM 4684. PPD A had a lower wax content than PPD B. In the oil with detergent A, PPD A was able to control the viscosity to 13,000 mPa s ($100 \text{ mPa s} = 100 \text{ cP} = 1 \text{ P}$), which was below the test specification of 30,000 mPa s. However, PPD A could not control the YS, which, at 105 Pa, exceeded the test specification of $<35 \text{ Pa}$. The excessive YS indicated that a gel network was forming. One explanation for this is that detergent A was waxy in nature, and the waxy side chains of PPD A interacted with detergent A leaving fewer PPD side chains available for interaction with the wax in the oil. PPD B, a higher WIF PPD than PPD A, controlled the wax crystallization. The results for both PPDs were comparable in detergent B testing, passing both viscosity and YS specifications.

Chemistry effects of VIIIs and a PPD in SAE 5W-30 oil are shown in Figure 12.16. The oils containing both VII 1 and VII 2 had comparable performance, and the oils met the test specification of $<30,000 \text{ mPa s}$ at -30°C . As the temperature was lowered to -35°C , a much larger change in viscosity was observed in the oil containing VII 2. The oil containing VII 1 doubled in viscosity, whereas the oil containing VII 2 tripled in viscosity. Although both VIIIs met the test specification of $<60,000 \text{ mPa s}$ at -35°C , this PPD was not able to control viscosity growth in the oil with VII 2. With proper PPD selection, VII 2 certainly can show equal performance to VII 1. This demonstrates the effect that different cold-temperature conditions can have on PPD selection and how seemingly small changes in an oil formulation, VII 1 or VII 2, can change the optimum PPD for a lubricant.

Olefin copolymers (OCPs) are used commonly as VIIIs. The ethylene content of the OCP can greatly affect the choice of PPD for optimum viscosity and structure control of a lubricant. The importance of testing PPDs and considering all pertinent tests is summarized in Table 12.3,

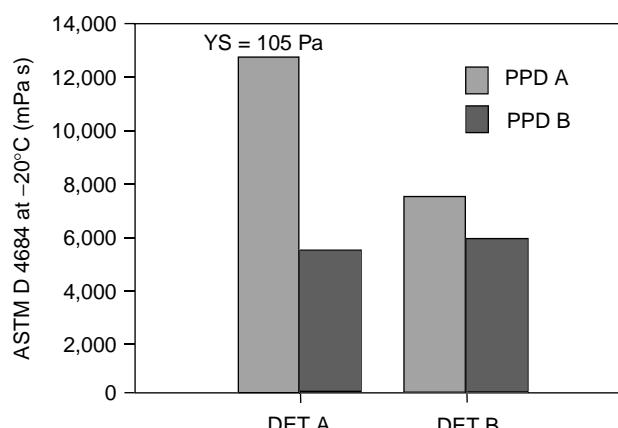


FIGURE 12.15 Detergent effects.

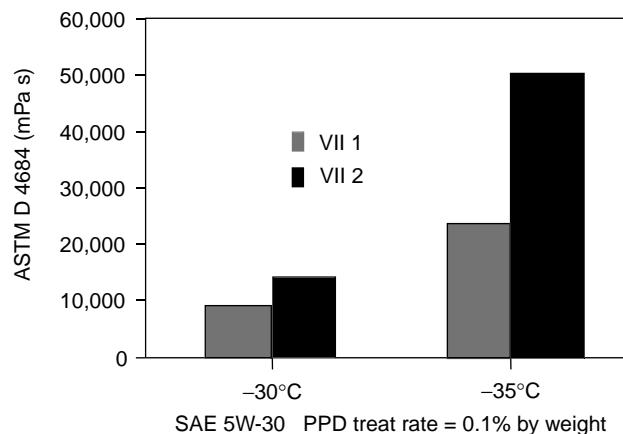


FIGURE 12.16 VII chemistry effects.

TABLE 12.3
VII Effects of HE OCP

VII	Traditional	HE OCP	HE OCP
PPD	1	1	2
Properties			
ASTM D 97 (°C)	-30	-27	-30
ASTM D 4684, viscosity (mPa s)	13,700	13,900	9,700
ASTM D 5133 (°C at 30,000 mPa s)	-28.8	-25.9	-30.2
Gelation index	4.6	9.8	4.8

Note: Oil source, SAE 10W-30, treat rate = 0.1% weight.

which presents the results of testing two different PPDs in SAE 10W-30 oil containing either a traditional OCP or a higher ethylene (HE) OCP. Using PPD 1, a lower-WIF PPD, the oil containing the HE OCP had results similar to the oil containing traditional OCP for all the tests except the gelation index, which approached the specification limit of 12, indicating a structure is starting to develop. When PPD 2, a higher-WIF PPD, was used with the HE OCP, the results were similar to or better than the oil containing traditional OCP and PPD 1. Assuming that the longer ethylene sequences in the HE OCP can contribute to wax interactions, these data demonstrate that a high-WIF PPD is needed to disrupt those waxy VII crystals as well as to interact with the waxy species in the base oil.

12.5.2.3 Fully Formulated Oil

It should be obvious from the previous discussion that another important aspect of PPD selection is the viscosity behavior of fully formulated oil versus base stocks. The fully formulated oil almost always contains additives and wax sources not present in the base oil, and these waxes may affect the viscosity behavior. The effect of two different PPDs on a 150N base oil and a SAE 10W-40, formulated with that same 150N oil, is shown in Figure 12.17. PPD 2 has a higher WIF than PPD 1. PPD 1 and PPD 2 gave similar viscosity results when tested in the base oil alone; however, YS was detected with PPD 2. These results indicate that PPD 1 would be a better candidate for the 150N base oil. With the fully formulated oil, however, PPD 1 resulted in a higher viscosity and a

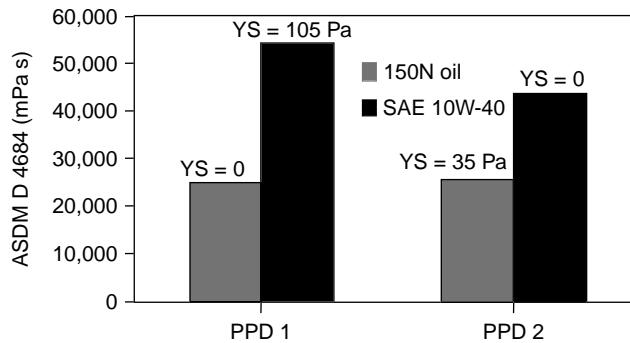


FIGURE 12.17 PPD selection in base oil versus fully formulated oil.

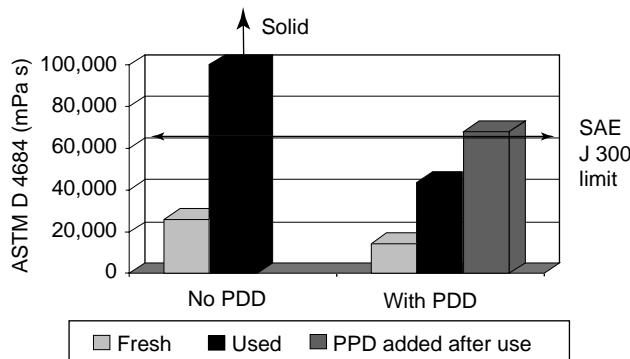


FIGURE 12.18 PPD stability after taxi field test. SAE 5W-30 as fresh oil (-35°C), SAE 10W-40 as used oil after 10,000 mi taxi service (-30°C), PPD at 0.1%—when present.

YS of 105 Pa, which exceeded the test specifications of <35 Pa. In this case, PPD 2 is the better choice because the additional waxy components from the DI or VII in the SAE 10W-40 formulated with that some 150N oil formulation required more waxy sites on the PPD polymer to effectively control the LTLS properties of the fully formulated oil.

12.6 POUR POINT DEPRESSANT ROBUSTNESS

The usefulness of PPDs has been clearly established through laboratory testing. However, the question of whether a PPD loses its effectiveness during use must be considered. The robustness of the PPD can be determined from field and laboratory tests. Experiments were performed to determine whether the PPD response was deteriorated by severe field and laboratory engine tests. The severe field test was a New York City 10,000 mi taxi test; the laboratory test was the Sequence IIIG test (ASTM D 7320) [11], a 100-hour, high-temperature engine test. The pumping viscosity (ASTM D 4684 MRV TP-1) was measured to evaluate the PPD response. Figures 12.18 and 12.19 depict the comparison of responses for fresh oil, used oil without the PPD, used oil with the PPD, and post-test addition of the PPD to used oil in the taxi test and the Sequence IIIG test, respectively. All fresh oil measurements were made at -35°C and used oil measurements at -30°C . Both tests demonstrate that, without the PPD, the used oil had a significantly higher viscosity than the fresh oil, becoming too viscous to measure during the testing at -30°C . On the contrary, the used oil containing PPD from both tests easily passed the SAE J 300 limit of 60,000 mPa s with no YS. Additionally, when PPD was added to the used oil without PPD from both taxi and Sequence IIIG tests, the used oil

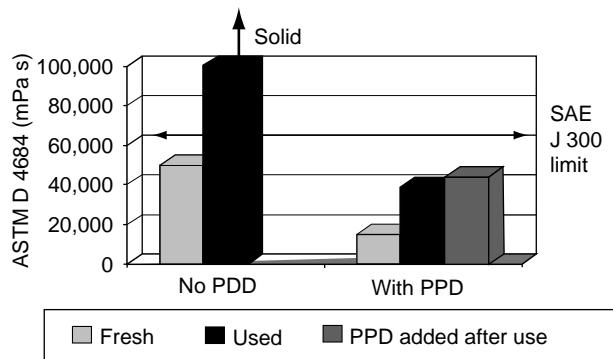


FIGURE 12.19 PPD stability after Sequence IIIGA testing. SAE 5W-30 as fresh oil (-35°C), SAE 10W-40 as used oil after sequence IIIGA (-30°C), PPD 0.3%—when present.

viscosity was greatly improved, showing slightly higher but similar results to the used oil with PPD results. Clearly, the PPD had not deteriorated during use as the PPD-pretreated used oil provides good MRV TP-1 viscosity, the untreated used oil has failing MRV TP-1 viscosity, and the postadded PPD used oil results are similar to the oil pretreated with PPD [12].

12.7 LUBRICANT APPLICATIONS

PPDs are selected and engineered for different lubricant applications ranging from automotive engine and transmission oils to industrial oils and biodegradable fluids. Engine oils tend to drive the PPD selection process for most blenders as engine oils are required to meet several LTLS specifications with severe limits, and they are often the high-volume products for a blend plant. Additionally, other lubricants more often are less selective for PPD.

12.7.1 AUTOMOTIVE ENGINE OILS

A PPD is always needed for automotive engine oils formulated with mineral oil base stocks, and given the complexity of these oils, the optimum PPD can usually only be identified by undertaking a PPD study on the fully formulated oils. The LTLS tests that are most often used today to access the pumpability of engine oils are ASTM D 4684, ASTM D 5133, and ASTM D 97. Various national, international, and OEM-specific engine oil specifications exist, each varying in the low-temperature test recommended or in the acceptable limits for a particular test.

12.7.2 AUTOMOTIVE TRANSMISSION OILS

Selection of PPDs for automotive transmission oils, including gear oils and ATFs, normally entails testing with ASTM D 2983 [13] (Brookfield viscosity) at -12 , -26 , and -40°C . ASTM D is also relevant. A PPD is always needed for mineral oil-based fluids, but it may be a constituent of the VII, if one is used.

12.7.3 INDUSTRIAL OILS

In contrast to the automotive oils, which typically require specialized low-temperature viscosity testing, industrial oils often have just a simple pour point (ASTM D 97) requirement. Therefore, the targets are often not difficult, and a low treat level of a traditional PPD may be suitable. For these oils, base stock choice is the primary driver for PPD selection. Some fluids, such as multigraded

hydraulic or tractor fluids, have additional LTLS requirements, namely Brookfield viscosity. These fluids generally need a low dose of PPD to meet requirements, and a PPD lab study will identify the optimum product and treat rate. Specific industrial oils, such as refrigeration oils, may be blended with synthetic or naphthenic stocks. These oils have excellent LTLS properties, and the addition of a PPD will not generally give further improvement.

12.7.4 BIODEGRADABLE FLUIDS

Another application of PPDs is in biodegradable fluids such as canola and soy oil. The PPDs for this application have to be specially designed and engineered because the mechanism of interaction for these biodegradable fluids is different from that of traditional automotive lubricants. For these biodegradable fluids, which consist almost exclusively of long-chain fatty acid triglycerides, the high wax content is responsible for the observed low-temperature viscosity problems, and therefore, the normal interference mechanism of small quantities of PPD containing long waxy side chains is not sufficient to address the observed problems. This leads to the need for different PPD structures and alternative approaches.

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Part 5

Miscellaneous Additives

13 Tackifiers and Antimisting Additives

Evaluating Tackiness of Polymer-Containing Lubricants by Open Siphon Method: Experiments, Theory, and Observations

Victor J. Levin, Robert J. Stepan, and Arkady I. Leonov

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13.1 INTRODUCTION

A tackifier is a lubricant additive that imparts a tack or stringiness to a substance and is typically used to provide adherence in fluid lubricants and stringiness in greases. Tackifiers function to discourage dripping, removal, flinging of oils, or impart texture in greases. For lubricant applications, most tackifiers are either mineral- or vegetable-based diluents combined with solubilized polymers. The polymers are usually PIB with a molecular weight of 1 to 4 million or rarely particular ethylene copolymers with a molecular weight of 200,000. The tackiness of a product generally increases with molecular weight. The lubricant's operational environment dictates polymer selection. High mechanical shear and high temperature favor ethylene copolymers over PIB. The oils may be paraffinic, naphthenic, or vegetable, depending on application. Typical applications for a tackifier include

bar and chain oil by limiting the oil slinging off during operation; way lubes by keeping oil in way, thus preventing contamination of coolant; grease by enhancing cling and tack and to mitigate water washout and spray off; and antimisting agents by coalescing the droplets and reducing mist. Specialty applications include food grade lubricants, aerospace, and biobased niches. Treat rates of tackifier ranges from 0.02% in antimist applications to 3% in grease applications. A key challenge among manufacturers and users of tackifiers is to evaluate and compare tackifier formulations in a systematic, repeatable manner. This chapter provides the theoretical foundation and practical test methods to address this challenge.

In particular, this chapter investigates tackiness of several lubricant fluids using familiar open siphon technique. In these experiments, evacuated sucking tube withdraws vertical free jet of liquids from a jar with a free surface. Dilute solutions of PIB of different molecular weights and polymer concentrations in lubricating fluids as well as the blends of PIB with ethylene-propylene copolymer were used in these experiments. Time dependences for the length and shape of free jet and flow rate in the process were recorded in the experiments for several values of vacuum pressure in sucking tube and for several lubricant fluids. The *tackiness* of lubricant fluids was quantified by the ultimate length of free jet just before it breaks up. Experimental data were described and interpreted by a nonsteady extension of an earlier stationary theory, modified for very dilute polymer solutions. Several specific phenomena were observed in the experiments, such as solvent exudation out of extended jet, maximum on the time dependence of flow rate during the process, maximum tackiness for solutions of blends of tackifier and nontackifier, and a two-phase flow in sucking capillary.

In many industrial applications, the lubricating oil must not drip or mist from the bearings. It can be practically achieved by increasing cohesion energy of lubricant fluid, which prevents its atomization, while keeping the oil viscosity as low as possible, which prevents the liquid from wasting energy in excess. Just the texture of such an optimal lubricating oil should be stringy, preventing oil loss and increasing lubrication time for machineries, where oil waste is a problem. To satisfy the aforementioned industrial needs, the lubricating industry has invented and utilized special types of lubricating oils containing tackifiers, which are solutions of polymers in oil. Till now, typical applications of tacky lubricants are limited to high-molecular-weight PIB dissolved in petroleum oil.

For polymer solutions to be tacky, the polymer chains should have a capacity to extend. It means that conventional tackifiers could also work as antimisting additives. Detailed analysis of antimisting was discussed by F. Litt [1]. Therefore, the tacky lubricant fluids should have elastic properties or should be viscoelastic liquids. To be less viscous and cheaper, they should also be very dilute polymer solutions in lubricant oils. It is well known that the viscoelastic properties of polymer solutions depend on polymer concentration and several molecular parameters of polymer determined by its chemical structure [2–4]. The most important parameters are the polymer molecular weight (and to some extent, the molecular weight distribution) and the flexibility of polymer chains, the latter being responsible for uncoiling of chains with smaller Kuhn segment or orientation of chains in the direction of extension for more rigid chains. Another important parameter of a tacky polymer solution is the viscosity of the base solvent. Preparation and testing of various lubricants with enhanced tackiness is in high demand for lubricant application. Yet to the best of the author's knowledge, there are no studies of the tackiness phenomena in lubricant polymer solutions.

This chapter investigates the tackiness of very dilute solutions of polymer-containing lubricants using the well-known open siphon method introduced and described in Ref. 5 (see also the monographs in Refs 6 and 7). In this method, elastic liquids are vertically withdrawn out of a jar by a vacuum-connected capillary. The suction pulls upward a tacky liquid out of the jar forming a free jet (string). More tacky fluids draw a longer jet in air than less tacky ones, whereas nontacky fluids are not drawn upward at all. Basic experiments and theory analyzing the open siphon phenomena on example of water solutions of polyethylene oxide (PEO) were initiated in Ref. 8, using

a viscoelastic approach. Prokunin [9], using the idea of relaxation of liquid–solid transition [10], developed the theory further, considering the free jet withdrawn from viscoelastic solution as a pure elastic gel. He found a good comparison between his calculations and experiments in Ref. 8. These results were later reviewed in a monograph [7]. The experimental and theoretical results in Refs 8 and 9 described, however, only the stationary processes of withdrawal of free viscoelastic jets by a rotating drum, where the constant speed of withdrawal and the flow rate of the fluid were controlled by the speed of drum rotation. Additionally, the experiments [8,9] were conducted on concentrated water solutions of very high-molecular-weight PEO with a polymer volume concentration of 0.5%. Thus, to analyze and describe the withdrawal of viscoelastic jets of very dilute polymer solutions in the nonstationary sucking open siphon process, the previously developed stationary theory [7,9] has to be modified.

It should also be mentioned that the problem of withdrawal of viscoelastic liquids seems similar to the withdrawal of viscous liquids by a vertically moving flat (or cylindrical) plate. In this problem, a viscous liquid forms a thin layer near the rigid plate under the action of viscosity, gravity, and surface tension. The solution of the problem mastered by Landau and Levich [10,11] uses a matching condition between viscous flow and static meniscus. Despite seeming similarity between these two problems, withdrawing of polymer solutions from a free surface is more complicated because the radius of extendable jet, varied with height, is *a priori* unknown.

This chapter is organized as follows. Section 13.2 describes the experimental setup, procedures, and the fluids used in experiments. Section 13.3 introduces some basic facts of viscoelasticity known for polymeric liquids. Section 13.4, using a quasisteady approach, modifies the theory [7,9] in the nonsteady case of the open siphon with sucking device and applies it to very dilute polymer solutions. Section 13.5 discusses the quantitative experimental findings and describes the data using the theory of Section 13.4. Section 13.6 applies the open siphoning method for evaluations of tackiness in two different lubricant oils. Concluding remarks are given in Section 13.7.

13.2 EXPERIMENTAL SETUP, PROCEDURES, AND FLUIDS

The experimental device used for testing tackiness of lubricating fluids is similar to those described in Refs 5 and 6. The setup is explained in Figure 13.1 in which the glass tube (capillary) with an inner diameter of 1.58 mm and a length of 120 mm is connected to the common vacuum equipment. In the experiments, we used three values of vacuum pressures p_v equal to 68, 77.3, and 84 kPa. The graduated glass cylinder (jar) filled with a tested fluid was of inner diameter 28 mm and height 190 mm. To quantify the jet profiles, we used the Konica Minolta A4 camera and computer, equipped with Adobe Photoshop CS2 program for enlarging pictures of the jet.

The experimental procedure was as follows. The capillary was lowered in the jar filled with the tested liquid, so that the lower sucking end of the capillary was initially below the liquid surface. Then the capillary was held in the position as shown in Figure 13.1. The suction pulled the liquid into the capillary and lowered the level of liquid in the jar. The experiment began at the moment when falling liquid surface in the jar reached the lower end of the capillary. Starting from this moment, a free jet of a tacky liquid was formed. The siphon draws down the level of liquid in the jar, increasing the length of free jet and making it progressively thinner. Flow rate q measured by graduated jar was dependent on applied vacuum; the higher the vacuum the higher was the flow rate. At small flow rates, the jet was broken, and at large enough flow rate, the jet lost its axial symmetry and the flow rate oscillated with time. We chose the aforementioned range of vacuum pressure to prevent breakage and high oscillation. But even in this range we observed some sporadic oscillations of the jet. Because of this, we repeated each measurement three times, recording an average value for calculations. The photos of the jets shown in Figures 13.2a and 13.2b demonstrate a very important characteristic feature of the jet, a relatively large viscoelastic meniscus near the free surface. Some traces of instability are also seen in the figures.

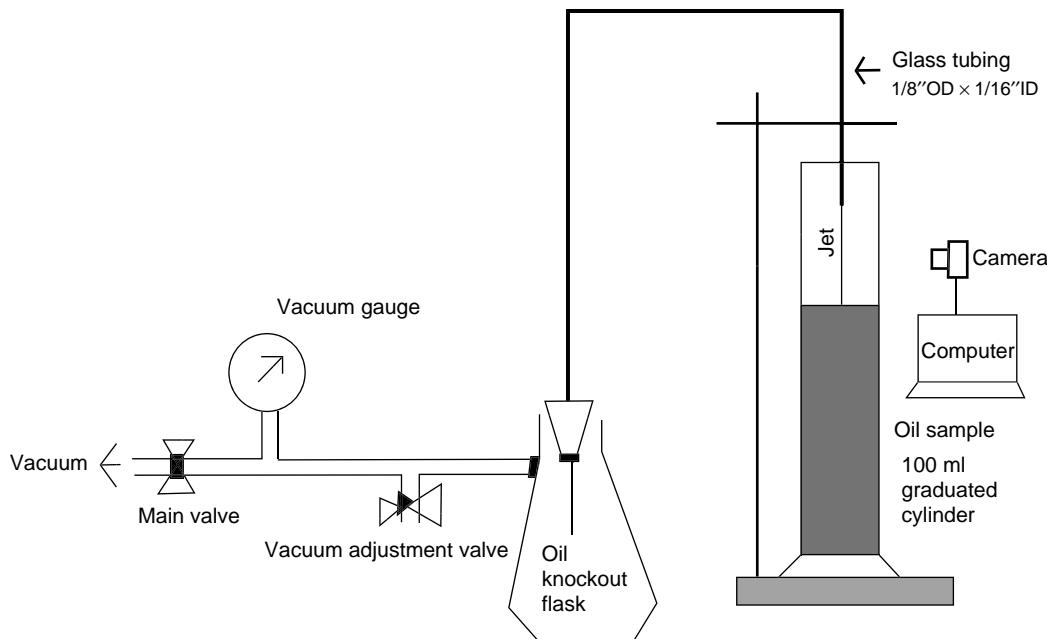


FIGURE 13.1 Experimental setup for testing tackiness.

We measured the size and shape of the jet by taking photographs every 25 s after the beginning of withdrawing. The maximum length of the free jet supported by the vacuum is recorded as a *string length* or *tackiness*. Photos were enlarged in the computer using Adobe Photoshop CS2 program. Using the printed pictures, we measured the jet radius r at different distances z from the liquid surface and at different flow rates q . Special attention was given to the measurements of parameters of meniscus that appears at the moment of disconnecting the capillary and fluid. These are the radius of meniscus R and radius of jet r_0 at the top of meniscus, measured at different flow rates q .

In the main part of the experiment discussed in Section 13.5, we used 0.025% (weight) PIB solution with viscosity average molecular weight $M_n = 2.1 \times 10^6$ [12] in the oil ISO 68, which has viscosities $\eta_s \approx 0.138$ Pa s, 0.0585 Pa s, and 0.0073 Pa s at 20, 40, and 100°C, respectively. Viscosities were measured by using capillary ASTM D 445 method. The density ρ_s of this oil at 25°C is equal to 0.86 g/cm³. Surface tension γ_s at 20°C is equal to 2.7 Pa cm [13].

In other industrially driven experiments, whose results are briefly discussed in Section 13.6, we also used various PIBs with $M_n = 0.9 \times 10^6$, 1.6×10^6 , and 4.0×10^6 , with weight concentration varying from 0.005 to 0.12%, dissolved in the mineral oil with viscosity η_s at 40°C equal to 0.068 and 0.022 Pa s. These are the standard ISO grades ISO 68 and ISO 22 oils widely used in lubrication industry. Solution of ethylene–propylene copolymer with a molecular weight of ~200,000 was also used. Polymers were granulated and then dissolved in oil in a glass container on hot plate with low-shear agitation. The time of dissolution was ~48 h.

13.3 VISCOELASTIC EFFECTS IN THE WITHDRAWAL OF TACKY LUBRICANTS

As viscoelastic polymer dilute solutions, the tacky lubricant liquids can be characterized by three basic parameters: solvent viscosity η_s , the polymer volume concentration c , and relaxation time θ . It is well known that at the very small concentrations of polymer additives, the viscosities η of polymer solutions practically coincided with those η_s for the mineral oil solvents. Nevertheless, adding

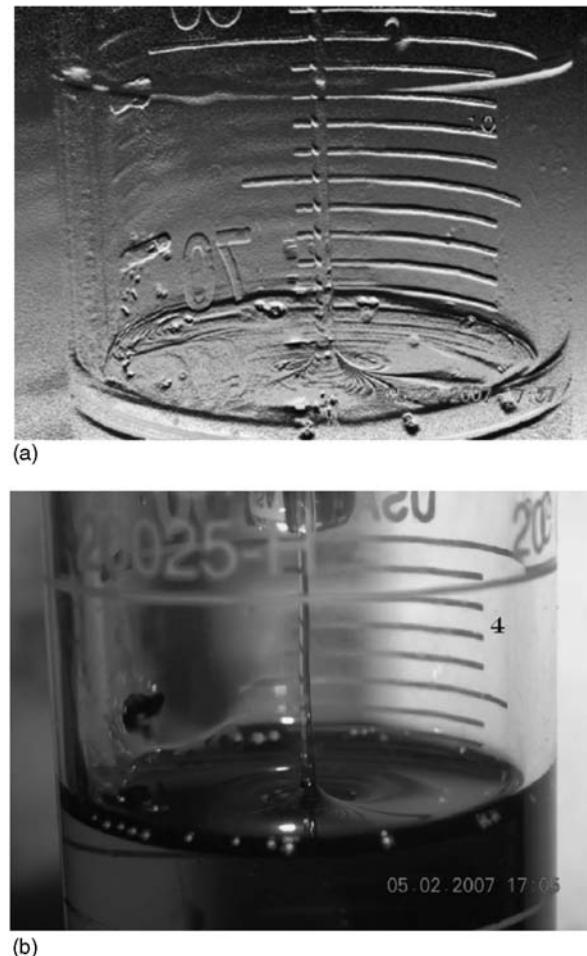


FIGURE 13.2 Photographs of free tacky jets for 0.025% PIB solution in lubricant oil.

very small concentrations of PIB into the mineral oil dramatically increases the relaxation time θ of the solutions.

Elastic liquids, by their reply to external actions, are in an intermediate position between viscous liquids and elastic solids. They behave as viscous liquids at low rates of external actions and as elastic solids when these rates are high. This type of behavior is commonly estimated by the non-dimensional Weissenberg number We . In extensional flows, including the problem of withdrawal, it is presented as [7]

$$We = \theta \cdot \dot{\varepsilon} \quad (13.1)$$

where $\dot{\varepsilon}$ is the elongation rate, that is, velocity gradient in the direction of extension (withdrawal). When extensional rate is low, $We \ll 1$, a viscoelastic liquid behaves as a viscous one. In the opposite case, when $We \gg 1$, the solidlike properties of viscoelastic liquids dominate, and they behave as elastic solids.

Along with well-known basic facts, many elastic liquids display a fast transition from the liquid-to the solidlike behavior when passing through a certain threshold We_c in the Weissenberg number. This phenomenon, called the *fluidity loss*, has been well documented for narrowly distributed polymers and treated as a *relaxation transition* (e.g., see the monograph in Ref. 7 and references therein).

The underlying physics of this transition is that the highly oriented polymer molecules in certain flows create physical cross-links that cause effective gelation of polymers and cease the flow. In case of withdrawal of dilute polymer solutions, the fluidity loss effect assumed in Refs 7 and 9 could also be caused by an increase in polymer concentration in intense extensional flows near the axis of extension. This might happen because the fluid trajectories in extensional flows cause the polymer macromolecules closely approach one another.

13.4 THEORETICAL MODEL

To make clear the basic physics of processes in the withdrawal of tacky lubricants, we now discuss modification of the theoretical model developed in Refs 7–9. This modification is based on the following assumptions: (1) the effect of *fluidity loss* plays a dominant role in the jet withdrawal, (2) the *inertia phenomena* are negligible in dynamics of polymer jet withdrawal, and (3) *exudation of solvent* out of withdrawn jet is important in case of dilute polymer solutions.

The first and second assumptions have been employed and proved valid in Ref. 9 on example of 0.5% water solution of very high-molecular-weight PEO. In case of dilute polymer solutions, the validity of these assumptions is *a priori* unknown. Neglecting inertia effects allows one to extend the stationary theory to the nonstationary case, using the quasisteady approach. The third assumption comes from the observations of withdrawn lubricant jets and plays an important role in the following modeling.

To develop a formal model, we introduce the vertical coordinate z , which coincides with the jet centerline and is counted off the moving free surface (Figure 13.3). So the origin $z = 0$ is located at the free surface, and the upper coordinate $z = l(t)$ at the capillary entrance indicates the length of visible jet at time t . It is convenient for theoretical treatment to roughly separate the whole domain of the liquid flow into three regions: *region 3* $\{z < 0\}$ located under free surface, *meniscus region 2* $\{0 \leq z \leq R(t)\}$ located from the free surface up to the end of meniscus, and the *region 1* of free jet motion $\{R(t) \leq z \leq l(t)\}$ (see Figure 13.3). Here the functions $R(t)$ and $l(t)$ are unknown and have to be determined. Basic flow effects that occur in the three regions of flow could be qualitatively described as follows [7–9].

In region 3, the sucking effect from capillary causes a specific extensional flow. This flow, slowly changing in time, looks like an effective undersurface jet, which narrows from the bottom to the surface. Therefore, the vertical velocity of jet and the characteristic extensional velocity gradient $\dot{\epsilon} \approx dV/dz$ are increased when approaching the surface from below. Substituting this value of $\dot{\epsilon}$ into Equation 13.1 explains the increase in the Weissenberg number, which might cause the relaxation fluid–solid transition. It was speculated in Refs 7 and 9 that the complete relaxation transition happens in region 2, where still viscoelastic polymer solution forms a free jet, which is squeezed under additional action of surface tension. In region 1, the free jet can be treated as an elastic gel swollen in solvent, which has a string-like shape, and is under the action of extensional force, gravity, and surface tension.

For describing the free jet behavior in region 2, we will use a semiempirical approach [7–9] instead of analyzing complicated viscoelastic flow in regions 2 and 3. This approach roughly approximates the shape of static meniscus by the expression

$$r(z,t) \approx r_0 + R - \sqrt{R^2 - (R - z)^2} \quad (0 \leq z \leq R) \quad (13.2)$$

where $R(t)$ is the maximum height of meniscus and $r_0(t)$ the initial (maximal) radius of the free jet.

The geometrical picture of this approximation is sketched in Figure 13.3, although the circle of radius R with a horizontal tangent at $z = 0$ surely cannot smoothly touch the meniscus surface

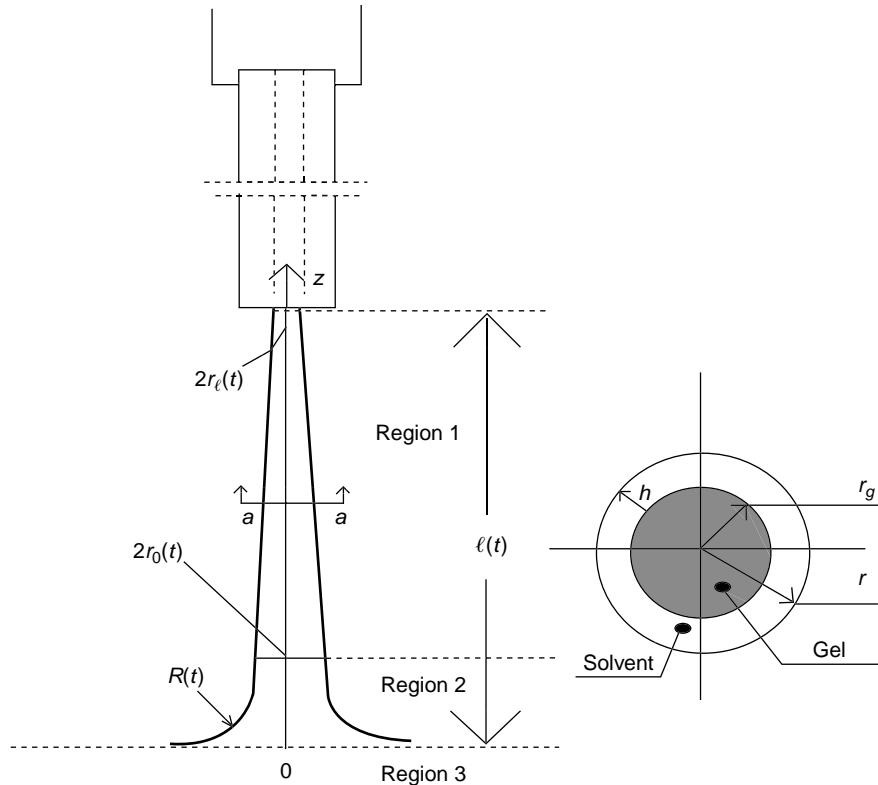


FIGURE 13.3 Schematics of jet withdrawal.

at $r = r_0$. Despite its very approximate character, Equation 13.2 allows to describe some critical phenomena at low flow rates and also interpret the measurements of jet radius near the free surface $z = 0$.

Despite very dilute character of polymer solutions in our study, we assume that the analysis of jet behavior in region 2 is identical to that in Refs 7 and 9. Utilizing dimensional and geometrical arguments, this approach yields the relations

$$R = \alpha(q\theta)^{1/3} \quad r_0 = \beta(q\theta)^{1/3} \quad (S_0 = \pi r_0^2 = \pi \beta^2 (q\theta)^{2/3}) \quad (13.3)$$

$$\sigma_0 \approx \rho g m R + \frac{2v\gamma}{R} = \rho g m v r_0 + \frac{2\gamma}{r_0} \quad (13.4)$$

where

σ_0 = stress at the initial jet radius r_0

$q(t)$ = flow rate

θ = characteristic relaxation time

ρ and γ = density and surface tension of solution, respectively, whose values will be evaluated by the corresponding values ρ_s and γ_s mentioned for solvent

Also in Equations 13.3 and 13.4, α and β are numerical parameters, whose values are estimated by fitting, and

$$v = \frac{\alpha}{\beta} \quad m = m(v) = v^2 \left[\frac{2}{3} + (1 + 1/v)^2 - \left(\frac{\pi}{2} \right) (1 + 1/v) \right] \quad (13.5)$$

The first and second terms in identical expression 13.4 for stress σ_0 describe, respectively, the contributions of weight and surface tension of the liquid column in the meniscus area 2. The bottom stress σ_0 , being due to Equation 13.4 a function only of R (or r_0), has a minimum at $R = R_c$ (or r_{0c}). The minimum value of initial stress $\sigma_{0\min}$ and corresponding values of R_c (or r_{0c}) and q_c are given by

$$\begin{aligned} \sigma_{0\min} &= (c_1 \rho g \gamma)^{1/2} \quad R_c = \left[\frac{c_2 \gamma}{\rho g} \right]^{1/2} \quad r_{0c} = \left[\frac{\hat{c}_2 \gamma}{\rho g} \right]^{1/2} \quad \theta q_c = \left[\frac{c_3 \gamma}{\rho g} \right]^{3/2} \\ c_1 &= 8mv \quad c_2 = \frac{2v}{m} \quad \hat{c}_2 = \frac{2}{vm} \quad c_3 = \frac{c_2}{\alpha^2} \end{aligned} \quad (13.6)$$

where numerical parameters c_1 , c_2 , \hat{c}_2 , and c_3 are calculated using Equation 13.5. The values of R_c (or r_{0c}) and q_c have a physical sense of critical parameters, below which the jet structure does not exist [7,9]. Remarkably, these values depend only on the equilibrium physical parameters of the fluid, its density ρ and surface tension γ , being independent of the withdrawal conditions and viscoelastic constants of liquid.

To analyze the jet behavior in region 1, we first mention unusual flow phenomenon in the sucking tube (capillary), recorded in experiments and shown by a photograph in Figure 13.4.

Here, the jet entered the tube with considerably less diameter than the inner capillary diameter and, at higher vacuum, seemingly continued its extension up to the upper capillary end. It means that instead of visible jet length $l(t)$ introduced earlier, the total jet length $L(t)$ at higher vacuum should be considered as the real dynamic variable, where

$$L(t) = l(t) + l_T \quad (13.7)$$

and l_T is the sucking tube length.

In case of withdrawal of dilute polymer solutions, an additional effect of *strain-induced exudation of solvent* should also be taken into account. Although the kinetics of this process is unknown, the flow of a thin film of solvent covering the gelled jet, swollen in the solvent, is guessed to be much the same as in the case of thin film withdrawn from a vessel by a vertical wall moving upward, that is, controlled by the vertical drag speed, viscosity, gravity, and surface tension [10].

To take into account solvent exudation, we introduce the *two-phase model* of jet sketched in the box of Figure 13.3, where the actual radius r of jet is represented as the sum of actual radius r_g of the gelled jet and the precipitated film thickness h , that is, $r = r_g + h$. At any radius r , we roughly treat the core of the swollen jet with radius r_g as an elastic solid with large deformations, whereas the peripheral thin film of solvent with thickness h as a viscous liquid. We neglect the contribution of the solvent film in axial stretching stress. Yet we consider in this two-phase model the local surface tension effect as acting on the total radius r .

We then roughly hypothesize that the film thickness h depends only on time. Using also the scaling argument, we assume that $h \approx \xi r_0(t)$, where $\xi = \xi(q_c/q)$ is a positive increasing function, and $r_0(t)$ is the maximum radius of the jet at time t (see Figure 13.3). Thus, this two-phase approach yields the kinematical relation

$$r = r_g + h(t) = r_g + \xi \left(\frac{q_0}{q(t)} \right) r_0(t) \quad (13.8)$$

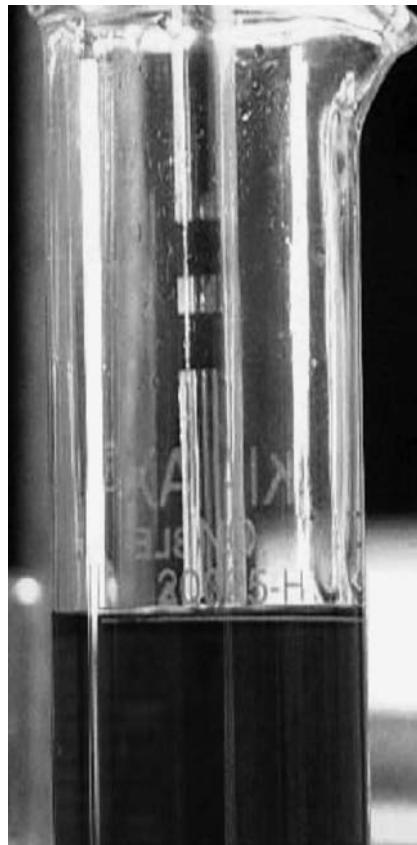


FIGURE 13.4 Photograph of two-phase motion of jet in capillary.

Neglecting a possible effect of the solvent film in the region 2, the dependence $r_0(t)$ will be calculated at the end of this section, using the kinetics of jet withdrawal and analyzing effects in the region 2. The function $\xi(q_c/q(t))$ will be proposed in Section 13.5.

We now use the aforementioned assumption that, in region 1, the core of gelled jet behaves as a weakly cross-linked purely elastic solid with a very low elastic modulus μ and very large elastic strain $\lambda (>>1)$. We employ in region 1 slightly inhomogeneous quasi-one-dimensional common approach, almost the same as in the homogeneous extension (e.g., see Refs 7 and 9). Then using Equation 13.8 yields

$$\lambda = \lambda_0 \left(\frac{r_{0g}}{r_g} \right)^2 = \lambda_0 \left[\frac{(1-\xi)r_0}{(r - \xi r_0)^2} \right] \quad (13.9)$$

$$\sigma \approx \left(\frac{\mu}{n} \right) \lambda^n - \frac{\gamma}{r} \quad (n > 1) \quad (13.10)$$

where

λ and σ = stretch ratio and stress, respectively

n = numerical parameter characterizing a specific elastic potential [9]

λ_0 = extensional stretch ratio attributed to the liquid–solid transition in region 2

The noninertial momentum and mass balance equations, averaged over the jet cross-section, can be written in the form similar to those used in Refs 7 and 9:

$$\frac{d}{dz} \left(\sigma S_g - 2\gamma\sqrt{\pi S} \right) = \rho g S \quad \left(S = \pi r^2, S_g = \pi r_g^2 \right) \quad (13.11)$$

$$uS = u_g S_g + u_f S_f = q(t) \quad \left(S_f = S - S_g \right) \quad (13.12)$$

where

S , S_g , and S_f = total, occupied by gel, and occupied by solvent film cross-sectional areas,
respectively

r = actual radius of jet

u , u_g , and u_f = total, gel, and solvent film vertical velocities, respectively

Note that if $u_g \approx u$, then $u_f \approx u$ either. It means that the solvent film is drawn upward with the same speed as the gel.

Substituting Equations 13.9 and 13.10 in Equation 13.11 yields the following solution of the stress-strain problem (Equations 13.4 through 13.6) described by the two-phase model:

$$\begin{aligned} \sigma &= G_0 \left(\frac{r_0(1-\xi)}{r-\xi r_0} \right)^{2n} - \frac{\gamma}{r} \quad z - R = \frac{n-1}{n} \cdot \frac{G_0}{\rho g} \left[\left(\frac{r_0(1-\xi)}{r-\xi r_0} \right)^{2n} - 1 \right] \\ &\quad - \frac{\gamma}{\rho g} \left(\frac{1}{r} - \frac{1}{r_0} \right) \quad (G_0 = \sigma_0 + \gamma/r_0) \end{aligned} \quad (13.13)$$

Equation 13.13 in the limit $\xi \rightarrow 0$ has the same form as in Refs 7 and 9. Parameters r_0 , S_0 , σ_0 , and G_0 in Equation 13.8 are slow functions of time. They represent the boundary values of respective variables at the level $z = R$. These boundary values should be determined by matching the behavior of liquid in regions 1 and 2. Also the function $\xi(q_c/q_0)$ is a slow function of time. As soon as these values are found, the jet profile and the stress distribution along the jet in the region ($R < z < L(t)$) are determined for any time instant from Equation 13.13.

We now consider the long jets with such large values of z that the surface tension effects on the stress are negligible as compared with the gravity. For these values of z , the solution of Equation 13.13 of the withdrawal problem has the asymptotic form found in Refs 7 and 9:

$$\sigma \approx \rho g \left(\frac{n}{n-1} z + \frac{m(c-1)}{c} R \right) \quad (c = m(n-1)/n) \quad (13.14)$$

where the numerical parameter c is again expressed through α and β using Equation 13.12. When the first term in the bracket in Equation 13.14 dominates, the following simplified expression will be used:

$$\sigma \approx \frac{\rho g z n}{n-1} \quad (z \gg R) \quad (13.15)$$

Equations 13.9 through 13.15 have been obtained in Ref. 9 for the stationary withdrawal problem in the limit $\xi \rightarrow 0$ using the noninertial approach. In Ref. 9, the characteristic sizes R and r_0 of the meniscus as well as the flow rate q have certain constant values. In the nonsteady case of

jet withdrawal under study, these formulae are still valid because of a slow noninertial approach, although the basic kinematical variables of the process, the length of withdrawn jet $L(t)$, and the flow rate q are now some functions of time t . To determine these functions $L(t)$ and $q(t)$, we will use two additional physical conditions.

The first, kinematical condition evident from Figures 13.1 and 13.3 is

$$q(t) = A \cdot \frac{dL}{dt} \quad (13.16)$$

where $A = \pi r_j^2$ is the cross-sectional area of the measuring cylinder (jar). Equation 13.16 shows that the change in length of the withdrawn jet is caused by the decrease of the liquid level in the jar.

The second, dynamic condition describes the dependence of flow rate on the pressure drop for the liquid flow in the sucking capillary. If there were a back gel–fluid transition in the sucking capillary, this dependence must be described by the well-known linear Poiseuille formula. However, this back gel–fluid transition was never observed in the sucking capillary. Instead, a very complicated two-phase flow shown in Figure 13.4 occurs there. It seems that at the highest vacuum, the jet continues to extend in the sucking capillary up to its very end. After that, the jet breaks down of the two-phase liquid–air mixture in the adjacent tube. At lower values of vacuum, this breaking process happens in the sucking capillary. Because of the relative slowness of the withdrawal process, this typically viscous, complicated flow could still be described by a linear hydraulic-type relation between the pressure drop and the flow rate:

$$q \approx k(\sigma_v - \sigma_L) \quad k = \text{constant} \quad \sigma_v = p_a - p_v \quad (13.17)$$

where

σ_v = pulling stress due to vacuum

p_v and p_a = absolute vacuum and atmospheric pressures, respectively

σ_L = acting elastic stress in the jet at the level $z = L(t)$

The constant k of dimensionality ($\text{cm}^3/\text{Pa s}$) describes the hydraulic resistance of jet at the end of sucking capillary. It should be evaluated by comparing theory with experimental data.

Determining σ_L from asymptotic equation 13.15 at $z = L(t)$ and substituting it along with Equation 13.17 in Equation 13.16 yields the kinetic equation describing the time evolution of $L(t)$:

$$\frac{dL}{dt} + sL = sL_u \quad (13.18)$$

where s is a parameter of dimensionality of one per second and L_u the ultimate length of the whole jet achievable with a given vacuum; these parameters are described as

$$s = \frac{n}{n-1} \cdot \frac{\rho g k}{A} \quad L_u = \frac{n-1}{n} \cdot \frac{\sigma_v}{\rho g} \quad (13.19)$$

Beginning with a time t_* where the asymptotic equation 13.15 is valid, solution of Equation 13.18 is presented as

$$L(t) = L_u \cdot \{1 - \exp[-s(t - t_*)]\} \quad (t \geq t_*) \quad (13.20)$$

Finally, Equations 13.16 and 13.20 yield the asymptotic expression for the flow rate

$$q = s \cdot L_u \cdot \exp[-s(t - t_*)] \quad (t \geq t_*) \quad (13.21)$$

Equations 13.19 and 13.21 will be used in Section 13.5 for the evaluation of parameters s and elastic constant of gel n . We should remember once again that these relations are reliable only after a certain time t_* elapsed from the beginning of the withdrawal process when Equation 13.15 is valid.

To describe the whole process from its very beginning, one should employ numerical calculations using Equations 13.3 through 13.7, where $z = L(t)$, $S = S(l(t)) \equiv S_t(t)$. Although these calculations can be performed relatively easily, the problem is that the beginning of withdrawal is accompanied by a poorly understood two-phase motion of jet in capillary.

13.5 EXPERIMENTAL RESULTS WITH A 0.025% PIB SOLUTION: COMPARISON WITH THE THEORY

We first attract attention to the jet photographs presented in Figures 13.2a and 13.2b made with 5.3 magnification. Some horizontal ripples on the jet are clearly seen, which might be explained by secondary instability of solvent film exuded out of solvent. This instability well known for the liquid films flowing down on inclined surfaces [11] indirectly confirms the very fact of exudation of the solvent from the withdrawn jet.

With increasing time of withdrawing, the diameter of jet dramatically decreases. The amount of liquid sucked from calibrated cylinder was measured every 5 s. Using these data, the time dependences of flow rate q (cm^3/s) were determined for different applied values of vacuum (Figure 13.5).

At the beginning of withdrawing, flow rate q substantially increases in time and reaches a maximum at ~ 25 s from the beginning of withdrawing. The higher the vacuum the higher is the q maximum and earlier its achieving. The possible explanation of the effect is as follows. The initial, just formed short jet is under the action of surface tension and extension from sucking capillary. The

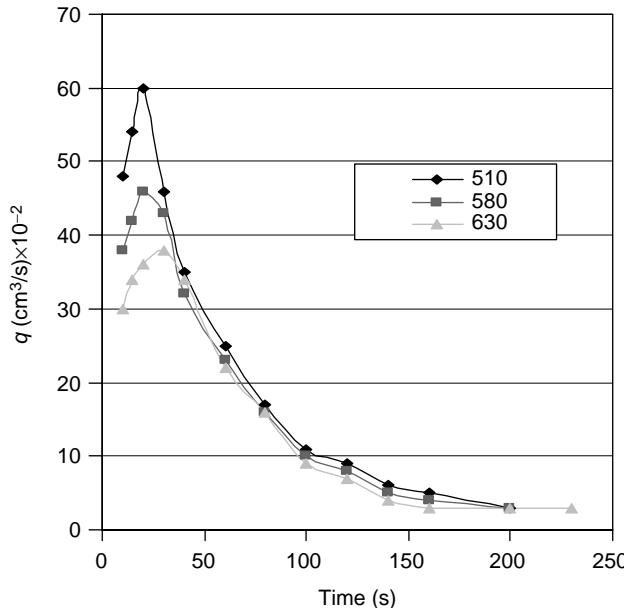


FIGURE 13.5 Time dependences of flow rate for different vacuum values (shown in the inset) for 0.025% PIB solution in lubricant oil.

action of surface tension squeezes the jet causing the increase in the flow rate. With increasing jet's length, the gravity force comes into play and soon overcomes the surface tension effect, causing the decrease in flow rate.

Figure 13.6 demonstrates that the flow rate is proportional to the speed of change in the length of jet dl/dt ($=dL/dt$). This is the direct confirmation of evident kinematical relation 13.16 on the example of the highest used vacuum.

After passing through the maximum, the flow rate exponentially decreases. This effect, predicted by Equation 13.21 is illustrated in Figure 13.7, where the time dependence of $\ln q$ is presented by a straight line with the slope equal to about -0.02 (s^{-1}). As seen from Figure 13.7, the decrease in applied (constant) value of vacuum also causes the decrease in flow rate, but after passing through the maxima, the differences between curves with different values of vacuum are negligible. Thus,

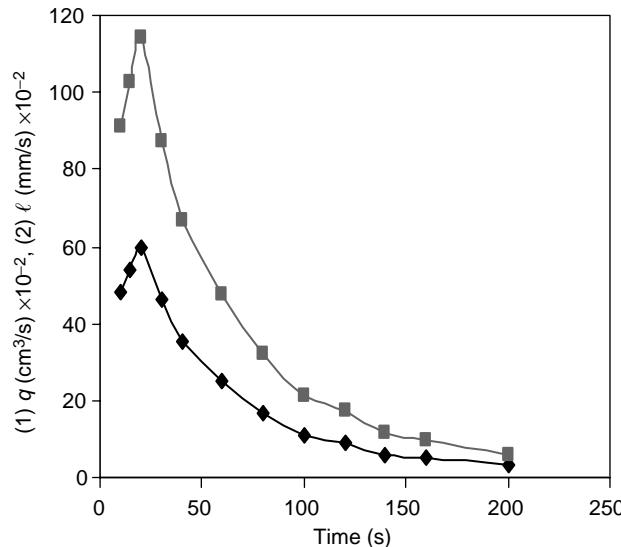


FIGURE 13.6 Comparison of time dependences of withdrawal rate $i(t)$ (curve 1) and flow rate (curve 2) with vacuum value $\sigma_v = 32$ kPa for 0.025% PIB solution in lubricant oil.

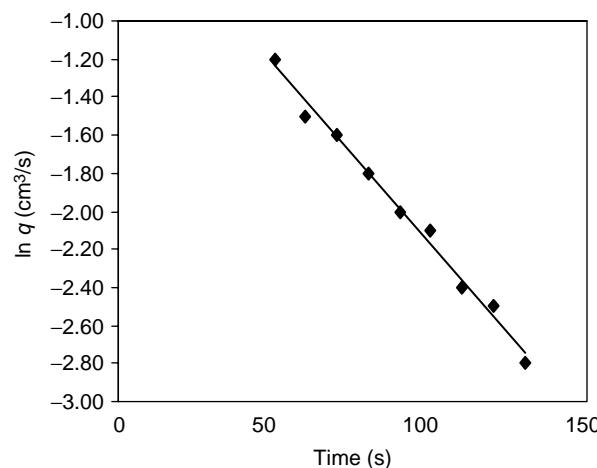


FIGURE 13.7 The decreasing branches time dependences of flow rate in Figure 13.5, represented in semilogarithmic coordinates.

the data presented in Figure 13.7 illustrate the changes of average flow rate with time for three different values of vacuum.

Another important fact found in this chapter is that independent of the vacuum values, all jets break at a flow rate of $\sim 0.03 \text{ cm}^3/\text{s}$. The very existence of a lower critical value of flow rate is predicted by the fourth formula in Equation 13.6. This fact will also be utilized in the following modeling.

Using the data presented in Figure 13.5, we choose on the decreasing branches $q(t)$ several flow rates, $q_1 = 0.35$, $q_2 = 0.25$, $q_3 = 0.20$, and $q_4 = 0.14 \text{ cm}^3/\text{s}$, corresponding to various time instances t_k . Making photographs at these t_k , we measured the *jet profiles* corresponding to the flow rates q_k related to these instances t_k . In this region of flow rates, the measured jet profiles were well reproduced. Figure 13.8 presents these jet profiles as decreasing dependences of the jet radius r versus distance z from the liquid surface, up to the maximal visible jet length at those time instances t_k . To describe the jet profiles shown in Figure 13.8, we had to find along with the function $\xi(q_c/q(t))$ describing the thickness of exuded solvent in Equation 13.13, three fitting parameters, numerical parameters v related to the meniscus (Equations 13.3 through 13.5), numerical parameter n describing the gel elastic potential (Equation 13.10), and parameter κ describing the stress-flow rate hydraulic relation (Equation 13.17).

We first evaluate the parameters of meniscus. Starting with the highest value of flow rate $q_1 = 0.35 \text{ cm}^3/\text{s}$, and using the aforementioned awkward procedure of meniscus approximation, we found the value $r_{01} \approx 0.49 \text{ mm}$ corresponding to the maximum flow rate q_1 . All other values r_{0k} corresponding to different values of q_k have been calculated using the scaling Equation 13.3 as $r_{0k} = r_{01}(q_k/q_1)^{1/3}$. As seen from Figure 13.8, the calculated data presented in Table 13.1 match well with the experimental values. Then, using the fact that the lower critical value of flow rate $q_{0c} \approx 0.03 \text{ cm}^3/\text{s}$, we calculated the lower critical value of r_{0c} as $r_{0c} = r_{01}(q_1/q_c)^{1/3} = 0.216 \text{ mm}$. Using this value, we employ Equation 13.6 for r_{0c} and Equation 13.5 for function $m(v)$ to yield the equation $vm(v) \equiv v(0.0959v^2 + 0.42v + 1) \approx 137$. Solution of this equation is $v \approx 9.7$ and $m \approx 14$, respectively. Using these data, we calculated the values of large meniscus radii $R = vr_0$, meniscus stress σ_0 due to Equation 13.4, and the values of parameter G_0 in Equation 13.13. These variables for the aforementioned four profiles are presented in Table 13.1.

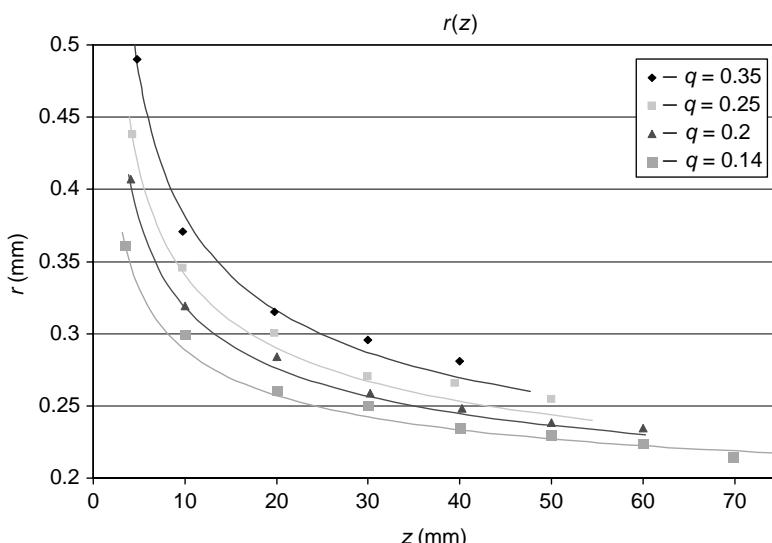


FIGURE 13.8 Jet profiles for several values of flow rate (shown in the box) for 0.025% PIB solution in lubricant oil established by photographing. Symbols—experimental data, solid lines—model calculations.

TABLE 13.1
The Values of Meniscus Variables in the Experimental Profiles (Figure 13.8)

q (cm ³ /s)	(q_c) 0.03	0.14	0.20	0.25	0.35
r_0 (mm)	0.216	0.361	0.407	0.438	0.490
R (mm)	2.10	3.50	3.94	4.25	4.75
$\sigma_0 \times 10^{-2}$ (Pa)	4.97	5.63	5.98	6.25	6.71
$G_0 \times 10^{-2}$ (Pa)	6.22	6.38	6.65	6.87	7.26

Elastic potential for the highly swollen elastic gel is unknown. It is characterized by the parameter n , which is determined by a fitting procedure as follows. Consider Equation 13.19 for the total ultimate length L_u of the jet. Using the values of vacuum pressure reported in Section 13.2, we found that the corresponding values of pulling vacuum stress σ_v are 32, 22.7, and 16 kPa, respectively. Consider the maximal value $\sigma_v = 32$ kPa. Experimental results show that for this value of vacuum, the visible maximal length of withdrawn jet $l_u \approx 10$ cm, so that the ultimate total jet value $L_u \approx 22$ cm. Thus from the Equation 13.19 for L_u , we found $n \approx 1.062$.

Being unaware of strain-induced exudation kinetics of solvent out of gel, we simply parameterize the function $\xi(q_c/q(t))$ by a power relation $\xi = (q_c/q)^a$. Fitting the jet profiles in Figure 13.8 with Equation 13.13, we quickly found that $a \approx 1/2$, that is, the thickness of the solvent film exuded out of gel under gel stretching is described as

$$h = \xi \cdot r_0 = r_0 \sqrt{\frac{q_c}{q}} \quad (13.22)$$

Simplicity of this result could indicate a fundamental physics of strain-induced solvent exudation out of the cross-linked swollen gel. Revealing this physics is, however, outside the scope of this chapter.

Using the aforementioned values of meniscus parameters and parameter n along with Equation 13.22, we calculated jet profiles according to the Equation 13.13. Figure 13.8 shows a good agreement between the calculations (solid lines) and experimental data (points).

We now consider the modeling of kinetics of long jet withdrawal, asymptotically described by Equations 13.16 through 13.20. Figure 13.6, discussed earlier, verifies the kinematical Equation 13.16 on the example of higher pulling vacuum stress. Finally, the parameter k introduced in the hydraulic Equation 13.17 is evaluated using Equation 13.18 and value $s = 0.02$ s⁻¹ as $k \approx 2.71 \times 10^{-5}$ cm³/(Pa·s). Data of Figure 13.5 by using Equation 13.20 and obtained values for s and L_u allow determine the time $t_* \approx 32$ s starting from which flow rate decays exponentially with time.

We now point out that the relaxation time θ could not be directly determined from the aforementioned experimental data. Using these data, we can calculate only the value

$$\beta\theta^{1/3} \approx 6.95 \times 10^{-2} \text{ (s)}^{1/3} \quad (13.23)$$

Direct measurement of relaxation time θ in our very dilute polymer solutions is very difficult. One possible way is to evaluate its value using the formula, roughly describing the longest relaxation time in the Rouse model (e.g., see Ref. 4, p. 222)

$$\theta_R = [\eta]_0 \frac{\eta_s M}{N_A k_B T} \quad (13.24)$$

TABLE 13.2
The Values of Basic Constants in Equation 13.21 Obtained Using Fitting Procedure

β	v	$\alpha = \beta v$	$m(v)$	n	$k (\text{cm}^3/\text{Pa s})$	$\theta (\text{s})$
0.215	9.7	2.08	14	1062	2.71×10^{-5}	3.38×10^{-2}

where

$[\eta]_0$ = intrinsic viscosity whose value is ~ 4 is known for the lubricant liquids [12]

η_s = solvent viscosity

M = polymer molecular weight

N_A = Avogadro number

k_B = Boltzmann constant

T = absolute temperature

At the room temperature, using these values of constants for 0.025% PIB solution in lubricant oil yields the value $\theta_R \approx 4.54 \times 10^{-4}$ s.

Another way of evaluating the relaxation time is hypothesizing that near the sol–gel transition, the polymer concentration in the jet highly increases causing cooperative relaxation effects. Then, we can speculate that the transition happens under the condition $We_c = \text{constant}$, with universal value of We_c . Roughly estimating the critical value $\dot{\epsilon}_c$ of strain rate in the transition as $\dot{\epsilon} = q/(\pi r_0^2 R)$ results in the relation

$$We_c = \theta_c \cdot \dot{\epsilon}_c \approx \frac{\theta_c q}{\pi r_0^2 R} = \frac{1}{\pi v \beta^3} \quad (13.25)$$

Using now the assumption of universality of We_c , we can use the data of Refs 8 and 9, where in case of 0.5% PEO water solution, $v_{\text{PEO}} = 2.6$ and $\beta_{\text{PEO}} = 0.334$, and calculate $We_c \approx 3.3$. Then, the value of β in our case where $v = 9.7$ is calculated as $\beta = (\pi v We_c)^{-1/3} \approx 0.215$. Substituting this value of β in Equation 13.22 yields: $\theta_c \approx 3.38 \times 10^{-2}$ s. Remarkably, the value of θ_c is almost two orders of magnitude higher than θ_R . In our opinion, the value θ_c and related value of parameter β seems preferable. The values of basic constants in Equation 13.21 obtained using fitting procedure are presented in Table 13.2.

13.6 USING OPEN SIPHON METHOD FOR THE EVALUATION OF TACKINESS OF LUBRICATING FLUIDS

As mentioned earlier, the ultimate jet length (or tackiness) strongly depends on the viscosity of oil, molecular weight of dissolved polymer, and its concentration in solution. Figure 13.9 shows the dependence of jet length l on the concentration of PIB with $M_\eta \approx 2,000,000$ in two paraffinic oils with respective viscosities 0.068 Pa s and 0.022 Pa s at 40°C.

One can see that the dependences of tackiness on polymer concentration in different oils are linear. These dependences are in fact linear for any molecular weight in different oils. It is clear from Figure 13.9 that decreasing oil viscosity is accompanied by a large decrease in tackiness. For example, at the concentration 0.025% of PIB, the jet length in oil with viscosity 0.068 Pa s is equal to 100 mm, whereas in oil with viscosity 0.022 Pa s, it is equal to 20 mm, that is, five times less than that in the first case.

Data presented in Figure 13.10 demonstrate what concentration of PIB with different molecular weights in oil with viscosity 0.068 Pa s should be used to reach the jet length of 100 mm. It is seen that, by simply increasing the molecular weight, it is possible to substantially increase the tackiness.

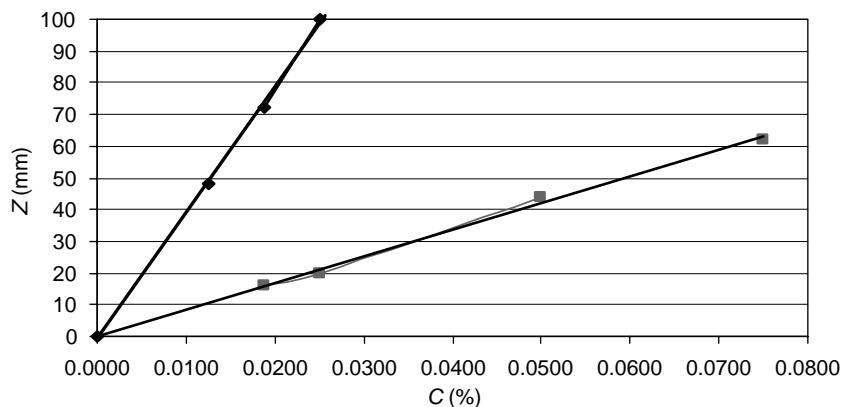


FIGURE 13.9 Ultimate jet length l versus the concentration of PIB with $M_n \approx 2,100,000$ in two paraffin oils with respective viscosities 0.068 and 0.022 Pa s at 40°C.

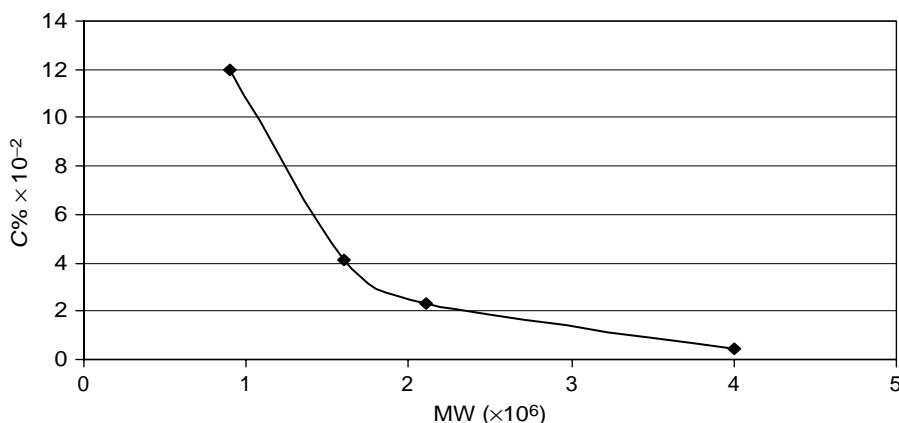


FIGURE 13.10 Concentration $C\%$ of PIB in oil with viscosity 0.068 Pa s corresponding to the jet length $l = 100$ mm versus viscosity average molecular weight M_n of polymer.

Increasing molecular weight causes, however, a decrease in both thermal/oxidative stability and shear stability.

Combining the data presented in Figures 13.9 and 13.10, it is possible to evaluate the jet length or tackiness for PIB solutions with different molecular weights at different polymer concentrations.

Unlike PIBs commonly used as tackifiers, the ethylene/propylene copolymers usually do not display tackiness. Nevertheless we obtained some unusual data for the blend of PIB with $M_n \approx 2,000,000$ with very small additive of ethylene/propylene copolymer. Figure 13.11 demonstrates that adding 0.01% of the copolymer to the PIB solution increases the jet length by ~30%. It should also be mentioned that addition of 0.01% of copolymer to the solution of 0.025% of PIB practically does not change viscosity of the solution. As seen from Figure 13.11, at higher concentration of the copolymer in PIB solutions, the tackiness decreases.

This effect might be explained as follows. Solutions that have 0.01% of copolymer could be considered as very dilute, with macromolecules well separated. During flow-induced orientation of long flexible PIB chains, much shorter and more rigid molecules of copolymer are involved in the process of orientation and support-oriented PIB macromolecules, causing increase in tackiness. With increase in concentration of copolymer, macromolecules form ensembles, which could not be

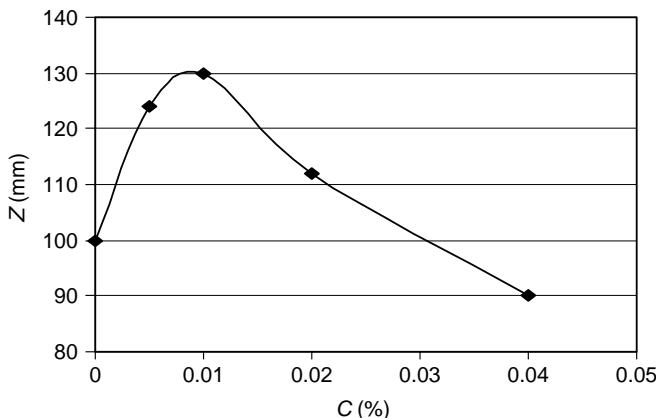


FIGURE 13.11 Tackiness effect versus concentration of ethylene–propylene copolymer added to the 0.025% PIB solution in lubricant oil.

involved in orientation process and moreover could restrict orientation of PIB macromolecules and decrease tackiness.

13.7 CONCLUSIONS

Theoretical model developed in this chapter is similar to that in Ref. 9, where the withdrawn jet is treated as a slightly cross-linked elastic gel. The model [9] was modified in this chapter by including two new features. First, we took into account the exudation of the swollen gel under extension, a common effect for dilute polymer solutions, observed in our experiments. Second, we made a nonsteady extension of an earlier stationary theory [9]. Fitting the theory with experimental data allowed us to well interpret and describe the data.

The results of this chapter clearly demonstrate that evaluation of tackiness by the open siphon technique presents a simple and reliable method useful for lubricant industry applications.

ACKNOWLEDGMENT

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14 Seal Swell Additives

Ronald E. Zielinski and Christa M. A. Chilson

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14.1 INTRODUCTION

The use of additives in lubricants, both military and civilian, began around 1930. Before that time, additives in lubricants were not required as most fluid systems operated at low pressure and low cycling rates. Seal swelling agents were not required because seals were generally made from leather or similar materials not subject to swelling by the petroleum-based fluids in use at that time. The use of additives to improve fluid performance began with the military fluids. Industrial fluid development paralleled or followed the military fluid development.

With the enhanced development of military aircraft and reciprocating engines spurred by World War II starting approximately in 1935, advanced fighters and bombers required new, high-performance lubricating fluids and seals. The new military fluids were based largely on petroleum base stocks or mineral oils for hydraulic systems. These consisted of paraffinic, aromatic, and alicyclic (naphthenic) components. Various additives including rust inhibitors, oxidation inhibitors, detergents/dispersants, viscosity index (VI) improvers, pour point depressants, antiwear components, and antifoam materials were used to develop additive packages for these hydraulic fluids depending on the aircraft type and intended missions. These development efforts resulted in the creation of a military specification—MIL-H-5606—for these fluids. The specification allowed for some flexibility in formulation for competitive purposes and guaranteed a performance band for the fluid and its compatibility with elastomer seals.

Similarly, new reciprocating engine lubricants based primarily on diesters of both aromatic and aliphatic acids and additive packages for fluids intended for each aircraft engine type, that is, high-flying bombers (B-17s) and fighters (P-47s), were developed. These were the early versions of MIL-L-7808.

High-acrylonitrile-content butadiene–acrylonitrile (NBR—Acrylonitrile-Butadiene Rubber) seals were used for these aircraft hydraulics and they worked fine except when strategic aircraft flew for long time periods at very high altitudes (i.e., >30,000 ft): the seals leaked, thus the base polymer had to be modified with a lower acrylonitrile content to improve low-temperature performance. Of course, seals made from NBR with reduced acrylonitrile content have higher butadiene content and thus

would have increased volume swell in petroleum-based fluids. This caused many problems. Programs driven by the military had material and chemical engineers working together and adjusting both fluid and seal formulations to solve the problems. The results of these coordinated efforts were the development of fluids and seals that were complementary.

It is very difficult to speak in specific terms with regard to seal swell additives, as commercial fluids have additive packages, which are considered very proprietary and highly confidential. To address seal swell additives, we will follow the development of military fluids and seals in three basic time frames: 1935–1960, 1961–1980, and 1981–2007. In general, specific information of compositions of most aircraft fluids, including seal swell additives, is extremely limited and is usually, again, company confidential. However, because these developments were, at least, in part supported by the military, more information is available. We describe what is known about swelling agents, yet recognize that generalities will have to suffice due to the confidential/proprietary nature of formulated fluids. Industrial fluid development, including seal swell additives, followed the military fluid development, and the additives used in military fluids were used in the industrial fluids, therefore, in essence, by following the military fluids, we are also following the industrial fluids as both used essentially the same seal swell additives.

14.2 FLUID/SEAL SWELL ADDITIVES DURING 1935–1960

During this period, petroleum-based fluids predominated as the fluid of choice for hydraulic fluids. The earliest versions of the military fluid designated MIL-H-5606 (mineral oil) had a higher aromatic content and thus provided sufficient volume swell for the high-acrylonitrile (ACN) NBR (nitrile) seals used in the low-pressure (~1500 psi) hydraulic systems in piston engine aircraft. As aircraft development proceeded, more powerful piston engines were developed for the very long-range bomber missions, primarily the B-17, to be used by the Army and Air Force for attacks on enemies in Europe and the Far East theaters. The long-range bombers flying at very high altitudes, 35,000–45,000 ft, caused oil thickening and seal leakage, which resulted in sluggish performance. The seals used were nitrile seals designated by the military as MIL-R-25732. Fighter aircraft, both land-based and aircraft carrier-based, did not experience problems because they flew at lower altitudes and for shorter missions. To solve the bomber fluid problem, the mineral oil base fluid was further refined to replace some aromatic content with aliphatic content to improve low-temperature viscosity at -65°F . This resulted in a revised version of MIL-H-5606 hydraulic fluid. Low-temperature sealing performance of the high-ACN NBR-content MIL-R-25732 seals was improved by replacing some of the high-ACN NBR with medium- or low-ACN NBR as the base polymer or replacing part of di-2-ethylhexylphthalate (DOP) processing oil used in seal compounding formulations with di-2-ethylhexylsebacate (DOS) oil. Fluid formulators added sufficient diester fluid, such as DOS, to the MIL-H-5606 to maintain 18–30% seal volume swell. Although very early piston engines used petroleum-based oils as lubricants, this gave way to pentaerythritol ester-based fluids to improve low-temperature performance at -65°F and maintain high-temperature performance at 275°F . MIL-R-25732 seals were used for engine lube sealing. For naval aircraft, antirust additives were added to fluid formulations for obvious reasons. Commercial aircraft versions of military aircraft were developed during this era, that is, Douglas DC-3 (C-47 military transport), Douglas DC-6, and Lockheed Constellation. These aircraft initially used military aircraft hydraulic oils/seals and engine lubrication oils/seals. However, because of the short flight duration and many takeoffs and landings of these aircraft, a new, more fire-resistant fluid was introduced. This new fluid had a phosphate ester base stock, which created the need for seals made with a polymer compatible with this new base stock.

14.3 FLUID/SEAL SWELL ADDITIVES DURING 1961–1980

As advanced military aircraft with enhanced performance (jet aircraft) and missions were developed, both hydraulic system and engine operating temperatures increased. Oil companies

and seal manufacturers responded by enhanced synthetic oil development and corresponding seal development to meet aircraft and gas turbine engine manufacturer's needs for -65 to 350°F performance. Oil companies synthesized thermally stable polyalphaolefin (PAO) fluids to meet the desired 350°F high-temperature fluid requirement; this was formulated with various additives such as antioxidants, lubricity additives, antiforms, metal deactivators, rust inhibitors, VIIIs, and seal swell materials to meet 18–30% volume swell. The first synthetic military hydraulic fluid developed was less flammable than MIL-H-5606 and was designated as MIL-H-83282. MIL-H-83282 had an operational range of -40 to 350°F . Seals based on sulfur-donor or peroxide-cured NBR were developed for this fluid. The new seals were designated as MIL-R-83461 and were developed to meet the -65 to 350°F operational requirements.

The MIL-H-83282 fluid contained a significant amount of diesters to achieve desired seal volume swell. This fluid found almost immediate use in most military aircraft, except for the Air Force strategic aircraft; for example, the B-52, B-1B, KC-135, and KC-10, which required -65°F viscosity, did not use this fluid, which became very viscous below -40°F . This shortcoming was later resolved by the development of a PAO-based fluid designated MIL-H-87257, which is currently being implemented. This low-temperature PAO fluid was achieved by the synthesis of lower-molecular-weight PAOs and replacing part of the higher-molecular-weight fractions present in MIL-H-83282. This approach caused a small loss in nonflammability capability but met the desired capability of a universal less-flammable hydraulic fluid for all military aircraft and with a -65 to 350°F range capability.

During this time frame, engine lubrication fluid requirements were also increased to -65 to 350°F , which led to the development of diesters of both adipic and sebacic acids, especially dioctyladipate (DOA) and DOS, with the latter predominating. These were formulated to later versions of MIL-L-7808 for both military and commercial aircrafts. During this time, seals were also formulated with fluorocarbon polymers to meet a -40 to 350°F operational requirement for these fluids. These seals were designated by the military specification MIL-R-83485. Seal swelling additives were not needed for the MIL-L-7808 lubrication fluids, as both NBR and fluorocarbon (FKM) seals exhibit swelling in these fluids.

During this 1961–1980 time frame, commercial aircraft were using the nonflammable phosphate ester fluids. Ethylene-propylene-(EPM) or ethylene-propylene diene-(EPDM)-based elastomeric seals were developed for these fluids. As the phosphate ester base stock acts as a plasticizer, there was no need for seal swell additives in these fluids.

14.4 FLUID/SEAL SWELL ADDITIVES DURING 1981–2000

As mentioned previously, MIL-H-83282, a PAO-based hydraulic fluid, was developed during the late 1960s and during 1970s, with implementations in most nonstrategic military (i.e., F-16, F-14, and F-18 fighters) aircraft beginning in the late 1970s after extensive flight-testing. The Air Force's strategic aircraft—long-range/high-altitude bombers, tankers, and reconnaissance aircraft—continued to use MIL-H-5606 to accommodate its need for a hydraulic fluid with a -65 to 275°F capability. The desire for a less-flammable fluid with better low-temperature viscosity led to the development of MIL-H-87257. This fluid balanced the PAO content with the proper molecular weight range of PAO components. With the proper additive package, including sufficient quantities of diesters (i.e., DOS) to achieve seal swell of 18–30%, dynamic cycling testing indicated that this new fluid had the desired capability of -65 to 350°F as well as compatibility with both MIL-R-82485 (fluorocarbon) and MIL-R-83461 (NBR) seals. Flight-testing was conducted on all military aircraft, including strategic aircraft, and it appeared likely that MIL-H-87257 would eventually be the universal hydraulic fluid (-65 to 350°F) for military aircraft. During this time, commercial aircraft continued to use phosphate ester fluids for hydraulics with the previously mentioned EPM/EPDM-based seals. Engine lubrication fluids were still primarily the DOS-type, MIL-L-7808, fluids for both military and commercial jet aircraft. Seal swelling materials are not required as the diester fluids accomplish this purpose.

14.5 FLUID/SEAL SWELL ADDITIVES DURING 2001–2007

MIL-H-83282, a PAO-based hydraulic fluid, has replaced MIL-H-5606 as the principal hydraulic fluid used in military aircraft. The advanced military fighter aircraft, namely, the F-22, F-35, and the latest model F-18, require MIL-H-83282. Currently, seals for these systems are MIL-P-83461 NBR and the higher-temperature capability MIL-R-83485 fluorocarbon materials. MIL-H-83282 is currently required in the main systems of all fleet aircraft previously using MIL-H-5606; however, MIL-H-5606 is still used in some areas, such as viscous dampers, due to its better low-temperature (-65°F) characteristics. Older aircraft that had been using MIL-H-5606 are gradually changing over to MIL-H-83282 by attrition.

Even with the trend of newer commercial aircraft, namely, Airbus' A380 and Boeing's 787, to have higher hydraulic system pressures up to 5000 psi, commercial aircraft continue to use phosphate ester fluids with the previously mentioned EPM/EPDM-based seals. Improvements in fire properties and other areas of performance continue to be made with these phosphate ester fluids; however, seal swelling materials are still not required because the diester fluids accomplish this purpose. No new types of fluids or seal swell additives have been introduced for engine lubrication fluids. The DOS-type, MIL-L-7808, fluids are still primarily used for both military and commercial jet aircrafts.

14.6 TRENDS AND THE FUTURE

It is very likely that advanced military fighter aircraft will continue to have the requirement of hydraulic fluid with a -40 to -350°F capability with a pressure of 4000 psi. As MIL-H-83282 meets these requirements, it should continue to be the primary hydraulic fluid for these aircraft. MIL-H-5606 will still be used in areas requiring better low-temperature (-65°F) performance until progress is made on improving the low-temperature properties of PAO-based hydraulic fluid or new base fluids are developed. Newer polymers are also investigated as potential seal materials for these systems as nitrile elastomers oxidize when exposed to temperatures above 250°F for extended periods of time, and fluorocarbon elastomers cannot achieve the low-temperature requirement of -65°F .

Strategic aircraft needs over the next 20 years will likely be met by the updated C-17 transport, the new A300, KC-10, or a tanker version of the C-17 (a KC-17), whereas strategic bomber needs are likely to be met by the B-1B, B-2, and an advanced version of the B-2 stealth aircraft. Although there could be some changing needs in both hydraulic and engine lubrication fluid needs, it is currently not possible to determine specific fluid/seal needs or seal swelling agent needs.

Commercial aircraft requirements over the next 20–30 years are not likely to involve major changes. Airframe designs and engine requirements will not change substantially but will likely feature incremental improvements in performance and, as always, be dependent on customer requirements. Therefore, a dramatic change is not expected in hydraulic or lubrication fluid/seal needs for commercial aircraft.

14.7 INDUSTRIAL FLUIDS

As stated earlier, industrial fluid development has closely followed the development of military fluids. Natural base oils including mineral oils have been used in industrial fluids. These fluids are not as controlled as military fluids, which have developed specifications to meet and essentially perform the same within a narrow band of additive variability, allowed by the specification for competitive bid requirements. Industrial fluids vary widely as a result of their crude source, for example, whether paraffinic, naphthenic, mixed, paraffinic–naphthenic, and the like, as well as their formation, for example, distillation range, straight run or cracked, hydrorefined, solvent extracted, and the like. Because these fluids vary widely, the additive packages are very proprietary, but again the seal swell additives parallel those used in military fluids.

DOS and DOP are used in industrial fluids. Other seal swell additives include mineral oils with aliphatic alcohols such as tridecyl alcohol. Oil-soluble, saturated, aliphatic, or aromatic hydrocarbon esters such as dihexylphthalate are very popular. Trisphosphite ester in combination with a hydrocarbonyl-substituted phenol is also used as a seal swell additive. As more highly refined mineral oils and synthetics based on PAO enter the market, it is not likely that there will be significant differences in seal swell additives.

14.8 SEAL SWELL DILEMMA

When a fluid is formulated, the usual concentration of seal swell additive is 0.6–1.0% by volume. During development, the fluid manufacturer uses standard test elastomers to determine fluid seal swell, which is normally targeted at 18–30%. These tests are normally 70–168 h in duration and do not allow for a full measure of fluid/seal compatibility evaluation. The fluid is then marketed as compatible with the elastomer seal. The dilemma is that the seal used in the actual system is much different than the elastomer used for seal swell determination, and swell beyond 20% is normally not allowed by elastomer specification or desired from a performance standpoint. Thus, we have fluid, developed to produce high seal swell, and an elastomer seal that is not allowed to swell beyond 20%. This dilemma occurs because fluid and seal development are no longer coordinated. In the past with the military driving parallel development programs, fluids and seals were simultaneously developed; this is not true in today's commercial arena. The fluid manufacturer has been taught that high seal swell is good. It allows for more seal force and less compression set. The problem is that seals that swell excessively soften and completely fill the seal gland. These conditions for dynamic seals lead to nibbling of the seal as it overflows the gland and to excessive seal wear. This leads to premature seal failure and leakage, which results in costly downtime while seals are replaced.

To put fluid developers on the same track as seal developers, ASTM International Committee D 02 has developed ASTM D6546. This specification details a fluid–elastomer seal test program, which involves the testing of commercially available elastomers in the new fluid at actual service temperatures for long periods of time (1000 h). These test conditions with recommended limits allow for a more complete evaluation of fluid–seal compatibility and should allow for optimized fluid formulations with a minimum amount of swell additive.

Changes to increase test times are also gradually made in new fluid specifications as more importance is placed on reliability and long-term performance. The commercial aerospace industry is becoming the driving force behind newer and updated specifications, such as SAE AS5780, with increased test times using commercially available fluids tested with commercially available seal materials. The military is slowly following.

14.9 COST-EFFECTIVENESS

It is important to minimize the amount of seal swell additive in fluid formulations. Seal swell additives increase the cost of mineral- and PAO-based hydraulic fluids. This is because the rather large amounts of DOS is expensive when compared to the cost of the base stocks, but it accomplishes the purpose of seal swell. It must be remembered that qualification testing of fluids and seals, not to mention quality control testing of both, is inherently expensive. This is why the implementation of ASTM D 6546 should be a cost-effective, integral part of the fluid development process. The fluid developer can also use the results of the tests to instill confidence in the fluid users that they are provided with a fluid and recommendations for seals substantiated by long-term testing.

The long-term testing can also provide useful information to the fluid user, which can help plan preventative maintenance programs, which would avoid or minimize costly downtime. Fluid stability tests are already performed for 1000 h; these additional tests would be extremely cost-effective in optimizing the fluid formulation and addressing total system needs—fluid and seals.

14.10 MANUFACTURE

Manufacturing of both fluids and seals is an extremely competitive and very proprietary business. This has not changed over the years and is not likely to change in the foreseeable future. In general, the following are true: (1) the competitive nature of the two business types has controlled product costs and (2) the fluids with the reputation for long life with a minimum of problems are the most successful. Fluid formulation plans that include testing to ASTM D 6546 or similar specifications can be very cost-effective over the long run as fluids would be developed with optimum concentrations of expensive additives, and long service life with compatible seals would be demonstrated.

14.11 SUMMARY

Seal swell additives are necessary in many fluid formulations; seal swell can be beneficial in slowing compression set. However, excessive seal swell can be deleterious to seal life and system performance. Seal swell additives add cost to the final fluid formulation, therefore, minimizing the concentration of these additives is important from a financial standpoint. For both the fluid and the seal developers, ASTM D 6546 represents a method to ensure that the seal and the fluid with its additive package are fully compatible. Whatever the proprietary formulation is, the fluid developers can demonstrate seal compatibility with confidence over a long period of time. They can also tailor the amount of seal swell additive for maximum seal performance and minimum cost.

SAE AS5780 Rev. A October 2005 Specification for Aero and Aero-Derived Gas Turbine Engine Lubricants.

15 Antimicrobial Additives for Metalworking Lubricants

William R. Schwingel and Alan C. Eachus

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15.1 INTRODUCTION

Metalworking fluids, the class of lubricants (along with water-containing hydraulic fluids) most susceptible to microbial attack, provide a number of vital functions in metal removal and forming operations. Designed as a coolant (to remove heat) and a lubricant (to reduce heat generation) and to provide corrosion resistance, electrochemical resistance, extended resistance to microbial degradation, and eventual biodegradability in the environment, a metalworking fluid must also be safe for human use and exposure. The failure of the fluid to perform any one of these has the potential to result in operational problems, process shutdowns, decreased tool life, and product-quality issues, all of which will result in increased costs. Perhaps one of the most common and controllable complications is microbial degradation. Metalworking fluids contain the nutrients that can permit unchecked microbial growth, including mineral oil base stocks, glycols, fatty acid soaps and esters, amines, sulfonates, and other organic components. Use-diluted emulsions, synthetic chemical solution fluids, and aqueous fluid concentrates are all vulnerable because they contain water, an important microbial growth requirement and the major source of microbiological contamination. Conversely, straight oils, although not immune to contamination problems, show greater overall

resistance to microbial degradation simply because they do not contain water or dilution. To ensure acceptable long-term performance of any fluid, protection against microbial degradation should be an integral part of the metalworking system.

15.2 MICROBIOLOGICAL GROWTH

The two types of microorganisms that contaminate metalworking fluids, bacteria and fungi, often proliferate independently, but they can also coexist in a fluid. The types of organisms present, and their ability to coexist in the same fluid, depend on fluid composition and environmental conditions.

15.2.1 BACTERIA

Bacteria, single-cell organisms that lack the internal cell organelles found in higher forms of life, are classified as either gram-positive or gram-negative depending on their cell wall structure, and as aerobic or anaerobic according to their requirement for oxygen. Anaerobic bacteria cannot grow in the presence of oxygen; however, strict anaerobes can tolerate very short exposure to oxygen before dying. Another group of bacteria, facultative anaerobes, is able to use metabolic pathways similar to those of aerobes when oxygen is present and then switch to anaerobic metabolism when oxygen becomes limited. The compounds produced from anaerobic pathways create unpleasant odors associated with the degradation of fluid quality and performance. The compounds produced through anaerobic pathways may include organic acids, as well as poisonous and explosive gases such as H₂S and H₂.

Not all bacteria are able to survive in the environment of metalworking fluids, and their occurrence is often specific to certain fluid formulations. However, *Pseudomonas aeruginosa*, *Enterobacter* spp., *Escherichia coli*, *Klebsiella pneumoniae*, and *Desulfovibrio* spp. are commonly found in all types of fluid. Because these bacteria are the species most predominantly found in rivers, streams, lakes, and soil, it follows that makeup water is viewed as a significant source of bacterial contamination. Other contamination sources include air, raw materials, and animals, including humans. When bacteria are present, they are generally distributed throughout the metalworking system and multiply rapidly when conditions are favorable.

15.2.2 FUNGI

Fungi may occur as either yeasts or molds. Yeasts, like bacteria, are unicellular and usually spherical in shape. Conversely, molds are composed of more than one cell and form complex mazes of filamentous hyphae with spore-bearing structures, which give them their powdery, matlike appearance. They are widespread in the environment and are commonly seen on decaying foods such as bread, fruit, and cheese. Fungi are often found in synthetic metalworking fluids but are usually found in lower concentrations and distributed less evenly than bacteria. They may be found in the fluid itself (planktonic), but they also tend to grow on solid surfaces (sessile) such as splash areas and in sluices, troughs, filters, and pipes, providing an important constituent of biofilm. Although many different species of fungi have been isolated from metalworking fluids, *Fusarium* sp., *Candida* sp., and *Cephalosporium* sp. occur most frequently.

15.2.3 BIOFILMS

Although microorganisms can exist in the free-flowing metalworking fluids in central systems, a large proportion of the microbial population exists within biofilms. Biofilms, often composed of diverse populations of microorganisms and complex in structure, adhere to system surfaces. Both chemical and biological materials can become trapped in the secretions of a biofilm's living cells. Biofilms, or *slime*, can vary in thickness but usually range from a few millimeters to several centimeters. The environment within the biofilm is highly influenced by the microorganisms present

and may be very different from the conditions in the fluid itself. Because the microorganisms growing within a biofilm are protected from the conditions that may be affecting the bulk fluid, the ability of antimicrobial agents to effectively control their growth is severely limited. This explains why chemical-control treatments shown to be effective in laboratory testing sometimes fail in field situations [1].

15.3 A MICROBE-FRIENDLY ENVIRONMENT

The primary factors affecting microbial growth are the availability of water and nutrients, system pH and temperature, and the presence of inhibitory chemicals [2]. With the introduction of water as an important component of metalworking fluids, microbial growth has become a major concern. Like all living organisms, bacteria and fungi require water for survival, which is present in all use-diluted emulsifiable, semisynthetic and synthetic metalworking fluids, as well as in some concentrates. In regard to nutrients, metalworking fluids are capable of providing all the essential nutrients needed to support microbial growth [3]. These include carbon, nitrogen, phosphorus, sulfur, and other trace elements. Small quantities of inorganic salts are also crucial for microbiological growth, which means variances in water hardness and quality can influence microbial survival. And, although at least some level of inorganic salts must be present, very high salt concentrations may actually inhibit growth.

In regard to pH, the ideal level for optimum bacterial growth is a neutral or slightly acidic pH of 6.5–7.5. Fungi prefer a slightly lower pH of ~4.5 to 5.0. However, both bacteria and fungi can survive in fluids with pH levels outside these ranges. A large contingent of microorganisms thrives in typical metalworking fluid pH ranges; however, species diversity decreases in fluids with pH levels of 8.5 and higher.

The optimum temperature range for mesophiles, the largest contingent of microorganisms, is 30–35°C, the bulk-temperature range of most metalworking fluid systems. However, many organisms can exist at extreme temperatures; for example, bacteria have been found growing in both Arctic climates and at the mouths of geysers and hot springs.

By manipulating these various growth factors, microbial survival and proliferation can be controlled and even prevented. Water quality and pH are the two factors most easily managed. However, the availability of nutrients can be regulated through the strategic selection of raw materials that are inherently more resistant to microbial degradation. Components such as borates, certain amines, and biocides can all inhibit microbial proliferation. Although little can be done economically to control bulk fluid temperature, factors such as oxygen availability can, if not slow microbial growth, at least alter microbial populations. For instance, a shift from aerobic bacteria to facultative or obligate anaerobe populations is likely to occur if metalworking fluids are not aerated or circulated.

15.4 DESIGN, MAINTAIN, AND MONITOR

In the ongoing quest for microbial control in metalworking fluids, system design, proper housekeeping, fluid maintenance, and microbiological monitoring programs all play an essential role. Microorganisms are less able to establish healthy populations in areas of high, uniform flow, therefore a well-designed system, one that eliminates or minimizes dead legs and stagnant zones, is ideal. For example, anaerobic bacteria are particularly likely to establish populations where flow is minimal, as this often limits the diffusion of O₂ into the fluid.

Good, consistent housekeeping practices at metalworking fluid end-use sites can significantly reduce the occurrence and proliferation of microbes. By preventing contaminants from entering the system, good housekeeping practices reduce the amount of chemical and human effort needed to maintain a system. An all-too-common scenario occurs when metalworking fluid splashes around machines. These small puddles of fluid can harbor concentrations of 10⁸–10⁹ microbes/mL. When

debris or built-up material is washed off or falls into central sumps, an extremely high microbiological burden is placed on the metalworking fluid's preservation package. Therefore, machine surfaces and work areas should be kept clean and free of debris or residue buildup. Operators should not rinse or sweep debris into return sluices, as this can inoculate central systems with contaminated material. Tramp oil is another significant cause of contamination that should be removed, as it introduces its own microbial population into the fluid and helps prevent oxygen contact with the fluid surface. High levels of tramp oil are associated with microbiological preservation problems in metalworking fluids and are known to reduce the efficacy of chemical and biological control agents [4].

Good housekeeping practices also require that workers wear clothing that is cleaned and kept on-site. This reduces the risk of workers introducing contaminants such as dirt into the plant and transporting contaminants and other possible chemical and biological irritants into their homes. Food and human waste should also be prohibited from entering fluid systems, as they both are likely sources of contamination.

15.5 COMPLICATIONS AND CHALLENGES

Uncontrolled microbiological growth can significantly impact both the performance of metalworking fluids and the operation of the central system. The poor fluid quality and performance that microbial degradation causes can result in corrosion of machines, tools, and workpieces; loss of lubricity and fluid stability; and the formation of slime, which can plug filters and delivery lines and cause unacceptable odors. Microbial growth may also contribute to skin irritation and respiratory problems.

Fluid deterioration can be defined as any change that adversely affects a fluid's utility. Direct deterioration of metalworking fluids can be caused by various microorganisms with the capability to degrade a number of organic compounds that make up the intricate formulation of a metalworking fluid [5,6]. Although components such as petroleum sulfonates, fatty acids and fatty-acid esters, organophosphorus products, and nitrogen compounds may or may not remain unaffected by any one singular group of organisms, they are all susceptible to attack from combinations of microbes. The degradation of these fluid components is responsible for loss of fluid performance. Resourceful groups of microorganisms may even develop the ability to attack and degrade biocides, especially if they are used at suboptimum levels.

Microbial contamination is also an indirect source of problems in fluid applications, including the generation of odors. The odors thus produced are associated with volatile organic acids (primarily acetate, propionate, and butyrate) and hydrogen sulfide—by-products of microbial metabolism. These compounds are formed when oxygen levels drop, allowing anaerobic bacteria to proliferate. A complication of weekend shutdowns occurs when fluids are not circulated, causing fluid oxygen levels to drop; odors generated by this means are often referred to as *Monday morning odor*, as fluid agitation at start-up volatilizes them. The odor can become so offensive that employees refuse to work until it is resolved.

Another complication of microbial contamination is a decrease in fluid pH. The organic acids generated from microbial metabolism have the potential to decrease the pH of the fluid, and a fluid with a lower pH can become corrosive to ferrous materials. A decrease in pH can also result in emulsion splitting and decreased efficacy of other fluid components, including antimicrobial agents or biocides. To maintain proper performance, the alkalinity of the fluid must be buffered at the desired pH.

Microorganisms can also have a direct effect on corrosion through a process known as microbially influenced corrosion (MIC). Here, certain bacterial populations either establish an electrolytic cell or stimulate anodic or cathodic reactions on metal surfaces. This can cause pitting and corrosion on both machining tools and workpieces, although it is more often associated with the pipeline, chemical process, and water-treatment industries [7]. Microorganisms can also degrade corrosion inhibitors, leaving metals more vulnerable to corrosion.

The formation of biofilm is a source of significant problems within the central system. Biofilm growth on machine surfaces can affect the heat-exchange characteristics of the system. Also, if it sloughs off, it can interfere with mechanical operations such as fluid flow and filtration. Fungal contamination, in particular, plays a major role in the clogging of lines and filters. Considerable time and effort are required to remove established biofilm from the system and resume efficient operations.

Microbial contamination is sometimes blamed for worker's skin irritation and dermatitis, but such issues may turn out to be chemically caused, instead. In recent years, respiratory problems among machine-shop workers have been thought to be linked to metalworking fluid microbial contamination. Hypersensitivity pneumonitis (HP), the most severe condition, has been attributed to the presence of *Mycobacterium immunogenum* in contaminated fluid mists [8]. Other possible causes of respiratory impairment include endotoxins, which are cell wall fragments of gram-negative bacteria that may be found in metalworking fluids, and mycotoxins, produced by fungi in contaminated fluids. These situations continue to be explored; Passman [9] has very recently provided a detailed discussion of worker health issues. The American Society for Testing and Materials (ASTM) Subcommittee E34.50 on Health and Safety Standards for Metal Working Fluids has produced standard test methods for enumeration of mycobacteria (E2564-07) [10] and determination of endotoxin concentration (E2250-02) [11] in metalworking fluids.

15.6 TESTING FOR CONTAMINATION

Test methods are vital in the fight to control and prevent microbiological contamination in fluid concentrates and coolant systems through the timely and accurate diagnosis and treatment of the problem. Many test methods exist, and each has its own set of advantages and limitations. The best method to use will vary by situation, but ideally it should balance ease of use with accurate, practical, and timely results. It is important to remember that different testing methods measure different aspects of microbial contamination.

Changes in fluid or system properties such as odor or slime formation, corrosion, emulsion splitting, and color changes are all good indicators of microbiological problems. However, by the time these symptoms are noted, microorganism populations may be very high and fluid properties significantly impaired. Other methods estimate the amount of microbial growth present through either direct or indirect measure of the biomass growing in the fluid.

The most common direct procedure includes taking microscopic counts. Requiring observation by a trained professional, this method is tedious and time-consuming but yields results within a matter of minutes. Another direct method that requires a skilled professional is staining. This identifies both living and dead cells among specific groups of organisms. Direct methods can also help account for organisms that will not grow on the various nutrient media specifically designed for enumerating microorganisms. However, because of their level of sophistication, direct test methods are not typically implemented in plants using metalworking fluids.

Indirect measures include obtaining estimates of the number of organisms present through the replication of these organisms and obtaining measurements of microbiological activity that translate into the amount of microbial biomass present in the system. Standard plate counts and dip-slide counts are the most common indirect methods for enumerating numbers of bacteria or fungi. Here, counts are estimated based on the development of bacterial or fungal colonies on the surface of solid nutrient media. In a standard plate count, a serial dilution is made of the metalworking fluid onto sterile petri dishes. The dishes are then filled with nutrient agar. Agar is a liquid above 45°C but solidifies at room temperature. After several days of incubation, bacteria and fungi form visible colonies on the agar and can be visually counted. Dilutions are taken into account in determining the number of organisms in the original sample.

Because plate-count methodology can be expensive and time-consuming, a similar method has been developed that uses paddles coated with the agar media to form a dip-slide. The dip-slide

is immersed in a fluid sample for a few seconds, returned to its sterile holder, and incubated for a few days at ambient temperature. Dip-slides generally contain a color indicator that changes color as bacteria or fungi begin to grow, providing a simple visual way to determine colony counts. An additional benefit of many dip-slide paddles is their ability to test for bacteria and fungi at the same time by offering a different growth medium on each side of the paddle.

In both standard plate-count and dip-slide methodology, the assumption is made that each colony comes from a single cell; however, cells often aggregate together, invalidating this conclusion. In addition, a given nutrient medium will only support the growth of certain microbes and may actually inhibit the growth of others, thereby limiting the ability to gain an accurate count of the total organisms present. It has been estimated that direct count methods may recover as few as 10% of the organisms present. Another major drawback to plate-count methods is the time required for the organisms to grow. Typically, results are available in 24–72 h, but they may take longer. This provides ample time for microorganism levels to reach detrimental levels in plant environments. The long lag times associated with both plate-count and dip-slide methods have prompted a search for more rapid techniques. Rapid test methods focus on the determination of the concentration of cell constituents such as proteins, enzymes, lipids, or adenosine triphosphate (ATP, the energy unit of living cells). Although these methods provide reliable estimates of microbial growth, they often require costly and complex instruments. However, as they become more commonplace, the cost of these technologies is likely to decline.

15.7 TREATMENT OPTIONS

Because metalworking fluids provide an environment conducive to microorganism growth, prevention techniques are vital to minimize the threat of contamination and facilitate trouble-free, consistent operations. Both chemical and physical methods are available, and often a combination of various methods is warranted when trying to establish and maintain microbiological control.

15.7.1 CHEMICAL METHODS

The use of biocides (also known as *antimicrobial pesticides*) is the most common method for controlling microbiological growth in metalworking fluids. The use of biocid reduces or maintains bacteria and fungi at acceptable levels in water-based concentrates and final use-diluted fluids, and ultimately maintains the integrity of the final product. Although they are capable of eradicating microbial growth at high concentrations, biocides are more often used at levels that control growth and manage contamination due to economic and toxicological considerations.

Governmental agencies in most countries regulate the use of biocides. In the United States, biocides are regulated by the Environmental Protection Agency (EPA), under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and must meet certain toxicological and environmental impact standards. Biocides are approved based on the relative risk resulting from their use. In the European Union, the Biocidal Products Directive (BPD, Directive 98/8/EC) performs a similar function. The EPA requires that all biocide labels include specific end-use applications, and it is up to the user to determine whether a registered biocide is appropriate for a specific application. Metalworking fluids are a specific EPA end-use application, and of the ~60 chemicals registered as biocides for this end use, fewer than two dozen are routinely used by fluid formulators and end users.

Two main biocide categories exist: bactericides and fungicides. Although some biocide chemistries possess both capabilities, it is common to use both antibacterial and antifungal functionality to preserve a fluid.

A brief summary of the most common chemistries follows. For a more complete listing of biocides and their properties, several excellent references on the subject exist, including Ross Moore [12], Ash and Ash [13], and Paulus [14]. Biocide suppliers are another valuable source of information and can supply product information and material safety data sheets (MSDS) that provide detailed

information on biocide chemistry, efficacy, toxicological properties, and handling. Additionally, appropriate biocide product labels must be consulted in determining dosages for a particular metalworking fluid application, as Federal law requires that biocide use-levels be within label limits. Dosage rates will also vary, depending on fluid formulation, housekeeping practices, time of year, operating temperature, pH, and type of contamination likely to be encountered. Testing should also be performed to determine the optimal biocide dosage.

15.7.2 POPULAR CHEMISTRIES

Formaldehyde condensates are by far the most popular and proven biocide chemistries for metalworking fluid applications. They control microbiological growth through their ability to generate formaldehyde *in situ*. Like other aldehydes, the antimicrobial activity of formaldehyde is derived from an electrophilic active group that reacts with nucleophilic cell sites. These targets include amino acids or proteins, which are often important components of enzymes or other functional proteins critical to cell function. Because of this more-generalized mode of action, formaldehyde-condensate biocides exhibit a broad spectrum of antimicrobial activity but are viewed as more effective against bacteria than against fungi. A general disadvantage of formaldehyde is the tendency of microorganisms to develop resistance to it [15,16].

Hydroxyethyltriazine (hexahydro-1,3,5-tris[2-hydroxyethyl]-*s*-triazine, CAS# 4719-04-4) is the most commonly used and most cost-effective formaldehyde-condensate biocide for metalworking fluids. Water-soluble and stable at moderately alkaline pH levels, it is the cyclic trimer made from formaldehyde and monoethanolamine (MEA). It is usually supplied as a 78% active aqueous solution, and its use can add significant alkalinity to a system. Hydroxyethyltriazine can be added tankside to an in-use fluid or incorporated into an aqueous concentrate. Viewed primarily as an antibacterial agent, its customary dose rate is ~1500 ppm (0.15%) in a use-diluted fluid.

Another frequently used formaldehyde-condensate biocide class is the oxazolidines, oxygen-nitrogen heterocyclic products formed by the reaction of formaldehyde with various alkanolamines. Representative materials include 4,4-dimethyl-1,3-oxazolidine (CAS# 51200-87-4) and 7-ethyl-bicyclooxazolidine (CAS# 7747-35-5). Being oil-soluble as well as water-soluble, these products can easily be incorporated into metalworking fluid concentrates or added tankside. Their alkaline nature will also aid in ferrous metal corrosion inhibition. Known primarily as antibacterial agents, customary dose rates for oxazolidine biocides are ~750 to 1500 ppm in working fluid systems.

Tris(hydroxymethyl)nitromethane (CAS# 126-11-4) is a water-soluble condensation product of formaldehyde and nitromethane. Chemically stable at acidic pH, it will decompose and release formaldehyde under alkaline conditions. Supplied as a 50% active aqueous solution, or sometimes in one-ounce solid tablets, its decomposition rate increases with increasing alkalinity levels, and it shows a rapid rate of kill against bacteria. Owing to its instability under alkaline conditions, resulting in lack of persistence of effect, this biocide is not incorporated into concentrates, but only added tankside to in-use fluids. It is often used in nonferrous applications such as aluminum rolling, due to its acidic, halogen-free nature and rapid kill rate. Tris(hydroxymethyl)nitromethane has been shown to work very well together with isothiazolinone biocides, especially in aluminum-rolling applications [17]. Recommended use rates are between 1000 and 2000 ppm active material.

Another reaction product of nitromethane and 2 mol of formaldehyde, and 1 mol of bromine, is known as bronopol (2-bromo-2-nitro-1,3-propanediol, CAS# 52-51-7). Bronopol, an antibacterial product, does not release free formaldehyde in its mechanism of antimicrobial action, and it is considered especially effective against resistant strains of *P. aeruginosa*. This water-soluble product is not chemically stable, long term, at pH levels above ~8.0. Its usual dosage rate is ~50 to 400 ppm active material.

A biocide consisting of 4-(2-nitrobutyl)morpholine (CAS# 2224-44-4) and 4,4'-(2-ethyl-2-nitrotrimethylene)dimorpholine (CAS# 1854-23-5) has proven effective as an antibacterial and antifungal metalworking fluid biocide. Although it is produced from formaldehyde, morpholine,

and nitropropane, this blend does not exert its antimicrobial effect through the release of formaldehyde. With limited water solubility and high oil solubility, the active ingredients formulate easily into many metalworking fluid concentrates, especially soluble oils. In fact, it is one of the few oil-soluble fungicides available. To optimize both its fungal and bacterial efficacy, it should be dosed at 500–1000 ppm active ingredient.

Phenolic compounds, including the commonly used phenolic active ingredient 2-phenylphenol (OPP, CAS# 90-43-7) as well as the sodium salt of OPP (CAS# 6152-33-6), have long been used as biocides in metalworking fluids. Although environmental concerns have at times lessened their popularity, these compounds have seen resurgence due to their proven favorable human toxicity profile and restrictions prohibiting the release of metalworking fluids into the environment. As a biocide, OPP can be used either tankside or in metalworking fluid concentrates. The sodium salt of OPP has greater solubility in aqueous systems. OPP is more easily formulated into concentrates with low water contents. The compound exhibits a very broad-spectrum, having efficacy against bacteria and fungi including both yeast and molds. Both OPP and sodium OPP can be used over a broad pH range; however, their performance and solubility are best at a pH > 9. Dosage rates range from ~500 to 1500 ppm active ingredient for OPP and from 500 to 1000 ppm active ingredient for the sodium salt of OPP. These active ingredients are available for various formulations in both solid and liquid forms. Another phenolic compound is *p*-chloro-*m*-cresol or 4-chloro-3-methylphenol (PCMC, CAS# 59-50-7). A very broad-spectrum biocide, PCMC is effective against bacteria, yeasts, and molds at dosages of 500–2000 ppm active ingredient. The active ingredient 4-chloro-3-methylphenol is effective in a pH range of 4–8 but is less stable at an alkaline pH than either OPP or sodium OPP. It can be added to metalworking fluid concentrates or used as a tankside additive. In tankside addition, it is generally preferable to make a solution rather than adding the dry powder directly. A closely related compound, *p*-chloro-*m*-xylenol (PCMx, CAS# 88-04-0), will behave in the same fashion as PCMC. Both PCMC and PCMx have received renewed interest recently as a result of their efficacy against mycobacteria.

The biocide 2,2-dibromo-3-nitrilopropionamide (DBNPA, CAS# 10222-01-2) has recently seen increased use in metalworking applications. This biocide chemistry is viewed as a bactericide with quick-killing properties that are achieved at very low dosage rates and is meant for use only as a tankside treatment. Because of the short half-life of DBNPA at a pH of >8, this chemistry is not persistent enough to provide prolonged preservation when added to metalworking fluid concentrates. An effective dosage rate for DBNPA in tankside applications is 1–2 ppm active ingredient. More recently, a timed-release tablet [18] has been developed that provides for a slow, continuous dose of DBNPA of 0.5–1 ppm active ingredient to central systems. The tablet eliminates the need for pumping liquid material tankside and is especially useful in smaller sumps.

A dialdehyde, known as glutaraldehyde (1,5-pentanediol, CAS# 111-30-8), also offers quick-kill properties and can be used in the cleanup of contaminated systems or as a tankside additive in fluids that do not contain amines, because its activity is impeded by the presence of amines. Its customary dose level in use-diluted fluids is 60–300 ppm active material.

In fluids that do not contain anionic emulsifiers such as sodium petroleum sulfonate, a polymeric quaternary-amine compound, poly[oxyethylene(dimethylimino)ethylene(dimethylimino)ethylene dichloride] (CAS# 31512-74-0) has shown efficacy against microbial contamination, at typical active levels of 180–300 ppm. The cationic nature of quaternary compounds is not considered compatible with anionic materials.

Several isothiazolinone chemistries have also seen extensive use in metalworking fluid applications. A blend of the active ingredients 5-chloro-2-methyl-4-isothiazoline-3-one (CMIT, CAS# 26172-55-4) and 2-methyl-4-isothiazolin-3-one (MIT, CAS# 2682-20-4) in a ratio of about 2.7:1 (CMIT/MIT) is the most commonly used isothiazolinone chemistry. Its typical dosage range for the total actives is 10–21 ppm. Offered in the form of a stabilized aqueous solution, this biocide is effective against bacteria and fungi, including both yeasts and molds, and can be used in all fluid types. Like formaldehyde condensates, isothiazolinones are strong electrophilic agents that react

with nucleophilic cell entities to exert their antimicrobial effect. Although resistance of microbial populations to isothiazolinones has been reported [19], its development was strongly affected by the dosing pattern of the biocide. When a regimen of fewer high-dose biocide treatments is compared with more frequent low-dose treatments, with the total biocide addition being equal, the low-dose treatment regimen is more likely to result in the selection of resistant microbial populations. Stable over a pH range of ~3 to 9, this chemistry shows greater stability at the lower end of the pH range. Although isothiazolinone chemistry is compatible with a wide variety of metalworking fluid additives, it is incompatible with reducing agents, various amines, mercaptobenzothiazole corrosion inhibitors, and the antifungal agent sodium 2-pyridinethiol-1-oxide.

Owing to the incompatibility of isothiazolinones with certain amines (especially at higher concentrations) and the issues of sensitization that could result from using high levels of isothiazolinones in concentrates, the CMIT/MIT blend is used only in tankside applications and is not added to metalworking fluid concentrates. Combining CMIT/MIT with formaldehyde condensates or copper [20] has been shown to stabilize the isothiazolinone molecules, indicating that these combinations may be better suited for fluid-concentrate incorporation. Recently, MIT alone has been offered as a fluid-concentrate biocide. While requiring a higher effective dose level than the CMIT/MIT blend (20–150 ppm active), it demonstrates significantly greater stability in aqueous solution and is less aggressive in human contact.

An aromatic isothiazolinone derivative, 1,2-benzisothiazolin-3-one (BIT, CAS# 2634-33-5), is well established as a metalworking fluid biocide. It can be incorporated into fluid concentrates or added tankside to use-diluted fluids. Its customary dosage level is ~40 to 360 ppm active ingredient in the final use-diluted fluid.

Another isothiazolinone chemistry, 2-*n*-octyl-4-isothiazolin-3-one (OIT, CAS# 26530-20-1) is also appropriate for use in metalworking fluids. Unlike CMIT/MIT, which demonstrates broad-spectrum activity, OIT functions only as a fungicide. Stable in the pH range of 2–10 and compatible with a wide variety of metalworking fluid additives, OIT products are often used in combination with other metalworking biocides including CMIT/MIT, triazine, oxazolidines, and sodium pyrithione. Its use with sulfides, mercaptans, bisulfites and metabisulfites, and strong oxidizing agents, however, should be avoided. It may be added to either concentrates or use-diluted fluids as a tankside addition. Dosage rates range from 25 to 75 ppm active OIT based on the final use-diluted fluid.

Another biocide chemistry used as a fungicide in metalworking fluid applications is 3-iodo-2-propynylbutylcarbamate (IBPC, CAS# 55406-53-6). Available in both powder and liquid forms, it has very limited water solubility but is miscible in both alcohols and aromatics. Effective dosage rates for IBPC range from 100 to 300 ppm active, and it can be formulated into metalworking fluid concentrates or used as a tankside additive.

Sodium 2-pyridinethiol-1-oxide (sodium pyrithione, CAS# 15922-78-8), a broad-spectrum fungicide, can be added either to water-based metalworking fluid concentrates or tankside into use-diluted fluids in metalworking fluid sumps. It has an effective pH range of 4.5–9.5 and is compatible with most metalworking fluid formulations; however, it is not recommended for use in combination with CMIT/MIT-based biocides. Strong oxidizing or reducing agents also impair the efficacy of sodium 2-pyridinethiol-1-oxide. The appearance of a blue color or black specks is common with this chemistry, as it reacts with ferric ions to form insoluble ferric pyrithione, which, incidentally, also has antifungal properties. Dosage rates range from 46 to 64 ppm active sodium 2-pyridinethiol-1-oxide.

A nonexhaustive listing of major producers of metalworking fluid biocides (ones that offer several different chemistries) includes Acti-Chem Specialties, Inc. (Trumbull, Connecticut); Arch Chemicals, Inc. (Norwalk, Connecticut); BASF Corporation (Florham Park, New Jersey); Buckman Laboratories International, Inc. (Memphis, Tennessee); Clariant Corporation (Mt. Holly, North Carolina); The Dow Chemical Company (Midland, Michigan); Lanxess Corporation (Pittsburgh, Pennsylvania); Rohm and Haas Company (Philadelphia, Pennsylvania); and Troy Corporation (Florham Park, New Jersey).

15.7.3 BIOCIDE COMBINATIONS

The use of more than one biocidal active ingredient is a well-known practice and works to broaden or complement the antimicrobial spectrum of a single product. Here, an antifungal product may be combined with an antibacterial product to provide a dual mode of action, or in cases where an antibacterial biocide may have limited efficacy against certain bacteria, another antibacterial agent may be added to expand the system's overall antibacterial spectrum. For example, sodium 2-pyridinethiol-1-oxide, a proven fungicide, is often blended with triazine or oxazolidines, both proven bactericides, to form a product effective against both types of organisms. An added benefit of commercial blends is that they reduce the number of products that an end user must hold in inventory.

Biocides may also be used together to improve the overall performance of either biocide. This concept, known as synergy, can boost efficacy in several different ways. One biocide molecule may stabilize another, while broadening the spectrum of antimicrobial coverage or providing additional modes of action for killing or inhibiting microorganisms. The use of isothiazolinones with certain formaldehyde-condensate biocides is an example of this type of synergistic blend [21]. Some isothiazolinone molecules, when used alone, have limited persistence in metalworking fluids. However, these formaldehyde condensates stabilize the isothiazolinones and increase the persistence of the blend.

It is important to remember that, in the United States, regulations regarding blending of registered biocides are stricter than current regulations in some other parts of the world. If a blend of registered active ingredients is sold in the United States, the blend itself must be separately registered by the EPA as a pesticide. The recently enacted European regulatory initiative known as the BPD will also result in more-restrictive biocide regulation and possibly fewer choices of biocide candidates.

15.7.4 METHODS OF BIOCIDE APPLICATION

Biocides can be either formulated into the metalworking fluid concentrates or added to a system tanksides. Each strategy has advantages and limitations, and the biocide chemistry may dictate which application method is best. A biocide added into a concentrate will not only protect the concentrate but will also provide antimicrobial protection in the use-diluted fluid. This method of biocide addition reduces handling of the concentrated biocide at plant locations and end-use sites and ensures that the biocide is added proportionally to the systems in the correct ratio to the fluid. The limitation to this type of addition is that different metalworking fluid systems may exert different demands on the biocide. For instance, there may be fluid ingredients in a central system which are not compatible with a certain biocide chemistry. Thus, the biocide in the newly diluted fluid may be deactivated and consequently fail. In systems that are already heavily contaminated, the organisms may create a heavy demand on the biocide and rapidly deplete it, leaving the remaining formulation components unprotected. Furthermore, adding a biocide to the concentrate for preservation of the use-diluted fluid assumes that the fluid will be diluted properly at the end-use site. If for any reason the fluids are over-diluted, biocide levels may not be sufficient to control microbiological growth.

Alternatively, tankside addition of a biocide at the plant site allows a more direct and specific way to address individual plant situations. With this method, biocide selection can be based on unique plant-operating parameters such as water quality (microbiological and chemical), house-keeping, fluid residence time, degree of expertise in personnel, and waste treatment processes used in the plant. Tankside treatment does require close, if not constant, monitoring, but the added benefit of this is the ability to respond immediately to problems as they arise. Routine tankside addition of a biocide, with specific targeted levels of biocide in the fluid, is more likely to provide effective control if these levels are maintained at all times. It is better to integrate biocide use into a planned

program than to just use it on an as-needed basis. Waiting until a microbiological problem is noted before providing treatment may result in large amounts of dead microbial biomass, which can plug pipes and filters and release odors associated with decaying microbial cells. Limitations associated with tankside treatment include user concerns about maintaining and handling undiluted (concentrated) biocide products due to the health and safety issues associated with these products, and the labor-intensive aspect of having to constantly monitor and maintain biocide levels. Tankside addition also requires more in-depth training in the proper handling of biocides, as well as a deeper understanding of how to properly calculate and add a given dose of biocide. When using tankside treatment methods, it is very important that all personnel in the plant be informed of the necessary precautions to take when neat biocides are present.

Many metalworking fluid operations use both methods of biocide application to provide a comprehensive treatment program. Although biocides added to fluid concentrates help preserve the concentrate and reduce the volume of tankside preservative that must be kept on-site, they may also become depleted in the working fluid over time. The routine addition of a tankside biocide, once the biocide provided in the concentrate has been depleted, prevents uncontrolled microbial growth and ultimately helps extend fluid life. However, compatibility between the concentrate biocide and the tankside biocide must be established.

15.7.5 BIOCIDE SELECTION

Although a seemingly straightforward task, biocide selection can prove challenging because of the number of options available and the fact that no single biocide will provide optimum performance in all situations. Of the various factors to consider when choosing a biocide, the first should be whether the product has an EPA end-use registration for metalworking fluid applications. In addition, the compatibility of the biocide with the fluid must be considered. The biocide must not affect the functional properties of the fluid, including lubricity, corrosion inhibition, and emulsion stability. Other factors such as cost, known chemical incompatibilities, and mode of application also need to be examined before laboratory or field evaluation of the biocide can begin. The type of metal on which the fluid is used should also be considered, as ferrous and nonferrous metals may have different compatibilities with various biocides. The ASTM document E2169-01 (2007), entitled Standard Practice for Selecting Antimicrobial Pesticides for Use in Water-Miscible Metalworking Fluids [22], provides a detailed discussion of the issues to be considered in matching the preservative with coolant chemistry and performance requirements. This document also lists the 57 chemicals registered by the EPA for use in the preservation of metalworking fluids.

Biocides must be cost-effective and also provide protection against the spectrum of microorganisms affecting the fluid. Although various laboratory test methods are available for measuring biocide performance, simulating real-use conditions in metalworking systems is difficult. The most rigorously documented laboratory test procedure is that published by ASTM. It is designated as ASTM E2275-03e1, Standard Practice for Evaluating Water-Miscible Metalworking Fluid Bio-resistance and Antimicrobial Pesticide Performance [23]. It replaces two previous ASTM methods, D3946 and E686, and can be used to evaluate initial fluid bioresistance, biocide speed of kill, and fluid resistance to repeated microbial challenges. In this test procedure, use-diluted fluid samples of <1 L in volume are inoculated with microbes and then aerated to simulate recirculation conditions. The samples may also contain metal chips. The test duration may range between 24 h and 3 months; for longer test periods, a portion of the test fluid is periodically replaced with fresh fluid to simulate fluid turnover in use. Fluid performance is determined by measuring properties such as increase in viable-cell recovery or biomass and changes in physical and chemical fluid properties. This test procedure is meant to compare relative performance of fluids and biocides, not as an absolute predictor of performance in the field. Despite the best efforts and assumptions, laboratory testing is not a perfect indicator of real-use conditions. Consequently, when a biocide has been

chosen for a system based on laboratory trials, it is imperative to confirm the laboratory results with a field trial.

15.7.6 BIOCIDE HANDLING

It is important to remember that biocide products are designed to control and arrest microbiological growth and, therefore, have toxic properties. Special precautions should always be taken when handling biocides. A product's MSDS is the best resource to consult, as it will present comprehensive information on the proper handling methods for that particular chemical hazard. The product label should also be consulted, as Federal law requires that registered pesticide labels provide detailed safety procedures and use instructions. Although the recommended types of protection will vary depending on biocide chemistry, in the interest of good chemical hygiene, protective gloves, aprons, and eye and face protection, at a minimum, are recommended when handling any biocide.

15.7.7 PHYSICAL AND NONCHEMICAL CONTROL METHODS

Although chemical methods are by far the most common means of controlling microbiological growth in metalworking fluids, several nonchemical methods have received some attention. These include heat treatment or pasteurization, UV treatment or irradiation, and filtration. Compared to chemical treatments, these technologies share some common disadvantages. Because these methods treat metalworking fluids at a single point in a system, microbiological growth that may not be circulating in the fluid, or is held up in dead areas of the system or in biofilms, is not treated.

Pasteurization of metalworking fluids heats the fluid to a temperature high enough to destroy the microorganisms responsible for fluid deterioration, but temperate enough not to damage the functional properties of the fluid. Although many microorganisms are particularly susceptible to heat treatment, others are more thermotolerant and can survive this treatment, leaving the remaining microorganisms to degrade the fluid. This process is also energy intensive, requiring fluids to remain at $\sim 142^{\circ}\text{F}$ (63°C) for periods >30 min. Consequently, the success of this method depends on the availability of an affordable energy source and the feasibility of heating the fluid in an entire system. Although Elsmore and Hill [24] obtained good results with heat treatment, they found that heat-resistant populations developed upon intermittent pasteurization. However, the use of fluid heating together with biocidal treatment is more effective in microbial control than either method alone [25].

Several types of radiation technology might appear to prove useful in controlling microbial growth in metalworking fluid systems, including UV irradiation, high-energy electron irradiation, and gamma irradiation. With all these methods, fluids flow through an irradiation bank, contained in a thin-film layer. The radiation causes lethal mutations or kills organisms by direct ionizing effects. All three methods have at least some degree of difficulty penetrating opaque materials such as metalworking fluids. UV technology is probably the least effective due to this challenge, followed by high-energy electron radiation, which is also energy intensive, making it less cost-effective. Gamma irradiation offers the most potential in penetrating fluids and killing organisms; however, handling of this radiation source is costly and requires well-trained personnel [26].

Filtration systems are designed to remove particulate material from fluid streams; however, they do not remove microbial cells directly. Microbial populations tend to grow on particulate surfaces rather than in free-flowing fluids. By removing these particles, filtration systems can keep metalworking fluids cleaner and, therefore, less vulnerable to microbial growth. Naturally, cleaner systems often require less biocide. It is important to remember, however, that filter media can also harbor microorganisms and may actually add to contamination problems.

Currently, nonchemical treatment methods remain largely unpopular for metalworking fluid applications because of their significant capital expenditures and energy costs, and the scarcity of well-documented technical success stories from the field. However, as pressure to remove toxic chemicals from fluid formulations increases, there may be a greater impetus for the industry to investigate more of these nonchemical treatment technologies.

15.7.8 ENHANCEMENT OF FLUID PROTECTION

Today's metalworking operations emphasize extending fluid life as long as possible. Not only does this reduce waste disposal costs, but customers also wish to eliminate or reduce the concentration of fluid components viewed as toxic, such as biocides. In an attempt to reach these goals, considerable effort has been spent on trying to formulate fluids with greater inherent biological stability.

One way to attack the problem is to incorporate nonbiocidal materials that will enhance biocide activity. The best-known example of such technology is the use of chelating agents such as ethylenediaminetetraacetic acid (EDTA) salts. Chelants are ordinarily used as conditioners in water treatment to soften hard water by complexing calcium and magnesium cations out of solution. However, EDTA has also been known for a long time as a potentiator of antimicrobial agent activity [27]. This is due to its effect in disrupting the cell wall of gram-negative bacteria (e.g., *P. aeruginosa*), rendering the cells more susceptible to damage from biocidal chemistries. Thus, the presence of EDTA in a use-diluted metalworking fluid could lower the level of actual biocide required for microbial control and lengthen the useful life of a working fluid. However, as is often the case in the development of chemical formulations, a balance must be maintained between desired properties and detrimental ones imparted by an ingredient. Too much EDTA or other chelating agent can lead to excessive fluid foaming and increased potential for corrosion of metal parts and machine tools.

Another approach is the use of bioresistant functional ingredients in the fluid. A bioresistant material is one that, although not actually killing microorganisms, is not readily decomposed by microbial attack. Bioresistant materials do not provide a readily available food source for microorganisms, but at the same time these materials cannot stand up to repeated insults of heavy microbial contamination without degradation. Bioresistant products are not subject to the requirements for U.S. EPA registration under FIFRA as long as no claims of antimicrobial efficacy are made. A metalworking fluid's overall potential for microbial degradation depends on the susceptibility of each of its components to microbial attack. A bioresistant component remains unchanged in structure and functional properties in the presence of a microbial population. Fluids with greater bioresistance do not necessarily show lower counts of microorganisms, and inhibition of microbial activity or growth is not ordinarily a property of a bioresistant raw material.

One metalworking fluid component chemistry that has received considerable attention in this regard is the alkanolamines, employed to maintain an alkaline pH and assist in corrosion protection. Although all alkanolamines eventually become susceptible to biodegradation, their specific bioresistance characteristics can vary [28,29]. In general, 2-amino-2-methyl-1-propanol (AMP, CAS# 124-68-5) appears more bioresistant than do 2-(2-aminoethoxy)ethanol (CAS# 929-06-6), MEA (CAS# 141-43-5), or triethanolamine (TEA, CAS# 102-71-6). However, differences exist in the bioresistance of these alkanolamines, depending on the fluid formulation and the situation in which the fluid is being used. At least some of the bioresistance attributed to alkanolamines appears to be related to pH. Rossmoore [30] showed that high pH attributed to alkanolamines provides a degree of bioresistance. However, in some fluids, bioresistance was maintained when pH was lowered, whereas in others bioresistance was lost. Sandin et al. [31] reported that bioresistance of metalworking fluids was directly proportional to pH and alkyl chain length of the particular alkanolamine tested. Other alkanolamines providing bioresistance include *N*-butylethanolamine (CAS# 111-75-1) and *N*-butyldiethanolamine (CAS# 102-79-4).

Amine reaction products with boric acid can be used as water-soluble inhibitors for corrosion of ferrous metals. A major additional benefit of these materials is that they resist microbial attack very

effectively [32]. However, on drying, they may tend to form hard or sticky residues that are difficult to remove from machines and parts [33].

15.8 THE FUTURE OF MICROBIOLOGICAL CONTROL

Although the metalworking fluid industry is not viewed as an aggressively expanding market, it is filled with impending changes and challenges. Metalworking operations and fluid technologies will continue to become more sophisticated. As many experts predict, this will drive the use of synthetic and semisynthetic fluids, increasing the demand for innovative and effective microbial control strategies. Environmental restrictions regarding fluid disposal are also likely to escalate, increasing disposal costs and creating even more pressure to extend fluid life. The popular option of simply adding more biocide to increase fluid utility will likely see counterpressure as safety-conscious workers demand the use of lower-toxicity fluids. As environmental and exposure concerns increase, the industry's biocide options will decrease, as more biocidal substances come under regulatory pressure. In addition, microbial resistance will continue to reduce the efficacy of current biocides. New chemistries coming to market are also anticipated to slow due to the high cost of registering new active ingredients. Furthermore, recent regulatory schemes such as the European law known as Registration, Evaluation and Authorization of Chemicals (REACH, Regulation 1907/2006/EC) may make it economically unattractive to either develop or continue to market some specialty-chemical materials, including biocide enhancers and bioresistant ingredients. At the same time, a recent trend in "green" chemistry is to replace at least a part of a hydrocarbon lubricant material with a vegetable oil or a vegetable-oil-derived ester or triglyceride. Although such materials offer greater lubricity *per se* than does mineral oil, their inherently biodegradable nature can provide new opportunities for microbiological attack in metalworking fluids. These are the industry's challenges, fighting more battles with fewer and more expensive weapons, but they will also serve as the impetus for the advancement of the industry and evolution of the next generation of microbial control strategies.

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16 Surfactants in Lubrication*

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16.1 INTRODUCTION

Surfactants are one of the most widely applied materials [1–9]. The application of surfactants varies from everyday mundane tasks such as cleaning to highly complex processes involving the formulation of pharmaceuticals, foods, pesticides, lubricants, etc. Although surfactants have been known and applied for centuries, they continue to be the subject of vigorous research and development effort. This is because of the continued development of new and complex applications (e.g., nanotechnology) that require new and improved surfactants and a deeper understanding of their performance.

The objective of this chapter is to provide an overview of the applications of surfactants in lubrication. However, before delving into the lubrication aspects of surfactants, the chapter provides basic information about surfactants. This basic information is critical to understanding the role of surfactants in lubrication discussed in the subsequent sections.

The chapter begins with a review of the basic information about the chemical structure of surfactants. Although there are thousands of surfactants being used in thousands of applications, they all have similar basic structures.

Another important property of surfactants is their ability to dissolve in both polar and nonpolar solvents. A brief description of this phenomenon is provided followed by a discussion of surfactant-organized assemblies. The ability of surfactants to spontaneously form various types of microstructures or organized assemblies is responsible for many of their applications [1–9].

* Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

Surfactants are used in lubrication to provide a number of desirable outcomes (e.g., lower friction, lower wear, better filtration, lower emission, and better cooling). The list of surfactant functions in lubrication is numerous, and a brief description of some examples is given. In addition, an in-depth review of two of the most important functions of surfactants in lubrication is highlighted. These two functions are solubilization and boundary lubrication.

Solubilization deals with the ability of surfactants to solubilize various polar and nonpolar ingredients [1–13]. This property of surfactants makes it possible to formulate the various water- and oil-based lubricants currently in use for various applications.

In boundary lubrication, friction surfaces are pressed together at very high load and rub against each other at low speeds. Such a process leads to the generation of high friction and wear. Surfactants adsorb on friction surfaces and prevent direct contact between the friction surfaces, thereby lowering both friction and wear. This property of surfactants is illustrated from a review of an extensive study into the boundary lubrication properties of agriculture-based surfactants [14–32].

16.2 STRUCTURE OF SURFACTANTS

The term *surfactant* is used to describe organic molecules that comprise two dissimilar groups in the same molecule. One group is a hydrocarbon chain of varying structures and is soluble only in nonpolar solvents. Examples of nonpolar solvents include benzene, toluene, and hexanes. Because it is soluble only in nonpolar solvents, the group is also referred to as the lipophilic segment or the lipophilic tail of the surfactant.

The second group in the surfactant is composed of polar groups that readily associate with or dissolve in polar solvents such as water, glycerol, formamide, and other similar solvents. Because of its strong affinity for polar solvents, the group is also referred to as the hydrophilic segment or hydrophilic head of the surfactant.

Figure 16.1 displays schematics of surfactant structure of varying complexity. The simplest surfactants comprise a linear or branched lipophilic chain directly attached to the hydrophilic component (Figures 16.1a and 16.1b). More complex structures include more than one lipophilic chain attached to one or more hydrophilic component (Figures 16.1c through 16.1e) or polymeric surfactants with various repeating hydrophilic and lipophilic components (Figure 16.1f).

Depending on the nature of the hydrophilic component, surfactants are classified into four categories: anionic, cationic, nonionic, and zwitterionic. Anionic surfactants are negatively charged and contain one or more positively charged organic or inorganic counterion. Similarly, cationic surfactants are positively charged with negatively charged organic or inorganic counterions. Nonionic surfactants have no charge, and zwitterionic surfactants have both positive and negative charges with no counterions. Examples of ionic and nonionic surfactants of varying hydrophilic and lipophilic structures are given in Table 16.1, along with their common names.

16.3 SOLUBILITY OF SURFACTANTS

Almost all ionic (anionic, cationic, and zwitterionic) surfactants display good solubility in water but poor solubility in nonpolar solvents. The reverse is true for most nonionic surfactants, except for ethoxylated surfactants ($C_{12}EO_6$ in Table 16.1). In the latter case, the solubility of the surfactant in hydrophilic (e.g., water) versus lipophilic (e.g., hexanes) solvents depends on the relative “strength” of the hydrophilic versus the lipophilic segments of the surfactant. Becher [9] developed the following empirical equation to quantify the net *strengths*, or the hydrophilic–lipophilic balance (HLB) of such nonionic surfactants.

$$\text{HLB} = \frac{20 \times (\text{MW} - \text{EO})}{\text{MW}} \quad (16.1)$$

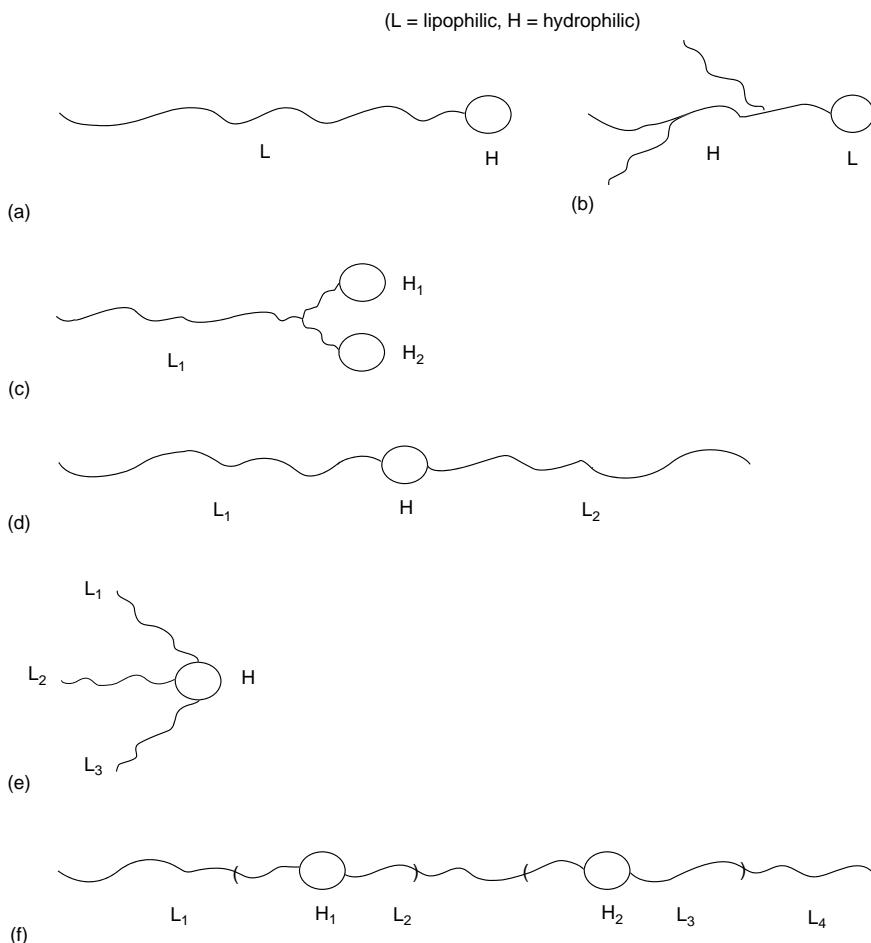


FIGURE 16.1 Schematics of surfactant structure of varying complexity. Hydrophilic and lipophilic segments are indicated by H and L, respectively.

TABLE 16.1
Examples of Surfactants of Varying Hydrophilic and Lipophilic Structures

General Structure: RXY

Type	R	X	Y	Name
Anionic	C ₁₁ H ₂₃ ⁻	COO ⁻	K ⁺	Potassium laurate (soap)
	C ₁₂ H ₂₅ ⁻	SO ₄ ⁻	Na ⁺	Sodium dodecyl sulfate (SDS)
Cationic	C ₁₆ H ₃₃ ⁻	(CH ₃) ₃ N ⁺	Br ⁻	Cetyltrimethyl ammonium bromide
	C ₈ H ₁₇ ⁻	(C ₈ H ₁₇) ₂ CH ₃ N ⁺	Cl ⁻	Tri(<i>n</i> -octyl)-methyl ammonium chloride
Zwitterionic	C ₁₂ H ₂₅ CH-	(CH ₃) ₂ N ⁺	-CH ₂ CO ₂ ⁻	Laurylbetaine
Nonionic	C ₁₂ H ₂₅ ⁻	OH		Lauryl alcohol
	C ₁₇ H ₃₃ ⁻	COOH		Oleic acid
	C ₁₂ H ₂₅ O ⁻	(CH ₂ CH ₂ O) ₆ H		C ₁₂ EO ₆ , ethoxylated lauryl alcohol

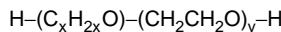


FIGURE 16.2 General structure of a polyethoxylated nonionic surfactant.

where MW – EO is the molecular weight of the ethoxylated segments of the surfactant and MW is the molecular weight of the surfactant.

To illustrate the application of Equation 16.1, let us examine the HLB of a hypothetical ethoxylated nonionic surfactant shown in Figure 16.2. According to Equation 16.1, the maximum value of HLB is 20, and it is for a nonionic surfactant without a lipophilic segment, that is, $x = 0$ in Figure 16.2. Using a similar argument, the minimum value of HLB is zero and is for a nonionic surfactant with no hydrophilic segments, that is, $y = 0$ in Figure 16.2. The general relationship between HLB and solubility of ethoxylated nonionic surfactants is as follows [9,10]: nonionic surfactants with high HLB (>11) are soluble in water and, hence, are good candidates for formulating oil-in-water (o/w) emulsions. On the contrary, nonionic surfactants with low HLB (<9) are soluble in oil and are good candidates for formulating water-in-oil (w/o) emulsions.

16.4 ORGANIZED SURFACTANT ASSEMBLIES

Surfactants form various types of structures when dissolved in hydrophilic and lipophilic solvents. The types of structures formed depend on various factors including the nature of the surfactant, type of solvent, surfactant concentration, temperature, and nature and concentration of cosolutes (e.g., salts and other surfactants).

At low concentrations, surfactants adsorb on the surface of the solvent, with one segment dissolved in the solvent and the other segment in contact with air. Which segment contacts the solvent depends on whether the solvent is hydrophilic or lipophilic. In hydrophilic solvents, the polar group is in contact with the solvent, whereas the lipophilic chain is in contact with air. The structure is reversed in a lipophilic solvent. These structures are depicted in Figures 16.3a and 16.3b.

When the concentration of the surfactant reaches a certain critical value, the surfactant molecules spontaneously form micelles or aggregate. The concentration at which such microstructures spontaneously form is called critical micelle concentration (CMC) or critical aggregate concentration (CAC). In hydrophilic solvents, normal micelles or aggregates are formed. In such systems, the lipophilic chains of the surfactants form the core of the spherical structures, away from the hydrophilic solvent, whereas the hydrophilic heads are in contact with the hydrophilic solvent. In lipophilic solvents, reverse micelles and aggregates are formed where the hydrophilic heads are buried in the core and away from the lipophilic solvent, whereas the lipophilic tails are in contact with the solvent. The structures of normal and reverse micelles are depicted in Figures 16.3c and 16.3d.

Micelles differ from aggregates in that they have a uniform size and a constant aggregation number, that is, they comprise the same number of surfactant molecules per micelle. Aggregates, on the contrary, have no fixed size or aggregation number but a range of sizes and aggregation numbers [11].

Incorporation of a cosurfactant (e.g., short-chain alcohol) allows normal micelles and reverse micelles to solubilize lipophiles (e.g., oils) and hydrophiles (e.g., water) in their cores, respectively. The resulting micelles have bigger diameters and are referred to as swollen micelles. Normal micelles with large volumes of solubilized oil are called o/w microemulsions, whereas reverse micelles with large volumes of solubilized water are called w/o microemulsions. The structure of o/w and w/o microemulsions are illustrated in Figures 16.3e and 16.3f.

The diameters of micelles and microemulsions are smaller than the wavelength of light. As a result, solutions with micelles and microemulsions are clear and transparent and remain so indefinitely since they are thermodynamically stable.

In the absence of cosurfactants, normal micelles dissolve little or no oil. As a result, mixing oil in micelle solutions will result in the formation of emulsions. Emulsions differ from micelles and o/w

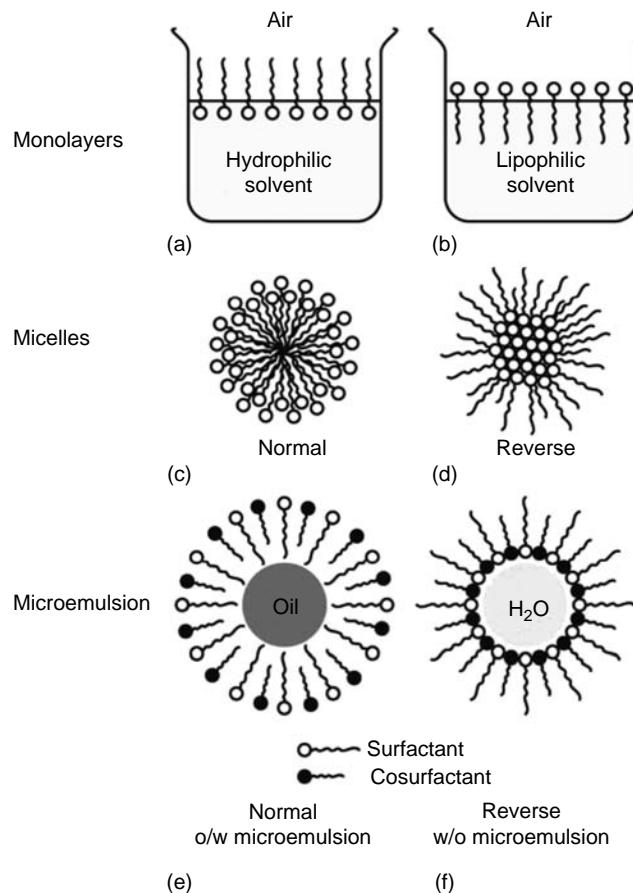


FIGURE 16.3 Microstructures of surfactant assemblies in solution: (a,b) monolayers, (c) normal micelles, (d) reverse micelles, (e) o/w microemulsions, and (f) w/o microemulsions.

microemulsions in that they comprise oil droplets with diameters larger than the wavelength of light. As a result, they reflect visible light and have a milky appearance. Emulsions are also thermodynamically unstable; as a result, they separate into their respective oil and water phases over time.

This distinction between micelles, o/w microemulsions, and o/w emulsion is very important in lubrication. In water-based lubricants, these three fluids are referred to by different names by lubricant suppliers and users [12]. Generally, emulsions are referred to as soluble oils because they comprise relatively large quantities of solubilized oils. Microemulsions are referred to as semisynthetic lubricants because they comprise relatively smaller quantity of solubilized oils. Micelles are called synthetic lubricants because they comprise no oil, and lubrication is achieved by synthetic ingredients dissolved in the water phase of the micelle. More detail about water-based lubricants is given in Section 16.6.

Increasing the concentration of the surfactant after the formation of micelles results in the formation of lamellar liquid crystals. These are three-dimensional surfactant multilayer structures. The exact orientation of the surfactants in these structures depend on whether the solvent is polar or nonpolar, as illustrated in Figures 16.4a and 16.4b.

Further increase in the concentration of surfactant leads to the formation of normal and reverse hexagonal liquid crystal structures, which are depicted in Figures 16.4c and 16.4d. Other surfactant-based microstructures include vesicles (Figure 16.4e) and foams (Figure 16.4f). Control of foam is a major problem in lubrication [12].

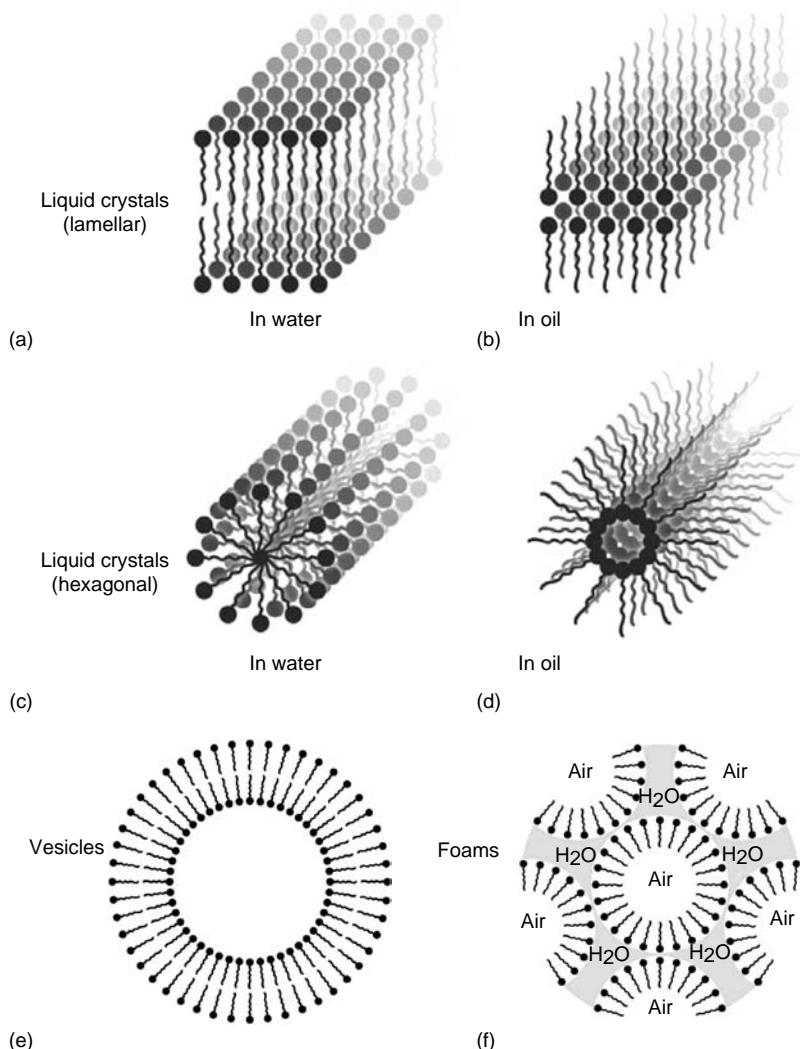


FIGURE 16.4 Microstructures of surfactant assemblies in solution: (a,b) lamellar liquid crystals, (c,d) hexagonal liquid crystals, (e) vesicles, and (f) foams.

16.5 FUNCTIONS OF SURFACTANTS IN LUBRICATION

Surfactants play a number of critical roles in lubrication and, thus, are important ingredients in lubricant formulations. Different types of surfactants are used to attain different lubrication objectives. Examples of lubrication objectives attained by surfactants include solubilization, antifriction, demulsification, dispersion of fines and debris, anticorrosion, defoaming, antiwear, and antimicrobes.

Sometimes, the performance objectives that surfactants are supposed to provide the lubricant are contradictory. Examples of contradictory objectives include emulsification versus demulsification, biodegradability versus bioreistance, and agglomeration versus dispersion of debris and fines. These contradictions occur because of the changing requirements of lubricant performance over time or process. For example, the performance requirements of the lubricant during use are different from that during waste treatment, disposal, or recycling. Another example is the difference in performance requirements of the lubricant during the lubrication process (e.g., hot rolling) versus lubricant handling process (e.g., filtration).

In this section, a brief description of some of the surfactant functions is given. Detailed description of two of the functions, solubilization and boundary friction, is provided in subsequent sections. It is clear that surfactants have numerous functions in lubrication, and it is beyond the scope of this chapter to provide detailed discussions of each. Readers are encouraged to go through the various references cited in this chapter for more detail.

Emulsification is one of the most important lubrication functions of surfactants and is discussed in detail in Section 16.6. Emulsification allows for preparing a stable dispersion of the lubricant formulation in water, so that the lubricant satisfies both lubrication and cooling functions of the process. The surfactants used in these functions are selected so as to provide the appropriate emulsion properties without interfering with the lubrication function of the formulation.

Demulsification is one of the requirements for waste treatment of used lubricants. In this process, a surfactant is used to help the oil and water in the lubricant to cleanly separate into their respective phases, so that they can be properly processed and disposed.

Dispersion of fines and debris is an important function of surfactants in lubrication processes that generate a lot of metal fines and debris. The function of the surfactant is to prevent fine metal particles and other debris from aggregating into large mass. If not dispersed, the fines and debris will agglomerate and accumulate on tool and workpiece surface. This can cause undesirable outcomes such as poor product quality (e.g., debris rolled into the workpiece), accelerated tool wear, and unsafe work conditions due to accumulation of debris on equipment and work area.

Agglomeration of fines and debris may be important in some processes where removing the fines and debris by filtration is important. Dispersed fines and debris are hard to filter out and might require the use of expensive filtration equipment and media to attain the degree of lubricant cleanliness required for the process. The function of the surfactant here is to allow the fines and debris to attract to each other, aggregate, and grow into large particles. Thus, the application of the proper surfactant to help the debris and fines agglomerate for easy filtration will save cost and result in cleaner lubricant.

Bioresistance is the property of a lubricant to resist attack by bacteria and fungi (mold and yeast) microbes. Attack by microbes will result in a number of undesirable outcomes (e.g., changes in pH, depletion of critical lubricant ingredients, bad odor, tool, and workpiece corrosion) that compromise the proper functioning of the lubricant. The function of the surfactant here is to protect the lubricant from attack by microbes. Surfactants used in such application are called biocides.

Biodegradability is the property of a lubricant to be easily and naturally degraded when disposed. This requires that the lubricant ingredients are easy to digest by microbes employed in composting and similar processes. Lubricants that are not biodegradable require expensive waste treatment processing before disposal to comply with tightening environmental laws. Surfactants that are easily biodegradable will improve the biodegradability of the lubricant in which they from a part.

16.6 SOLUBILIZATION WITH SURFACTANTS

Liquid lubricants are broadly classified into two groups: oil-based and water-based. Oil-based lubricants comprise a base oil of appropriate viscosity with various solubilized additives. The function of the additives is to reduce friction and wear as well as to impart the lubricant other important characteristics such as oxidation stability, low pour point, and bioresistance. Oil-based lubricants are used in processes where the heat generated during lubrication does not cause concern about tool wear, product quality, productivity, safety, and other issues. Another reason for the use of oil-based lubricants is when the presence of water causes undesirable outcomes such as poor product quality (e.g., water stain), corrosion of tools and machine elements, and rust.

Water-based lubricants comprise 0–20% of all or portions of the oil-based lubricant ingredients mentioned above, solubilized in 80–99% water. Water-based lubricants are employed when the lubrication process generates excessive heat capable of damaging tools, negatively affecting product quality, causing fire, and other undesirable results. Examples of such lubrication processes

include metal forming (e.g., hot rolling of aluminum and steel) and metal removal (e.g., grinding and machining).

Various types of surfactants (e.g., cosurfactants and coupling agents) are employed to achieve proper dissolution of the oil phase in water. Water-based lubricants are classified into the following categories depending on their composition and physical properties [12,13].

1. *Soluble oils.* These are o/w emulsions with up to 20% of the oil phase in water. They are produced by vigorously mixing the oil and water phases in the presence of surfactants. These emulsions comprise large droplets of oil stabilized by surfactants in water. Unlike o/w microemulsions, the o/w emulsions have large diameter of oil droplets. As a result, o/w emulsions reflect visible light and hence appear milky to the naked eye. Another major difference between o/w emulsions and microemulsions has to do with their stability. O/w emulsions are thermodynamically unstable and, hence, separate into the respective oil and water phases over time. A schematic comparing o/w emulsions and o/w microemulsions is given in Figure 16.5.
2. *Semisynthetic oils.* These are water-based lubricants with 1–5% (w/w) of solubilized oil phase. These are the o/w microemulsions that have been discussed previously (Section 16.4) and depicted in Figure 16.3e. Semisynthetic oils are clear and transparent solutions. This is attributed to the fact that the size of the oil droplets is smaller than the wavelength of light. As mentioned earlier, semisynthetic oils are thermodynamically stable (see Figure 16.5 for comparison of o/w emulsions versus o/w microemulsions).

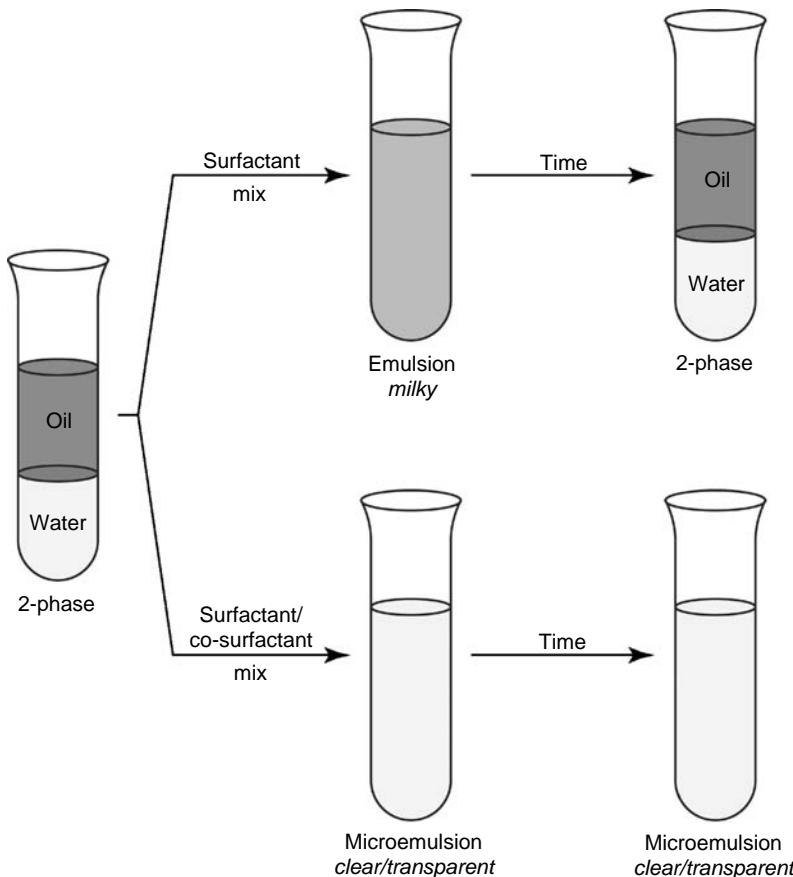


FIGURE 16.5 Emulsions versus microemulsions.

3. *Synthetic oils.* These are normal micellar solutions discussed previously (Section 16.4) and depicted in Figure 16.3c. Synthetic oils contain no solubilized oil. However, they contain additives solubilized in the continuous water phase and the lipophilic core of the normal micelle, to provide the necessary friction, wear, and other properties to the synthetic oils. Because of the presence of solubilized additives, synthetic oils can be considered as swollen micelles. Again, because of the small diameter of the swollen micelles relative to the wavelength of light, synthetic oils are transparent and clear solutions. They are also thermodynamically stable, that is, various additives will not appear as a separate phase over time.

16.7 BOUNDARY LUBRICATION PROPERTIES OF SURFACTANTS

Boundary lubrication occurs in processes where the friction surfaces are rubbing at relatively low speeds and under very high load [13]. Under such conditions, no lubricant film is formed to separate the rubbing surfaces from each other. The rubbing surfaces contact each other, but direct contact is prevented by surfactants adsorbing on the friction surfaces. This is another important function of surfactants in tribology. The effectiveness of surfactants at reducing friction and wear under boundary conditions is highly dependent on the chemistries of their polar and nonpolar segments, concentrations, properties of the friction surfaces, and process conditions (e.g., temperature). This will be illustrated by a brief review of an extensive study into the boundary properties of agriculture-based surfactants.

Proteins [14,15], starches [16,17], and vegetable oils [18–22], obtained from plant-based agricultural products, with or without further modification (through enzymatic, chemical, or other methods), have been found to possess surface-active properties. This has dramatically increased the potential application areas where these materials can be used to develop new uses from surplus agricultural crops. Surface-active materials are used in a wide range of consumer and industrial products including food, cosmetics, pharmaceuticals, paints, coatings, adhesives, polymers, and lubricants [1–9].

Among the various ag-based products, vegetable oils are the most widely investigated raw materials for lubricant applications [18–23]. This is because most vegetable oils are liquid at room temperature. This, along with the fact that they are surface active, allows vegetable oils to be used in lubrication processes that occur in all the lubrication regimes, that is, boundary, hydrodynamic, and mixed-film.

Vegetable oils have two types of chemical structures: triglycerides and waxy esters (Figure 16.6). However, most vegetable oils are triglycerides. In both triglycerides and waxy esters, the structure

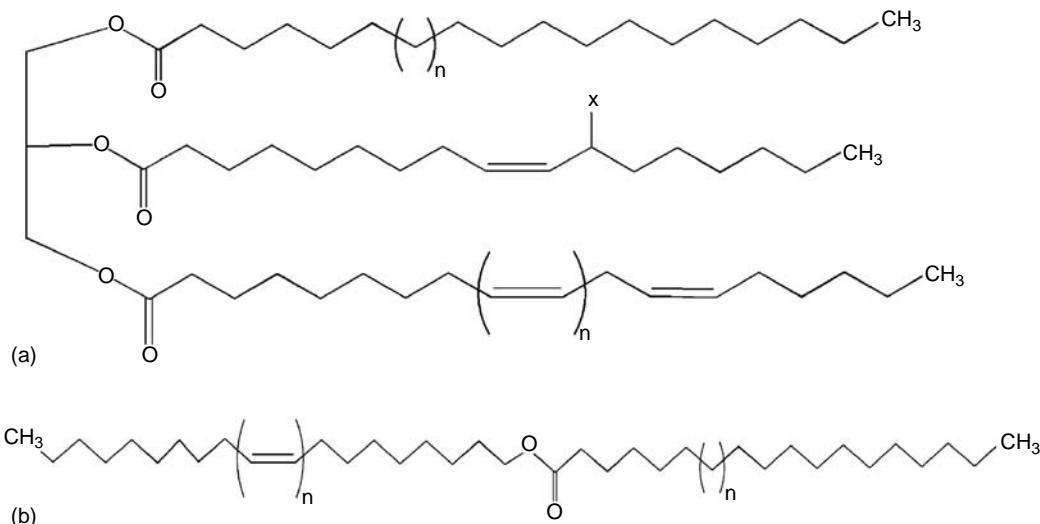


FIGURE 16.6 Chemical structures of vegetable oils: (a) triglycerides, and (b) waxy esters.

of the polar segment of the molecules comprises one or more ester linkages of fatty acid with glycerol or long-chain fatty alcohols. In all cases, various structures of fatty acids are involved. The structural variations of the fatty acids include chain length; degree, position, and stereochemistry of unsaturation; and presence of additional functional groups (such as hydroxy or epoxy groups), on the fatty acid chain. As a result, triglycerides and waxy esters can have a multitude of structures. In addition, the triglycerides and waxy esters from specific crops (e.g., soybean oil) are mixtures of various structures. Despite these enormous possible structural variations, the structural composition of triglycerides from a specific crop (e.g., soybean oil) is fixed and well-known [23]. Thus, for example, triglycerides of regular soybean oil comprise 23% oleic acid and 54% linoleic acid, whereas regular canola oil comprises 61% oleic acid and 23% linoleic acid [23].

The boundary lubrication properties of vegetable oils were investigated in steel/steel and steel/starch contact. In addition to varying the properties of the contacting surfaces (steel/steel versus steel/starch), vegetable oils of varying chemical structures were employed. Also, simple methyl esters of fatty acids were included in these studies as model compounds to the more complex triglycerides and waxy esters. A summary of these studies along with subsequent data analysis is reviewed next.

16.7.1 BOUNDARY FRICTION OF VEGETABLE OILS IN METAL/METAL CONTACT

The boundary lubrication properties of vegetable oils, in metal/metal contact, were investigated using a ball-on-disk tribometer. A schematic depiction of the ball-on-disk tribometer is shown in Figure 16.7. In these studies, the steel ball and steel disk were immersed in a lubricant of hexadecane, with varying concentrations of vegetable oils. Friction between the stationary steel disk and the rotating steel ball were measured under the following conditions: speed, 5 rpm or 6.22 m/s; load, 1788N or 400 lb; temperature, room temperature; test duration, 15 min. The concentration of the vegetable oils in hexadecane varied in the range 0.0–0.6 M. A typical data from a ball-on-disk tribometer are shown in Figure 16.8. The data show that the coefficient of friction (COF) increases with time and levels off after ~6 min. The COF for the specific lubricant is obtained by averaging the COF values in the steady-state region.

The effect of vegetable oil concentration on boundary COF from a ball-on-flat tribometer is shown in Figure 16.9. The data in Figure 16.9 have four important features that need pointing out: (1) the COF without vegetable oil is very high (>0.5); (2) addition of vegetable oil results in a sharp reduction of COF; (3) the COF decreases with increasing concentration of vegetable oil and reaches a minimum value; and (4) once the minimum value is attained, the COF remains constant and independent of any further increase in vegetable oil concentration. These observations are important for understanding the mechanism of boundary lubrication by vegetable oils. It also provides the basis for proper analysis of the friction data to elucidate the effect of vegetable oil and substrate properties on boundary friction.

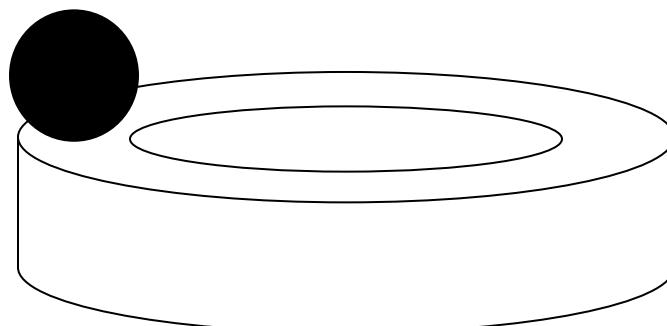


FIGURE 16.7 After schematic of ball-on-disk tribometer. (From Biresaw, G., Adharyu, A., Erhan, S.Z., Carriere, C.J., *J. Am. Oil Chem. Soc.*, 79(1), 53–58, 2002. With permission.)

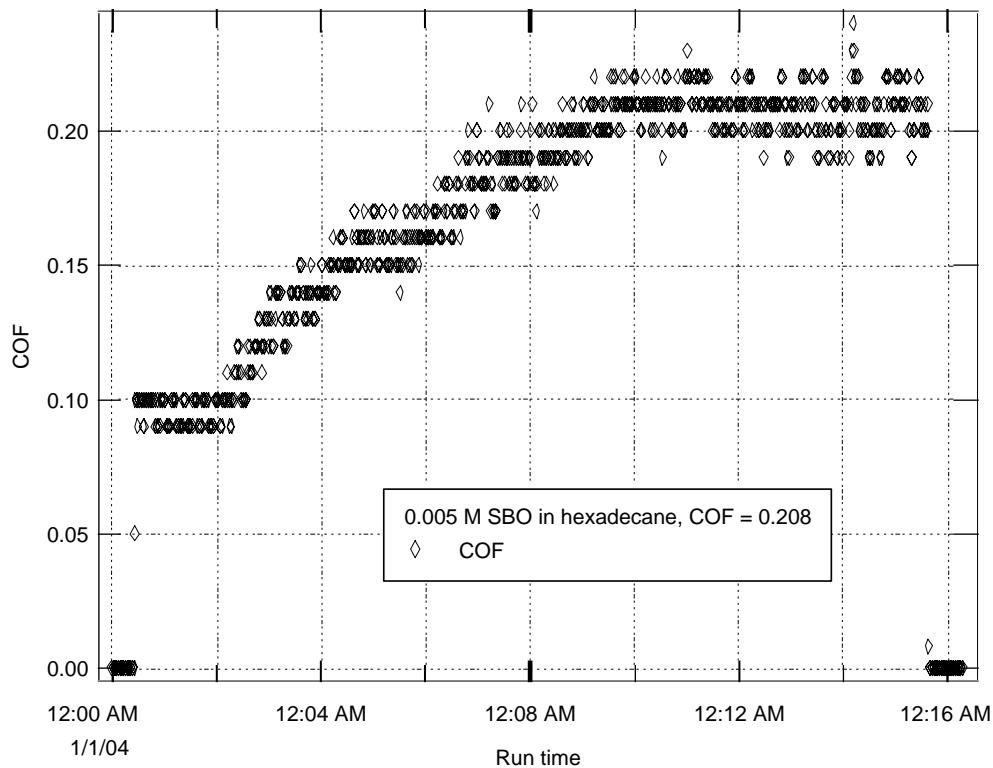


FIGURE 16.8 After typical data from a ball-on-disk tribometer. (Biresaw, G., Adharyu, A., Erhan, S.Z., Carriere, C.J., *J. Am. Oil Chem. Soc.*, 79(1), 53–58, 2002. With permission.) (SBO, Soybean oil.)

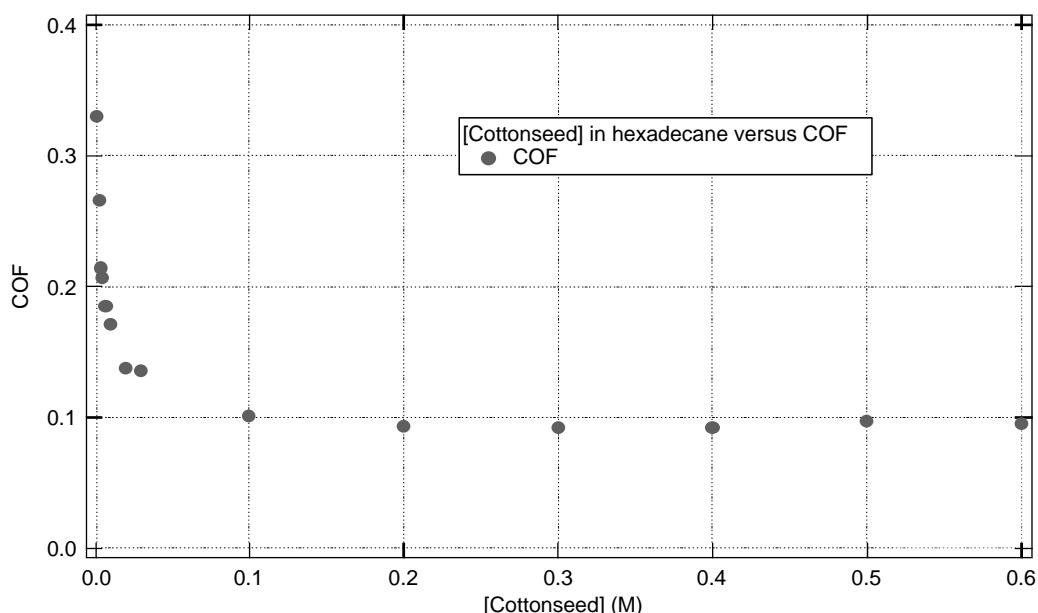


FIGURE 16.9 After effect of vegetable oil concentration in hexadecane on steel/steel boundary friction. (Adharyu, A., Biresaw, G., Sharma, B.K., Erhan, S.Z., *Ind. Eng. Chem. Res.*, 45(10), 3735–3740, 2006. With permission.)

16.7.2 BOUNDARY FRICTION OF VEGETABLE OILS IN STARCH/METAL CONTACT

Vegetable oils can be encapsulated into a starch matrix by a steam-jet cooking process called Fantesk™ [24]. The resulting starch–oil composite can be redispersed in water and applied on sheet metal surfaces as a dry film lubricant [25–28]. Dry film lubricants are those that are applied on sheet metals to help protect the surface from damage (dents, rust, and corrosion) during transportation, storage, or as lubricants in subsequent forming processes [13]. Studies were conducted to investigate the friction properties of vegetable oils in starch–oil composites. In this investigation, composites with varying concentrations of vegetable oil (0–40 parts per hundred) were redispersed in water, applied (using various methods) onto steel surfaces, and its friction properties evaluated. Boundary friction of the dry film was measured using a ball-on-flat tribometer (Figure 16.10) at room temperature and the following conditions: speed, 2.54 mm/s; load, 14.7 N (1500 gf); temperature, room temperature; test duration, 24 s. A typical data from a ball-on-flat tribometer are shown in

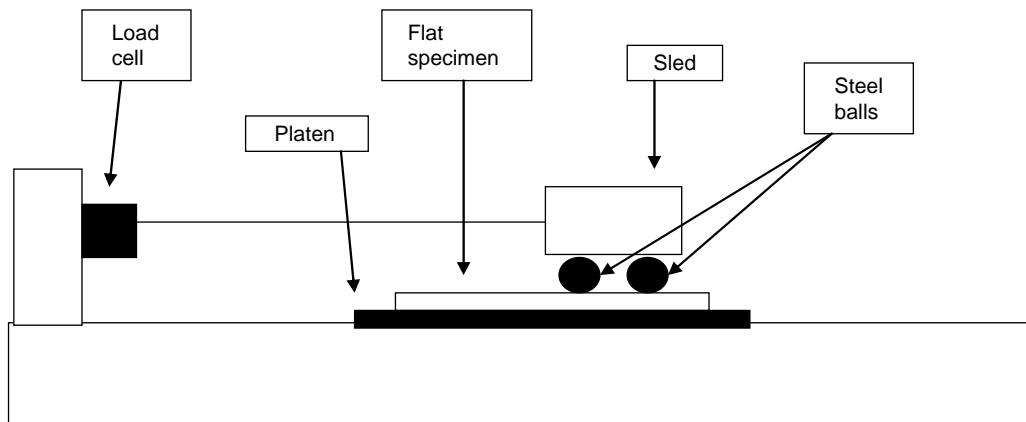


FIGURE 16.10 After schematic of a ball-on-flat tribometer. (Biresaw, G., Erhan, S.M., *J. Am. Oil Chem. Soc.*, 79, 291–296, 2002. With permission.)

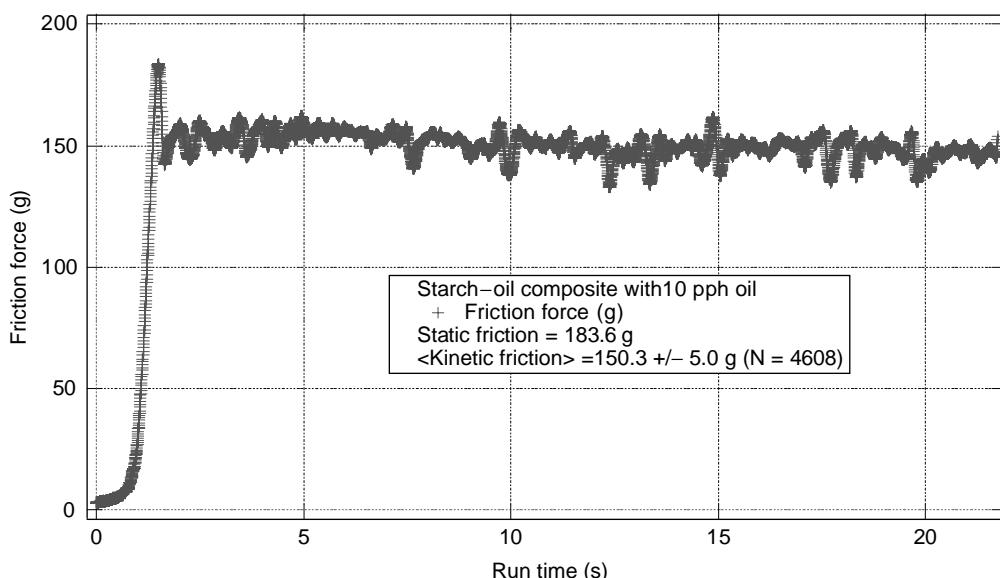


FIGURE 16.11 After typical data from a ball-on-flat tribometer. (Biresaw, G., Erhan, S.M., *J. Am. Oil Chem. Soc.*, 79, 291–296, 2002. With permission.)

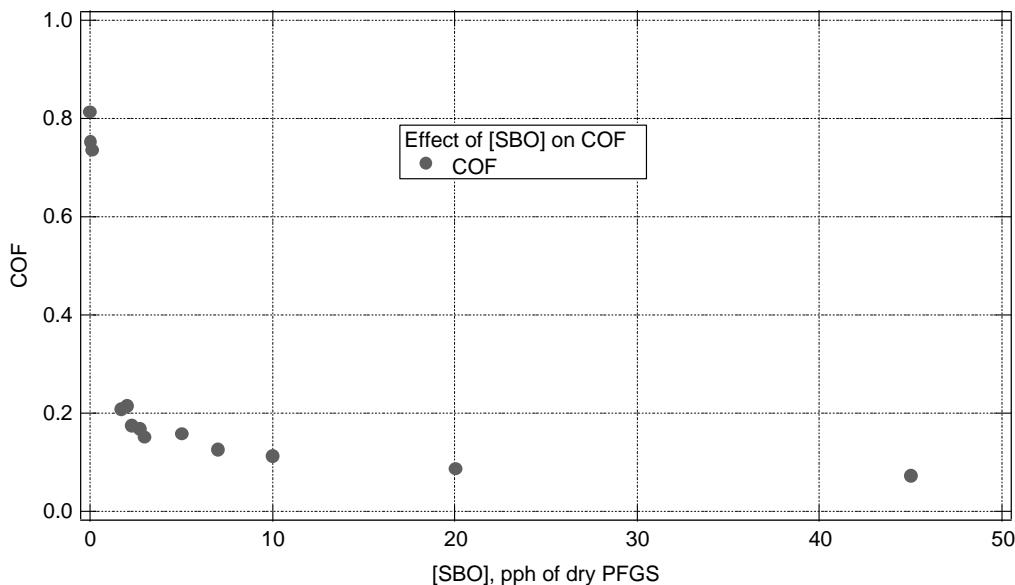


FIGURE 16.12 After effect of vegetable oil concentration in starch matrix on starch/steel boundary friction. (Biresaw, G., Erhan, S.M., *J. Am. Oil Chem. Soc.*, 79, 291–296, 2002. With permission.) (PEGS, purified food grade starch.)

Figure 16.11. As can be seen in Figure 16.11, initially, the friction force rose sharply to a maximum and immediately went down to a steady-state value for the remainder of the test period. The maximum value corresponds to the static friction of the steel ball against the starch, whereas the steady-state value corresponds to the kinetic friction. The COF for the dry film lubricant is obtained by dividing the average of the steady-state friction force data by the load.

The effect of vegetable oil concentration in starch matrix on starch-steel boundary friction is illustrated in Figure 16.12. The data show that, in the absence of vegetable oil, the COF between starch and steel is very high (~0.8). However, incorporation of vegetable oil into the starch matrix results in a sharp decrease in COF, which eventually levels off to a constant value. Further addition of vegetable oil will cause no change in COF. The vegetable oil concentration versus COF profile in starch/metal contact shown in Figure 16.12 is similar to that discussed before for metal/metal contact (Figure 16.9). Thus, it is reasonable to assume that a similar mechanism may be responsible for the boundary friction properties of vegetable oils in both systems.

16.7.3 MECHANISM OF BOUNDARY LUBRICATION OF VEGETABLE OILS

The effect of vegetable oil concentration on metal/metal and starch/metal boundary COF can be explained using an adsorption model [29,30]. According to this model, in the absence of vegetable oil, high COF is observed because of rubbing between two high-energy surfaces (metal/metal or starch/metal), which are in direct contact (boundary conditions). When vegetable oil is introduced into the lubricant, the COF is reduced because the vegetable oil adsorbs on the rubbing surfaces (metal or starch) and prevents direct contact between the two high-energy surfaces.

Adsorption occurs due to a strong polar–polar interaction between the polar groups of the vegetable oils and the polar adsorption sites on the starch or metal surfaces. According to the adsorption model, there are a finite number of adsorption sites (S_i) on the surfaces, and once all adsorption sites are occupied, full surface coverage is attained, and no further adsorption occurs and friction remains unchanged. The adsorption sites could be oxides or hydroxides in the metal surfaces and hydroxyl groups on starch. Depending on the concentration of the vegetable oil in hexadecane or

starch matrix, the adsorption sites on the steel or starch surface may be fully or partially occupied by the vegetable oils. The surface concentration of vegetable oils is expressed in terms of fractional surface coverage, θ , which is defined as follows:

$$\theta = \frac{[S_o]}{[S_t]} \quad (16.2)$$

where $[S_t] = [S_o] + [S_u]$; S_o and S_u are occupied and unoccupied adsorption sites, respectively.

The fractional surface coverage is obtained from boundary friction data as follows [17–21,28–30]:

$$\theta = \frac{f_s - f_o}{f_s - f_m} \quad (16.3)$$

where

f_s = COF without vegetable oil

f_m = minimum COF or COF at full surface coverage

f_o = COF at various vegetable oil concentrations

Note that in Equation 16.3, without added vegetable oil, $f_o = f_s$ and $\theta = 0$; at full surface coverage, $f_o = f_m$ and $\theta = 1$. Thus, the value of θ varies in the range of 0–1.

The adsorption model also stipulated that adsorption of vegetable oil is an equilibrium process between vegetable oil in solution (O_b) and that on the surface as follows:



where K_o is the equilibrium constant in moles per liter, defined as follows:

$$K_o = \frac{[S_o]}{[O_b][S_u]} \quad (16.5)$$

K_o in Equation 16.5 can be used to calculate the free energy of adsorption (ΔG_{ads}) of vegetable oils using an appropriate adsorption model. However, to be able to do that, two things have to be accomplished. First, an adsorption isotherm must be constructed. An adsorption isotherm shows the relationship between the concentration of vegetable oil in solution (moles per liter) and that on the surface, expressed as fractional surface coverage, θ . Second, the adsorption isotherm must be analyzed using an appropriate adsorption model. An adsorption model is a mathematical expression describing how surface concentration is related to solution concentration. The equilibrium constant K_o is obtained by analyzing the adsorption isotherm data with the adsorption model.

Typical adsorption isotherms (vegetable oil concentration in hexadecane or starch versus fractional surface coverage, θ), calculated from boundary coefficient of friction data using Equation 16.3, are given in Figures 16.13 and 16.14. θ represents the concentration of the vegetable oil on the metal or starch surface and the COF data are used in the calculation of θ (Figures 16.13 and 16.14). As can be seen in Figures 16.13 and 16.14, the concentration versus θ profile (or the adsorption isotherm) is a mirror image of the concentration versus COF profile.

Various models are available for analyzing adsorption isotherms [5,6]. The simplest such model is called the Langmuir adsorption model [31], which assumes that adsorption is only due to primary interaction between the vegetable oil and the surface. The model assumes no contribution to adsorption from lateral interaction between the adsorbed molecules. The Langmuir model predicts the following relationships between surface and solution concentrations of vegetable oils:

$$\frac{1}{\theta} = 1 + \left(\frac{1}{\{K_o[O_b]\}} \right) \quad (16.6)$$

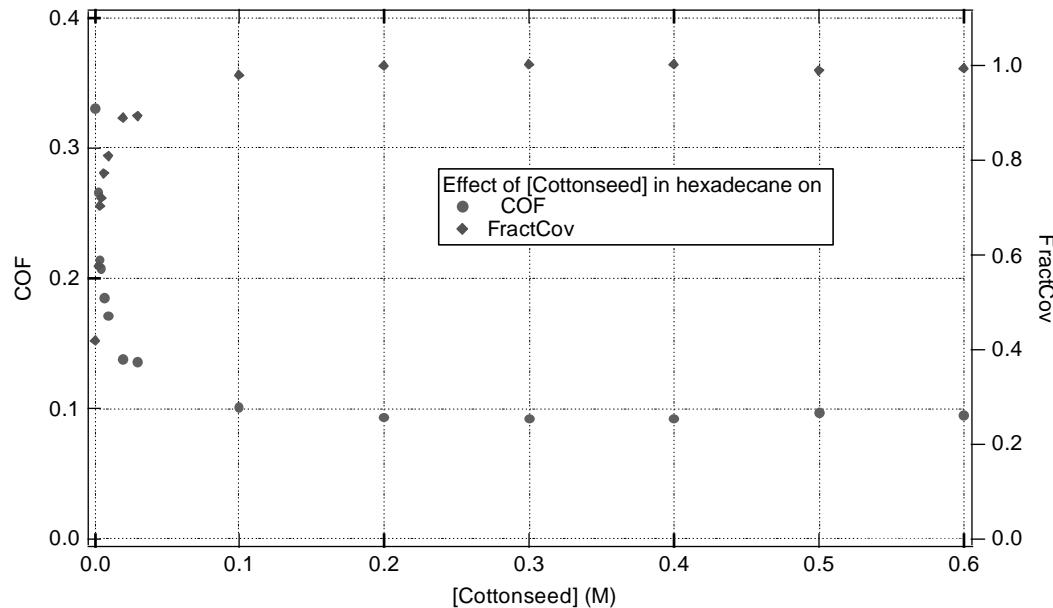


FIGURE 16.13 Concentration in hexadecane versus fractional surface coverage, θ , of vegetable oil from boundary friction data on a ball-on-disk tribometer.

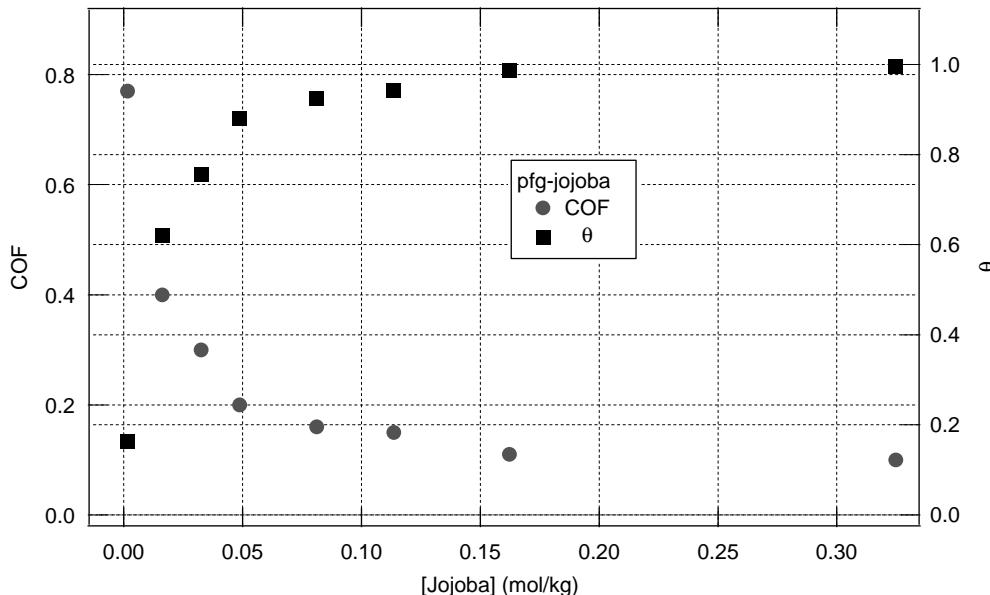


FIGURE 16.14 Concentration in starch versus fractional surface coverage, θ , of vegetable oil from boundary friction data on a ball-on-flat tribometer.

According to Equation 16.6, a plot of $[O_b]^{-1}$ versus θ^{-1} should give a straight line with a slope of K_o^{-1} and an intercept of 1. The free energy of adsorption, ΔG_{ads} , is then obtained by substituting the value of K_o obtained from Equation 16.6 in Equation 16.7:

$$\Delta G_{ads} = \Delta G_o = -RT[\ln(K_o)] \text{ (kcal/mol)} \quad (16.7)$$

where

ΔG_o = free energy of adsorption due to primary interaction in kilocalories per mole

R = 1.987 cal/K mol is the universal gas constant

T = absolute temperature in Kelvin

Figures 16.15 and 16.16 show analysis of boundary friction data of vegetable oil in steel-steel and starch-steel contact using the Langmuir model. In all cases, plots of $[O_b]^{-1}$ versus θ^{-1} gave

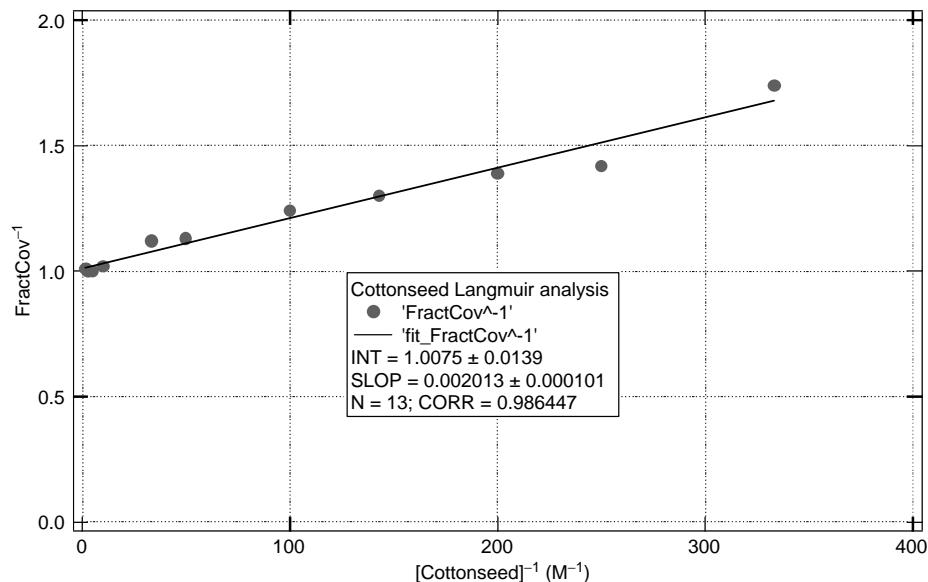


FIGURE 16.15 Langmuir analysis of adsorption isotherms derived from steel/steel boundary friction of vegetable oils in hexadecane. (Adhvaryu, A., Biresaw, G., Sharma, B.K., Erhan, S.Z., *Ind. Eng. Chem. Res.*, 45(10), 3735–3740, 2006. With permission.)

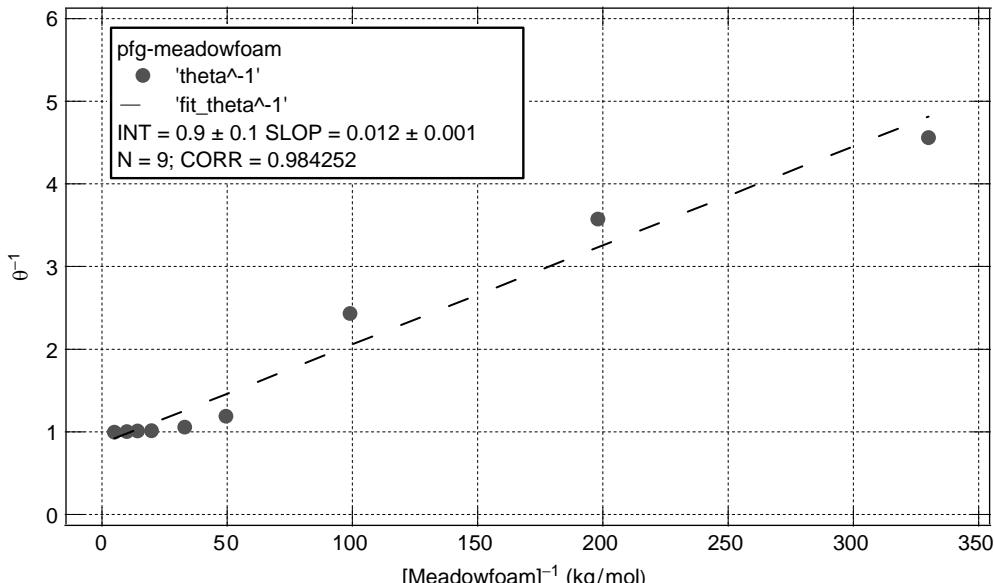


FIGURE 16.16 Langmuir analysis of adsorption isotherms derived from starch/steel boundary friction of vegetable oils in starch–oil composites.

straight lines, with intercepts close to 1. From the slopes, K_o values were obtained and used to calculate ΔG_{ads} using Equation 16.7.

Another model that has been used to analyze friction-derived adsorption isotherms is the Temkin model [32]. Unlike the Langmuir model, the Temkin model assumes a net repulsive lateral interaction, and the free energy of adsorption is given as follows:

$$\Delta G_{ads} = G_o + \alpha\theta \text{ (kcal/mol)} \quad (16.8)$$

where ΔG_o is free energy of adsorption due to primary interaction calculated using Equation 16.7 and α the free energy of adsorption due to lateral interaction ($\alpha > 0$).

Estimation of ΔG_{ads} using the Temkin model (Equations 16.7 and 16.8) requires values of K_o and α . For $0.2 \leq \theta \leq 0.8$, the Temkin model predicts the following relationship between solution concentration, $[O_b]$, and surface concentration, θ , of vegetable oil [32]:

$$\theta = \left(\frac{RT}{\alpha} \right) \ln \left(\frac{[O_b]}{K_o} \right) \quad (16.9)$$

According to Equation 16.9, a plot of $\ln([O_b])$ versus θ in the specified θ range will result in a straight line. K_o and α are then obtained from the analysis of the slope and intercept of the line using Equation 16.9. The values of K_o and α are then used to calculate ΔG_{ads} using Equations 16.7 and 16.8.

Figure 16.17 shows the results of Temkin analysis of adsorption isotherms data derived from boundary friction measurements of vegetable oils in steel-steel contact. As can be seen in Figure 16.17, the analysis gave a straight line in the range $0.2 \leq \theta \leq 0.8$, as predicted by the Temkin model. From the slope and intercept of such analysis, K_o and α are obtained and used to calculate ΔG_{ads} using Equations 16.7 and 16.8.

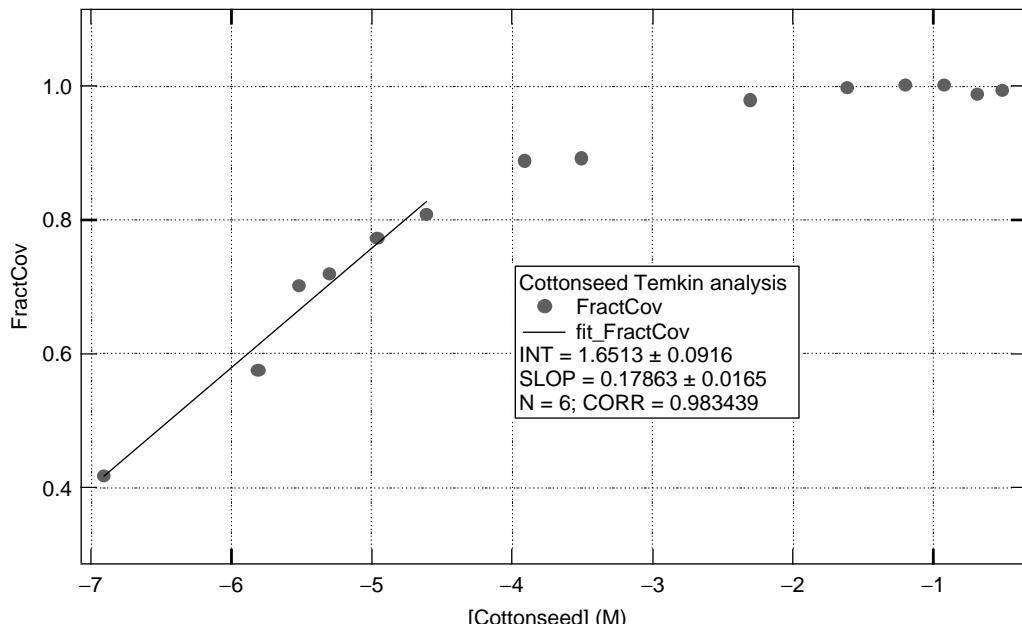


FIGURE 16.17 Temkin analysis of adsorption isotherms derived from steel/steel boundary friction of vegetable oils in hexadecane.

Table 16.2 summarizes ΔG_{ads} values for various vegetable oils obtained from Langmuir and Temkin analysis of steel-steel boundary friction data obtained using the ball-on-disk tribometer. The data in Table 16.2 show that the Temkin model predicts a weaker adsorption (a smaller negative number) than the Langmuir model. This observation is consistent with the fact that the Temkin models assume a net repulsive lateral interaction ($\alpha > 0$), which will counter the strong primary interaction. Table 16.2 also shows that triglycerides generally adsorb stronger than the waxy ester jojoba, or the simple fatty acid methyl esters. This has been attributed to the ability of the triglycerides to engage in multiple binding with the surface, whereas the waxy esters and the methyl esters cannot do so since they have only one functional group per molecule. The data in Table 16.2 also indicate that the adsorption of methyl esters weakens with decreasing fatty acid chain length. This may be an indication of decreasing van der Waals interaction due to the decreasing molecular weight of the oil molecules.

TABLE 16.2
 **ΔG_{ads} Values Obtained from Langmuir and Temkin Analyses
 of Steel/Steel Boundary Friction Data Obtained on a Ball-
 On-Disk Tribometer**

Oil	Friction Pairs	Test Geometry	ΔG_{ads} (kcal/mol)	
			Langmuir	Temkin
Cottonseed	Steel/steel	Ball-on-disk	-3.68	-2.16
Canola	Steel/steel	Ball-on-disk	-3.81	-2.04
Meadowfoam	Steel/steel	Ball-on-disk	-3.66	-2.28
Jojoba	Steel/steel	Ball-on-disk	-3.27	-1.31
Methyl oleate	Steel/steel	Ball-on-disk	-2.91	-1.02
Methyl palmitate	Steel/steel	Ball-on-disk	-2.7	-1.63
Methyl laurate	Steel/steel	Ball-on-disk	-1.9	-0.6

TABLE 16.3
 **ΔG_{ads} Values of Vegetable Oils Obtained from Langmuir Analysis of
 Steel/Steel and Starch/Steel Boundary Friction Data**

Vegetable Oil	Friction Pairs			
	Starch Matrix	Starch/Steel (Starch-Oil Composite Dry Film Lube)		ΔG_{ads} (kcal/mol)
		Base Oil	Starch/Oil	
Meadowfoam	PFGS	-2.41 ^a	Hexadecane	-3.57 ^b
Jojoba	PFGS	-2.63 ^a	Hexadecane	-3.27 ^c
Soybean	PFGS	-2.96 ^a	Hexadecane	-3.6 ^d
Soybean	Waxy	-2.91 ^a		

^a Biresaw, G., Kenar, J.A., Kurth, T.L., Felker, F.C., Erhan, S.M. Investigation of the mechanism of lubrication in starch-oil composite dry film lubricants, *Publ. Sci.* 19(1): 41–55, 2007.

^b Adharyu, A., Biresaw, G., Sharma, B.K., Erhan, S.Z. Friction behavior of some seed oils: Bio-based lubricant applications, *Ind. Eng. Chem. Res.* 45(10): 3735–3740, 2006.

^c Biresaw, G., Adharyu, A., Erhan, S.Z. Friction properties of vegetable oils, *J. Am. Oil Chem. Soc.* 80(2): 697–704, 2003.

^d Biresaw, G., Adharyu, A., Erhan, S.Z., Carriere, C.J. Friction and adsorption properties of normal and high oleic soybean oils, *J. Am. Oil Chem. Soc.* 79(1): 53–58, 2002.

Table 16.3 compares ΔG_{ads} data obtained from the Langmuir analysis of boundary friction data from steel/steel and starch/steel contact. The data in Table 16.3 show that, in general, ΔG_{ads} is smaller for adsorption on steel than on starch. This means that vegetable oils will adsorb stronger on metal than on starch. This observation is consistent with the fact that steel has much higher surface energy than starch and will result in a stronger interaction with the polar ester groups of vegetable oils.

16.8 CONCLUSION

Surfactants are widely used in various consumer and industrial applications. They are invaluable in various products ranging from simple cleaning to complex formulations of pharmaceuticals, foods, lubricants, etc.

Surfactants owe their success to their unique chemical structure, which involves the presence of two dissimilar segments in the same molecule. One segment is hydrophilic and is soluble only in hydrophilic or polar solvents such as water, whereas the other is lipophilic and is soluble only in lipophilic or nonpolar solvents such as hexanes. As a result, surfactants display various degrees of solubility in both hydrophilic and lipophilic solvents. By varying the structures of the hydrophilic and lipophilic segments, thousands of surfactants have been developed and used in thousands of applications.

Depending on the nature of the hydrophilic component, surfactants can be broadly categorized into anionic, cationic, zwitterionic, and nonionic. In general, ionic surfactants are more soluble in hydrophilic solvents such as water than in lipophilic solvents. The reverse is true with nonionic surfactants except for polyethoxylated alcohols. In the latter case, solubility depends on the relative "strength" of the hydrophilic and lipophilic segments, which can be systematically varied and quantified using the HLB system. The HLB of polyethoxylated alcohols varies from 0 to 20, those with low HLB (<7) are oil-soluble, whereas those with high HLB (>11) are water-soluble, and those in between are soluble in both oil and water.

An important property of surfactants is their ability to spontaneously organize into various assemblies when in solution. The structures of these assemblies depend on the nature of the surfactant, the nature of the solvent, the concentration of surfactant, the presence of cosolutes (e.g., salts and cosurfactants), temperature, etc. At low concentrations, surfactants form monolayers. Progressive increase of surfactant concentration leads to the formation of aggregates, micelles, lamellar, and hexagonal liquid crystals. Other organized assemblies of surfactants in solution include vesicles and foams.

With proper selection of surfactant combinations, micelles can be used to solubilize large quantities of oil in water, or large quantities of water in oil. The resulting single-phase solutions, which are transparent due to the small size of the droplets, are called o/w or w/o microemulsions.

Surfactants perform a number of functions in lubrication so that the lubricant can meet its lubricity, cooling, handling, waste treatment, disposal, and other requirements. Some requirements of lubricants are contradictory and require proper selection of surfactant combinations to achieve the desired objectives. An example of a contradictory requirement is that the lubricant possesses both biostability and biodegradability. During use, the lubricant should be biostable, and the purpose of the surfactant is to protect it from attack by microbes (bacteria and fungi). On the contrary, used surfactants that are subjected to waste treatment and disposal processes should be biodegradable, that is, easy to be broken down by composting microorganisms, and the purpose of the surfactant is to enhance biodegradation.

Lubricant formulations can be broadly categorized into oil-based (straight oils) and water-based. Formulation of water-based lubricants is one of the most important functions of surfactants in lubrication. Water-based lubricants are used in processes that generate a lot of heat and must be cooled to prevent tool wear, workpiece damage, fire, and other undesirable outcomes. Surfactants allow dispersion of the oil-phase lubricant formulation in water, without interfering with the lubrication function of the oil phase and the cooling function of the water phase. Depending on the concentration of solubilized oil phase, water-based lubricants are classified into three groups: soluble

oils, with up to 20% oil; semisynthetic, with up to 5% oil; and synthetic, with no solubilized oil. Soluble oils are o/w emulsions, which, unlike o/w microemulsions, are milky and thermodynamically unstable. Semisynthetic oils are o/w microemulsions, thermodynamically stable single-phase clear solutions. Synthetic oils are micellar solutions with solubilized additives that provide lubricity and other functions.

Another important function of surfactants in lubrication is adsorbing on solid and liquid surfaces, and interfaces, and modifying surface and interfacial properties. Agriculture-based surfactants derived from farm products such as proteins, starches, and vegetable oils are effective at reducing surface tension, interfacial tension, surface energy, and boundary friction. Boundary friction investigations in metal/metal and starch/metal contacts revealed that vegetable oils are effective boundary additives. Free energy of adsorption values obtained from the analysis of friction-derived adsorption isotherms was consistent with the expected effect of vegetable oil chemical structures and friction surface properties on adsorption.

Surfactants have been known, investigated, and applied for centuries. Despite that, the current rapid development of new and complex products, processes, and equipments have produced a great deal of demand for new and improved surfactants and a deeper understanding of their performance. As a result, surfactants will continue to be the subject of vigorous research and development effort well into the future.

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17 Corrosion Inhibitors and Rust Preventatives

Michael T. Costello

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17.1 INTRODUCTION

Since the observation by Plato that “things in the sea ... are corroded by brine” in the fourth century BC, the prevention of corrosion of metal parts has been a concern to manufacturers and is the cause of serious economic loss estimated in billions of dollars per annum. The exact mechanism of corrosion remained unclear for centuries after Plato. Then, in 1675, Robert Boyle wrote the first scientific description of the mechanism of corrosion: “The Mechanical Origine or Production of Corrosiveness and Corrosibility.” Subsequently, another century passed before Luigi Galvani, in 1780, described the mechanism of bimetallic or Galvanic corrosion. After this advancement, the study of corrosion progressed more rapidly, and W.H. Wollaston introduced the “electrochemical theory of acid corrosion” around 1800 to explain the corrosion resistance of platinum boilers used to make concentrated sulfuric acid [1]. Finally, in 1903, W. R. Whitney [2] published a complete chemical description of corrosion in which he stated that oxygen and carbonic acid were necessary for the formation of rust when iron was dissolved into solution and that the addition of base inhibited corrosion. Whitney’s paper firmly placed corrosion as a chemical and electrochemical phenomenon.

In the 1920s, methods to reduce corrosion involved the coating of a metal part with various natural products such as petrolatum, wax, oxidized wax, fatty acid soaps, and rosin [3–5]. By the 1930s, petroleum sulfonates derived as by-products from oil-refining processes were commonly used and during World War II (WWII) the military demand expanded so rapidly that synthetic sulfonates were produced to supplement the supply [6]. After the war, it was found that barium and overbased barium sulfonates were very effective as rust preventatives (RPs) in slushing oils, and this became the *de facto* standard [7,8]. In the 1940s and 1950s, it was discovered that corrosion could be prevented in gas pipelines by injection of NaNO_2 , whereas in aqueous systems by using chromates and polyphosphates [9,10]. Subsequently, after WWII, the chemistry and various corrosion inhibitors that are in current use have grown exponentially and expanded to a multitude of applications.

Corrosion inhibitors can be divided into several categories depending on their duration of use, chemical composition, and end-use application. The common chemistries used for corrosion inhibitors include nitrites, chromates, hydrazines, carboxylates, silicates, oxidates, sulfonates, amines, amine carboxylates, borates, amine borates, phosphates, amine phosphates, imidazoles, imidazolines, thiazoles, triazoles, and benzotriazoles, and depending on the application different product families are desired (Table 17.1). Primarily the performance property that determines the type of chemistry desired for a corrosion inhibitor is the intended duration of use of the RP coating. In particular, some coatings require long service periods due to outdoor exposure in extreme climates where reapplication is difficult, whereas other corrosion inhibitors are only intended for short-term storage before a part is manufactured or painted. There are essentially three broad classes of corrosion inhibitors, which can be divided into the following areas:

Oil coatings. These are temporary liquid coatings used to prevent corrosion during transport of the metal part or for temporary indoor (months) or outdoor (weeks) storage. The RP oil (or slushing oil) can be applied during the metal-forming operation or after the part is completed.

Soft coatings. These are temporary soft solid coatings typically made of wax, petrolatum, or grease. These coatings are used to coat structures exposed to the elements such as bridges, cars, or trucks and last from a few months up to many years.

TABLE 17.1
Common Rust-Preventative Chemistries and Applications

	Water Soluble	Soluble Oil	Oil Soluble
Oil coatings	Carboxylates		Carboxylates
	Sulfonates	Carboxylates	Sulfonates
	Alkyl amines	Sulfonates	Alkyl amines
	Alkyl amine	Alkyl amines	Phosphates
	Phosphates	Alkyl amines	Alkyl amines
	Alkyl amines	Borates	Imidazolines
Soft coatings	Borates		Thiazole
			Benzotriazoles
			Triazole
	—	Oxidates	Oxidates
Hard coatings		Sulfonates	Sulfonates
	Nitrites	Alkyl amines	Alkyl amines
	Chromates		
	Hydrazines	—	—
	Phosphates	—	—

Hard coatings. These coatings are typically applied as an alkyd resin or as an inorganic coating (or galvanized coating) and are used to form a hard permanent barrier from corrosion. These products are typically used as a pure barrier to prevent corrosion and do not possess the RP additives used in lubricants.

Although the hard coatings are generally applied using aqueous solvents, the oil and soft coatings are applied to the metal surface by various methods. Many oil and soft coatings are typically applied using oil or solvent (naphtha)-based systems, but they can also be emulsified or solubilized in an aqueous system where the volatile solvent is allowed to dry and cast a film of the RP oil. The coatings can be classified into three different categories based on the method of application to the metal surface as follows:

Water soluble. The additives are mainly inorganic materials (nitrite or arsenate) used for aqueous systems such as water treatment or drilling muds.

Soluble oils. The additives used are mainly oil-soluble sulfonates and organic amines that can be used in emulsions used for metal deformation and metal removal processes.

Oil soluble. The additives used are mainly oil-soluble additives that can be used in lubricant oils for machinery or slushing oils.

In this chapter, the study of corrosion inhibitors will be restricted to the use of additives that are used to prevent corrosion in lubricating oils or additives used to prevent corrosion in aqueous systems. In particular, although water treatment, refinery, drilling, and vapor-phase corrosion inhibitors (VCIs) are not strictly lubricating oil applications, many of the additives used in these aqueous systems have been adapted to oil-based systems and have been used as additives in lubricants.

17.2 INHIBITOR TYPES

Corrosion is a chemical or electrochemical reaction between a material, usually a metal, and its environment, which produces a deterioration of the material and its properties. For our purposes, it is instructive to envision corrosion as an electrochemical process in which the metal is oxidized at the anode, and a reduction takes place at the cathode (Figure 17.1). Depending on the pH of the system, the cathodic reaction can produce either H_2 in acidic media or OH^- in neutral/alkaline media.

The oxidized metal ions (Fe^{2+} or Fe^{3+} in the case of iron) formed at the anode then diffuse through the system to react with either an inhibitor or the products of the reduction process at the cathode. The end result is the formation of corrosion products (scale or rust) of poorly defined stoichiometry (Figure 17.2). In this standard model, inhibitors are used to prevent either the oxidation of metal or the reduction of oxygen (or H^+).

The mechanism of corrosion inhibition has been extensively investigated, and three basic mechanisms are prevalent. The inhibitor disrupts the anodic process, cathodic process, or a combination of both processes (Figure 17.3). The mechanism of inhibition of the process is significantly

Acidic media		
Anode:	$Fe \rightarrow Fe^{2+} + 2e^-$	$E_{ox} = -(-0.44) V$
Cathode:	$2H^+ + 2e^- \rightarrow H_2$	$E_{red} = +0.00 V$
	<hr/>	$E_{cell} = +0.44 V$
Neutral or alkaline media		
Anode:	$Fe \rightarrow Fe^{2+} + 2e^-$	$E_{ox} = -(-0.44) V$
Cathode:	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	$E_{red} = +0.40 V$
	<hr/>	$E_{cell} = +0.84 V$

FIGURE 17.1 Corrosion reactions in acidic and neutral/alkaline media.

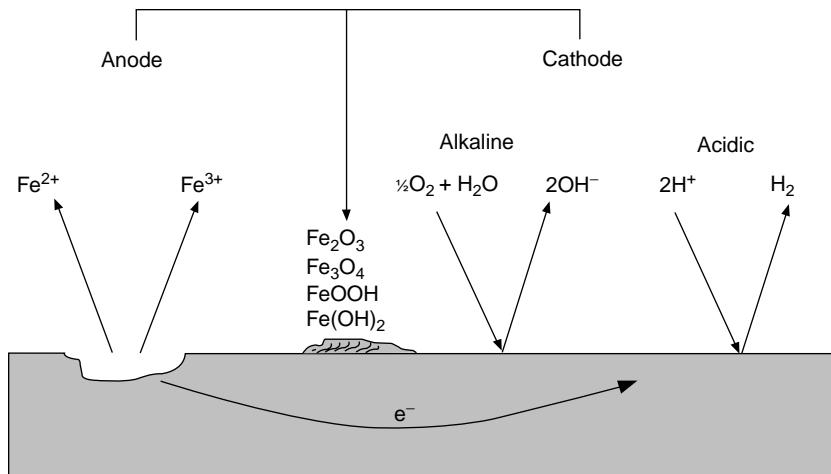


FIGURE 17.2 Formation of corrosion products in acidic or alkaline/neutral media.

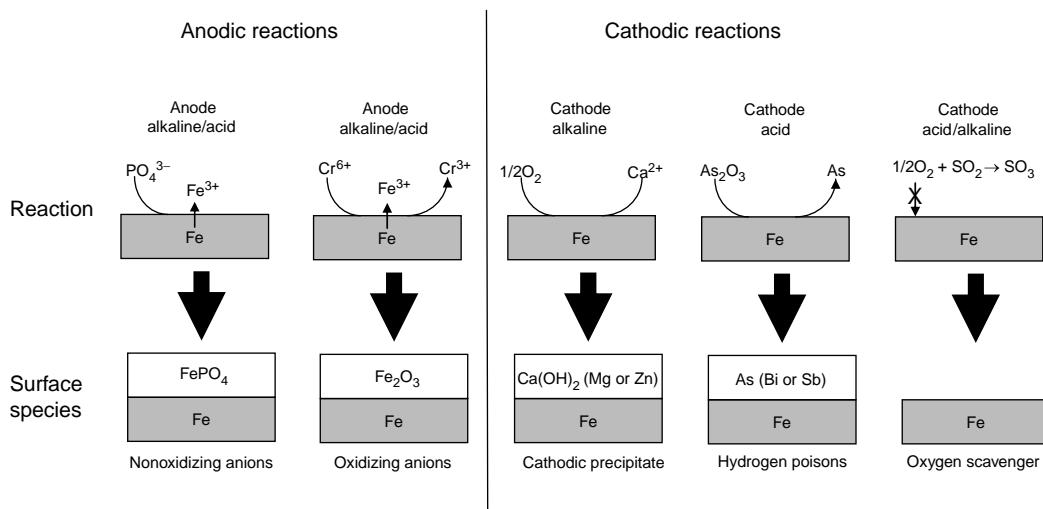


FIGURE 17.3 Schematic mechanism of cathodic and anodic corrosion inhibitors.

affected by the pH of the system and ultimately determines the type of protective film that is formed.

Anodic inhibitors (passivating inhibitors or dangerous inhibitors). Anodic inhibitors produce a large positive shift in the corrosion potential of a metal through the production of a protective oxide or hydroxide film (Figure 17.3). These can be quite dangerous since they can be corrosive at low concentration and need to be carefully monitored. There are two main modes of action that serve to disrupt the anodic processes.

Oxidizing anions. Oxidizing anions passivate a metal in the absence of oxygen. Typical examples include chromates and nitrites, which function by shifting the potential into a region where insoluble oxides or hydroxides are formed. For example, the commonly used chromates will be reduced from Cr^{6+} to Cr^{3+} , which in turn oxidizes the Fe^{2+} on the surface to Fe^{3+} . The Fe^{3+} , which is less soluble in aqueous solutions than the Fe^{2+} , then forms a protective oxide coating and passivates the metal surface [10,11].

Nonoxidizing anions. Nonoxidizing anions contain species that need oxygen to passivate a metal. Typical chemistries include silicate, carbonate, phosphate, tungstate, and molybdate. The mode of action appears to promote the formation of a passivating oxide film on the anodic sites of the metal surface [11].

Cathodic inhibitors. Cathodic inhibitors act to retard the reduction of O₂ or H⁺ or selectively precipitate onto cathodic areas (Figure 17.3). Although the cathodic inhibitors are not as effective at low concentration as their anodic counterparts, the cathodic inhibitors are not corrosive at low concentrations. There are three main modes of action that serve to disrupt the cathodic reaction.

Hydrogen poisons. Hydrogen poisons such as As (as As₂O₃ or Na₃AsO₄), Bi, or Sb primarily act in acidic media (Figure 17.3) to retard the hydrogen reduction reaction by reducing at the cathode and precipitating a layer of the poisoning metal. Unfortunately, they also promote hydrogen absorption in steel and can cause hydrogen embrittlement if not carefully monitored.

Cathodic precipitates. Cathodic precipitates are used in neutral or alkaline solutions (Figure 17.3) and act to form insoluble hydroxides (such as Ca, Mg, or Zn) that will reduce the corrosion rate where the metal is exposed. Typically when the hydroxyl ion (OH⁻) concentration increases in the cathodic areas, cathodic precipitates such as the calcium or magnesium carbonates will react to absorb the excess hydroxide and precipitate Ca(OH)₂ or Mg(OH)₂ on the surface of the cathode which in turn inhibits the reduction of oxygen.

Oxygen scavengers. Oxygen scavengers reduced corrosion by capturing excess oxygen in the system. Typical aqueous oxygen scavengers used for water treatment include hydrazine, SO₂, NaNO₂, and Na₂SO₃, but there are also many organic antioxidants based on alkylated diphenylamine or alkylated phenols that are used in lubricating oils to scavenge oxygen, which could also be considered in this category.

Mixed (or organic) inhibitors. Mixed inhibitors are organic materials (not inorganic ions such as anodic and cathodic inhibitors) that absorb on a metal surface and prevent both anodic and cathodic reactions. These materials are the typical corrosion inhibitors used in lubricating oils and are more difficult to remove by chemical or mechanical action than the monolayer films formed by the anodic and cathodic inhibitors.

17.3 MECHANISM

The basic description of the mechanism for corrosion inhibition by additives was first proposed by Baker et al. as the adsorption of a monolayer of the inhibitor on the metal surface to form a protective barrier. This barrier is impervious to water and prevents contact with the outside environment. They found that the amount of rust prevention depended on a complex interaction of several variables including the lifetime of the adsorbed film, presence of oxygen, thermal and mechanical desorption, solubility (in water), and surface wettability [7,8]. Subsequently, Kennedy [12] added that there is a complex equilibrium between the water on the metal surface and the micellar or solubilized water; he found that the concentration of water in the system effects the corrosion inhibition of a sulfonate. Later, Anand et al. [13] found that lowering the interfacial surface tension also improved the corrosion resistance.

Subsequently, it was found that the monolayer of adsorbed additive was oriented with the polar head adsorbed on the surface and the nonpolar tail closely packed and vertically aligned [14]. The matched chain lengths of the inhibitor and the basestock (e.g., C₁₆-fatty acid matched with C₁₆-alkane) prevent rust due to tight surface packing, which makes the inhibitor more difficult to remove through chemical action (Figure 17.4) [15]. Further investigation revealed that the absorption was accomplished by either an electrostatic (physisorption) or an electron transfer to a coordinate type of bonding (chemisorption) [13,15]. The film was found not only to restrict the access to the

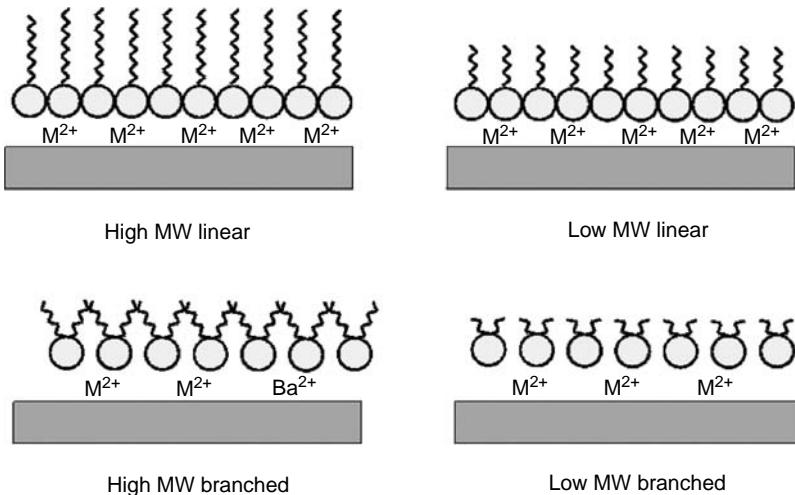


FIGURE 17.4 Schematic diagram of adsorbed films.

surface of aggressive species but also to prevent the passage of metal ions into solution, which restricts the cathodic process to prevent the evolution of H_2 or reduction of O_2 (Figure 17.4) [14].

Early studies on rust inhibitors focused on the widely used dinonylnaphthalene sulfonates. It was found that in water-saturated solutions the cation does not effect the adsorption of the sulfonate, whereas in anhydrous solutions the cation possesses a significant effect, where it is proposed that the cation coordinates directly with the oxide film (not solubilized in the aqueous phase) [16]. In the general trends for sulfonate, it was observed that the corrosion inhibition of the cations increased in the order: $Na < Mg < Ca < Ba$ [13,14,16].

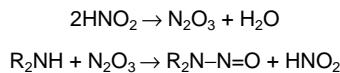
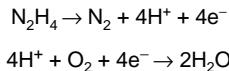
Overall, it can be stated that a corrosion inhibitor is a substance that forms a protective barrier and creates a mechanical separation between the metal and environment. This barrier cannot be easily removed and prevents transport of aggressive agents from contact with the surface, as well as corrosion products from leaving the surface.

17.4 CHEMISTRY

17.4.1 NITRITES

Wachter and Smith first described the use of sodium nitrite ($NaNO_2$) as an anodic inhibitor to prevent internal corrosion by water and air in steel pipelines for petroleum products [17,18]. It was first speculated that the mechanism involved the formation of a tight oxide layer of oxygen and nitrite to prevent corrosion by forming a passivating layer [19], but subsequently it was proposed that the nitrite accelerated the production of Fe^{3+} on the metal surface and formed a less-soluble protective barrier than the Fe^{2+} species [20].

Historically, nitrites were primarily used in aqueous systems such as water treatment or concrete emulsions as an anodic inhibitors [20], but subsequently they have also been used in soluble oils for metalworking applications. Since the 1950s, the reaction of amines commonly used in the soluble oils with nitrite (Figure 17.5) was found to form the carcinogenic nitrosamines (R_2NNO) under acidic conditions [21,22]. As a result, the use of nitrites as RPs in metalworking fluids containing ethanol amine carboxylate salts was banned by the U.S. Environmental Protection Agency (EPA) in 1984, and the industry quickly modified their formulations to replace the nitrite with other inhibitors [23]. Typical replacements used were the borate, carboxylate, or phosphate salts of triethanolamine (TEA) [24,25]. Subsequently, it was found that of the three common

**FIGURE 17.5** Nitrosamine formation.**FIGURE 17.6** Hydrazine decomposition.

amine ethoxylates (monoethanolamine [MEA], diethanolamine [DEA], and TEA), DEA was the most prone to the reaction with nitrite, whereas there was no evidence of nitrosamine formation in the TEA-containing soluble oils [26]. Despite low nitrosamine formation with TEA, the use of nitrite has been widely discontinued in metalworking applications.

17.4.2 CHROMATES

Chromates are another inhibitor that is part of the class of anodic passivators, which appear to inhibit corrosion through the formation of an oxide coating [19,27]. Historically, chromates have been used in steel plating and finishing, aqueous corrosion inhibition, and leather tanning, and although there have been attempts to make oil-soluble chromate derivatives [28], they have not been widely used in lubricants due to their instability in the presence of organics. In water treatment, these products were applied as chromic acid, sodium chromate (Na_2CrO_4), or sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), all of which contain hexavalent chromium. Subsequently, the hexavalent chromium (Cr^{6+}) was found to be a powerful respiratory carcinogen and possessed high aquatic toxicity. As a result, the use of chromates in aqueous water treatment was banned in 1990, and interest in using them in lubricants has disappeared [29].

17.4.3 HYDRAZINES

Hydrazine (N_2H_4) has been historically used for water treatment as a corrosion inhibitor and oxygen scavenger. The hydrazine prevents corrosion in a boiler by (1) reacting with O to form N_2 and H_2O ; (2) reacting with Fe_2O_3 (hematite) to form the harder (passive) Fe_3O_4 (magnetite), which makes a protective skin over the iron surface; and (3) forming NH_3 at high temperatures and pressures to maintain a high alkalinity (Figure 17.6) [30]. Although it has been demonstrated that derivatives of hydrazine can be used to inhibit copper corrosion in sulfuric acid [31], due to health concerns there relatively few new oil-soluble derivatives have been developed, and the main focus has been to use alternative organic treatment chemicals [32].

17.4.4 SILICATES

These materials are mainly used as inhibitors in water treatment for potable water due to their low cost. Owing to their poor oil solubility, silicates have limited use as inhibitors in lubricant formulations.

17.4.5 OXIDATES

Oxidates are one of the oldest classes of RP additives and were historically made from oxidized oils, waxes, and petrolatums obtained from the refining process [3–5]. The production of oxidates can be accomplished by either heating the petroleum product air in a closed vessel in the presence of a catalyst or chemical treatment using nitric acid, sulfuric acid, or KMnO_4 . Both these methods typically make a combination of polar compounds (including carboxylic acids, esters, alcohols,

aldehydes, and ketones), where the total acid number (TAN) of the resulting mixture is between 10 and 200 mgKOH/g and the saponification number (SAP#) is between 10 and 200 mgKOH/g. Typically, commercial grade products possess a TAN of 50 and 100 mgKOH/g and a SAP# of 10 and 50 mgKOH/g. Depending on the application, oxidates can be applied to a surface in various methods as follows:

1. *Aqueous dispersions.* The oxidate can be dissolved or suspended in a water-based formulation that is then applied to the surface. Either the water is removed with washing or the film is allowed to dry to make an RP coating.
2. *Solvent based.* The oxidate is dissolved in a low-boiling solvent (like naphtha), and the solvent is allowed to quickly evaporate to form the RP coating.
3. *Solid film (typically wax).* Either the oxidate is heated to apply the coating as a liquid and then allowed to cool to solidify or the solid oxidate is applied through mechanical methods as a solid at ambient temperatures.

Although these materials can be used as effective RP additives in their acid form, they are typically neutralized to form more effective coatings. It has been found that oxidized wax neutralized with Ca(OH)₂ or Ba(OH)₂ are effective RPs [33], and that the use of Ca(OH)₂ as a neutralizing agent is effective at preventing gelation [34]. Basic materials that contain CaCO₃ have also been found to be effective when combined with petroleum oxidate. The combination of petroleum oxidates and overbased calcium sulfonates has demonstrated both improved lubricity and corrosion protection in forming and engine oils [35,36]. Additionally, the petroleum oxidates can be neutralized with amines to form the carboxylate amine salts. Although there are various amines listed in the patent literature (piperadines [37] and polyamines [38]), the most common amines used are the simple alkanolamines [3–5].

17.4.6 SULFONATES

The sulfonates comprise a class of compounds that can be derived from petroleum (natural) or synthetic feedstocks. The sulfonic acids are formed in the reaction of SO₃ with a feedstock and can be neutralized with various bases to form the Na, Ca, Mg, or Ba salts, all of which have demonstrated activity as RPs in various applications. Additionally, the neutral salts can be *overbased* by the addition of excess base and carbon dioxide. For example, in the case of a calcium petroleum sulfonate, an excess of Ca(OH)₂ and CO₂ can be added to the sulfonic acid to form a colloidal suspension of CaCO₃ in oil, where calcium sulfonate serves to disperse the CaCO₃ in the oil carrier (Figure 17.7). The overbased sulfonates serve a dual role in rust prevention, where the sulfonate acts to form a protective layer, and the calcium carbonate acts to absorb any acidic by-products of corrosion. As a result, a combination of neutral and overbased sulfonates can be a quite effective RP.

The two types of sulfonates that are commonly manufactured are as follows:

1. *Petroleum (natural) sulfonates.* The petroleum sulfonates were originally made from the by-products of the acid treating of petroleum oil but have also been intentionally made as coproducts from the acid-treating process to manufacture technical and medicinal white oil [6,39]. In this process, the oil-soluble petroleum sulfonic acids formed are typically isolated from the oil layer as the sodium salts by treatment with sodium carbonate followed by extraction with alcohol, where the typical activity of the extracted product is 60%, which significantly reduces the viscosity and facilitates easier storage and handling.
2. *Synthetic sulfonates.* The synthetic sulfonates are made from the sulfonation of long-chained alkyl aromatics. Depending on the aromatic structure used, the alkyl chain length varies, but it is important for the overall alkylation to be sufficient to render the compound oil-soluble. The alkylbenzene sulfonate derivatives are typically monoalkylated with a long-chained (C16–40) moiety, whereas alkylnaphthalene derivatives are typically

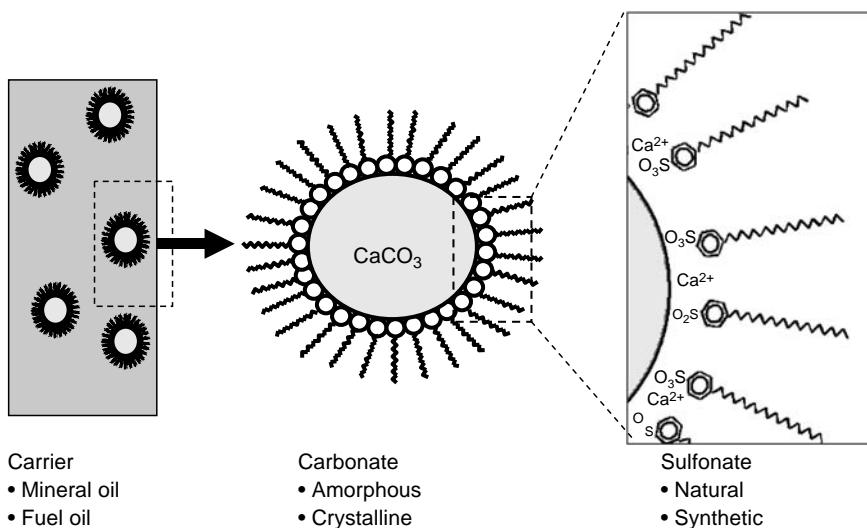


FIGURE 17.7 Overbased sulfonate structure.

dialkylated with short-chain (C9–10) lengths, where barium dinonyl naphthalene sulfonate (BaDNNS) is a common structure [6,40,41].

A natural or synthetic sulfonate can be neutralized and overbased with various cations depending on the application. For example,

Sodium sulfonate. In general, the high equivalent weight (500–550 EW) petroleum or (390–700 EW) synthetic alkylbenzene sulfonic acids are neutralized with NaOH to form sodium sulfonates, which are commonly used in soluble oils for metalworking applications, where the divalent cations (Mg, Ca, and Ba) are detrimental to the stability of the soluble oil. The sodium salts of the synthetic dialkyl naphthalene sulfonates have been used, but their high cost has limited their use in this application.

Calcium sulfonate. Both the synthetic and natural sulfonic acids have been neutralized with CaO or Ca(OH)₂ to form the neutral calcium sulfonates, but generally these products are more effective when they have been overbased. The overbased calcium sulfonates can contain either amorphous or crystalline form of calcium carbonate. The amorphous calcium carbonates are easily soluble in oil and are commonly used as a detergent in engine oils [42,43], whereas the crystalline form of calcium carbonate, called calcite, typically contains colloidal particles that are too large to be held in suspension in the fluid and precipitate to form a gel or gelled solid and are commonly used in RP coatings and greases [44–47].

Magnesium sulfonate. Both the natural and synthetic sulfonic acids can be neutralized with MgO or Mg(OH)₂ to form the magnesium sulfonates. Although magnesium sulfonates have not been generally used in RP oils, the overbased magnesium sulfonates are extensively used as fuel oil additives [48,49]. In particular, the undesirable contaminants in fuel oil such as V and Na can form low-melting corrosive slags on the fireside of a commercial boiler used for power generation. The molten V₂O₅ can act as an oxygen carrier and can accelerate corrosion. The addition of the overbased magnesium sulfonate to the fuel oil serves to react with low-melting sodium vanadates to form high-melting magnesium vanadates that increase the viscosity, reduce the oxygen uptake, and counteract the destruction of the protective oxide film. Additionally, magnesium sulfonate reacts with sulfur oxides (SO₃/SO₂) forming high-melting friable MgSO₄, which can be easily removed by washing, whereas the carbonate neutralizes any free acids to reduce the pH and lower the acid deposition rate (ADR) [50,51].

TABLE 17.2
Ionic Radii of Cations

Type	Solubility Product (K _{sp})	Ionic Radius (pm)	ΔH _{soln} (kJ/mol)	ΔH _{lattice} (kJ/mol)
MgCO ₃	6.82 × 10 ⁻⁶	65	-25.3	3180
CaCO ₃	4.96 × 10 ⁻⁹	99	-12.3	2804
SrCO ₃	1.1 × 10 ⁻¹⁰	113	-3.4	2720
BaCO ₃	2.58 × 10 ⁻⁹	135	4.2	2615

Barium sulfonate. Both the natural and synthetic sulfonic acids can be neutralized with BaO or Ba(OH)₂ to form the barium sulfonates. The barium sulfonates have been found to be effective when both neutral and overbased barium sulfonates are combined in a formulation and applied to a metal surface, where these products are generally used as RPs in mill and slushing oils [8,13,39–41,52,53]. The BaDNNS was found to be very effective at low concentrations [6,39–41] compared to Ca and Na derivatives, and, in general, the RP effectiveness of the sulfonate increases with ionic radius (Table 17.2) where Ba > Ca > Mg > Na.

The effectiveness of alkaline earth metals can be correlated to their ionic radius, which is inversely proportional to the solubility of the metal carbonate (and metal sulfonate) of the additive. For example, the large ionic radius of Ba results in a small release of energy (enthalpy of solution) due to the small amount of solvation necessary for this large polarizable cation. As a result, the large cations require more energy to solubilize and are more difficult to remove from a metal surface by a humid atmosphere or aqueous washing.

17.4.7 CARBOXYLATES

Carboxylates are some of the oldest known corrosion inhibitors and can be made from animal (lanolin, lard, or tallow), vegetable (tall oil fatty acids [TOFAs]), or mineral (naphthenic or aromatic acids) oils and were commonly used in early slushing oil formulations [3–5]. The carboxylic acids can be neutralized with many exotic cations (such as Bi [54]), but they are commonly reacted with NaOH to form the sodium carboxylate salts.

Owing to their corrosivity in aqueous systems [55], carboxylates are more typically combined with alkanolamines to form the alkanolamine salts *in situ* in soluble oil applications for metalworking. In metalworking, the use of the alkanolamine carboxylates provides good coupling with other lubricity additives, enhanced lubricity, and the formation of soft (noncalcium containing) residues, but the alkanolamine carboxylates do suffer from hard water sensitivity, and many short-chained derivatives can cause odor and excessive foaming. The dicarboxylates, which possess good corrosion protection and low foam, can remedy this problem, but they are not popular due to their high cost and poor coupling with other lubricity additives.

In other applications, carboxylates have been used with varying amounts of success, and it had been found that a small amount of the C₆–C₁₈ carboxylic acids prevented corrosion in turbines, whereas acids with chain length <C₆ promoted corrosion [56]. Additionally, in stamping applications, it was found that a simple fatty acid ester provides good lubricity as well as possesses inherent RP properties [57].

17.4.8 ALKYL AMINES

The alkyl amines represent the largest and most diverse chemistry of all the RP types and are used in various metalworking and industrial oil applications. The most common alkylated amines that are used include MEA, DEA, and TEA, fatty amines, diamines, phenylene diamine, cyclohexylamine, morpholine, and ethylenediamine, triethylene tetramine (TETA), and tetraethylene pentamine

(TEPA). It had initially been recognized that the amine was preferentially adsorbed onto the metal surface and inhibited the reaction of the corrosive species and the metal [58], but now it is believed that the alkyl amines first displace the water on the metal surface to form a bond between the lone pair on the nitrogen and the unoccupied orbitals on the metal through defects present in the oxide coatings. As a result, the amines provide cathodic protection by creating a barrier and inhibiting H₂ formation in acidic environments [59–62]. In general, it has been found that longer-chained amines are more effective than the shorter-chained amines [60] and that the nucleophilicity of the nitrogen strongly correlates with rust inhibition effectiveness where the tertiary is more effective than the secondary or primary amine [61].

Owing to their high volatility and low ash formation, products such as cyclohexyl amine, morpholine, and piperidine can be used as VCIs. In systems that are unsuitable for oil, grease, or hard coatings, they expand in the vapor phase to fill the void space in a metal enclosure to form an extremely thin film over the entire metal surface (including intricate interior parts in a fired engine) [59,63]. Owing to the absence of inorganic salts (such as the phosphates, borates, or carboxylates), they do not have the tendency to leave dry residues on the surface [64]. They are also commonly found in sweet (CO₂) and sour (H₂S) gas applications where they volatilize to fill the entire void space of the pipeline [65].

Unfortunately, it has also been found that the amines tend to cause occupational skin diseases (including irritant and allergic contact dermatitis) in workers exposed to metalworking fluids [66–68]. In particular, the commonly used mono- and diethanol amines were found to elicit a significant amount of positive reactions [69], and as a result, they have been largely phased out of this application in favor of the tertiary amines such as TEA. The tertiary amines possess the added benefit of low ecotoxicity and are used environmentally sensitive applications. For example, they are particularly effective in oil field acidizing operations as corrosion inhibitors where they are directly introduced to the outdoor environment [70].

17.4.9 ALKYL AMINE SALTS

Although the alkylamines are commonly used in the gas phase, the amine salts of the carboxylates, borates, and phosphates are most commonly used in metalworking fluids where they are formed *in situ* by reaction with the corresponding acid. For example, the combination TOFA neutralized with triethanol amine to form the amine carboxylate salt is commonly used as a RP. Each amine salt formed for metalworking and RP applications possesses its own unique chemistry and performance issues, each of which will be discussed.

17.4.10 AMINE CARBOXYLATE SALTS

In metalworking formulations, typically tertiary amines such as TEA are neutralized with organic fatty acids to form the amine carboxylates *in situ* to not only provide corrosion inhibition but also improve lubricity and emulsification. Although there have been many combinations of carboxylic acid and amines proposed, the most effective combinations include the long-chained carboxylic acids from C₁₈ to C₂₂ [71–73].

17.4.11 AMINE BORATE SALTS

The borates represent the most chemically diverse and least understood of the RP classes. Although the structure of the borates and borate esters can be written empirically as B(OR)₃, where R is a H or alkyl group, the actual three-dimensional structure of the borates are complex chains and rings that contain both sp² (3-coordinate)- and sp³ (4-coordinate)-hybridized boron species. For example, the species Na₂(B₄O₅(OH)₄) contains both sp³ and sp²-hybridized species, where two of the sp²-hybridized B have empty p-orbitals that can be used to bond to an amine or any other lone pair of electrons as well as use the terminal oxygen to form borate ester linkages (Figure 17.8).

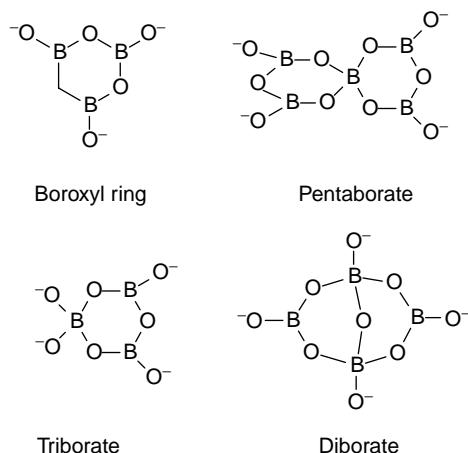


FIGURE 17.8 Proposed structures of borates.

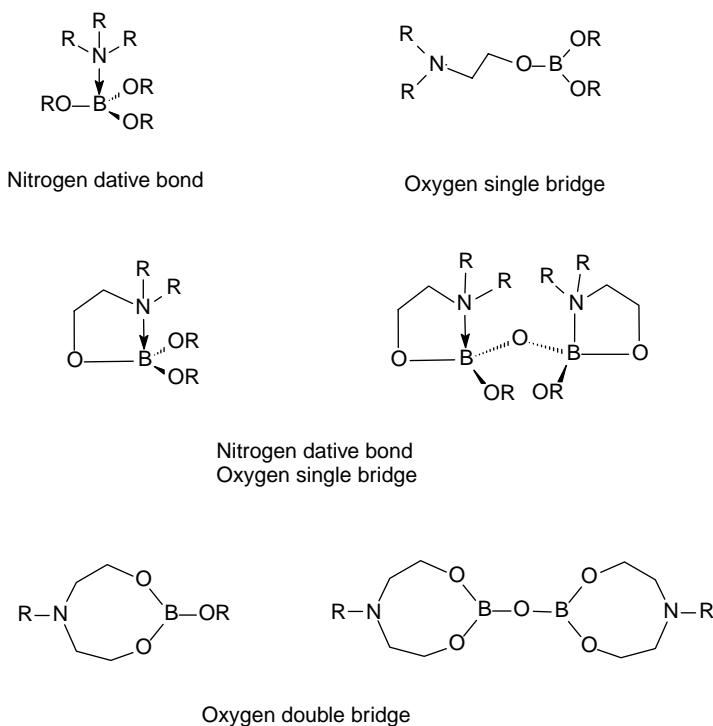


FIGURE 17.9 Proposed structures of borated amines.

As a result, common ethoxylated amines, such as the triethanol amine, can bond to the borate using four different modes of connectivity (Figure 17.9), which can be described as follows:

1. The TEA can datively bond to the unoccupied sp^2 -hybridized orbital of the boron to make the borate salt that is nominatively of the form $R_3N:B(OR)_3$.
2. The TEA can bond through one oxygen on an sp^2 -hybridized boron to form the monodentate $-(N-CH_2-CH_2-O-B)-$ bond.

3. The TEA can datively bond to the unoccupied sp^2 -hybridized orbital of the boron to make the borate salt and can bond through one oxygen on an sp^2 -hybridized boron to form the bidentate $-(N-CH_2-CH_2-O-B)-$ bond.
4. The TEA can bond through two oxygen on an sp^2 -hybridized boron to form the bidentate $-(N-(CH_2-CH_2-O)_2-B)-$ bond.

The advantages of the borate salts are their low cost, low toxicity, hard water stability, excellent antiwear, and reserve alkalinity. The large disadvantage is the possible formation of a tacky residue that remains after the part is machined due to the partially dehydrated products such as *meta*-boric acid and its esters depositing on the surface [74].

The borates not only serve to inhibit corrosion but have also been found to be bacteriostatic (biostatic) agents, and a large synergistic inhibitory effect has been found when combined with amines. Although the mechanism of the effect is still unclear, it is believed that it may be due to the release of boric acid at low pH that may react to form *cis*-diols with the ribonucleotides to promote the antimicrobial activity [75–77].

Although the borated amines have been cited for use in engine oils [78,79], hydraulic fluids [80], and slushing oils [81,82], they are most commonly used in metalworking fluids [83] for both their rust inhibition and biostatic properties.

17.4.12 PHOSPHATES

The phosphating of metals is a well-known technique to improve both wear and corrosion resistance and is primarily used as a surface preparation before painting. The process of phosphate coating is the treatment of iron, steel, or a steel-based substrate with a solution of phosphoric acid or as K, Na, or Ca phosphate salts, in the presence of heavy metal accelerators (Zn or Mg) whereby the surface of the metal is converted to a mildly protective layer of insoluble crystalline phosphate. Phosphating is considered the heart of pretreatment operations in a steel mill and where the top surface of the metal is converted into a highly insoluble, corrosion-resistant coating [84]. The mechanism of this cathodic inhibitor is believed to be the precipitation of a phosphate film on the surface of the steel that prevents the corrosive action of acids and water. Additionally, phosphates have been extensively used in water treatment where the phosphate combines with calcium to form calcium phosphate precipitates [10].

Although the inorganic phosphates (mono-, ortho-, or polyphosphates) are not oil soluble, the phosphate esters can be synthesized to provide oil-soluble derivatives for lubricants. In particular, the tertiary and secondary phosphate esters of the form $(RO)_3P=O$ or $(RO)_2OHP=O$, where R is typically an alkylaryl group have been used in slushing oils alone or in combination with other additives (Figure 17.10) [84–90]. The most common alkylaryl derivatives include the tricresyl phosphate (TCP) and trixylyl phosphate (TXP). Although the trialkyl phosphates (such as tributyl or trioctyl) could be used for this application, the instability of these species due to facile thermal, oxidative, and hydrolytic degradation makes them less desirable as RPs [91,92].

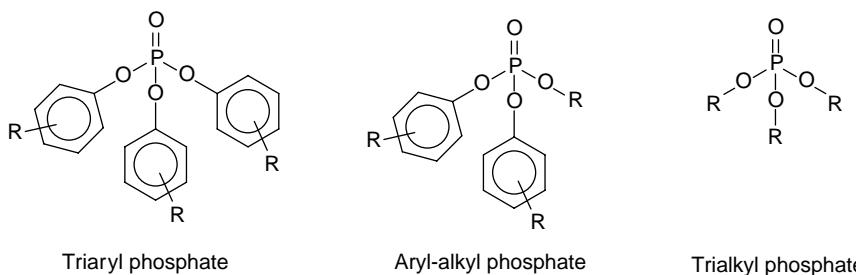


FIGURE 17.10 Phosphate ester structures.

The use of phosphates in soluble oils is less extensive, but there are a few examples of trialkyl phosphates being used in drawing and ironing operations [93,94]. Although the phosphates possess low toxicity and excellent EP/AW and RP properties, their use in soluble oils for metalworking additives has been limited due to their stimulation of microbial growth that can lead to contact dermatitis or worse after prolonged worker exposure [10,69,95,96].

Phosphates have also been used in combination with amines, and this provides not only additional EP/AW protection but also both anionic (phosphate) and cationic (ammonium) RPs in a single salt [85].

Another area where phosphates have been extensively used is in aviation turbines in which low ash properties of TCP are desirable [97]. Although the TCP produced in the 1940s and 1950s did possess a considerable amount of triorthocresyl phosphate (TOCP), which increased concerns of neurotoxicity, the TCP now commercially available can have TOCP levels as low as parts per billion (ppb) and are not a significant concern [98].

17.4.13 NITROGEN RING STRUCTURES

Although tertiary amines have gained wide acceptance in various RP formulations for their ability to neutralize acids, the nitrogen heterocycles have also found use in many common RP applications. The most common type of nitrogen ring structures are imidazolines, benzotriazoles, thiazoles, triazoles, imidazoles, and the mercaptobenzothiazoles (Figure 17.7), as well as any of their common derivatives that include a basic nitrogen in their structure. Owing to the volatile nature, these materials can be used as VCIs and are particularly effective in metal equipment such as engine blocks made from cast iron or aluminum [99]. Additionally, the absence of an inorganic salt minimizes the possibility of dry residue formation.

It has also been found that some imidazoline derivatives have low toxicity in the marine environment and are useful in offshore oil and gas production [64,100]. Although the mechanism is still unclear, it appears as if the highly basic nitrogen in the ring structure is converted to a less basic salt (by reaction with organic acids), which renders the molecule less toxic in the marine environment [64].

Although many amine heterocycles have been proposed, due to their relative low cost and high RP effectiveness, primarily imidazoline and its derivatives have found use in grease, soluble oils, rolling, cutting, drilling, turning, grinding, wire drawing, stamping, and sheathing with varying levels of success. Additionally, the imidazolines can be used alone or combined with a number of organic acids to make the ashless amine salt, which have been demonstrated to be very effective in RP (Figure 17.11).

17.5 CORROSION TESTING

RPs can be used in various end-use lubricant applications, and as a result, there are a wide variety of industry standard rust and corrosion tests available to the formulator. Although industrial organizations such as the American Society for Testing and Materials (ASTM) list many commonly performed test methods, there are a host of international (Deutsche Norm Test Methods [DIN], International Standards Organization [ISO], Association Française de Normalisation [AFNOR], or Institute of Petroleum [IP]) and Original Equipment Manufacturer [OEM] methods that are commonly used to screen corrosion and RPs. The most common ASTM corrosion testing used for RPs and corrosion inhibitors are listed in Table 17.3 along with cross-references to various industry and international methods.

ASTM D1401—Water separability characteristics of petroleum and synthetic fluids. This test determines the ability of lubricating fluids, such as rust and oxidation-inhibited industrial gear lubricant, hydraulic oils, and turbine oils that have viscosities in the range of

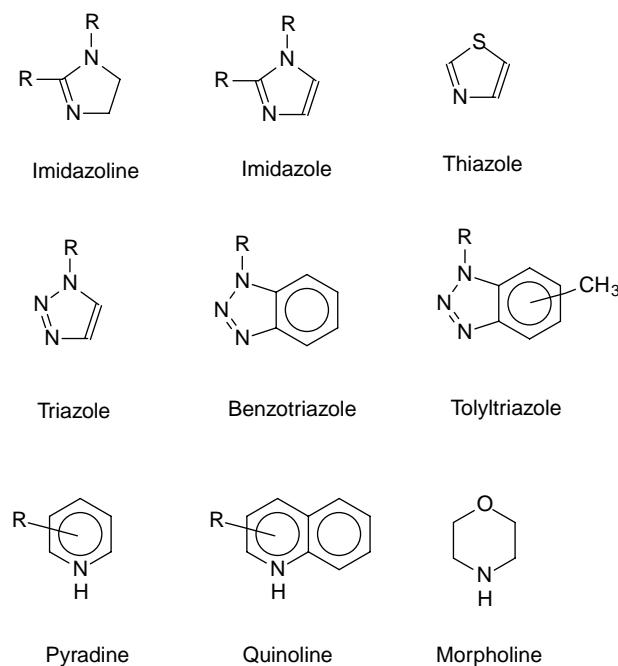


FIGURE 17.11 Common nitrogen ring structures.

28.8–90 cSt at 40°C to separate from water. Although not a standard corrosion test, it is widely used in the lubricant industry to screen potential RP lubricant formulations where in some applications water shedding is desired (slushing and rolling oils), whereas in other applications, emulsification is required (soluble oils for metalworking). The demulsibility characteristics of lubricating oils (ASTM D2711) measures an industrial gear lubricant's ability to separate from water, similar to the ASTM D1401 method, whereas the demulsibility characteristics of lubricating oils (ASTM D2711) test is primarily used to test medium and heavy-viscosity (ISO 220–ISO 1500) industrial gear lubricants' ability to separate from water.

ASTM D130—Copper strip corrosion test. This test is used to evaluate the corrosive tendencies of oils to copper-containing materials, while ASTM D4048 is used for grease. A result of 1b slight tarnish or 2a moderate tarnish is considered a passing result in most applications. This test is particularly sensitive to active sulfur (ASTM D1662) and can be easily passed if an inactive sulfur additive is used in the RP formulation.

ASTM D665—Turbine oil rust test. This test is designed to measure the ability of industrial oils to prevent rusting under conditions of water contamination. To pass the test, the specimen must be completely free from visible rust when examined without magnification under normal light. This test was developed for steam-turbine oils and is one of the oldest standard corrosion tests and has found utility in various applications (aviation oils, RP oils, gear oils, and hydraulic fluids).

ASTM D1748—Standard test method for rust protection by metal preservatives in the humidity cabinet. This test method is used for evaluating the rust-preventive properties of metal preservatives under conditions of high humidity at 49°C. The polished steel panels coated with RP oil are hanged vertically in a humidity cabinet where the water vapors from the bottom of the cabinet contact the panel. At different time intervals, the panels are removed from the cabinet and observed visually for any rust or stains. The time is recorded when the rust or stains are observed or alternatively the area percent rust can be noted at a

TABLE 17.3
Corrosion Test Cross-Reference

Description	Test Method				
	ASTM	DIN	ISO	IP	FTM
<i>Oil</i>					
Detection of copper corrosion from petroleum products by copper strip tarnish test	D130	51 759, 51 811	2160	154	791 5225
Standard method for rust-preventing characteristics of inhibited mineral oil in the presence of water	D665, D3603	51 355, 51 585	7120	135	791 4011, 791 5315
Standard test method for water separability of petroleum oils and synthetic fluids	D1401	—	—	—	—
Standard test method for rust protection by metal preservatives in the humidity cabinet	D1748	50 017*	—	366	791 5310
Standard test method for iron chip corrosion for water-dilutable metalworking fluids	D4627	51 360P2*, 51 360P1*	—	287*, 125*	—
Standard test method for corrosiveness of lubricating fluid to bimetallic couple	D6547	—	—	—	791 5322.2
Standard practice for operating salt spray (Fog) apparatus	B117	50 021-SS*	9227-SS*		791 4001.2
Method of acetic acid-salt spray (Fog) testing	B287	51 021- ESS*	9227-AASS*	—	—
Standard method for copper-accelerated acetic acid-salt spray (Fog) testing (CASS Test)	B368	50 021- CASS*	9227-CASS*	—	—
Standard practice for conducting moist SO ₂ tests	G87	50 018- SWF*	3231	—	—
<i>Grease</i>					
Standard test method for determining the corrosion preventative properties of lubricating grease	D1743	—	—	—	791 4012
Standard test method for detection of copper corrosion from lubricating grease	D4048	—	—	—	791 5309
Standard test method for corrosion-preventive properties of lubricating greases in presence of dilute synthetic sea water	D5969	—	—	—	—
Standard test method to determine the corrosion preventative properties of lubricating greases under dynamic wet conditions (Emcor test)	D6138	51 802	—	220	—
<i>Transport</i>					
Standard test method for the evaluation of corrosiveness of diesel engine oil at 121°C	D5968				791 5308.7
Standard test method for evaluation of rust preventative characteristics of automotive engine oil	D6557				

* Similar test conditions to ASTM method

specified time interval. Depending on the application 1000, 2000, or 4000 h are considered passing results.

ASTM B117—Standard practice for operating salt spray (fog) apparatus. Although not a specific method, this practice covers the apparatus, procedure, and conditions required to create and maintain the salt spray (fog) test environment at 35°C. This practice prescribes neither the type of test specimen or exposure periods to be used for a specific product nor

TABLE 17.4
Typical Corrosion Test Conditions

Method	ASTM D665A&B	ASTM D1748	FTM 4001.2	CASS
Type	Rust test	Humidity cabinet	Salt spray	Acetic acid — salt spray
Time (h)	4	100	24	5
Temperature (°C)	60	49	35	35
Conditions	Distilled water or synthetic sea water	Distilled water	5% NaCl	5% NaCl + 0.2% acetic acid
Test panel	Steel rod	Sandblasted cold rolled steel	Cold finished steel	Cold rolled steel
Grade	AISI/SAE 1010 (BS 970)	AISI/SAE 1009C	AISI/SAE 1010	AISI/SAE 4130
Dimensions	5" × 2 × 11/16"	4" × 2" × 1/3"	3" × 2" × 1/8"	6" × 4" × 1/8"

the interpretation to be given to the results. As a result, there are many OEM, military, and international variations to this method, and specifications must be agreed by the buyer and the seller. The most common form of this test is the FTM-791C 4001.2; it describes the most common time, temperature, and salt concentrations used for this testing. It is considered as an industry standard test procedure and is used to compare different RP formulations on a relative basis. A typical passing rating can range from 100 to 2000 h, but an absolute number is generally not specified as the test formulation is most commonly related to a standard reference fluid for performance evaluation.

A list of the standard test conditions for the most common RP tests is provided in Table 17.4, where the order of severity increases as follows:

$$\text{ASTM D665A} < \text{ASTM 665B} < \text{ASTM D1748} < \text{FTM 4001.2} < \text{CASS}$$

ASTM D4627—Test method for iron chip corrosion for water-dilutable metalworking fluids. This method was designed to determine the relative corrosion rate of a water-dilutable metalworking fluid by using typical cast iron chips found during machining as the test specimen. The procedure uses ~2 g of clean cast iron chips that are spread onto a filter paper in a petri dish, the fluid mixture is then pipetted on to the chips, and the dish is covered. After a certain period of time (typically 24 h), the chips are removed, and the paper is examined for staining. The test is typically evaluated as a pass or fail criterion using successive dilutions of a water-dilutable metalworking fluid. There are many slight variations of this basic procedure (IP-287 or DIN 51 360P1 and IP-125 or DIN 51 360P2), and typically, the method is modified to accommodate prevailing conditions of the end user. Results are evaluated by determining the lowest concentration of soluble oil necessary to prevent rust appearing on the filter paper or on the iron chips where typically a concentration of 2–5% is considered acceptable. This procedure remains an excellent low-cost screening tool to evaluate relative effectiveness of an RP in water-dilutable metalworking fluids.

ASTM D6547—Standard test method for corrosiveness of lubricating fluid to bimetallic couple. This test method covers the corrosiveness of hydraulic and lubricating fluids to a bimetallic galvanic couple and replicates Fed-Std No. 791, Method 5322.2. It uses the same apparatus, test conditions, and evaluation criteria, but it describes test procedures more explicitly.

ASTM D1743—Standard test method for determining corrosion preventive properties of lubricating greases. This test method covers the determination of the corrosion-preventive properties of greases using grease-lubricated tapered roller bearings stored under wet conditions. This method distributes a lubricating grease sample in a roller bearing by running a bearing under a light thrust load. This test method is based on CRC Technique L 41² that shows correlations between laboratory results and service for grease-lubricated aircraft wheel bearings.

ASTM D5969—Standard test method for corrosion-preventive properties of lubricating greases in presence of dilute synthetic sea water environments. This test method covers the determination of the corrosion-preventive properties of greases using grease-lubricated tapered roller bearings exposed to various concentrations of dilute synthetic sea water stored under wet conditions. It is based on test method D 1743, which is practiced using a similar procedure and distilled water. The reported result is a pass or fail rating as determined by at least two of the three bearings.

ASTM D6138—Standard test method for determination of corrosion-preventive properties of lubricating greases under dynamic wet conditions (Emcor test). This test measures the ability of a grease to protect a bearing against corrosion in the presence of water. This test method covers the determination of corrosion-preventive properties of greases using grease-lubricated ball bearings under dynamic wet conditions. It is a dynamic test where two sets of grease-coated bearings are immersed in water and a series of running and resting periods are in rotation. At the end of the test, the raceways of the bearing outer rings are inspected for rust and evaluated. This method is equivalent to IP-220, DIN 51 802, and the Emcor/SKF water wash test.

ASTM B368—Standard test method for copper-accelerated acetic acid salt spray (fog) testing (CASS test). Although the ASTM B368 method is typically used for hard coatings (galvanized or painted surfaces), extended outdoor exposure oil and soft coatings can be tested as an alternative to the milder conditions of the salt spray (fog) method. In ASTM B368, the corrosiveness of the standard salt spray test is increased by lowering the pH or increasing the operating temperature. Several domestic automotive OEMs have their own versions of this test (Ford BG105-01 and GM 4476P), which address their own specific materials requirements.

ISO 6988—Metallic and other nonorganic coatings, sulfur dioxide test with general condensation of moisture. The Kesternich Cabinet (with SO₂ added) is used for metallic and organic hard coatings for long-term outdoor exposure. The Kesternich test simulates the detrimental effects of acid rain and the test calls for dissolving sulfur dioxide in distilled water. The chamber is heated for 8 h at 100% relative humidity. After 8 h, the chamber vents the excess sulfuric dioxide and returns to room temperature. The cycle is repeated every day, and the results are reported as pass/fail after specified duration after a visual inspection for rust (Table 17.5).

17.6 FUTURE REQUIREMENTS

The demand for RPs in lubricants will continue for many years, in part due to higher demand in the developing countries such as Brazil, Russia, China, and India (BRIC) and the aging of existing OEM equipment that is currently used in the developed world. The current market drivers for new RPs will continue to be environmental and health concerns.

New environmental requirements for RPs address various shortcomings of the current commercial chemistries. For amine-based products, there is a desire for lower marine toxicity (ecotoxicity), which is driving the industry toward alternative eco-friendly products, whereas for the classic barium-based products, there is a drive to reduce the heavy metal content and replace them with less-hazardous metals (i.e., Na, Ca, or Mg). Additionally, the waste disposal of the final

TABLE 17.5
Commercial Rust Preventatives/Corrosion Inhibitors

Manufacturer	Chemistry	Trade Name
Air Products	Alkylamine	
Akzo Nobel	Fatty imidazoline	Armohib
Akzo Nobel	Amine sulfonate	Armohib, Armeen, Duomeen,
Akzo Nobel	Alkylamine	Triameen
Akzo Nobel	Ammonium thiocyanate	
Akzo Nobel	Quaternary ammonium compounds	Arquad
Akzo Nobel	Ethoxylated alkyl amine	Ethomeen, Ethoduomeen
Arch Chemical	Hydrazine	Scav-Ox
Arizona Chemical	Dimerized fatty acid	Century, Unidyme
BASF (formerly PPG/Mazer)	Alkylamine	Mazon
Chemtura	Calcium sulfonate	Calcinate
Chemtura	Barium sulfonate	Surchem, Petronate
Chemtura	Oxidized petrolatum	Oxpert
Chemtura	Sodium sulfonate	Petronate
Ciba	Succinic acid ester	Irgacor
Ciba	Polycarboxylic acid	Irgacor
Ciba	Sodium sebacate	Irgacor
Ciba	Nonyl phenoxy acetic acid	Irgacor
Ciba	Amine phosphate	Irgalube
Ciba	<i>N</i> -acyl sarcosine	Sarkosyl
Ciba	Imidazoline derivatives	Amine
Cognis	Dimer acids	
Cognis	Fatty acid ethoxylate	Eumulgin
Cognis	Alkylamine	Texamin
Dover (formerly Keil)	Carboxylic acid salt	Synkad
Dover (formerly Keil)	Boramide	Synkad
Dover (formerly Mayco)	Carboxylic acid salt	Mayco
Dover (formerly Mayco)	Barium sulfonate	Mayco
Dow (Angus Chemical)	Amino alcohol	AMP AEPD, Corrguard
Dow (Angus Chemical)	Oxazoline	Alkaterge
Dupont	Dilauryl acid phosphate	Ortholeum
Dupont	Dibasic acids	Corfree
Grace Construction	Calcium nitrite	DCI Corrosion Inhibitor
Georgia Pacific	Ethanolamine borate	Actracor
Georgia Pacific	Ethanolamine carboxylate	Actracor
Georgia Pacific	Alkanolamide	Actramide
Halox	Alkyl ammonium salt	Halox
Halox	Alkanol amine/boric acid/phosphoric acid	Flash-X
Huntsman	Amine borates	Diglycol amine
Huntsman	Ethanol amines	MEA, DEA, TEA
Huntsman	Polyether amines	Jeffamines
Huntsman	Castor oil ethoxylates	
Huntsman	Aminomethyl propanol	AMP
King Industries	Dinonylnaphthalene sulfonate	Na-Sul
King Industries	Alkyl amines	K-Corr
King Industries	Acid amine salts	K-Corr
Lonza	Quaternary ammonium carbonate	Carboshield
Lonza	Quaternary ammonium chloride	Uniquat
Lonza	Imidazoline derivatives	Unamine

(continued)

TABLE 17.5**(Continued)**

Manufacturer	Chemistry	Trade Name
Lubrizol	Calcium sulfonate	Alox, Lubrizol
Lubrizol	Barium sulfonate	Alox, Lubrizol
Lubrizol (Alox)	Oxidized petrolatum	Alox
Oxy-Wax	Oxidized wax	Hypax
Pilot Chemical	Sodium sulfonate	Aristonate
Pilot Chemical	Ethanolamine sulfonate	Aristonate
Pilot Chemical	Calcium sulfonate	Aristonate
PMC Specialties	Benzotriazole	Cobratec
PMC Specialties	Tolytriazole	Cobratec
PMC Specialties	Carboxybenzotriazole	Cobratec
PMC Specialties	Sodium tolytriazole	Cobratec
PQ Corporation	Sodium silicate	PQ
R.T. Vanderbilt	Succinic acid ester	Vanlube
R.T. Vanderbilt	Barium sulfonate	Vanlube
R.T. Vanderbilt	Imidazole	Vanlube
R.T. Vanderbilt	Amine phosphate	Vanlube
Rohm & Haas	Alkylamines	Primene
Uniqema	Proprietary	Perfad
Uniqema	Fatty acid derivatives	Prifac, Priolene, Pripol
Uniqema (formerly Mona)	Borate esters	Monacor
Uniqema (formerly Mona)	Amine carboxylate	Monacor
Uniqema (formerly Mona)	Amine phosphate	Monacor
Uniqema (formerly Mona)	Phosphate ester	Monalube
Uniqema (formerly Mona)	Imidazone	Monazoline

end product has been a great concern in both lubricant and metalworking applications and has driven the market to pursue more biodegradable products that could be based on new chemistries or natural fats and esters.

Although the majority of the severe health effects such as the carcinogenicity of the hexavalent chromium products have, for the most part, been addressed, there are still concerns for sporadic outbreaks of acute and chronic symptoms. In particular, the public health concerns for the reduction of contact dermatitis for machine shop workers has lead to increase demand for *amine-free* lubricant and metalworking fluids, using alternative technologies such as sulfonate or low-toxicity amines. Additionally, although contact dermatitis is generally viewed as an acute symptom, the occurrence of hypersensitivity pneumonitis (HP or machine operators lung) can lead to a chronic condition that may require hospitalization in its most extreme cases. As a result, regular worker health checkups and air quality monitoring are standard practices now in many metalworking shops.

Generally, workers employed in industrial manufacturing are safer now due to tougher regulations from industrial and governmental bodies, which has led to the search for alternative chemistries. As a result of both environmental and health concerns, the RP suppliers will continue to develop alternative technologies that incorporate a cradle-to-grave approach to product stewardship.

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18 Additives for Bioderived and Biodegradable Lubricants

Mark Miller

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18.1 INTRODUCTION

There is increasing interest in biobased and biodegradable lubricants as alternatives to petroleum-based products. According to the National Oceanic and Atmospheric Administration (NOAA), 700 million gallons of petroleum is released into the ocean each year. Over half of that, 360 million gallons, is because of irresponsible maintenance practices as well as routine leaks and spills.

As environmental enforcement agencies increase pressures and costs for petroleum lubricant spills, many equipment operators are using or considering environmentally safer products. These types of fluids can protect the users against fines, cleanup costs, and downtime, but care must be given in selecting the right product for each specific application.

The benefits of biodegradable hydraulic fluids are well known. Their biodegradable properties allow them to break down in the environment reducing the negative impact from leaks and spills. They can be nontoxic, meaning they will not hurt operators, animals, or plants that come into contact with the fluid. They are renewable and reduce dependence on foreign petroleum oil.

Conventional knowledge has focused on the limitations of vegetable oils as base stocks for lubricants. The weakness of the oxidative stability, the cold temperature performance, and incompatibility with elastomers are well documented. Early generation biobased lubricant formulators utilized performance chemistry similar to those used in petroleum-based fluids creating lubricant products that did not meet industrial performance requirements. Over the past decade, however, improvements in vegetable base stocks, performance chemistry, and formulation expertise have allowed for the development of biodegradable products with performance similar to or better than conventional petroleum fluids.

Although there is a wide range of *biobased products*, most are readily biodegradable, meaning that they are biodegradable above 60% in 28 days as measured by the ASTM D5864 biodegradability

test. Petroleum hydraulic fluids are either not biodegradable (<30% in 28 days) or inherently biodegradable (30% < X < 59% in 28 days, where X is biodegradability).

Most of these biobased products are free of toxic performance chemicals such as sulfated ash, zinc, calcium, and other heavy metals. Biobased products are also usually formulated to be *virtually* nontoxic and frequently measure 5–10 times less toxic compared with the ASTM *nontoxicity* specification. A conventional petroleum lubricant typically contains a zinc and calcium additive performance system and will generally be considered toxic. These fluids are toxic and persistent as the additive system kills the microbes responsible for biodegradation, and the petroleum fluid itself is not readily consumed by the microbes. There are, however, some *inherently biodegradable* petroleum hydraulic fluids containing ash-free additive systems and as such are less toxic than standard petroleum hydraulic fluids. However, these products are still petroleum-based, and the microbes cannot readily degrade (digest) these types of fluids. They will persist in the environment for many months or years and will dramatically reduce water quality, harming local wildlife and ecosystems.

Furthermore, standard petroleum products contain aromatic, cyclic (ring structure) hydrocarbons. These *aromatics* cause the familiar rainbow sheen on a water surface. Biobased products do not contain aromatics and as such do not produce a *rainbow* sheen on a water surface when spilled. Severely hydrotreating petroleum oil during the refining process will remove most aromatics. These fluids might not produce a sheen but will persist on the water surface harming the aquatic wildlife and ecosystem.

There are no universal definitions of biobased, environmental, or biodegradable for lubricants. The focus of this chapter is on vegetable or biobased lubricants with the vegetable oil content maximized at >60%. The Farm Security and Rural Investment Act (FSRIA or Farm Bill) was signed into law in 2002. A goal of that legislation is to increase the government's purchases and use of biobased products. Under this legislation, the United States Department of Agriculture (USDA) has selected and prioritized items for designation as *preferred* biobased products and set minimum biobased content levels. Each level of prioritization is issued in a *round* of designated products. In the first round, lubricant-related products were specified (Table 18.1) [1].

Despite the levels required by *federal minimum biobased content*, high-performance vegetable-based products can sometimes contain >90% biobased content. As a result, they will be readily (rapidly) biodegradable [2].

Also, this chapter looks primarily at environmentally compatible performance chemistry, which is defined as no heavy metals, no ash, low treatment volume, low toxicity, and low environmental persistence. Use of these types of chemistries will not adversely affect the environmental performance of biobased products and are very less toxic. One standard of measuring toxicity of a substance is the LC 50, that is, the concentration, in parts per million (ppm), of a substance that is lethal to 50% of the laboratory animals exposed to it in a 96 h test [3]. Therefore, the higher the LC 50, the lesser the toxicity. As most commercially available biobased lubricants can be formulated at LC 50s ranging from 5,000 to 10,000 ppm, only formulations less toxic than 5,000 ppm will be considered. This chapter, however, touches lightly on chemistry that seems to have a positive effect

TABLE 18.1
Government-Specified Minimum Biobased Content

Product	Minimum Biobased Content (%)
Diesel fuel additives	90
Hydraulic fluids (mobile equipment)	44
Penetrating lubricants	68

Source: Extracted from United States Department of Agriculture Biopreferred Web site, <http://www.biopreferred.gov>.

on vegetable-based products yet might be < 5000 ppm LC 50 level. The additives will include both traditional petroleum oil-type additives and other novel additives.

Significantly, more work has been done in hydraulic and tractor transmission fluids as well as total loss lubricants, that is, lubricants that are consumed through their use. Engine oils, although a large market, typically do not present an environmental threat due to leaks or spills. They require extremely high operating temperatures that are not suitable for vegetable oils. Although some work has been done with engine oils to date, the Chemical Manufacturers Association (CMA) or International Lubricant Standardization and Approval Committee (ILSAC) has certified no vegetable-based engine oil. Some of the development work on engine oil performance has shown the performance of several additive types and will be addressed.

The use of refined, bleached, and deodorized (RBD) *food-grade vegetable* oils in industrial lubricant applications has been limited due to their inherent performance deficiencies regarding oxidative and thermal stabilities and their limited cold temperature flow properties. The use of genetically modified vegetable base stocks such as high oleic, reaction modification such as esterification, and chemical modification combined with improved vegetable oil-specific performance additives can fully address the concerns surrounding the use of vegetable oils in hydraulic applications. Commercial applications and previous research have demonstrated that mixtures of modified vegetable oils provide performance levels required for hydraulic original equipment manufacturers (OEM). Much work has been done evaluating the performance benefits of genetically modified vegetable oils and mixtures of base fluids including ester and polyalphaolefins, but it is outside the scope of this chapter. For the most part, the benefits that an additive provides to a conventional vegetable oil will also apply to genetically modified oils and mixtures.

Before modern additives are explored, the history of vegetable oils will be reviewed.

18.2 HISTORY

Early generation biobased lubricant formulators utilized performance chemistry similar to those used in petroleum-based fluids creating lubricant products that frequently did not meet industrial performance requirements.

Historically, vegetable-based lubricants have not exhibited sufficient performance for industrial applications. There were several reasons for this inability. The first reason is that vegetable-based lubricants were misformulated. Traditionally, a lubricant is compounded from base oil and various performance chemistries. Early formulators in the vegetable-based lubricant market used the same chemistry that was used for petroleum lubricants for vegetable base oils. This approach was not effective as the characteristics of vegetable oils are vastly different than those of petroleum oils. Typical characteristics of vegetable oils as compared with petroleum are summarized in Table 18.2.

TABLE 18.2
Typical Characteristics of Various Base Fluids

Characteristic	Petroleum Oil	Vegetable Oil	Saturated Ester	PAO
Lubricity	Low	High	High	Low
Oxidative stability RPVOT	300	50	180	300
Viscosity Index (VI)	100	200	165	150
Hydrolytic stability	High	High	Low	High
Polarity	Low polar	Highly polar	Polar	Low polar
Saturation	Saturated	Unsaturated	Saturated	Saturated
Flash point (°F)	200	450	400	350
Pour point (°F)	-35	-35	-40	-50

Source: Derived from Terresolve Technologies In-house Knowledge Base.

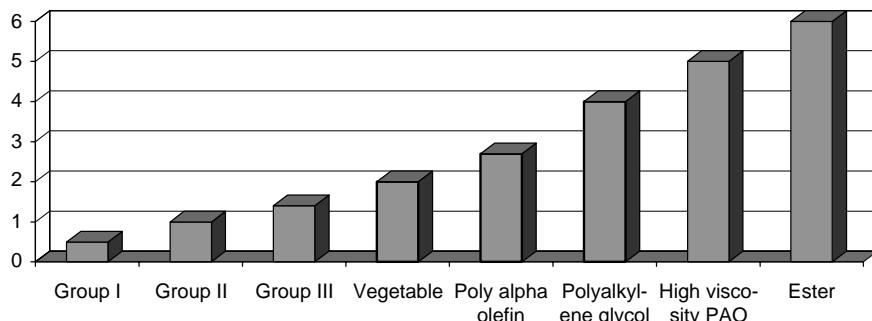


FIGURE 18.1 Relative cost of various base fluids. (Derived from Terresolve Technologies In-house Knowledge Base.)

Vegetable oils have to be formulated for their individual characteristics. Some modern vegetable-based products currently in the market offer good performance and a fair price. Figure 18.1 shows relative costs for a wide range of lubricants.

Although all triglyceride vegetable-based lubricants have temperature limitations, there are some that are better than others. Although most vegetable-based lubricants have a maximum operating temperature of 140°F, there are some that offer protection as high as 220°F. Similarly, most vegetable-based lubricants offer good performance down to 30°F, yet there are some that flow below -30°F.

These temperature limitations led to another major reason for early technical failures and that was the wrong fluid choice. Even the highest-performing biobased fluids have operating limitations in terms of temperature and life expectancy. Using a biobased fluid in an application over 220°F (and as low as 160°F for some fluids) will cause premature and possibly catastrophic equipment failure. This, combined with sensitivity to moisture, which is another characteristic of vegetable-based lubricants, has caused numerous cases in which using a vegetable-based fluid was a major contributor to the failure. In extreme high-temperature, environmentally sensitive applications, readily biodegradable synthetic fluids should be utilized.

Finally, biobased fluids require special care to maximize its useful life. Water in any lubricant system is bad for many reasons, which include causing many additives to fall out, increasing the onset of acid formation, deteriorating seals, creating rust, and accelerating wear. Most biobased fluids are more susceptible to hydrolytic breakdown, the result of which can be acid formation, more susceptible to additive precipitation, and as previously mentioned are prone to oxidative instability.

Over the past decade, however, improvements in vegetable base stocks including low-euricic acid rapeseed oils, high oleic soy and rapeseed oils, and improved low-temperature castor oil; improvements in additive chemistry; and improvements in formulation expertise have allowed the development of biodegradable products with performance similar to or better than conventional petroleum fluids.

18.3 VEGETABLE BASE FLUIDS

Vegetable oils and other fats are triglycerides that are essentially triesters of fatty acids and glycerol. They are soluble in most organic solvents and are insoluble in polar substrates such as water. They can have a broad range of fatty acid profiles, but most commonly used vegetable oils will be C18—oleic, linoleic, or linoleic acids. The proportion of each of these acids depends on the vegetable type, the growing season, and the geography. These factors can dramatically affect the performance of the vegetable oil in terms of oxidative stability, cold flow, hydrolytic stability, and other features of the final product. For example, the higher the oleic acid content, the better the oxidative stability but the higher (worse) the pour point. Further discussion of acid content and oil performance is reviewed in other sections.

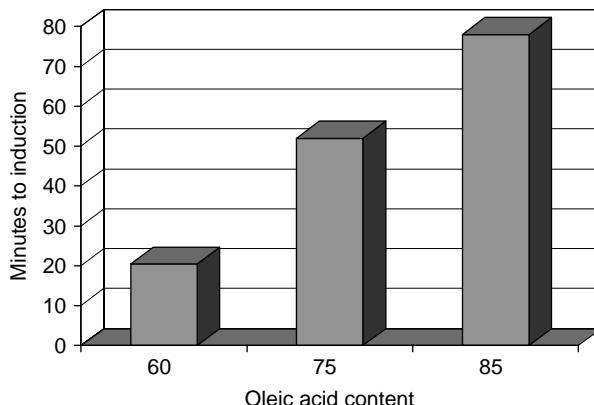


FIGURE 18.2 PDSC oxidation stability. (Based on Bergstra, R., *Emerging Opportunities for Natural Oil Based Chemicals*, MTN Consulting Associates, Plant Bio-Industrial Workshop, Saskatoon, Saskatchewan, Canada, February 27, 2007.)

18.4 OIL TYPES AND PERFORMANCE

The following chart shows the effect of oleic acid level on oxidative stability as measured by the pressure differential scanning calorimeter (PDSC). The PDSC is a test frequently used to evaluate thin-film oxidation of lubricants and base fluids. It is also known as the CEC L-85-T-99. The test measures the *minutes to induction time*, and the longer the time, the better the oxidative stability.

Figure 18.2 [4] shows that there is a direct correlation between the oleic acid content of a vegetable oil and its oxidative stability and that the higher the oleic content the higher the oxidative stability.

18.5 ADDITIVE PACKAGES

As previously mentioned, early vegetable oil formulators used performance additives similar to the performance additives used for petroleum base fluids. Petroleum oils are, for the most part, nonpolar, whereas triglycerides are highly polar. As such, conventional petroleum additives sometimes have solubility problems with vegetable oils. Frequently, to utilize typical additive packages, a solubilizing agent must be used. Additive packages without metals, such as *ashless* additives, are more soluble in vegetable oils.

Even today, several additive manufacturers try to promote additive packages targeted to vegetable oils. Although major additive companies are highly skilled at performance chemistry for petroleum base oils, the expertise needed for formulating vegetable oils is highly specialized. Adding to it is the complication of maintaining environmental integrity, which makes it a daunting task.

Most additive packages supplied by the major additive companies are specifically designed for petroleum base oils. Even those targeted toward vegetable oils utilize core chemistry tailored for petroleum. Additionally, the carrier fluid from the various components is usually petroleum, and when a multicomponent package is created, several percent of petroleum is included. This will reduce biodegradability and increase toxicity of the final fluid, that is, counter the objective of the product.

To make high-performance fluids from vegetable oils, a *clean sheet approach* must be utilized, and the fluid must be designed with the specific characteristics of the base fluids and the specific requirements of the end products. Some typical petroleum additives can be utilized and are effective in vegetable oils. Frequently food-grade additives are superior and have lower toxicity. When formulating vegetable-based lubricants, it is useful to expand the search into food additive and other nonlubricant industries. Table 18.3 [5] summarizes the performance of some conventional additive packages designed for both petroleum and vegetable base oils as compared with a custom-designed

TABLE 18.3
Performance of Various Additive Packages in Vegetable Oil

Custom Formulation	Vegetable Additive Package 1	Vegetable Additive Package 2	Petroleum Additive Package 1	Petroleum Additive Package 2
Petroleum additive package 1			X	
Petroleum additive package 2				X
Vegetable additive package 1	X			
Vegetable additive package 2		X		
RPVOT D2272	125	76	16	41
Rust D665B	Pass	Pass	Fail	Pass
				Fail

Source: Derived from In-house Terresolve Technologies Proprietary Development Research, October 11, 2005 through January 8, 2007.

TABLE 18.4
Sequence VII Performance

Engine Test Result	Weight Loss (mg)	Stripped Viscosity (cSt) at 10 h
GF 4 Spec limit	26	Stay in grade
Traditional package	108.6	11.51
Unique package	4.0	11.09

Source: Based on McCoy, S., United Soybean Council Technical Advisory Panel, The Valvoline Company, September 20, 2005.

performance formulation using vegetable oil and specific additives. The rotary pressure vessel oxidation test (RPVOT) known as the ASTM D-2272 is a common test procedure that compared the oxidative stability of lubricants and base fluids. The ASTM D-665B rust test is also a typical indicator of the rust protecting characteristics of a finished fluid.

For the past several years, Valvoline has been working toward the development of a bio-containing engine oil. In this work, they compared results of a mid-oleic soy oil and petroleum oil mixture with a conventional additive package with the results from a *clean sheet* design. Taking the characteristic of biofluid under consideration, they were able to achieve vastly superior results in the Sequence VII bearing corrosion test (Table 18.4) [6].

18.6 DETERGENTS

Vegetable oils have a high level of solvency and by themselves act as a detergent for many applications. Vegetable oils and methyl esters of vegetable oils have been successfully used as solvents and cleaners for many years.

When attempting to add detergent performance, phenates and sulfonates should be avoided, as they are frequently toxic for *environmentally safe* fluids. The phenate and sulfonate functional groups are not the problem, but conventional petroleum detergent additives that are typically attached to heavy metals, such as calcium, sodium, and barium, are highly toxic. Specialty *metal-free* phenates and sulfonates have been used as a component to protect seal materials. These products have shown collateral benefits. For example, some classes of phenates have shown improvements in thermal stability to natural oils, and some sulfonates show an additional side benefit of corrosion inhibition.

Low amounts of phosphate and phosphate esters have been used successfully in vegetable products showing good performance without adversely affecting the environmental performance.

Sulfurized phenates and salicylate chemistries are typically not used in bio oils as they adversely affect the environmental benefits of a vegetable oil. There has been some work, although very sparse, on the detergent and antiwear benefits of thiophosphates, phosphonates, and thiophosphonates. These additives and their benefits, however, are of limited value in formulating vegetable-based lubricants because vegetable oils on their own have sufficient detergent and antiwear capabilities and do not require supplementation.

18.7 DISPERSANTS

Almost all dispersants found are designed for petroleum oils. They typically contain a long *tail* that will be soluble in the oil and *polar head* to keep certain contaminants in the oil. These contaminants can be filtered out later or are swept away during an oil change. The vegetable oil molecular size is too small to act as a dispersant, and while the *polar head* is highly polar, the molecular chain length is too small to accommodate dirt and sludge.

Typical vegetable-based lubricant applications such as hydraulic fluids and total loss lubricants (bar-chain oil and 2-cycle oil) have little need for dispersants. There has, however, been some work done evaluating dispersants for vegetable oil-containing engine oils. This work has shown that the most effective way to add dispersancy without significantly reducing other performance characteristics is through a dispersant polymer. As it is one additive that can be used for multiple purposes, a side benefit to a dispersant polymer is that it keeps the amount of nonbiodegradable, nonbiobased products to a minimum. Conventional high-molecular-weight dispersants such as polyisobutylene (PIB), PIB succinimide, and PIB succinate ester are not used as they adversely affect the environmental performance.

18.8 CORROSION INHIBITORS/ANTIRUST

Rust is a chemical reaction between water and ferrous metals, whereas corrosion is a chemical reaction between chemicals (usually acids) and metals. As previously mentioned, water in any lubricant system is bad. It can cause rust on metal surfaces and reacts with chemicals in the system to produce acids that cause corrosion. Vegetable oils can utilize more novel (expensive) acidic rust inhibitors helping to protect against corrosion and rust. Typically, acid inhibitors in conventional additive packages form precipitates that cause filter plugging. Sulfonates and acid rust inhibitors are more surface active and perform better in vegetable-based oils.

18.9 ANTIOXIDANTS

Vegetable oil's primary weakness for use in industrial applications is its oxidative instability. Oxidation occurs with the interaction of oil and oxygen. Vegetable oils (triglycerides) have a number of double bonds depending on the type of the oil. Through use, these fluids develop free radical ions. The double bonds in the oil are *searching* for ions (free electrons). The double bond reacts with the free electrons and will change the characteristics of the vegetable oil. This will open a double bond and allows for degradation of by-products. There is a very good correlation between the degree of unsaturation of a vegetable oil and its oxidative stability. Table 18.5 [7] summarizes several oil types and their oxidation characteristics as measured by the PDSC (see Section 18.4 for a detailed description). The onset oxidation temperature and the oxidative stability can be predicted using fatty acid composition rather than individual fatty acid percentage.

Vegetable oils have significantly lower oxidative stability than petroleum fluids. The stability can be improved through the proper choice of vegetable type, chemical modification, and antioxidant additives.

TABLE 18.5
Degree of Saturation and PDSC Onset Temperature in Soybean Oils

Base Fluid	Name	Unsaturation	PDSC Onset Temperature (°C)
Soybean oil	SO	1.5	173
High linoleic SO	HLSO	1.4	179
Mid oleic SO	MOSO	1.14	190
High oleic SO	HOSO	0.94	198

Source: Extracted from Erhan, S. Z., *Oxidative Stability of Mid-Oleic Soybean Oil: Synergistic Effect of Antioxidant-Antiwear Additives*, National Center for Agricultural Utilization Research, USDA/ARS, Peoria, IL, 2006.

TABLE 18.6
Effect of Various Antioxidants on Vegetable Oil Formulations

	1 Custom Formulation	2 Vegetable Additive Package	3 Vegetable Additive Package + Supplement 1	5 Petroleum Additive Package + Supplement 3	6 Petroleum Additive Package + Supplement 2
Petroleum additive package 1				X	X
Vegetable additive package 1		X	X		
AO supplement 1			X		
AO supplement 2					X
AO supplement 3			X	X	
RPVOT D2272	125	76	100	41	52
Rust D665B	Pass	Pass	Pass	Pass	Not tested

Source: Derived from In-house Terresolve Technologies Proprietary Development Research, October 11, 2005 through January 8, 2007.

The study on oxidative stability (Section 18.5, Table 18.3) mentioned earlier was continued to include antioxidant additives to both the vegetable additive package and the petroleum additive package. One can see from Table 18.6 that although both additive packs can have oxidative stability improvements, neither was able to reach the performance level of a custom formulation hydraulic fluid.

Some unique antioxidants such as zinc diethyl dithiocarbamate (ZDDC), alkylated diphenyl amines (ADPA), and butylated hydroxytoluene (BHT) improve in both PDSC and RPVOT in soy oils. These also have shown a synergistic effect with some antiwear agents such as antimony dialkyl dithiocarbamate (ADDC) as shown in Figure 18.3.

These chemistries can have a positive effect on the oxidative performance of vegetable oils. However, they can be toxic and persistent and reduce the environmental benefits of the fluids.

There are two other widely used methods for oxidation control. The first is free radical scavenging and the other is hydroperoxide decomposition. Radical scavenging will lock up free radicals and prevent oxidation. Commonly used free radical scavengers for vegetable oils are arylamines and hindered phenol. Zinc dialkyldithiophosphate (ZDDP) is a widely used free radical scavenger and an excellent antiwear agent but is not often used in vegetable oil formulations due to its high level of toxicity.

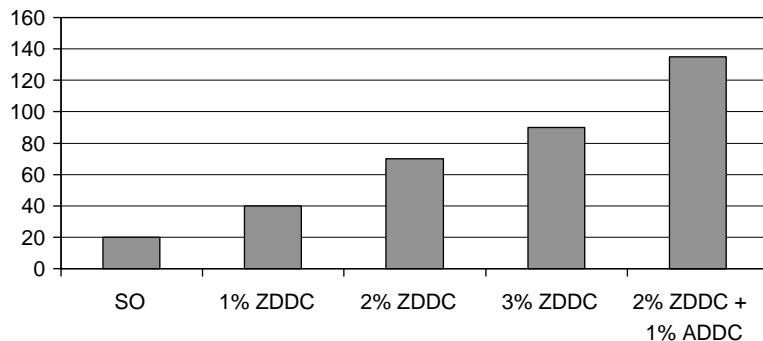


FIGURE 18.3 Effects of antioxidant and antiwear on soy oil RPVOT. (Extracted from Erhan, S. Z., *Oxidative Stability of Mid-Oleic Soybean Oil: Synergistic Effect of Antioxidant-Antiwear Additives*, National Center for Agricultural Utilization Research, USDA/ARS, Peoria, IL, 2006.)

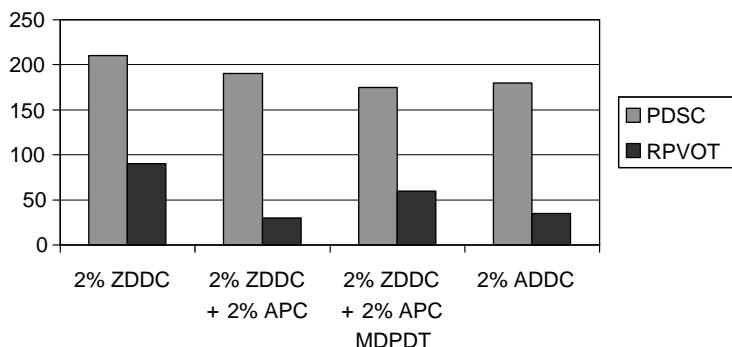


FIGURE 18.4 Oxidation effects of various antiwear additives in vegetable oil formulations. (Extracted from Erhan, S. Z., *Oxidative Stability of Mid-Oleic Soybean Oil: Synergistic Effect of Antioxidant-Antiwear Additives*, National Center for Agricultural Utilization Research, USDA/ARS, Peoria, IL, 2006.)

The other widely used oxidation inhibitor mechanism is *hydroperoxide decomposition*. Hydroperoxide is another precursor to oxidation, and *breaking it down* can significantly improve oxidation stability. The main additive components for hydroperoxide decomposition are phosphorus-based additives as they are mostly environmentally benign and very effective. Other types of hydroperoxide decomposers such as sulfides, phosphates, and olefins are not used due to environmental incompatibility.

18.10 ANTIWEAR

Vegetable oils can have excellent lubricity, far superior than that of mineral oil. The polarity of vegetable oil improves antiwear characteristics as they have an affinity to metal and protect the surface. Some RBD vegetable oils have passed hydraulic pump wear tests, such as ASTM D2882 and ASTM D2271, in their natural state with no additives. These unadditized oils thermally break down due to their oxidative instability but perform well in the wear tests.

Amine phosphate compounds (APCs) are used in readily and inherently biodegradable products. They do not work well in refined petroleum as they do in vegetable oil.

Some commonly used antiwear additives have been utilized in vegetable oils and found to reduce oxidative stability when combined with certain antioxidants. These include, for example, APC and molybdenum dialkyl phosphordithioate (MDPDT) with ZDDC (Figure 18.4).

These additives as well as other molybdenum, zinc, and boron compounds are excellent chemicals for antiwear and friction reduction, but are typically designed for petroleum fluids. They will work well in vegetable oils and highly refined petroleum oils, but will increase overall toxicity of these blends.

18.11 ANTIFOAM

Vegetable oils need additional antifoam agents to prevent air entrainment. Conventional antifoam agents have only a minor effect on vegetable oils. Silicon foam inhibitors are very effective and widely used. Silicon is very nonpolar and is an excellent foam inhibitor. The silicon chemicals are usually diluted in either petroleum oil base stock or vegetable oils and may need an additional solubility agent such as an ester to maintain solubility. Silicon acts as a surfactant and prevents air from reacting with the lubricant surface. Other foam inhibitors used with vegetable oils are dimethylsiloxane, alkylmethacrylate, and other alkylacrylates.

18.12 VISCOSITY MODIFIERS/POUR POINT DEPRESSANTS

Viscosity is commonly known as resistance to flow. Vegetable oils normally have a good natural viscosity for industrial lubricants. Some formulators will utilize this natural characteristic and the very high viscosity index (VI) and not use any additional viscosity modifiers.

VI is the change in viscosity compared to the change in temperature. A high VI indicates small viscosity changes with temperature changes. Vegetable oils have very high VI usually ~200 when compared to petroleum oil, which has a VI of ~100. This means that vegetable oils maintain their design viscosity over a broader temperature range.

Finding an environmentally safe viscosity modifier is very difficult. Typically, the long-chain polymers do not break down in the environment and therefore reduce biodegradability. Most viscosity modifiers are nonpolar and hard to solubilize in vegetable oils and will create hazy mixtures. Ethylene propylene diene monomer (EPDM) polymers are especially difficult to solubilize due to their *diene* double bond. There are some viscosity modifiers, however, that can be dispersed in vegetable oils including olefin copolymer (OCP) and polymethacrylate (PMA).

The pour point is the lowest temperature at which oil will flow. Most pour point depressants (PPDs) reduce the size and cohesiveness of the crystal structures and will thereby reduce pour point and improve the flow at reduced temperatures. PPDs are base oil specific. While the steric effect of the carbon side chains of vegetable oils have more of an effect on the pour point than any other factor, some ppds can reduce the pour sufficiently for industrial usage.

Styrene esters, methacrylates, and alkylated naphthalenes work well for vegetable oils as well as petroleum fluids. Methacrylates typically are more effective for group II petroleum oils.

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Part 6

Applications

19 Additives for Crankcase Lubricant Applications

Ewa A. Bardasz and Gordon D. Lamb

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19.1 INTRODUCTION

Engine oil lubricants make up nearly one-half of the lubricant market and therefore attract a lot of interest. The principal function of the engine oil lubricant is to extend the life of moving parts operating under different conditions of speed, temperature, and pressure. At low temperature, the lubricant is expected to flow sufficiently in order that moving parts are not starved of oil. At higher temperatures, they are expected to keep the moving parts apart to minimize wear. The lubricant does this by reducing friction and removing heat from moving parts. Contaminants pose an additional problem, as they accumulate in the engine during operation. The contaminants may be wear debris, sludges, soot particles, acids, or peroxides. An important function of the lubricant is to prevent these contaminants from causing any damage.

To function effectively, the lubricant needs chemical additives as well as base oils. Depending on the application, various combinations of additives are used to meet the required performance level; the most important ones are listed as follows:

- Detergents
- Dispersants
- Antiwear
- Antioxidants
- Viscosity modifiers
- Pour point depressants
- Foam inhibitors

In addition to these additives, there are several other additives for anticorrosion, antirust, seal swelling, biocide, and demulsibility.

19.2 DETERGENTS

19.2.1 INTRODUCTION

Detergents play an essential role in protecting various metallic components of internal combustion engines by neutralizing acidic compounds formed during combustion processes [1–3]. Gasoline and diesel engine oils account for more than 75% of the total detergent consumption. Detergent treatment in engine lubricant can reach 6–10 wt%, with marine diesel engine lubricants containing the

highest concentration levels due to combustion of high-sulfur fuel, which leads to the formation of inorganic acidic combustion products such as sulfuric acid.

The purpose of detergents in crankcase oils is

1. To suspend/disperse oil-insoluble combustion products such as sludge or soot and oxidation products
2. To neutralize combustion products (inorganic acids)
3. To neutralize organic acid products of oil degradation processes
4. To control rust, corrosion, and deposit-forming resinous species [4]

Why are these specific functions critical to engine durability? Coke and varnish-like deposits can restrict the free movement of the piston rings, allowing a portion of the combustion gases to pass into the crankcase or combustion chamber, leading to heavy contamination of the oil, impacting engine out emissions and even causing piston seizure if the engine operates at high loads [5]. Heavy sludge can plug oil filters, leading to oil starvation and thus to catastrophic wear especially during cold temperature start-ups [6]. Acidic fuel combustion products can cause corrosion.

Detergents can react with hydroxyacids, deposit precursors, formed during the oxidation of the oil. Deposit precursors are attracted to detergent micelles and trapped within them and, thus, cannot settle onto metal surfaces and form resinous deposits. The cleaning action of detergent additives is attributed to chemisorption processes and formation of metal salts.

To satisfy the abovementioned requirements, practically all detergent additives contain

- *Polar head.* Hydrophilic, acidic groups (e.g., sulfonate, hydroxyl, mercapton, carboxylic, or carbonamide groups) that react with metal oxides or hydroxides
- *Hydrocarbon tail.* Oleophilic aliphatic, cycloaliphatic, or alkyaromatic hydrocarbon radicals that provide oil solubility
- One or several metal ions

Idealized representation of the detergent structures is shown in Figure 19.1.

Although several metals have been incorporated into detergents, only three metal cations are now commonly used—calcium, magnesium, and sodium. Heavy metals such as barium are no longer used.

Detergents are described chemically in terms of their metal ratio, soap content, percent sulfate ash, degree of overbasing or conversion, and total base number (TBN) [2]. The *metal ratio* is defined as total equivalents of metal per equivalent of sulfonate acid. *Soap content* refers to the amount of neutral salt and reflects the detergent's cleansing ability or detergency. The *percent sulfate ash* is the ash obtained after treating the detergent with sulfuric acid and complete combustion. The *degree of overbasing (conversion)* describes the ratio of equivalents of the metal base to equivalents of the acid substrate and is usually expressed as conversion. Conversion provides the amount of inorganic material relative to that of the organic material and is expressed as number of equivalents of base per equivalent of acid times 100. The overbased part of detergent is needed to neutralize acid

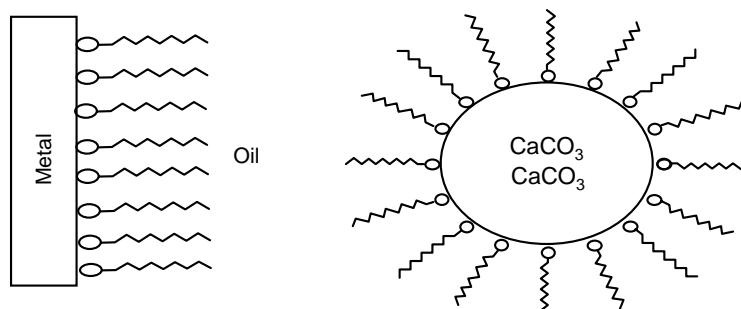


FIGURE 19.1 Idealized representations of neutral and overbased detergents.

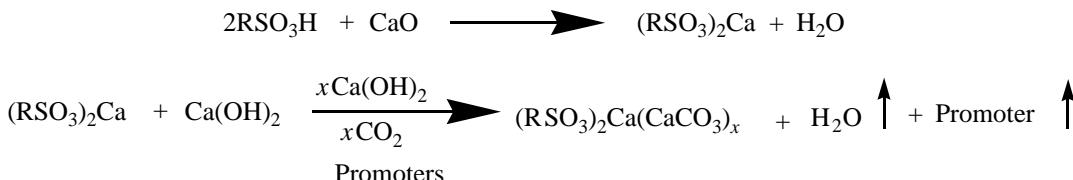
by-products. The TBN indicates its acid-neutralizing ability and is expressed as milligrams of KOH per gram of additive. It is measured using a potentiometric method (e.g., ASTM D-2897).

The alkaline reserve of all modern detergents may vary considerably. Neutral detergents contain the stoichiometric amounts of metals, corresponding to the basicity of the acids. Basic (or overbased) detergents contain a significant excess of metal oxides, hydroxides, carbonates, etc., in colloidally dispersed form. The structure of detergents can be envisioned as a reverse micelle, with an amorphous carbonate molecule encapsulated by metal soap molecules with their nonpolar ends extended into the oil (Figure 19.1).

In practice, virtually all commercial detergents are overbased to some extent. For example, commercial *neutral* sulfonates have a TBN of 30 or less. *Basic* detergents have a TBN in the range of 200–500.

Some detergents can act as oxidation inhibitors, depending on the nature of their functional group. Most modern motor oils contain combinations of several detergent types, which are selected to give optimum performance.

Preparation of calcium detergents be represented schematically as follows:



19.2.2 SULFONATES

The salts of long-chain alkylarylsulfonic acids are being widely used as detergents. Basic calcium sulfonates make up 65% of the total detergent market.

As the demand for sulfonic acids has rapidly increased, synthetic products with the general structure $(\text{RSO}_3)_v\text{Me}_w(\text{CO}_3)_x(\text{OH})_y$ are also used besides the sulfonated alkylaromatics from petroleum refining known as *natural* sulfonates. Synthetic products are produced by the sulfonation of suitable alkylaromatics, for example, the di- and polyalkylation products from the dodecylbenzene production; their alkyl radicals should contain together at least 20 C atoms. Other starting materials are alpha-olefin polymers with mean molecular mass of ~1000.

The *neutral sulfonates* (schematically shown in Figure 19.2) contain the stoichiometric amounts of metal ion and acid. Besides Na, Ca, and Mg, patents have been issued describing detergents containing

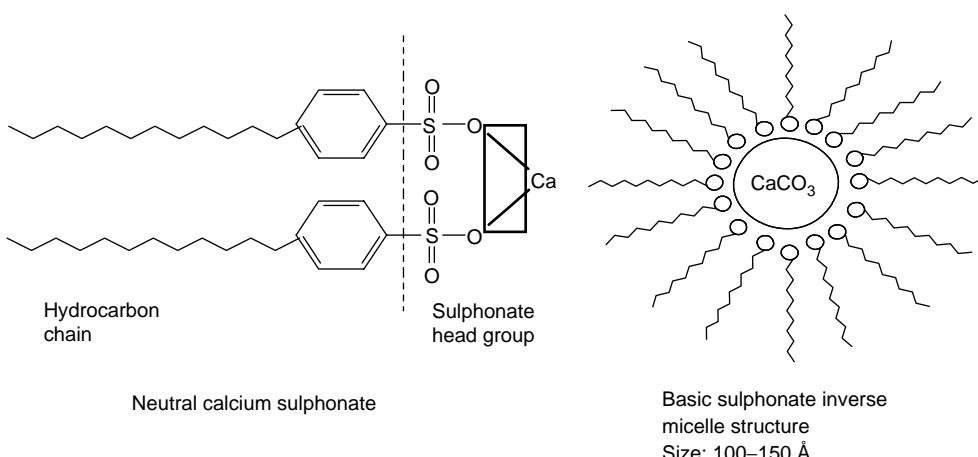


FIGURE 19.2 Neutral and basic sulfonates structures.

tin, chromium, zinc, nickel, and aluminum; however, the importance of these metals is inferior to that of the alkaline earth metals.

Neutral oil-soluble metal petroleum sulfonates can be converted into *basic sulfonates* by mixing and heating with metal oxides or hydroxides, followed by filtration. In these products, the metal oxides and hydroxides are present in colloidally dispersed form (Figure 19.2). Such basic sulfonates have a considerably increased alkaline reserve and thus a higher neutralizing power.

Treatment with carbon dioxide converts basic sulfonates into metal sulfonate–carbonate complexes that have the same alkaline reserve, yet a lower basicity. Efforts to produce additives with even higher neutralizing power have led to the development of the *overbased sulfonates*. Besides high neutralizing power, these additives also possess a high dispersing capacity due to the large amount of polar inorganic bases present.

Overbased sulfonates are produced, for instance, by heating an oil-soluble sulfonate with metal oxides in the presence of substances that act as catalysts such as phenols and phosphoric acid derivatives.

19.2.3 PHENATES, SULFURIZED PHENATES, AND SALICYLATES

Basic phenates make up 31% of the total detergent market. Schematic structures of phenates and sulfurized phenates are shown in Figure 19.3.

Phenate detergents are available as calcium and magnesium salts. Metal salts of alkylphenols and alkylphenol sulfides, $(R)(OH)C_6H_3S_xC_6H_3(OH)(R)$, where $x = 1$ or 2 and R is ~ 12 C, can be prepared at elevated temperatures by the reaction of alcoholates such as magnesium ethylate with alkylphenols or by the reaction of phenols or phenol sulfides with an excess of metal oxide or hydroxide (particularly of Ca) sulfides with an excess of metal oxides or hydroxides in neutral phenates. Besides their neutralization power, phenates also possess good dispersant properties.

As in the case of the sulfonates, the phenates can be overbased. Overbased phenates are often used as components of marine diesel cylinder lubricants.

In many commercial lubricant applications, sulfonate and phenate detergents are used in combination and often contain various metals to obtain an optimum detergent action and neutralizing power. Besides better neutralizing power, the main incentive for the use of basic phenates is lower manufacturing cost compared with the normal phenates.

Salicylates are less commonly used as detergents in crankcase lubrication. The typical structure of salicylate detergent is given in Figure 19.4.

Besides their detergent properties, the metal alkylsalicylates also possess oxidation-inhibiting and anticorrosion properties. Their solubility in mineral oils can be improved in the case of esters by extending the chain length of the alcohol radicals or generally by alkylation of the aromatic ring.

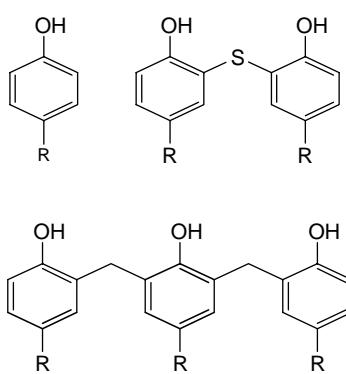


FIGURE 19.3 Phenates and sulfurized phenates structures.

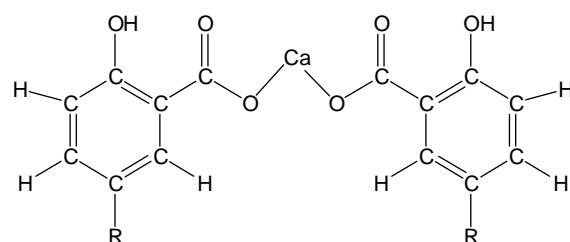


FIGURE 19.4 Calcium salicylate structure.

The alkaline earth salicylates are usually overbased by the incorporation of alkaline earth carbonates, stabilized in the form of micelles.

19.2.4 OTHER DETERGENTS: PHOSPHATES, THIOPHOSPHATES, PHOSPHONATES, AND THIOPHOSPHONATES

Besides their use as oxidation inhibitors, phosphates and thiophosphates also serve in various variations and combinations as detergents. Thiophosphonates are obtained by the reaction of phosphorus pentasulfide with polyisobutenes (PIBs), olefins, fatty alcohols, and esters are neutralized after hydrolysis with metal hydroxide.

19.2.5 PERFORMANCE IN LUBRICANTS

For crankcase engine oils, which include passenger car, heavy-duty diesel, marine diesel, and stationary gas applications, detergents provide several key performance functions. One of the primary functions of overbased detergents is to neutralize acidic combustion by-products [2–4]. In all reciprocating piston internal combustion engines, gases from the combustion chamber are forced around and through the piston rings and into the crankcase where they interact with the lubricant. These combustion gases and by-products contain such components as oxides of sulfur, derived from the sulfur content of fuels. Particularly in diesel engines, these sulfur oxide compounds interact with oxidized components from the fuel and base oil to produce sulfuric acid and organic acids [6].

Another form of combustion by-products comes from oxides of nitrogen, derived from the high-temperature combination of nitrogen and oxygen from the intake air. These by-products are predominant in gasoline engines in which the oxides of nitrogen materials can further react with water (from the combustion process), oxidized oil and fuel, and soot (if present) to produce engine sludge and piston varnish [5]. Obviously, these acidic combustion gases and by-products are detrimental to the extended life of both the engine components and the lubricant itself. They can give rise to increased rusting of steel parts and corrosion of bearings.

The use of high TBN, overbased detergents can combat these problems. However, one must be careful in formulating with an appropriate mix of detergents for acid control and corrosion performance. The use of several appropriate detergents in a lubricant for excellent engine rust and bearing corrosion performance may not necessarily be favorable to maintain good valve train wear performance, such as in the well-known gasoline engine specification tests, the Sequence VE and Sequence IVA.

Figure 19.5 plots data from a recent passenger car field test showing the decrease in TBN and the increase in total acid number (TAN) with use. Original equipment manufacturer (OEM) oil drain recommendations are often determined by this type of testing. Typically, it is considered desirable

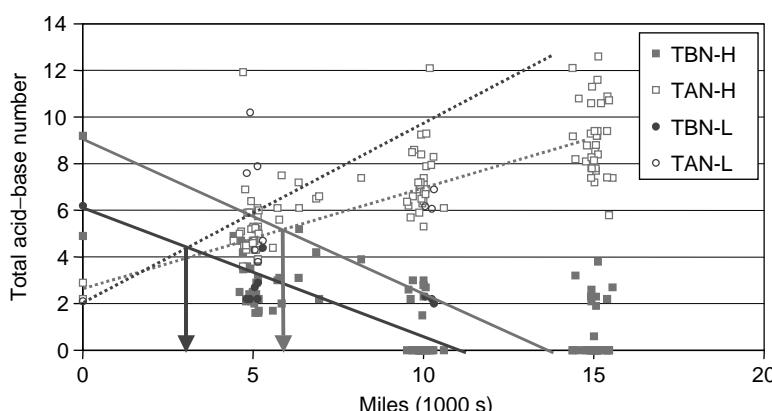


FIGURE 19.5 Passenger car field testing: TBN/TAN relation.



FIGURE 19.6 Detergents keep upper pistons clean.

to change the oil before the TBN and TAN cross. In this “severe service” example, the oil that starts at a TBN of 6 would need to be changed twice as often as the oil that has an initial TBN of ~ 9 .

Evidence such as this results in oils with higher TBN being recommended for longer drain intervals.

A second function of a detergent is to retard deposit formation on engine parts, especially parts that are operating at high temperatures, such as pistons and piston rings (Figure 19.6). Detergency of North American diesel engine oils is evaluated using both single-cylinder engine tests (Caterpillar 1N, 1K, 1P, and 1Q) and multicylinder engine tests (Cummins M11, Mack T-9, and T-10). The selection of detergents to give the best piston and ring cleanliness is highly dependent on the temperature of the piston ring area, the metallurgy of the piston, the ring pack design, and the base stock of the lubricant being tested. Metallurgy variances in engine designs such as aluminum versus articulated steel diesel pistons complicate proper detergent selection. A particular mixture of detergents may be excellent with aluminum hardware but may only perform marginally with steel hardware.

Some types of detergents perform additional functions in an engine oil formulation. For example, coupled-coupled alkyl phenols enhance high-temperature oxidation inhibition. Owing to their specific structure and thermal stability, these detergents help prevent oxidation of the lubricant under high speed and high-load engine conditions; the result is a lower viscosity increase of the oil. Of course, high-temperature oxidation inhibition synergizes with the detergent’s ability to enhance *cleanliness*.

In summary, the best overall cost and performance by using a selected combination of detergents in a lubricant depends on many factors. Several of these factors entail complete engine performance, customer desires, and regulations including the maximum total amount of metal or metal ash allowed in a lubricant as set by specification requirements.

19.3 DISPERSANTS

19.3.1 INTRODUCTION

Dispersants are typically the highest treat additive in an engine oil formulation. They are similar to detergents in that they have a polar head group with an oil-soluble hydrocarbon tail. Although detergents are used to clean engine surfaces and neutralize acidic by-products, their effectiveness is limited when it comes to dispersing oil-insoluble products resulting from the by-products of combustion. The principal function of a dispersant is to minimize the deleterious effects of these contaminants. The most obvious contaminants related to engine lubricants are black sludge and soot particles. Sludges range from thick oil-like deposits to a harder deposit; soot is composed primarily of carbon particles and is typically found in diesel engines. Dispersants are used to disperse these contaminants within the engine thereby ensuring that the oil flows freely. The dispersing ability of the dispersants helps keep the engine clean and, in some cases, will maintain piston cleanliness. Some formulators will actually refer to certain dispersants as ashless detergents.

Over many years, dispersants have played a major part in keeping the engine clean, and they continue to play an important part in the oil formulation. In modern top-quality engine oil formulations, dispersant will range from 3 to 6% by weight. Typically, this would account for ~50% of the total oil additive in the lubricant.

19.3.2 DISPERSANT STRUCTURE

Dispersants consist of an oil-soluble portion and a polar head group. The polar group is attached to the oil-soluble group by means of a *hook*. The schematic in Figure 19.7 gives a simple representation of a dispersant structure based on the reaction of a polyisobutlenyl succinic anhydride (PIBSA) with either a polyamine or a polyol.

Many different types of dispersants have been used in lubricant additive packages. Over the years, these have evolved as the lubricant requirements for both OEMs and the testing organizations have become more demanding. The following list, although not exhaustive, covers the most popular types of dispersant chemistries in use today:

- Polyisobutlenyl succinimide
- Polyisobutlenyl succinate ester
- Mannich dispersants
- Dispersant viscosity modifiers (VMs) (e.g., dispersant olefin copolymer [dOCP], dispersant polymethacrylate [dPMA])

By far the most common group of dispersants is polyisobutlenyl succinimides. These are the preferred dispersants for tackling the black sludge problem that occurred in gasoline engines during the 1980s. During the 1990s and up to the present day, they have also been used in ever increasing levels to reduce oil thickening, which is the result of high levels of soot in diesel engine oils.

To prepare a polyisobutlenyl succinimide dispersant, a hook is attached by reacting maleic anhydride (MA) with PIB to make PIBSA. The PIBSA is then typically neutralized with a polyamine mixture to yield the succinimide dispersant (Figure 19.8).

The reaction between the PIB and the MA occurs through the unsaturated end group of the PIB. This can be achieved by directly reacting the PIB with MA at temperatures in excess of 200°C (direct alkylation or DA for short). Once the PIBSA is formed, it can react again to make the disuccinated product. The reaction of PIB and MA depends on the unsaturated end groups of the PIB being reactive enough to add to the MA. As the reaction proceeds, the addition of MA to the PIB slows as all

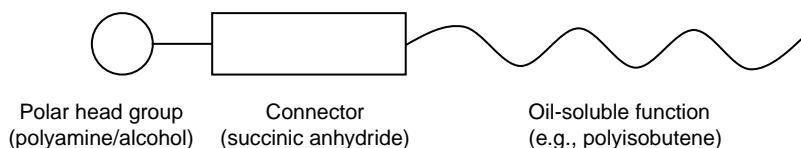


FIGURE 19.7 Schematic of a dispersant molecule.

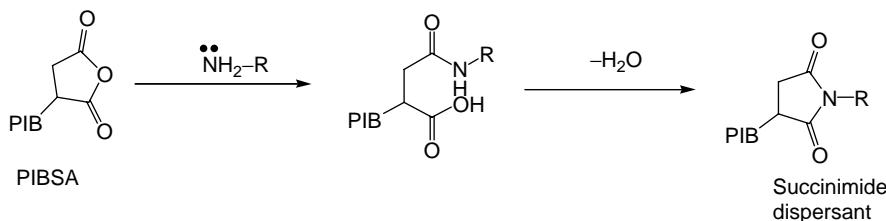


FIGURE 19.8 Imidation of a PIBSA.

the reactive end groups in the PIB are used up. With some types of PIBs, this will leave a relatively large amount of unreacted PIB. In recent years, this problem has been overcome by using PIBs with very high levels of terminal vinylidene groups, in some cases >80%. These vinylidene groups are more reactive through the DA route, enabling DA PIBSAs to be prepared with relatively low levels of unreacted PIB (see Figure 19.9).

The key to the PIB-MA reaction is to ensure that the PIB is completely converted into PIBSA. Any unreacted PIB in the finished lubricant will result in a formulation with poor low-temperature viscometric properties. In addition, the dispersant will be less effective in preventing sludge formation and in dispersing soot since not all the oil-soluble PIB will contain active dispersant chemistry.

For these reasons, it is beneficial to maximize the conversion of the PIB to the succinic anhydride. The addition of MA to the PIB is made easier by using chlorine, which catalyzes the reaction through a PIB diene intermediate that reacts more readily with the MA yielding a highly converted PIB with minimal unreacted PIB. A schematic of the reaction is shown in Figure 19.10.

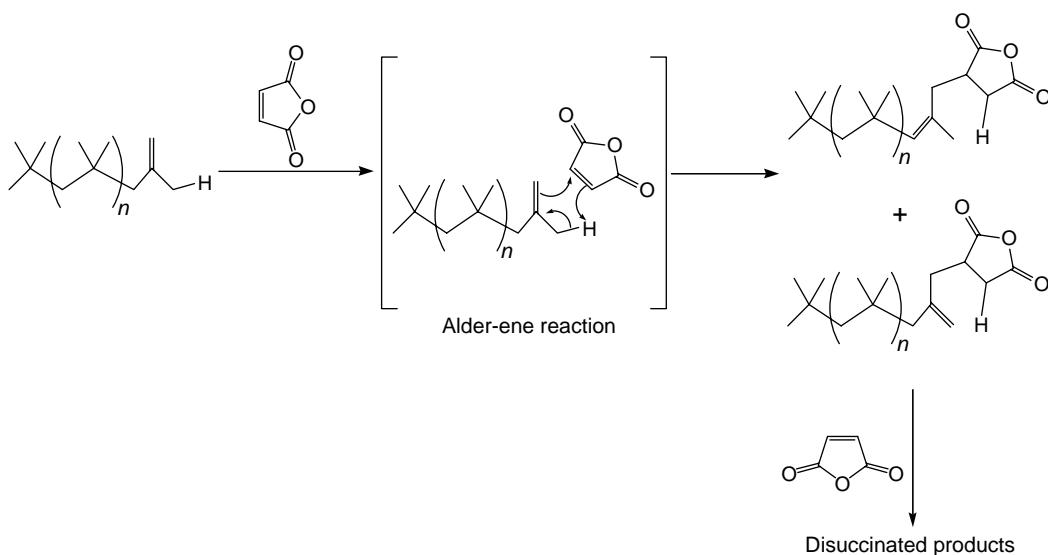


FIGURE 19.9 Direct alkylation reaction of PIB with MA.

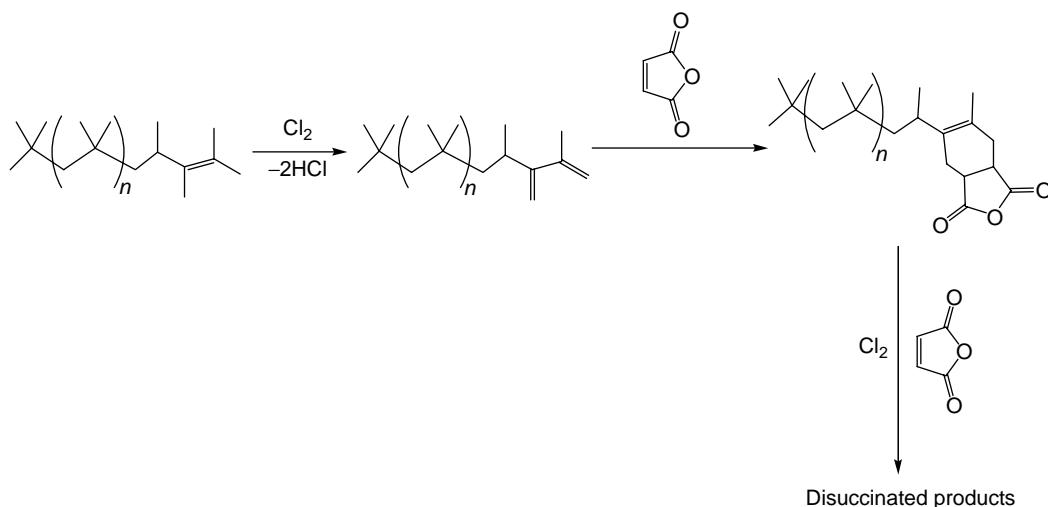


FIGURE 19.10 Chlorination/succination of PIB.

19.3.3 POLYISOBUTENE SYNTHESIS

PIB is produced by cationic polymerization of either pure isobutene or C₄ stream from an oil refinery. The isobutene in the C₄ refinery stream reacts preferentially, whereas other compounds such as *n*-butenes and butanes do not. Typical catalysts for these reactions include AlCl₃ and BF₃.

The molecular weight of the PIB is very important and can have a significant effect on the dispersant performance. Typically, the number average molecular weight (M_n) of PIB ranges from 500 to 3000 although there are instances where PIBs outside this range may be used. The higher-molecular-weight PIB dispersants have VM properties and aid the formulation of multigrade oils. In addition, they are much more effective in the handing of black sludge and soot. Although lower-molecular-weight dispersants have found use as sludge and soot dispersants, they are clearly less effective. Dispersants made using higher-molecular-weight PIB (M_n > 2500) have an adverse effect on the low-temperature viscosity properties of the finished lubricant, particularly the cold crank viscosity, and for this reason are not normally used. In addition, they are more difficult to react with MA due to their higher viscosity.

19.3.4 DISPERSANT BASICITY

The amount of polyamines added to the PIBSA will determine the basicity of the dispersant. This is referred to as TBN and is measured by the ASTM D-2896 method. The unit of measurement for TBN is milligrams of KOH per gram. The TBN of the dispersant will give a good indication of the dispersant structure. Higher levels of polyamines, that is, more base, will predominately yield a monosuccinimide structure, which is the most basic of the PIBSA dispersants (see Figure 19.11). When there is a molar excess of PIBSA more of the bis and tris structures will predominate (see Figure 19.12).

19.3.5 SUCCINATE ESTER DISPERSANTS

These dispersants are prepared from a PIBSA and a polyol as shown in Figure 19.13. Ester-based dispersants are used to reduce sludge and piston deposits and function in a similar manner to the succinimide-based dispersants.

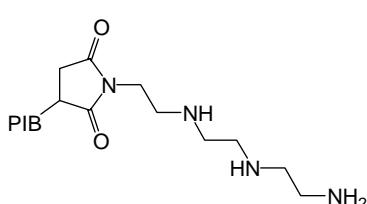


FIGURE 19.11 Example of monosuccinimide from triethylenetetramine (TETA).

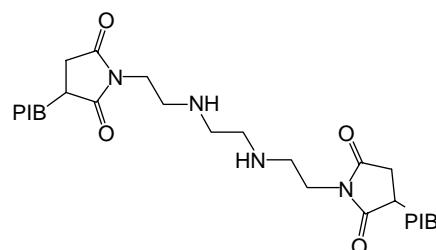


FIGURE 19.12 Example of bis-succinimide from TETA.

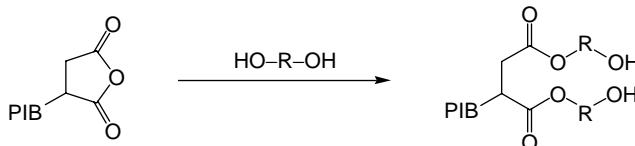


FIGURE 19.13 Example of a simple succinate ester dispersant.

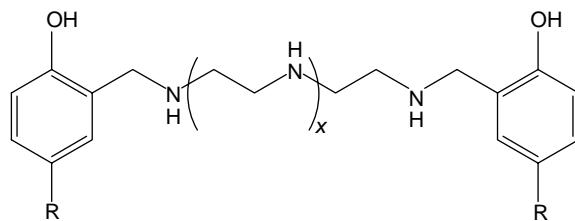


FIGURE 19.14 Mannich dispersant.

19.3.6 MANNICH DISPERSANTS

These types of dispersants are prepared by reacting a PIB phenol with a polyamine in the presence of formaldehyde. The resulting dispersant has some antioxidant properties (Figure 19.14). This family of dispersants is typically used in gasoline engine oils.

19.3.7 SOOT CONTAMINATION IN DIESEL ENGINE OILS

The soot contaminants in heavy-duty diesel engines usually appear when the engine is operating under very high loads or when the fuel injection is retarded (i.e., injected late in the cranking cycle). Under specific engine conditions, the small soot particles, typically <200 nm, will agglomerate into a larger macrostructure leading to a significant rise in oil viscosity. The structure of the dispersant is key to the lubricant's ability to minimize these structures from forming. Thus, with the correct choice of dispersant, it is possible to reduce the soot-related viscosity increase and also to maintain cleanliness throughout the engine by preventing the large soot structures from settling out.

Over the past 10–20 years, the main reason for adding dispersants to diesel engine oils has been the increasing levels of soot, especially in the modern low-emission engines. During the 1990s, the level of soot in diesel engine oil has trended higher as a result of new engine technologies designed to reduce NO_x and particulate emissions. This trend accelerated in the United States as older engine designs were changed to meet the U.S. 1990 exhaust emission regulations and then more latterly in Europe during 1992 for the Euro I regulations. During this period, retarded fuel injection has been one of the main strategies employed by OEMs to reduce NO_x emissions, which has resulted in more unburned fuel entering the crankcase oil as soot particles. Combined with extended oil drain intervals, it is not unusual to see soot levels as high as 5% in certain types of duty cycles. This trend is set to continue as more legislation appears on the horizon aimed at reducing diesel exhaust emissions.

One of the most important factors in dispersing soot is the dispersant TBN. Typically, as the base number of the succinimide dispersant tends to higher values, the dispersant molecular weight tends to lower values as more of the monosuccinimide structure prevails with more primary nitrogen. This type of dispersant is the most efficient for use in diesel engines, especially modern low-emissions engines where there are high levels of oil soot. The effectiveness of the dispersant is determined by its ability to separate soot particles and thus prevent them from agglomerating. The mechanism whereby this occurs can be represented by the basic dispersant molecule attaching itself to an acidic site on the surface of the soot particle. Assuming that there are sufficient dispersant molecules attached to the soot particle, the PIB chains will prevent the soot particles from coming together. The stability of the soot dispersion is influenced by the molecular weight of the PIB and the level of reactive amines (primary and secondary) per molecule of PIB. A very simplistic representation of a soot-dispersant interaction is given in Figure 19.15. It is fair to say that a lot of energy has been spent finding the most optimum dispersant for dispersing soot as the patent literature demonstrates. Each individual additive company will have their favored structures.

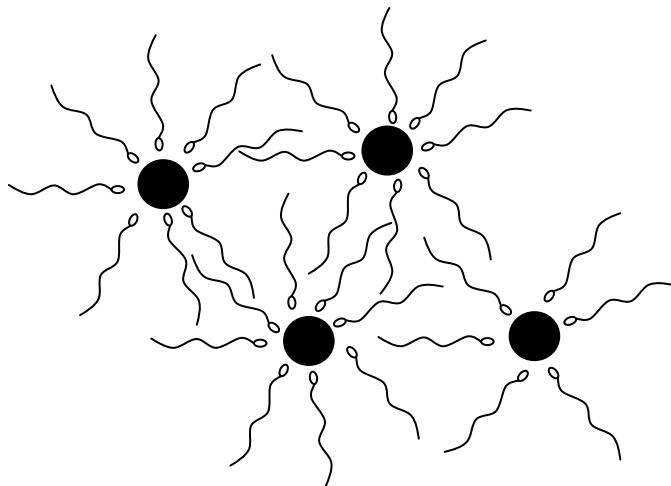


FIGURE 19.15 Dispersant–soot interaction.

TABLE 19.1
Mack Engine Tests to Evaluate Soot-Mediated Oil Thickening

Engine Oil Category	Engine Test	Limits
API CF-4	Mack T-7	$\leq 0.04 \text{ cSt/h}$ (last 50 h of test)
API CG-4	Mack T-8	$\leq 11.5 \text{ cSt}$ at 3.8% soot
API CH-4	Mack T-8E	$\leq 2.1 \times$ sheared viscosity ^a at 4.8% soot

^a Sheared viscosity for Mack T-8E = $(KV_{\text{initial}} + KV_{\text{DIN sheared}})/2$.

19.3.8 SOOT-THICKENING TESTS

As the soot levels of heavy-duty diesel engine oils increased, OEMs, particularly in North America, introduced engine tests to evaluate the oils' ability to disperse soot. One of the tests used to evaluate soot-mediated oil thickening for a low-emissions engine was the Mack T-7. This is included into the Mack EO-K and API CF-4 specifications. As the engine technologies progressed to lower-emission levels, more severe tests were introduced into API CG-4 and API CH-4 specifications. Table 19.1 summarizes the progression of the Mack engine tests and the limits applied to the API C categories.

For light-duty diesel applications, Peugeot introduced the XUD-11 soot-thickening test for the Association of European Automotive Manufacturers (ACEA) passenger car diesel oil approvals. This test, now in its second generation and called the XUD11 BTE, is used to measure oil thickening at soot levels up to 4%. Because the level of soot is much higher compared with what is typically found in European passenger car diesels pre-Euro 2 (1996), the test makes a good measure of the ability of the oil to minimize oxidative soot thickening for small European diesel engines. Criteria have also been applied to the Mercedes OM602A, OM364LA, and OM441LA diesel engine tests in respect of soot-related oil thickening and sludge control. Despite all these tests, the engines that have driven oil formulations to ever-higher levels of basic dispersant are still the Mack engines. A comparison of an API CG-4 formulation and an API CH-4 formulation in the Mack T-8 is shown in Figure 19.16. This demonstrates the progression of dispersant characteristics from API CG-4 to API CH-4.

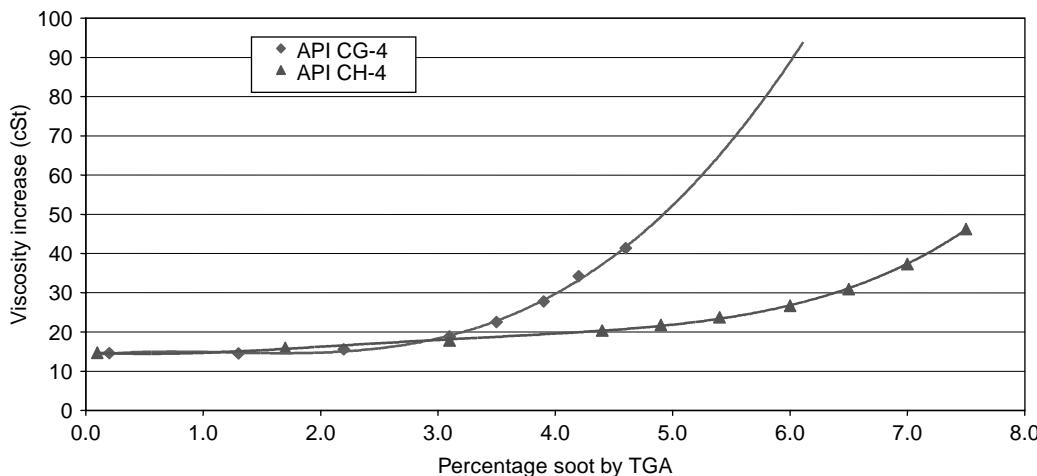


FIGURE 19.16 Comparison of an API CG-4 formulation versus an API CH-4 formulation in the Mack T-8 engine test.

TABLE 19.2
Effect of Dispersant TBN on Mercedes-Benz Fluoroelastomer Seals

Formulation	A	B	C
Max variation of AK6 Viton			
Hardness (Shore A)	-3	0	1
Volume (%)	1	1	0.9
Tensile strength (%)	-8	-32	-46
Elongation rupture (%)	-15	-33	-38
	Pass	Pass	Borderline fail

Note: A, European passenger car gasoline/diesel formulation; B, North American heavy-duty diesel formulation (API CG-4); C, North American heavy-duty diesel formulation (API CH-4).

19.3.9 SEAL TESTING

The balance between soot handling and seal compatibility has provided lubricant formulators with significant challenges over the past 10 years especially as seal testing is a major part of the oil approval process in Europe.

The most difficult issue to contend with is that the highly basic dispersants, used in diesel oil formulations to disperse soot, are aggressive toward fluoroelastomer seals. There are many fluoroelastomer seal tests, one common example being the Volkswagen PV3344 test, which is a requirement for Volkswagen oil approvals. There are also seal test requirements for most of the European engine manufacturers, for example, Mercedes-Benz, MAN, and MTU and collectively through the ACEA. A comparison of three formulations with different dispersants in a Mercedes-Benz seal test is summarized in Table 19.2. This clearly shows that as the soot dispersancy is increased for API CH-4, the MB fluoroelastomer seal test worsens.

19.3.10 CORROSION

Another potential drawback with high TBN dispersants is that they tend to be more aggressive toward Cu/Pb bearings. This has led some additive companies to treat their dispersants with boron compounds,

for example, boric acid to reduce Cu/Pb corrosion. In some cases, this can improve the antiwear properties but usually reduces the effectiveness of the dispersant at dispersing soot. Clearly a balance has to be found, and formulators will use different dispersants to meet the various requirements.

19.3.11 SLUDGE

Under certain conditions, sludge will accumulate in an internal combustion engine. During the 1980s, this problem intensified throughout the world, particularly in gasoline engines in Germany, the United Kingdom, and the United States. The origins of the problem are most likely related to fuel quality, drive cycles, extended oil-drain intervals, and the redirection of blowby gas into the rocker cover. Sludge build up, if left unchecked, can spread throughout the engine, leading to reduced oil flow through the filter and drain-back holes on the valve-deck. In extreme situations, this will lead to engine seizure. The problems were not linked to poor-quality lubricants. However, as lubricant technology evolved, it was found that newer lubricant formulations could help alleviate the problem.

Sludges can be split into low-temperature sludges and high-temperature sludges. Sludges formed at low temperatures will tend to be soft and easily removable from surfaces by wiping. As previously mentioned, the sludge-forming mechanism is thought to be accelerated by the transfer of blowby gases into the oil. Blowby gases contain water, acids, and partially burned hydrocarbons in the form of oxygenates and olefins. The olefins react further with nitrogen oxides to form oil-insoluble products. Fuels with high-end boiling points or with high aromatics also tend to contribute to more sludge. Once formed, highway driving will exacerbate the problem as the engine runs hotter, thereby causing the sludge to bake on.

Sludge formation is reduced by the addition of basic succinimide dispersants particularly the high-molecular-weight types. The addition of boric acid to a succinimide dispersant to make a lower TBN dispersant will reduce the effectiveness of a dispersant in dispersing sludge [7]. Although this indicates that basic dispersants are required to neutralize sludge precursors, it has been found that very high levels of basic nitrogen are not necessarily required for sludge dispersion in gasoline engines. For Sequence VE performance, high-molecular-weight PIB bis-succinimide dispersants have demonstrated excellent performance. This would appear to indicate that the mechanism of sludge formation in a gasoline engine is different from the agglomeration of soot in a diesel engine, which do require high levels of basic nitrogen especially in low-saturate mineral base stocks. Although bis- and monosuccinimide dispersants are used in both gasoline and diesel engine oils, it would be fair to say that, more recently, diesel engine oils have tended to higher levels of basic dispersants, with correspondingly higher levels of PIB monosuccinimides compared with gasoline engine oils. One of the big challenges for formulators since API CG-4 has been to develop lubricants that meet the requirements of both gasoline and diesel engine oils, the so-called universal engine oils. This requires careful formulation with both bis- and monosuccinimide dispersants.

When formulating engine oil, it is also important to consider the interactions between the succinimide dispersant and other additives such as zinc dialkyldithiophosphate (ZDDP). A complex between ZDDP and succinimide polyamine has been observed in laboratory tests especially where there is a high basic nitrogen to ZDDP ratio [8]. As the level of basic dispersant is increased, sludge and wear will improve. Above a critical concentration of dispersant, the antiwear properties of the ZDDP will be dramatically reduced as the basic nitrogen forms a stable complex with the ZDDP effectively reducing its antiwear capability. It has been demonstrated that the ZDDP–amine complex retards the rate of peroxide decomposition by ZDDP [9], which in turn accelerates the formation of sludge. Sludge will usually increase in line with wear, so clearly a high level of ZDDP with a sufficient dispersant level to disperse the sludge is required. High levels of ZDDP permit high levels of dispersant to be used in the lubricant thereby giving superior engine sludge and wear performance. However, phosphorus has been implicated in exhaust catalyst poisoning. Because of this, a maximum phosphorus limit of 0.1 wt% in the lubricant has been applied to recent API and ILSAC specifications. This means that where phosphorus limits are imposed for API SJ and ILSAC

GF-3 lubricants, careful choice of dispersant and ZDDP are required. The phosphorus limits are set to be reduced further for ILSAC GF-4 thereby providing more challenges for the lubricant to meet the sludge and wear requirements in future engines.

19.3.12 SLUDGE ENGINE TESTS

Although sludge tests have been around for many years, the most significant lubricant tests to address the sludge problems during the 1980s and 1990s were the Sequence VE and Mercedes M102E. More recently, the Sequence VG and the MB M111E have superseded these tests and have become the current benchmarks for measuring lubricant sludge-handling performance in Europe and North America. Table 19.3 lists the test conditions for the various gasoline sludge tests. The Sequence IIIE and Sequence IIIF are also included since high-temperature sludge is a rated parameter in these gasoline engine tests.

High-temperature sludges are also present in diesel engines and are a rated parameter for several engine tests, particularly the Cummins M11 for API CH-4. Dispersants based on high-molecular-weight PIB are essential in minimizing sludge build up in this test. Sludge is also a rated parameter for the Mercedes-Benz OM364LA and OM441LA engine test although it is not as critical parameter as the Cummins M11 engine test.

19.4 ANTIWEAR

19.4.1 INTRODUCTION

As the power of engines has risen, the need for additives to prevent wear has become more important. Initially, engines were lightly loaded and could withstand the loading on the bearings and valve train. Corrosive protection of bearing metals was one of the early requirements for engine oils. Fortunately, the additives used to protect bearings usually had mild antiwear properties. These antiwear agents were compounds such as lead salts of long-chain carboxylic acids and were often used in combination with sulfur-containing materials. Oil-soluble sulfur-phosphorus and chlorinated compounds also worked well as antiwear agents. However, the most important advance in antiwear chemistry was made during the 1930s and 1940s with the discovery of ZDDPs [10–12]. These compounds were initially used to prevent bearing corrosion but were later found to have exceptional antioxidant and antiwear properties. The antioxidant mechanism of the ZDDP was the key to its ability to reduce bearing corrosion. Since the ZDDP suppresses the formation of peroxides, it prevents the corrosion of Cu/Pb bearings by organic acids.

19.4.2 WEAR MECHANISMS

Antiwear additives minimize wear in a mixed or partial lubricant film operating under boundary conditions (Figure 19.17). A classic example of boundary lubrication is in a nonconforming contact such as a cam on a follower. The partial lubricant film is most likely to occur when the oil is not sufficiently viscous enough to separate the two surfaces completely.

The tendency to boundary lubrication increases as the temperature rises due to the viscosity-temperature dependence of the lubricant. Low contact speeds, high contact pressures, and rough surfaces will also contribute to more boundary lubrication. If these circumstances are taken to the extreme and minimal or if no lubricant film exists, then the maximum surface contact will exist (Figure 19.18). This is defined as an extreme-pressure (EP) contact and is usually associated with very high temperatures and loads. Additives that prevent wear in an EP contact typically require higher activation temperatures and load than an antiwear additive.

Antiwear and EP additives function by thermally decomposing to yield compounds that react with the metal surface. These surface-active compounds form a thin layer that preferentially shears under boundary lubrication conditions.

TABLE 19.3
Sludge Engine Test Comparison

Test	Cylinder Configuration	Displacement (cc)	Test Duration (h)	Test Operation	Duration (h)	Speed (rpm)	Power (kW)	Coolant Temperature (°C)	Oil Temperature (°C)	Fuel type
Sequence IIIE (Buick)	V-6	3800	64	Steady speed	64	3000	50.6	115	149	Phillips GMR leaded gasoline Howell EEE unleaded
Sequence IIIF (Buick)	V-6	3800	80	Steady speed	80	3600	75.0	115	155	Phillips J unleaded
Sequence VE (Ford)	1.L.-4 Slider Follower	2290	288	Cyclic	2.00 1.25 0.75	2500 2500 750	25.0 25.0 0.75	51.7 85.0 69 kPa	68.3 98.9 46.1	Phillips J gasoline Unleaded
Sequence VG (Ford)	V-8 Roller Follower	4600	216	Cyclic	2 1.25 0.75	1200 2900 700	69 kPa 66 kPa Record	57 85 45	68 100 45	Unleaded gasoline
Mercedes-Benz M-111E Sludge	1.L.-4	1998	224	Cyclic	48 h cold 75 h WOT 100 h cyclic	Idle to maximum	40–98	45–130	45–130	CEC RF-86-T-94 (ULG)
Nissan VG-20E		2000	200	Cyclic	200	800–3500	2–9 kgf m	38–100	50–117	Unleaded gasoline
Toyota 1G-FE		2000	48	Steady speed	48	4800	6 kgf m	120	149	Unleaded gasoline

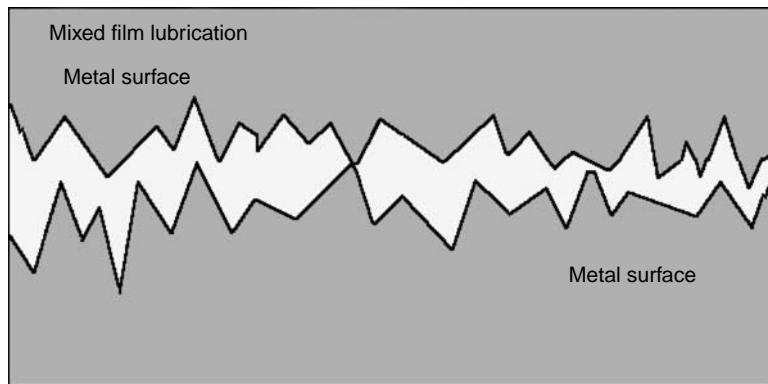


FIGURE 19.17 Mixed film lubrication.

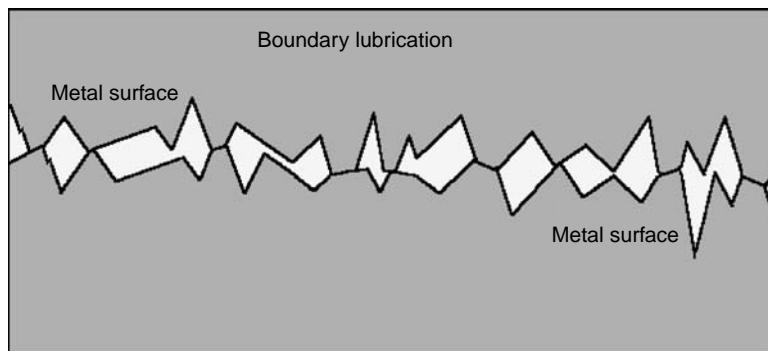
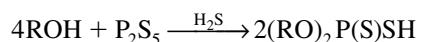


FIGURE 19.18 Boundary lubrication.

After the discovery of ZDDP, it rapidly became the most widespread antiwear additive used in lubricants. As a result, many interesting studies have been undertaken on ZDDP with many mechanisms being proposed for the antiwear and antioxidant action [13–17]. The performance of the ZDDP is strongly influenced by the decomposition pathways. These pathways are thermolysis, oxidation, and hydrolysis, which in turn depend on the conditions under which the ZDDP is working. In general, it can safely be assumed that the degradation products of the ZDDP form a film on the metal surface, typically rich in phosphorus and oxygen and possibly polymeric. As mentioned earlier, this layer preferentially shears under boundary lubrication, thus reducing the wear on the metal surfaces. As this layer needs to be constantly replenished, the concentration of ZDDP in the lubricant is critical. It is therefore not unusual to find up to 2 wt% of ZDDP in a modern lubricant. This equates to a maximum level of ~0.15% phosphorus in the lubricant.

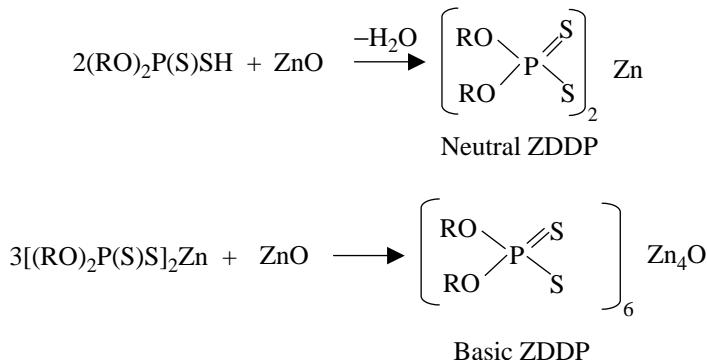
19.4.3 ZDDP PREPARATION

ZDDP is prepared by reacting a dialkyldithiophosphoric acid with zinc oxide. The first stage of the process involves the preparation of the acid. The acid is prepared from an alcohol and phosphorus pentasulfide:



dialkyldithiophosphoric acid

The acid is then neutralized with zinc oxide to yield ZDDP at ~70 to 90°C. There are two types of ZDDP structure, neutral and basic, both of which can be observed by ^{31}P NMR (nuclear magnetic resonance). The basic salt is observed at 104 ppm with the neutral salt at 101 ppm. The neutral salt exists as an equilibrium mixture of monomer, dimer, and oligomers. The basic salt consists of a central oxygen atom surrounded tetrahedrally by four zinc atoms and six dithiophosphate groups attached symmetrically to the six edges of the tetrahedron. In most industrial processes, the ZDDP is left slightly basic for providing improved stability.



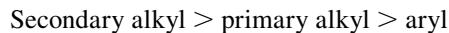
19.4.4 ZDDP DEGRADATION MECHANISMS

The type of alcohol used to prepare the ZDDP will determine its thermal and oxidative stabilities. The most reactive ZDDPs are derived from secondary alcohols and especially those that are lower in molecular weight. Solubility is a limiting factor at carbon numbers less than five; therefore, most ZDDPs will use alcohols with carbon numbers greater than five. Alcohols with a lower carbon number may be used if they are combined with a higher alcohol during synthesis.

The type of alcohol used in the preparation will have a significant effect on the stability. In most cases, the thermal stability of the ZDDP is as follows:



The least stable ZDDPs tend to provide improved wear at lower engine oil temperatures. Therefore, the following applies for antiwear action:



Tables 19.4 through 19.6 indicate the performance of various ZDDPs in a range of gasoline engine wear tests.

TABLE 19.4
Comparison of ZDDP Types in Sequence VE Wear Test

Alcohol Type	Zn (%) as ZDDP	Sequence VE Wear	
		Average (μm)	Maximum (μm)
Mixed	0.127	36	203
C ₃ secondary			
C ₈ primary			
C ₈ primary	0.124	121	495

TABLE 19.5
Comparison of ZDDP Types in Sequence VD Wear Test

Alcohol Type	Zn (%) as ZDDP	Sequence VD Wear Average (μm)
C ₆ secondary	0.13	18
Mixed		
C ₆ secondary		
C ₈ primary	0.13	48

TABLE 19.6
Comparison of ZDDP Types in Sequence IID Wear Test

Alcohol Type	Zn (%) as ZDDP	Sequence IID Wear Average (μm)
Mixed	0.13	25
C ₆ secondary		
C ₈ primary		
C ₈ primary	0.13	175

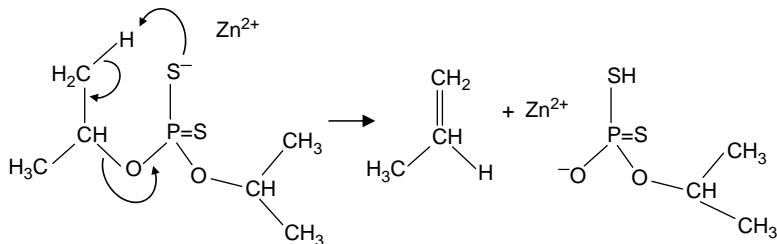


FIGURE 19.19 β -Elimination (secondary ZDDP).

The mechanism by which secondary alcohol ZDDPs thermally degrade is shown in Figure 19.19. The degradation mechanism proceeds rapidly as the temperature rises and is made easier as a hydrogen on the β position readily leaves to form the alkene. This mechanism may explain why the secondary ZDDPs are much more active antiwear agents particularly at lower temperatures.

In contrast, the primary alcohol ZDDPs are more stable due to the absence a tertiary hydrogen on the β carbon and therefore more useful for higher-temperature operation and wear such as that found in diesel engines. The mechanism of thermal degradation is through sequential alkyl transfers and relies on an intermolecular alkyl transfer (Figure 19.20).

19.4.5 SEQUENTIAL ALKYL TRANSFERS (PRIMARY ZDDP)

Other additives will affect the rate of thermal degradation of the ZDDP. For instance, it is known that succinimide dispersants will complex with the ZDDP, making it more resistant to thermal degradation. It is therefore important to recognize this when formulating an oil additive. Too much dispersant may tie up the ZDDP, leaving it unable to form an effective antiwear film. A balance has to be found, which is dependent on the ZDDP type and the dispersant structure.

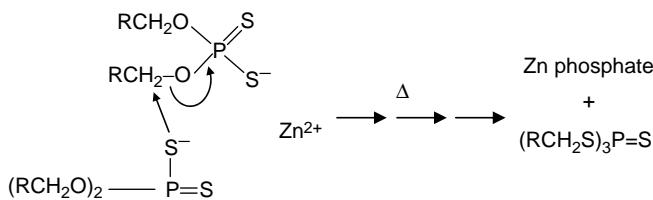


FIGURE 19.20 Sequential alkyl transfers (primary ZDDP).

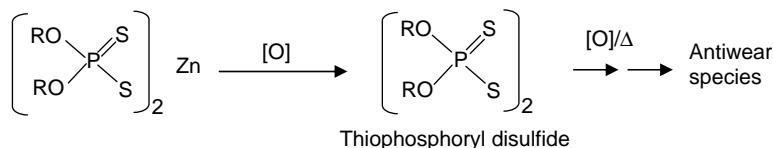


FIGURE 19.21 Thiophosphoryl disulfide formation. ([O] can be almost any oxidant such as O_2 , $ROOH$, H_2O_2 , Cu^{2+} , and NO_x .)

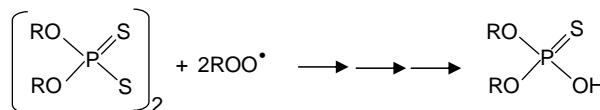


FIGURE 19.22 Thiophosphoryl disulfide decomposition of peroxy radical.

ZDDP, also degrades at lower temperatures by oxidation ($<100^\circ\text{C}$), yielding compounds that are beneficial antiwear agents (see Figure 19.21). This leads to the mechanism of oxidative inhibition by ZDDPs, which occurs through the thiophosphoryl disulfide intermediate (see Figure 19.22). A more detailed mechanism of the antioxidant function of the thiophosphoryl disulfide intermediate has been reported [18].

The effectiveness of ZDDP in decomposing hydroperoxides has been linked to wear rates in a motored engine test [19]. Secondary ZDDPs were better at decomposing peroxides than their primary counterparts. There is a plethora of papers in the literature with detailed analyses of the various degradation pathways for the ZDDP molecule and its subsequent effect on the wear and oxidation properties of the lubricant [13,14,20–22]. Although these give an excellent insight into the ZDDP degradation mechanisms, it must be remembered that the degradation pathways are strongly dependent on the test conditions, that is, temperature and amount and type of oxidants.

19.4.6 ANTIWEAR TESTS

The Sequence VE and Sequence IVA gasoline engine tests (for API SJ and ILSAC GF-3, respectively) are designed to test the ability of a lubricant to prevent low-temperature sliding wear in the valve train of a gasoline engine. Secondary ZDDPs will usually perform better than primary ZDDPs in both tests. However, there are certain cases where it is possible to achieve a passing test result with primary ZDDP especially with formulations in which a low level of detergent is present. High-temperature gasoline wear is measured in the Sequence IIIE and Peugeot TU3 scuffing test and responds well to most types of ZDDP.

Wear in a diesel engine is usually accelerated by the presence of soot. There are several tests to measure wear in diesel engines of which the four most common tests are listed in Table 19.7.

TABLE 19.7
Diesel Wear Tests

Engine Test	Specification	Wear Measured
GM roller follower wear test	API CG-4, CH-4	Roller follower wear
Cummins M11	API CH-4	Valve bridge wear
Mercedes OM602A	MB Sheet 228.X, 229.X	Cam nose wear
	ACEA B and E sequences	Cylinder wear
Mitsubishi 4D34T	Global DHD-1, JASO DH-1	Cam nose wear

In addition, field tests such as the Volvo VDS and Scania LDF specifications also specify limits for wear on critical engine components. Depending on the operating temperature of the oil, primary or secondary ZDDPs will be used. For heavy-duty diesel engine oils, both primary and secondary ZDDPs are widely used. In certain cases, an aryl ZDDP may be used for maximum thermal stability.

19.4.7 OTHER ANTIWEAR AGENTS

Boron is widely used to provide antiwear properties in lubricants. A common method is to react boric acid with the amine moiety of a succinimide dispersant. The boron works by reacting at the metal surface to form boric acid, which has a layered structure with weak interlayer bonds [15]. On its own, it is unlikely to give the same level of antiwear performance as ZDDP, but when used in combination with other antiwear additives, it will reduce wear.

19.5 ANTIOXIDANTS

19.5.1 INTRODUCTION

Most of the lubricants, by virtue of being hydrocarbon based, are susceptible to oxidation [23,24]. If oxidation is not controlled, lubricant decomposition will lead to oil thickening; sludge formation; and the formation of varnish, resin, and corrosive acids [25,26].

The oxidation reactions that occur in a lubricant at elevated temperatures in the presence of atmospheric oxygen may lead to declined lubricant performance such as significant increase in kinematic viscosity observed in severe service conditions or during extended drain intervals (Figure 19.23).

In general, all types of base oils require addition of antioxidants depending on the amount of unsaturation and *natural inhibition* present. The refined mineral base oils contain *natural inhibitors* in the form of sulfur and nitrogen compounds sufficient for many applications. The oxidative stability of such oils shows a distinct, relative long induction period. In contrast, hydrorefined oils do not contain these natural inhibitors or contain them only in small quantities. Besides sulfur and nitrogen compounds, other compounds such as aromatics or partially hydrogenated aromatics and phenolic oxidation products can be of importance; their inhibiting effect is lost during various refining processes. Traditional mineral oils, such as group I and group II base stocks, show moderate oxidative resistance. Synthetic oils such as polyol esters and hydrogenated polyalpha-olefins (PAOs) exhibit the highest oxidative stability due to their low unsaturated content. The most unstable oils include highly unsaturated vegetable triglycerides such as corn, sunflower, canola, and peanut.

An overall scheme of lubricant oxidation starts with the conversion of hydrocarbon substrates to carbonyl compounds (Figure 19.24). Coupling of these polar compounds through aldol and related reactions builds molecular weight. Eventually, at very high molecular weight (i.e., >1000), the oil is converted into insoluble sludge, which can precipitate on the engine hardware.

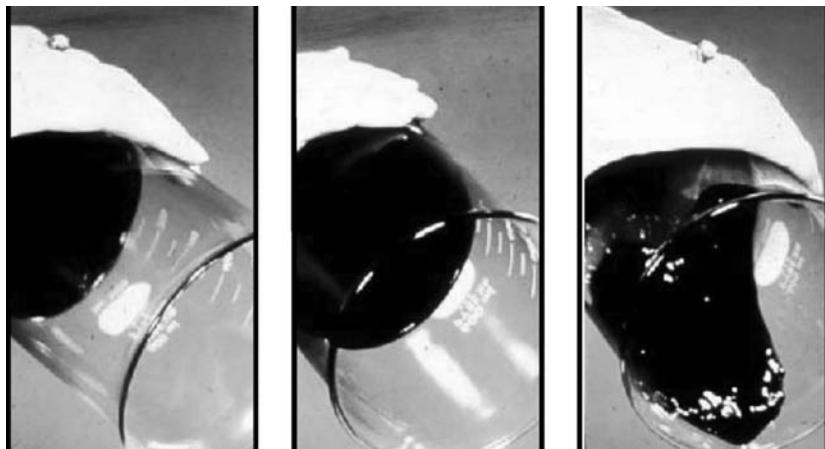


FIGURE 19.23 Antioxidants can prevent premature oil thickening.

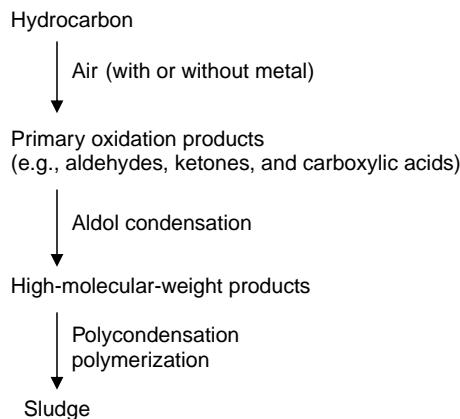
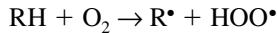


FIGURE 19.24 Degradation of mineral oils.

19.5.2 MECHANISM OF OXIDATION OF LUBRICATING OILS

The oxidation of petroleum hydrocarbons proceeds according to a radical chain mechanism through alkyl and peroxy radicals in three stages [27].

19.5.2.1 Initiation

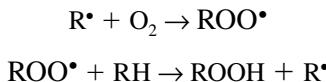


The initiation step starts by the slow abstraction of a hydrocarbon proton by molecular oxygen to form alkyl and hydroperoxy free radicals. This process is also referred to as *autooxidation* and is favored by time, higher temperature, and transition metal (i.e., iron, nickel, and copper) catalysis.

19.5.2.2 Propagation

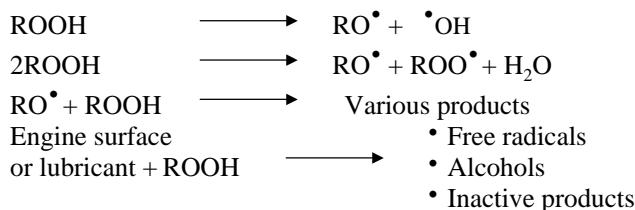
Propagation starts by the rapid reaction of more oxygen with an alkyl-free radical to form an alkyl peroxy radical, which is also capable of hydrocarbon abstraction to form hydroperoxide

and another alkyl radical. The alkyl radical then may react with more oxygen starting the chain over [25].



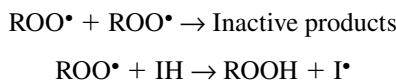
19.5.2.3 Peroxide Decomposition

Alkyl hydroperoxides are quite reactive and may decompose, especially at higher temperature, to form additional radical species. These can undergo further abstraction and chain propagation reactions that increase the overall oxidation process. Alkyl peroxides and alkyl peroxy radicals also decompose to neutral oxidation products such as alcohols, aldehydes, ketones, and carboxylic acids. Hydroperoxide decomposition to neutral oxidation products can be viewed as a chain termination step, since free additional radicals are not formed.



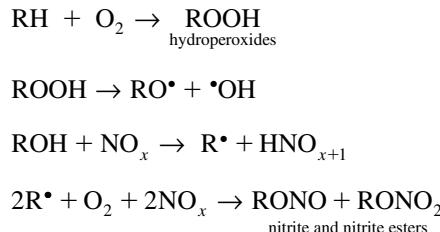
19.5.2.4 Termination (Self and Chain Breaking)

During termination stage, the radicals either self-terminate or terminate by reacting with oxidation inhibitors [23].



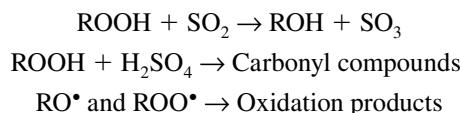
Alternative oxidation pathways are listed later.

19.5.2.5 Radical Formation



Nitrogen oxides can react with alcohols (an oxidation product) to form alkyl free radicals, which react with NO_x and oxygen to form nitrate and nitrite ester oxidation products.

19.5.2.6 Decomposition and Rearrangement



The action of sulfur dioxide and H_2SO_4 (from $\text{SO}_3 + \text{water}$) on alkyl hydroperoxides also leads to neutral oxidation products such as alcohols and carbonyl compounds. Aldehydes and ketones can react further and form polymers. Carboxylic acids can attack metallic hardware: rings, valve train, and bearings leading to extensive wear. Furthermore, they can form metal carboxylates, which further increase the oxidation rate. Wear metals can also enhance the rate of oxidation [26].

19.5.3 OXIDATION INHIBITORS

Oxidation inhibitors can be classified into the following manner:

1. Radical scavengers
 - a. Nitrogen-containing inhibitors—aryl amines
 - b. Oxygen-containing inhibitors—phenols
 - c. ZDDPs
2. Hydroperoxide decomposers
 - a. Sulfur-containing inhibitors—sulfides, dithiocarbamates, and sulfurized olefins
 - b. Phosphorus-containing inhibitors—phosphites and ZDDPs

Note that ZDDPs function by both antioxidant mechanisms in addition to providing antiwear protection (covered in Section 19.4.2). This dual- (or tri-) functional ability of ZDDPs to provide antiwear performance and antioxidantcy by two different pathways explains why these additives are by far the most effective inhibitors, especially on a cost/performance basis.

Phenols or amines of specific structures function as radical acceptors by transfer of a hydrogen atom from the oxygen or nitrogen atom to the hydrocarbon or peroxy radical. The inhibitor radicals thus formed react through radical combination or electron transfer to give ionic compounds or by addition reactions or formation of complexes that do not maintain the radical chain mechanism of the autoxidation reaction. In further reactions, very often ethers, betones, polyaromatic systems, etc. are formed.

19.5.4 HINDERED PHENOLS AND ARYLAMINES

Hindered phenols and arylamines are two prominent examples of inhibitors that act as radical scavengers through hydrogen transfer. Figure 19.25 illustrates the mechanism of phenol performance.

Among various types of phenols, polyalkylphenols have significant performance advantage over nonalkylated compounds (Figure 19.26). The effect of substituents demonstrates the role of

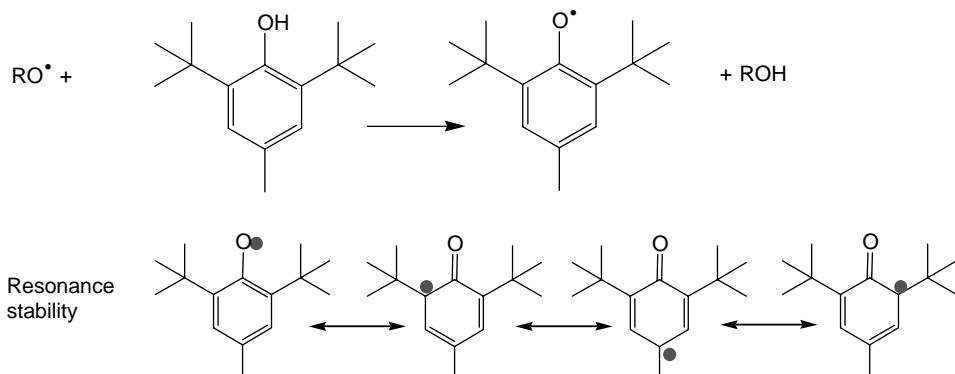
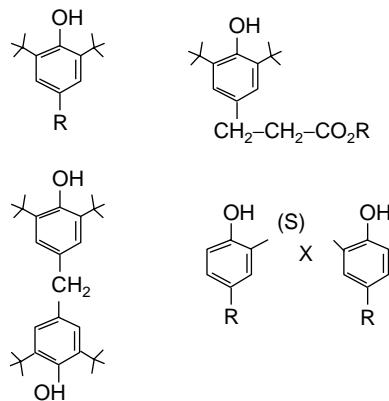
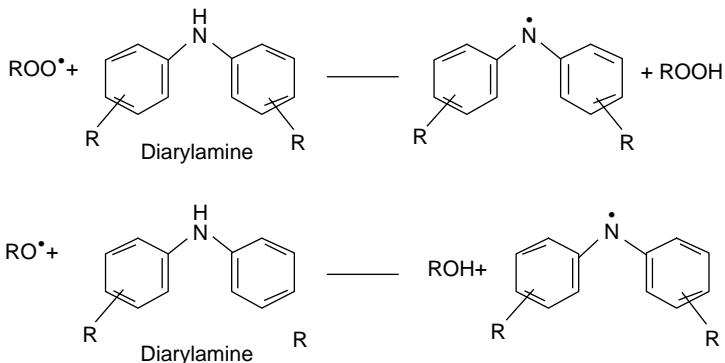


FIGURE 19.25 Mechanism of inhibition by hindered phenols.

**FIGURE 19.26** Major types of phenolic antioxidants.**FIGURE 19.27** Mechanism of inhibition by arylamines.

electron density and steric hindrance at the phenolic oxygen; an increase in the number of alkyl radicals and the introduction of electron donors in the *o*- and *p*-positions increase the efficiency, whereas the introduction of electron acceptors reduces it. α -branching of alkyl groups in *o*-position or increasing the alkyl group to C4 in *p*-position has a beneficial effect [27].

A new type of antioxidant involves the base-catalyzed addition of hindered phenol to Michael acceptors such as acrylate esters. Although more expensive than simple alkylphenols, the originators of this chemistry claim improved upper piston deposit control in certain diesel engine tests and better seal compatibility than arylamines.

S-coupled ($X = 1,2$) alkylphenols combine the antioxidant benefits of the phenol and sulfide groups.

The mechanism of oxidation inhibition (based on generation of nitrogen radicals) by arylamines is presented in Figure 19.27.

In general, the alkylated arylamines are more effective antioxidants than alkylphenols because they are

- Able to trap more equivalents of radicals: four versus two
- Able to better stabilize nitrogen or nitroxyl radicals (by two aryl rings instead of one)
- Able to operate at both low and high-temperature mechanisms (the latter of which regenerates the alkylated arylamine)

Oil-soluble amines such as diphenylamine, phenyl- α -naphthylamine are the most common type of amine antioxidants used in lubricants. Diphenylamine can be alkylated with aluminum chloride catalyst and a mixture of branched nonene olefins. A mixture of mono- and dialkylate (Figure 19.28) is intentionally targeted by the reactant charge ratio to produce a liquid product. Diphenylamine is particularly suited for applications at elevated temperatures. Therefore, it is often used to lubricate supersonic aircraft engines and bearings. In these applications, arylamines prevent sludge formation in synthetic ester oils.

19.5.5 SULFUR AND PHOSPHORUS CONTAINING ANTIOXIDANTS

Sulfur, phosphorus, and compounds containing both the elements decompose peroxides by reducing the hydroperoxide in the radical chain to alcohols; the sulfur or phosphorus atoms are correspondingly oxidized (Figure 19.29). Bivalent sulfur compounds (sulfides, etc.) yield sulfoxides and sulfones; trivalent phosphorus compounds (phosphates) are transformed into pentavalent ones (phosphates). Organic compounds of tetravalent sulfur act as peroxide decomposers, but the corresponding hexavalent, in line with theory, do not. Destruction of hydroperoxides is important so that these intermediates do not decompose into radicals, which can continue the chain oxidation process.

Phosphates are somewhat hydrolytically unstable, and due to limits on phosphorus level in crankcase oils, these additives are generally limited to application in gear lubricants. ZDDPs are more efficient phosphorus-containing antioxidants for crankcase oils, with the added benefit of antiwear performance.

ZDDPs convert hydroperoxides to one equivalent of an alcohol and a carbonyl compound (Figure 19.30). The ZDDP is regenerated intact and is available to convert another hydroperoxide molecule. Many cycles of hydroperoxide decomposition are carried out by the ZDDP, before its eventual breakdown.

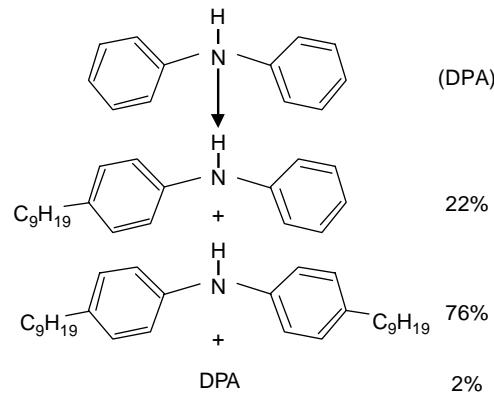


FIGURE 19.28 Alkyl aromatic amine as antioxidant.

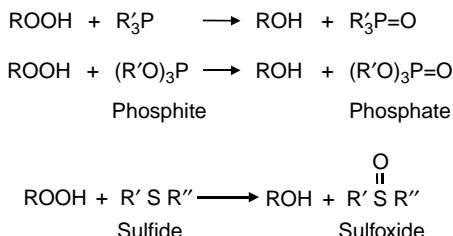
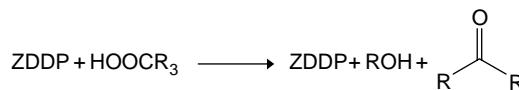


FIGURE 19.29 Mechanism of S- and P-containing antioxidants.

**FIGURE 19.30** ZDDPs hydroperoxide destruction.

19.5.6 SULFUR COMPOUNDS

Elemental sulfur is an efficient oxidation inhibitor; however, it shows a strong corrosion tendency. From the practical approach, numerous dialkyl sulfides and polysulfides, diaryl sulfides, modified thiols, mercaptobenzimidazoles, thiophene derivatives, xanthogenates, zinc dialkyldithiocarbamates, thioglycols, thioaldehydes, and others have been examined as inhibitors. Dibenzyl disulfide must be mentioned among the alkyaromatic sulfur compounds.

Alkylphenol sulfides that are formed in the reaction of alkylphenols such as butyl-, amyl-, or octylphenol with sulfur chloride are more active than the compounds of the dibenzyl disulfide type, due to the position of sulfur next to the OH group.

Modern compounds of this type contain mostly *tert*-butyl radicals besides the methyl groups, as for instance, 4,4'-thio-bis-(2-*tert*-butyl)-5-methylphenol. Sulfur–nitrogen compounds are also suited as oxidation inhibitors for lubricating oils (2-mercaptopbenzimidazole, mercaptotriazines, reaction products of benzotriazole alkylvinyl ethers or esters, phenothiazine, and its alkyl derivatives). Among the sulfur-containing carboxylic acid esters, 3,3'-thio-bis-(propionic acid dodecyl ester) and bis-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-malonic acid-bis-(3-thio-pentadecyl) ester have been applied with success. These compounds have been replaced by the dialkyldithiophosphates due to their broad application spectrum. Sulfoxides, sometimes in combination with aromatic amines, have also been utilized.

19.5.7 PHOSPHORUS COMPOUNDS

Red phosphorus possesses oxidation-inhibiting properties but cannot be used because of its corrosivity toward nonferrous metals and alloys. Triaryl and trialkyl phosphates have been proposed as thermally stable inhibitors; however, their applications are limited. Combined phosphoric acid–phenol derivatives such as 3,5-di-*tert*-butyl-4-hydroxybenzyl-phosphonic acid dialkyl esters or phosphonic acid piperazides have a better effect.

19.5.8 SULFUR–PHOSPHORUS COMPOUNDS

Today, metal salts of thiophosphoric acids are used predominantly as oxidation inhibitors for crankcase oils. In principle, compounds that contain sulfur and phosphorus are significantly more efficient than inhibitors that contain only sulfur or phosphorus. Most widely used are the ZDDPs that are prepared by the reaction of P_2S_5 with the respective higher alcohols (e.g., hexyl, 2-ethylhexyl, and octyl alcohols), followed by the reaction with zinc oxide. The temperature of the exothermic salt formation is kept at 20°C by successive addition of zinc oxide and cooling and is limited even at the end of the reaction to 80°C because of the thermal ability of the free dialkyl dithiophosphoric acids. They react very corrosively with metals and are toxic. Metal dialkyldithiophosphates are prepared in mineral oil solution. Their solubility in hydrocarbon oils increases with the increasing number of carbon atoms of the alkyl residues and is satisfactory with the diamyl compounds and higher. Longer-chain derivatives act as solubilizers for short-chain products. Metal dialkyldithiophosphates act not only as antioxidants but also as corrosion inhibitors and EP additives.

The efficiency of Zn dialkyldithiophosphates (with octyl or cetyl and, respectively, propyl, butyl, or octyl radicals in various combinations) decreases with increasing molecular mass of the alcohol substituents. The best results have been obtained with isopropyl and isoamyl radicals.

Reaction products of P_2S_5 with terpenes (dipentene, pentene), polybutenes, olefins, and unsaturated esters belong to the same group; among these, the terpene and polybutene products have been proposed for crankcase oils. Metal dialkyldithiophosphates serve at the same time as detergents, EP additives, and anticorrosion agents, when the corrosion is caused by oxidation products; in this case, the metal is protected from attack by organic acids by the formation of sulfide or phosphate films. 2,5-Dimercaptothiadiazole derivatives have a similar effect.

19.5.9 ANTIOXIDANT SELECTION, SYNERGISM, AND TESTING

Most of the crankcase engine antioxidant needs are met by the ZDDP. Today's higher-temperature engines (Table 19.8) require supplemental ashless antioxidants to pass the Sequence IIIE engine. Therefore, modern engine oils use three or more different types of antioxidants, with the highest level (0.1–0.15 wt%) being the ZDDP.

The previous generation engine to measure lubricant oxidation was the Sequence IID, which required a maximum oil kinematic viscosity increase of 375 cSt at 80 h of operation. A fail result is shown for the base formulation at less than half way through the test (30 h). Addition of 0.5 wt% arylamine antioxidant to base formulation results in easily meeting the kinematic viscosity increase requirement. The same pass result could be obtained by increasing the ZDDP level, but the current limits on phosphorus level prevent this option.

Another important antioxidant phenomenon is known as inhibitor synergism. Another way of stating the definition shown here is “1/2 (or partial) levels of two compounds produces a greater benefit than a full level of either alone.” Synergistic combinations of inhibitors can extend a lubricant's temperature and use ranges thereby boosting its performance.

Either formulations containing 0.5 wt% of alkylphenol (rating = 63) or 0.5 wt% of arylamine as inhibitor (rating = 60) alone do not provide a sufficient deposit control to pass this test. However, a mixture of two inhibitors at 0.25 wt% each offered an outstanding rating, 71, which is a pass result.

The efficiency of antioxidants in lubricating oils is tested on the laboratory scale in a battery of bench tests and engine tests under more severe conditions. This is particularly true for motor oils, where only the practical test in the engine can assess, for instance, the high-temperature efficiency of dithiophosphates and the frequently antagonistic effects of dispersants and oxidation inhibitors in a given additive combination.

As a rule, however, the final formulations of products are subjected to time-consuming field testing.

TABLE 19.8
Approximate Temperature of Internal Surfaces in a V-8 Engine

Area of Engine	Temperature Range (°C)
Exhaust valve head	650–730
Exhaust valve stem	635–675
Combustion chamber gases	2300–2500
Combustion chamber wall	204–260
Piston crown	204–426
Piston rings	149–315
Piston (wrist) pin	120–230
Piston skirt	93–204
Top cylinder wall	93–371
Bottom cylinder wall	Up to 149
Main bearings	Up to 177
Connecting rod bearings	93–204

Some screen and engine oxidation performance tests are as follows

The ASTM D-943 or turbine oil oxidation test is used for hydraulic oils. In this screen, molecular oxygen is blown through a quart of the oil at 95°C containing an iron and copper coil. The time taken to reach an oil TAN of 2 are recorded, with a pass result considered to be anywhere from 1000 to 3000 h, depending on the specific customer approval.

The ASTM D-2272 (rotary bomb oxidation test [RBOT]) and ASTM D-4742 (thin-film oxygen uptake test [TFOUT]) are two other industry-recognized bench tests. These screens use pressure to accelerate the oxidation process to simulate the lubricant's extended service or "real-world" conditions. The RBOT also finds utility for formulating industrial oils, whereas the TFOUT is used to measure the oxidation performance of passenger car and heavy-duty diesel engine oils.

Indiana stirred oxidation test (ISOT) has several versions, with temperature ranging from 150 to 165°C. The beaker of oil is stirred vigorously for 24 h in the presence of iron and copper catalysts. Measurements include the oil's kinematic viscosity increase, TAN built up, and amount of pentane insoluble sludge generated.

Pressure differential scanning of calorimetry (PDSC) is designed to predict the improvement inhibitors add to an oil of poor oxidative stability.

Passenger car motor oil (PCMO) engines for oxidation performance consist of

- The Sequence IIIE and Sequence IIIF to measure an oil's viscosity built up
- The Sequence VE and Sequence VG to measure sludge control (Table 19.3)

The extreme temperature ranges reached in Sequence VE engine are given in Table 19.8. The oil bulk temperature does not reach these high temperatures, but the fluid operates in proximity of these parts. Since the oxidation process is accelerated by temperature, one can see why an oil's antioxidant system must be specially designed to be effective.

Typical passenger engine design has been undergoing dramatic changes since it has been introduced to the public in the early 1920s.

Table 19.9 summarizes several major design/fluid system changes observed. The two critical parameters affecting lubricant stability and projected life are

1. The large increase in the engine oil temperature (2×)
2. Steady decrease in the amount of lubricant (~5×)

These two factors have put extra demands on the lubricant's antioxidant system, whereas somewhat recent limits on phosphorus level have "capped" the use of ZDDP.

TABLE 19.9
Changes in the V-8 Engine over Past Seven Decades

	1920	1960	1990
Engine capacity (L)	6	2	1.6
Brake horse power	50	70	130
Engine speed (rpm)	1200	5000	7000
Oil temperature (°C/°F)	60/140	90/194	130/266
Oil capacity (L)	14	4.5	3.5
Valve train	Side valves	Push rod, overhead valves	Twin overhead camshafts four valves
Fueling system	Single-choke carburetor	Multichoke carburetor	Fuel injected

19.6 VISCOSITY MODIFIERS

19.6.1 INTRODUCTION

VMs are added to a lubricant formulation to reduce the viscosity–temperature dependence of the base oils. This class of lubricant additives is the technology that enabled the development of multigrade lubricants in the 1960s. The primary feature of multigrades is that they allow the engine to start at low temperatures while providing sufficient viscosity at elevated temperatures to protect the engine against wear.

A lubricant oil formulation based on a group I mineral base stock without a VM additive will have a limited range of temperature operation since it has a relatively strong viscosity–temperature relationship. VMs are oil-soluble polymers that, when added to a base oil and additive mixture, will thicken the mixture at high temperatures while having a minimal thickening effect at lower temperatures (Figure 19.31). A very simplified mechanism to explain this phenomenon would be that the polymer–oil interaction at low temperature is minimal but increases as the temperature rises. This interaction of the polymer with the base oil at elevated temperatures increases the effective hydrodynamic volume of the polymer thereby increasing the effective volume fraction of the VM. This, in turn, leads to an increase in lubricant viscosity. To make use of this phenomenon, a low-viscosity base oil mix is used to which the VM and additive mixture is added. The low-viscosity base oils permit the oil to flow freely at low temperatures, whereas the VM increases the viscosity at higher temperatures.

19.6.2 VISCOSITY MODIFIER TYPES

There are several types of VMs available to the oil formulator. Each of these has strengths and weaknesses. Therefore, it is sensible to select the correct type for the intended application. Table 19.10 details some of the most common VMs in use today.

OCPs are prepared by either Ziegler–Natta or metallocene catalysis. Besides containing ethylene and propylene, diene monomers may be added to improve the handling characteristics of the solid form of the polymer. The relative amounts of each monomer will dictate the solubility of the copolymer. As the level of ethylene in the copolymer increases, polymer solubility decreases especially at low temperatures. This effect at low temperatures has the beneficial effect of lowering the polymer contribution to subambient viscosity. But one must be careful not to go too far because, at very high ethylene contents, the OCP will drop out of solution or form gels at low temperature. This may only manifest itself after several month storage at low temperatures. The monomer sequence distribution is also critical and can be carefully controlled to maximize the amount of ethylene in the copolymer and hence give minimal low-temperature thickening. OCPs are the most popular type of VM in use today due to their high thickening efficiency and relatively low cost.

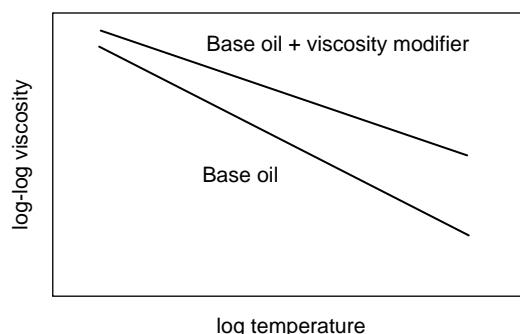


FIGURE 19.31 Effect of VM on base oil viscosity–temperature dependence.

TABLE 19.10
Viscosity Modifiers

VM Name	Abbreviation	Polymer Structure
Olefin copolymer poly(ethylene/propylene) (may contain diene comonomer)	OCP	Linear copolymer (can contain long-chain branching)
Polyalkylmethacrylate	PMA	Linear copolymer
Hydrogenated radial polyisoprene (can contain styrene as comonomer)	HRI	Star polymer
Hydrogenated styrene-isoprene	HIS	Linear A-B block copolymer
Hydrogenated styrene-butadiene	HSB	Linear tapered block copolymer
Polyisobutylene	PIB	Linear homopolymer
Styrene-ester, alternating copolymer of styrene and alkylmaleate	SE	Linear copolymer

Styrene–diene copolymers are prepared by an anionic polymerization of styrene with either butadiene or isoprene. The residual unsaturation in the backbone is removed by hydrogenation. Tapered block copolymers are prepared by charging both monomers together at the beginning of the reaction. To synthesize A-B block copolymers, the monomers are added sequentially. Anionic polymerization yields polymers with very narrow molecular weight distributions especially when compared with those of OCPs and PMAs. A narrow molecular weight distribution yields the maximum shear stability to thickening efficiency ratio for a linear polymer. Because styrene–diene copolymers also possess excellent low-temperature properties and good thickening efficiency, they have found widespread use in engine oils. One of the few drawbacks is that, relative to OCPs, they are relatively expensive to make due to the two-stage synthesis process and more expensive starting materials. Another issue is that A-B block copolymers undergo more temporary viscosity loss under high-temperature, high-shear-rate (HTHS) conditions (such as in lubricated journal bearings), especially when compared to OCPs.

Star polymers are prepared by an “arms-first” process whereby isoprene (and an optional comonomer) is anionically polymerized to a predetermined molecular weight. The *arms* are then linked together by adding divinylbenzene that forms an ill-defined gel core. The number of arms per star is defined by the amount of divinylbenzene relative to the polymer *arm* concentration. Finally, the star polymer is hydrogenated. These polymers have exceptional low-temperature properties but undergo more permanent viscosity loss under severe operating conditions when compared to OCPs at the same nominal shear stability index (SSI).

PMAs are prepared by free-radical polymerization of alkylmethacrylate monomers. This produces a polymer with a relatively broad molecular weight distribution. To reduce molecular weight and hence increase shear stability of the polymer, the initiator concentration is increased. In addition, a chain transfer agent may be added during the polymerization process. This stops the polymer chains from growing and enables the production of a polymer with low molecular weight and exceptional shear stability. The composition of the monomers in the polymer backbone is chosen to optimize low-temperature properties viscosity index (VI) and thickening efficiency. PMAs are frequently used because of their exceptional low-temperature viscometric properties. Because of this, they are used extensively as VMs in gear oils, automatic transmission fluids, and hydraulic oils as well as pour point depressants. In recent years, OCPs have gained market share from PMAs in engine oils due to their relatively low cost and acceptable performance. PMAs can also be manufactured with dispersant functionality, which adds another performance attribute to an already highly versatile additive. The most direct method for preparing dispersant PMAs is to incorporate a nitrogen-containing monomer into the polymer during copolymerization. Alternately, various nitrogen-monomer grafting techniques can be used.

19.6.3 DISPERSANT VISCOSITY MODIFIERS

Various VMs can be prepared with the incorporation of dispersant properties. These dispersant VMs (dVMs) have been used to provide improved sludge and soot handling performance to engine oil lubricants. They can either substitute for or add to the existing dispersant in the formulation. As a replacement for dispersant, they are required to provide equivalent performance. As a top treat to the existing additive, they will provide a boost in performance especially in areas of sludge and soot handling. Examples include dPMAs and dOCPs.

19.6.4 SHEAR STABILITY OF ENGINE OILS

Polymeric VMs are susceptible to mechanical and in some cases thermal shearing, leading to a loss in oil viscosity. The SSI of an engine oil VM is defined by the following equation. The SSI gives an indication of the mechanical stability of the VM.

$$\text{SSI} = \frac{m_i - m_f}{m_i - m_o} \times 100$$

where

m_i = initial viscosity of lubricant with the VM (cSt)

m_f = final viscosity of lubricant after shear*

m_o = viscosity of lubricant without the VM (cSt)

Numerically, the SSI can be explained as follows: a VM with a low SSI number is more shear stable, whereas a VM with a high SSI number is less shear stable. The SSI value of the VM will depend on its molecular weight. Higher-molecular-weight VMs will have the greatest thickening efficiency for a given weight of polymer but will have the lowest shear stability (highest SSI). 55 SSI represents the lowest shear stability acceptable for modern engine oils. Although this is not unusual for North American PCMO, it is quite uncommon to find this shear stability being used in Europe where minimum shear stability is specified in the ACEA and OEM specifications. A VM with 25 SSI or less is typical for European diesel and gasoline applications, whereas a 35 SSI VM or less is preferred for North American diesel formulations.

19.6.5 VISCOSITY GRADE

A lubricant's viscosity grade, which defines the useful operating temperatures under which it may be used, is defined by the number of viscometric measurements that are given in various Society of Automotive Engineers (SAE) specifications. Polymeric VMs are crucial in allowing many viscosity grades to be made. Most OEMs will use the viscosity grade to define the lubricant that best works in their equipment. For engine oil lubricants, the viscosity grade is defined by the SAE J300 specification.

In general, an OEM will aim to use the lowest viscosity oil possible, to reduce energy losses due to friction. However, they will usually recommend a minimum oil viscosity with which their equipment will work comfortably. These limits may not always coincide with the SAE J300 specification especially in the case of the high temperature and high shear viscosity. European OEMs have historically been more conservative and most have specified a minimum HTHS

* Note that the SSI value is dependent on the particular shearing device used to measure shear stability. Common devices include the Kurt Orbahn fuel injector rig, CRC L-38 engine test, sonic shear device, and the KRL tapered bearing rig. The latter is primarily used to measure the SSI of driveline fluids such as highly shear-stable ATF and gear oils.

viscosity of 3.5 cP for their engine oils irrespective of viscosity grade. This limit is still applied by European heavy-duty diesel OEMs since bearing wear is seen as a critical performance parameter. This would mean that an SAE 10W-30 oil would not only have to meet the SAE viscosity grade but also have to be >3.5 cP in the HTHS viscosity test. North American diesel oils are similar to their European counterparts with 15W-40 making up the majority of the market. However, there are some 10W-30 oils in use for which there are no HTHS viscosity minimum limits other than that specified in SAE J300.

For some European passenger car OEMs, there has been some relaxation in the OEM limits applied to the HTHS viscosity as engine designs have changed to accommodate lower-viscosity oils. Lower-viscosity oils enable improvements in fuel economy to be made. For example, Volkswagen has published oil specifications VW 503 and 506 for their gasoline and diesel engines. These specify an SAE 0W-30 with an HTHS from 2.9 to 3.4 cP together with a fuel economy target. The reduction in HTHS viscosity for PCMO in Europe is moving in line with North America where most of the gasoline oils are 5W-30s with HTHS limits in line with the SAE J300 specification. In addition to this, some OEMs are now using 5W-20 oils for factory fill to ensure even better fuel economy. This is important since some VMs have poor temporary viscosity loss performance at high temperatures. If an HTHS of >3.5 cP is required, then it is easier to formulate this oil with an OCP. If the HTHS target is <3.5 cP, then most VMs will suffice.

19.6.6 VISCOSITY MODIFIER REQUIREMENTS

The necessary attributes for polymeric VI improvers are as follows:

- Good thickening for cost-effectiveness
- Proper shear stability to stay in grade
- Temporary shear stability to meet high-temperature, high-shear requirements (especially where it is specified)
- Minimum low-temperature viscosity for cold cranking and pumping
- Minimal deposits at high temperature, for example, pistons and turbochargers

Correct selection of the VM will allow all the viscometric requirements to be achieved at the optimum cost. This being done, it is then necessary to evaluate the formulation in various engine and field tests. The performance of VM in the engine and service duty requirements will then define whether the VM is suitable for the intended application.

19.7 POUR POINT DEPRESSANTS

All mineral base oils contain some paraffinic components. These have very good viscosity-temperature dependence, but they are liable to form waxes at lower temperatures. Although the effective volume of these waxes is low, they can still form a network of wax crystals that prevents the oil from flowing. One way to investigate this phenomenon is to measure an oil's ability to flow at low temperatures by way of its pour point. The pour point temperature of an oil is defined as the lowest temperature at which the oil is still capable of flowing and is measured according to ASTM D-97. Additives used to reduce the pour point temperature may also benefit the low-temperature pumping viscosity.

Pour point depressants work at low temperatures, not by preventing the formation of wax crystals, but by minimizing the formation of wax networks and thereby reducing the amount of oil bound up in the network. Examples of pour point depressants include polyalkylmethacrylates, styrene-ester polymers, alkylated naphthalenes, ethylene vinyl acetate copolymers, and polyfumarates. Treat rates are typically $<0.5\%$ (Figure 19.32).

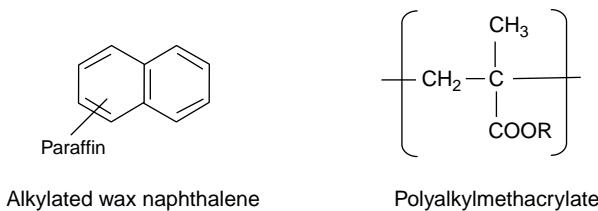


FIGURE 19.32 Examples of pour point depressants.

19.8 FOAM INHIBITORS/ANTIFOAMS

Entrained gas or foaming of a lubricant will reduce its effectiveness and needs to be minimized and at best stopped from building up during engine operation. In engine oils, the presence of foams can result in reduced oil pressure leading to engine damage particularly for hydraulic lash adjusters or for hydraulically actuated unit injectors. Air entrainment is another problem. This may lead to cavitation of the oil film in bearings and possible failure. The performance of hydraulically actuated unit injectors is also sensitive to the amount of entrained air.

For simple oil formulations, a foam inhibitor may not be necessary. However, the stability of foams increases as more additives are added to the lubricant. This has necessitated the use of foam inhibitors such as those listed as follows:

- Dimethylsiloxane polymers
- Alkylmethacrylate copolymers
- Alkylacrylate copolymers

These compounds are borderline soluble in the lubricant and function by reducing the surface tension at the interface of the air bubble, thus allowing the bubble to burst more easily. To function effectively, they must be present as a fine dispersion.

Foam inhibitors are usually added to the lubricant at very low levels typically <20 ppm. At higher levels, the solubility becomes an issue and is noticeable by an increase in the cloudiness of the lubricant and possible drop out of the foam inhibitor.

Foaming is measured according to ASTM D-892, which uses air flowing through a porous ball to create foam in the test oil sample. The amount of foam and its stability are measured at 24 and 94°C. ASTM D-6082A is a variation of this test but measures foaming at 150°C. Additional engine tests such as the Navistar HEUI have also been introduced for diesel oils since API CG-4. This test measures a diesel oil's ability to minimize air entrainment that could affect the performance of unit injectors, which are hydraulically actuated. Gamma ray detection techniques are also used to monitor the entrained air in an engine by way of the oil density. This method is used by BMW for their oil approval system.

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20 Additives for Industrial Lubricant Applications

Leslie R. Rudnick

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20.1 INTRODUCTION

The objective of this chapter is to provide a review of additives and additive chemistry specifically for industrial lubricant applications. This chapter reviews the history of additives and some types of additives used to improve performance of lubricants in industrial applications. This chapter also describes the chemistry and mechanisms of action of these additives and some of the important test methods used to evaluate formulated oils.

An additive is a chemical substance added to a lubricant to improve its properties and performance. Additives can function by physical and chemical interactions. Some additives remain essentially unchanged as a lubricant is used and others are depleted during use. Still others must chemically change to perform the desired function. Additives are used widely in many of the largest industries including the food, soap and detergent, pharmaceutical, paint, plastics, fuel, and

automotive industries. In fact, many of the antioxidants that are used in plastics are also used to stabilize automotive and industrial lubricants.

Today, most additive (and lubricant) companies have corporate websites that provide information. Some provide only cursory information and would do well to expend the effort to provide the scientist, formulator, and potential customer with more useful information. Other companies publish almost encyclopedic detail on all of their commercially available additives. Some include detailed chemistry, properties and performance characteristics, and examples of formulations. The internet over the past several years has become a repository of information on additives and lubricants for the lubricant industry. A list of additive suppliers and the Uniform Resource Locators (URLs) for the corresponding website can be found in Chapter 31 and in the CD accompanying this book. In addition to websites from the individual companies, industry organizations such as Noria, Society of Tribologists and Lubrication Engineers (STLE), and others provide information on lubrication, which includes discussion of additive interactions and depletion during use. Book publishers have also placed online, the contents of entire books that can be purchased to download in their entirety or only the desired chapter(s). Several recent examples of books specifically related to additives and lubricant fluids have been published [1–3].

20.2 HISTORY OF ADDITIVES

The Egyptians around 1500 BC may have used animal fats with or without water-based additives to move the huge stones and statues to the building sites of the early pyramids on lubricated wooden sledges [4]. Most certainly, there were earlier applications involving the lubrication of wheels and axles with mixtures of animal fats and natural oils. The earliest reported evidence of solid film lubrication were metal inserts in wooden implements found in the Middle Ages, around AD 500 [5].

The use of additives and additive industry has grown as a result of the larger use of lubricants and the more stringent requirements placed on lubricating fluids. The Industrial Revolution, ~1700 to 1800, resulted in the greater need for both lubricants and lubricant additives. Addition of inorganic chemicals to water and the use of animal fats, vegetable, and fish oils were common.

The discovery of oil at Titusville, Pennsylvania, in 1859 resulted in not only the growth of a new petroleum-based industry but also a need for an additives industry to supply chemical components that would impart improved properties and performance to the oils being used as lubricants at the time [6]. Early use of additives to improve lubricating oils was in metalworking fluids required by the rapid expansion of the railroad and automobile industries [7]. Animal fats, fish oils, vegetable oils, and blown rapeseed oils were added as friction modifiers. Rosin oil, mica, and wool yarn were among the early grease additives. Sulfur was added to metalworking oils as early as 1916 and shortly thereafter phosphorus additives came into use.

Petroleum refining continued to grow in scale and in process technology during the beginning of the twentieth century. At first, refining operations were aimed at improvements in the quality and quantity of fuel, heating oils, and asphaltic components for road paving. Between these ends of the spectrum, there were petroleum distillates that found their way into use as lubricants. These were high-boiling components and contained various amounts of sulfur and nitrogen that were later found to retard oxidation and wear when these fluids were used as lubricants. So one might consider the natural nonhydrocarbon components of petroleum as the first modern lubricant additives. Chemists at the major oil companies worked to isolate these materials and identify their structures so that they could be made as desired and added in optimum concentrations depending on the application requirements. There is an analogy here to the pharmaceutical industry where natural plant substances are extracted, isolated, and characterized as a prelude to direct chemical synthesis of these materials or improved analogues. Process engineers at the same time were developing processes to eliminate these materials so as to produce more stable, clearer lubricants. Synthetic chemists were also working to develop synthetic oils formed from basic chemicals derived from petroleum and other sources. All of these resulted in lubricant fluids that contained lower concentrations of naturally

TABLE 20.1
Chronological History of Additive Developments

Period	Application	Additive	Comments
BC	Wheels	Animal fats, oils	Chariots, carts
	Construction	Water	Pyramids, moving heavy stones
1500	Wire drawing	Wax	Au, Ag metals
1750	Industrial	Water	Industrial revolution, cooling
1800	Industrial, metalworking	Water and inorganics	Rust prevention
1900	Industrial	Phosphorus, sulfur	Oxidation, wear protection grease
1920	Metalworking	Emulsifiers	Soluble oils
	Automotive, engine oils	Fatty acids	Friction reduction
1930	Engine oils	Isoparaffins, polymethacrylates	Pour point depressants
	Gears	Lead soaps	EP/wear protection
1940	Engine oils	Calcium carboxylates	Detergents
	Engine oils	Zinc dithiophosphates	AW/antioxidant
	Engine oils	Sulfonates, phosphonates, phenates	Detergents, dispersants
1950	Metalworking	Soluble oils	Cooling capability
	Engine oils	Viscosity modifiers, basic sulfonates	Temperature–viscosity improvers, detergents
		Overbasing, salicylates	Dispersants, acidity, oxidation control
1970	Industrial	Solid additives	EP/wear protection
		Phosphate glass	
		Boron nitride	
		Fluorocarbons	<i>Teflon-like</i> additives
		Low toxicity	
		Biodegradable	<i>Environmentally friendly</i>
1990	Industrial	Low volatility	Reduced emissions
		Food grade	Safety in food processing/handling
		Nanomaterials	Improved microlubrication

occurring antioxidants and antiwear (AW) and corrosion components. This made these oils more susceptible to degradation and less-effective lubricants, and therefore there arose a need to develop specific additives to protect these new fluids from all of the degradation processes that occur under the newer, more severe operating conditions. It should be noted that in general for petroleum-derived lubricants, the greater the extent of hydroprocessing the lower the amount of heteroatom components, and therefore the more nonpolar and hydrocarbon-like the fluid.

Improvements in the performance of industrial lubricants since the late 1930s, for the most part, resulted from the development and use of synthetic additives. These developments occurred initially by researchers in major oil companies, but as the industry developed, many additive companies came into existence and flourished. A chronology of the development of some additives is given in Table 20.1.

Several reviews of lubricant additives and their applications have been published [3,8–12]. Companies interested in protecting their research investments and technology patented their new innovations, and by the 1950s, over 3000 additive patents had been issued. The rapid growth of the additive market in the 1900s has slowed in recent years because the world's finished lubricant market continues to remain flat. It is predicted that global additive demand will grow at only a 1–1.2% per year until about 2015 [13].

20.3 THE FUNCTION OF ADDITIVES

As evidenced by the plethora of structures for additives described in the first 19 chapters of this book, the lubricants industry has had the advantage of the talents of many excellent organic chemists able to provide new organic and inorganic components as additives. Many of these structures, or slight modifications, are used to stabilize similar materials in other industries. Naturally occurring materials or synthetic versions are also used. For example, alpha-tocopherol, vitamin E, is used as an antioxidant both in food products and in lubricant products to maintain the stability of highly isoparaffinic base fluids that are used in food-grade and nonfood-grade industrial and automotive lubricants. Antioxidants, in particular, are employed to protect raw materials used in lubricant formulations as well as to protect the fully formulated oil during storage and use.

Although most industries have specific performance requirements related to their use of additives, there are some general requirements of additives that apply to all applications.

The overriding criterion for additives in lubricant formulations is that it be effective for the application. That said, there are certain criteria that make this possible.

These include the following:

1. *Solubility.* The additives must all be soluble in the formulated oil, and in some applications, this may require solubility in water. Additive solubility is critical in a lubricant throughout the temperature range that the lubricant will experience. This includes conditions of storage as well as the lowest and highest temperatures the oil will experience during use. Lubricants must be formulated such that the additives remain in solution as the oil is used so that the additives do not drop out and lower their effective concentration in the lubricant and so that they do not cause any deleterious effects by virtue of their insolubility.
2. *Stability.* The additives should have good stability to ensure acceptable performance over the useful life of the lubricant product. Lack of additive stability can affect the color and odor of the product. Breakdown of additive components caused by heat or light or moisture can result in reduced product stability and therefore performance. Many additives, especially arylamine antioxidants, are susceptible to darkening on exposure to light. This can affect product performance in terms of stability and also affects personal acceptance of the product in terms of quality.
3. *Volatility.* Low volatility is generally required for most industrial lubricant applications. This reduces the nonuniform loss of oil from the system and therefore thickening of the oil caused by the heavy components remaining in the system. Furthermore, this is often not considered when formulating; the additives that are chosen must be nonvolatile under the conditions of use to maintain the concentration of these additives in the lubricating fluid. This is especially true of lubricants that are to be used in high-temperature applications. In some particular applications, there is a need for a certain degree of volatility of the additive, for example, vapor-phase corrosion inhibitors must have a controlled rate of volatility.
4. *Compatibility.* Additives must be compatible with other components in the systems, including base oils and other additives. One of the most important considerations is compatibility with the base fluids being used in the formulation. This also involves compatibility with system components such as seals, gaskets, and hoses. Incompatibility is initially observed as a haze or cloudiness during formulation. This should be the first clue that something is insoluble or reacting. Bench tests that include visual observation of the oil after testing can also provide information as to the compatibility of additives in the formulated oil.
5. *Odor.* Odor must be acceptable for the particular application. This is especially true in food-processing applications in which any odor from the base oil or additives can affect food product quality due to adsorption of odorous oil components, including additives. The same may be true for lubricants that are used in the manufacture of textile or paper or other fibrous materials that can absorb odors.

6. *Activity.* The additive must have functional activity over the lifetime of the application. For example, a very reactive antioxidant that is depleted in a short time period will render a lubricant susceptible to oxidation sooner than a product formulated with long-term acting antioxidants as part of the additive chemistry in the product.
7. *Environmental compatibility.* Three issues to consider here are biodegradability of the additive, disposal constraints, and toxicity. These issues are important both from the standpoint of use and proper disposal and also in the event of a spill. Many industries are now using life cycle analysis to understand and control the use of all components that enter and leave their products and processes [14–16]. Green chemistry is also applied to the manufacture of additives to minimize the environmental impact of these processes and the disposal of waste products.
8. *Health and safety issues.* These issues are concerned with any of the aspects of human contact and transportation of the additives as raw materials or as components in finished products. Health and safety issues are particularly important for additives when used in food-grade lubricants for use in food processing plants. Every additive that is allowed for use in food-grade H-1 (incidental contact) lubricants has an upper concentration limit. Lubricants formulated with quantities higher than these limits are not considered food grade because of the potential for unsafe levels of the additive to contact the food.

Before describing the chemistry of the various classes of additives used in the wide variety of industrial applications, it is appropriate to consider the additive types in terms of how they function as part of the formulated oil, that is, physical interaction or chemical interaction. Additives that function by physical interaction act through physical adsorption–desorption phenomena. These additives include pour point depressants, additives that impart lubricity, color stabilizers, additives that change in structural form with changes in temperature (viscosity index improver [VII]), additives that cause changes in surface or interfacial tension (antifoam and emulsifiers), those that cause the formation of structures that trap base fluid (tackifiers, thickeners, and fillers), antimisting additives, water repellants, or additives that affect the perceptive qualities of a lubricant (odorants, color stabilizers or dyes, and chemical marking agents) (Table 20.2).

Table 20.3 describes those additive types that act by chemically reacting with surfaces and are consumed or chemically changed during use. Chemical processes can also change the physical

TABLE 20.2
Additives That Function by Physical Interaction

Additive	Function
Antifoam	Prevents the formation of stable foam
Antimisting	Reduces the tendency to mist or aerosol
Color stabilizer	Slows darkening of fluids
Demulsifier	Enhances the separation of water and oil by promoting drop-coalescence and gravity-induced phase separation
Dyes	Impart color, mask color, product identification
Emulsifier	Reduces interfacial tension and allows dispersion of water
Friction modifier	Associate with the metal surface and improve sliding between surfaces
Odor control	Prevent or mask undesirable odors or maintain odor level
Pour point depressant	Lowers low-temperature fluidity by reducing the formation of wax crystals
Tackiness	Improve cohesion of fluid and nondrip quality
Thickener, solid filler	Converts oil into solid or semisolid lubricant
VII	Improve viscosity–temperature characteristics
Water repellent	Impart water resistance to greases and other lubricants

TABLE 20.3
Additives That Function by Chemical Interaction

Additive	Function
Antibacteria (biocides)	Prevents or slows growth of bacteria in systems
Anticorrosion (corrosion inhibitors)	Protects surfaces against chemical attack
Antioxidant	Reduces the rate of lubricant oxidation and deterioration and increases oil and machine life
Antirust	Eliminates rusting due to water or moisture
AW	Reduces thin-film, boundary wear
Basicity control	Neutralizes acids from oxidation processes
Detergent	Maintains surface cleanliness
Dispersant	Suspends and disperses undesirable combustion, wear, and oxidation products
EP (temperature)	Prevents seizing and increases load-carrying ability
Friction modifiers	Reduce friction and increase lubricity
Metal deactivator	Counteracts catalytic effects of surfaces by passivating surfaces

properties of the lubricant. For example, oxidation of the base fluid in a formulation results in degradation, producing smaller molecules that are more volatile than the original molecules. This has the effect of increasing the viscosity of the oil as the lower-molecular-weight components volatilize and can result in a decrease in oil volume if the process continues.

One should note that the chemical structure of the base fluid and that of the additives used in a lubricant formulation are all crucial to the properties and performance of the lubricant. The polarity of the base fluids and the additives is very important because each component of the mixture is competing for the metal surfaces. A polar additive that would normally adsorb and desorb reversibly from a metal surface in a nonpolar base fluid and has a reasonable steady-state concentration on the surface might have a much lower, even ineffective, concentration on the surface when in a formulation that contains a high concentration of polar base fluid such as ester or vegetable oil.

The AW performance of tricresyl phosphate has been studied in 11 different base fluids. When molecular weight, dielectric constant, and solubility parameters were considered, correlations for optimum concentration of additive were obtained [17].

20.4 CLASSES OF ADDITIVES

20.4.1 ANTIOXIDANTS

Antioxidants chemically interact with free radicals and hydroperoxides to slow the chain reactions that result in oxidation of the base fluid. The two most common classes of compounds that are used as antioxidants are hindered phenols and aromatic nitrogen compounds. Some phenolic antioxidants commonly used in industrial applications include di-*tert*-butyl *p*-cresol (BHT) and 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamic acid, C7–C9 branched alkyl ester. Examples of aryl amines include diphenylamine, dioctyl diphenylamine, styrenated diphenylamine, phenyl-alpha-naphthylamine (PANA), and polymerized versions of trimethylquinoline. These types of additives are described in detail in Chapter 1. In general, these types of antioxidants are used in gear oils, turbine oils, hydraulic oils, compressor oils, and various greases. Some additive molecules containing different chemical structures, such as phenothiazines, are sometimes used in ester formulations and can react many times with oxygen molecules before they are depleted. Other additives such as

zinc dithiophosphates (ZDTPs) and ashless phosphorus-containing additives can also function as antioxidants in addition to other functions. These are described in Chapters 2 and 3, respectively.

20.4.2 ANTIWEAR AND EXTREME-PRESSURE (ANTISCUFFING) ADDITIVES

AW- and extreme-pressure (EP)-type (antiscuffing) additives react with metal surfaces to form a chemical film that is sheared more easily than the moving metal surfaces. Additives that perform these functions, ZDTPs, ashless phosphorus additives, ashless AW and EP additives, and sulfur carriers, are described in detail in Chapters 2, 3, 8, and 9, respectively. Two criteria differentiate AW from EP additive. The differences depend on the load the additive film formed can carry and how it survives the high temperatures generated by the friction forces. Although bulk oil temperatures may be low, the temperatures at the metal-to-metal interfaces in the contact zone can exceed 300°C. At extreme loads, the frictional heat can exceed the melting temperature of the metal. In fact, during four-ball EP testing, the weld load is that load that caused the balls to actually weld to each other.

Some additives, for example, ZDTPs and alkyl amines, perform multiple functions. These additives can function as antioxidants and AW additives or as AW and surface deactivators. ZDTPs are some of the most economical and effective additives. The largest application is in the formulation of automotive and diesel engine oils; however, they are used in some industrial hydraulic fluids. The temperature at which zinc dialkyldithiophosphates (ZDDPs) are most effective depend on the mix of hydrocarbon group, that is, primary alkyl, secondary alkyl, or aryl. Therefore, both the amount and structure of the ZDDP components affect the performance of the fully formulated oil.

ZDTP has come under scrutiny from an environmental viewpoint in automotive engine oils. Phosphorus and sulfur in the additive are suspected of being detrimental to the effectiveness of after-treatment catalysts in spark (gasoline) and compression ignition (diesel) engines. Research is ongoing to develop a cost-effective chemical alternative to ZDDPs. Alternative additives, evaluated to date, are not as effective and are significantly more expensive than the ZDTPs. As combustion in the presence of lubricants and after-treatment catalysts are not factors in industrial applications, there is no problem with use of ZDDPs.

The adsorption and desorption of dibenzyl disulfide and dibenzyl sulfide on steel have been investigated. This involved the study of the rate of uptake of labeled additives onto stainless steel disks. The kinetics of both adsorption of these additives and the desorption from the metals was examined. Two processes, reversible physisorption and irreversible chemisorption, were identified, and the implications in AW and EP behavior were described [18].

20.4.3 FRICTION MODIFIERS

Friction modifiers or lubricity additives (see Chapter 7) absorb on the surface to form films that reduce the friction between the moving surfaces. These additives are generally polar molecules having a polar functional group (alcohol, aldehyde, ketone, ester, and carboxylic acid) and a non-polar hydrocarbon *tail*. The polar portion of the molecule adsorbs onto the surface with the long hydrocarbon chains exposed to the moving surfaces, reducing the friction. They can also contain polar elements that adsorb and chemically react with the surface to form a protective film. Vegetable oils, fats, and animal based have structures that make these materials excellent friction modifiers. In addition to liquid organic friction modifiers, there are various solid lubricants that reduce friction. These materials are reviewed in Chapter 6. A recent example from the literature reports on the influence of graphite, molybdenum disulfide, and perfluoropolyalkylethers (PFPAE) on changes in the shear stress values in lubricating greases [19].

20.4.4 VISCOSITY MODIFIERS/VISCOSITY INDEX IMPROVERS

VIIIs are very high-molecular-weight compounds (polymers) that function by physically changing form with changes in temperature. VIIIs can be depleted chemically through thermal or oxidative

breaking of bonds. Higher-molecular-weight versions can be mechanically sheared to form smaller, less-effective molecules. The stability of the VII depends on both the chemical structure and the size of the molecule. There are two main structural types of molecules used as VIIIs—the nonpolar olefin copolymers (Chapter 10) and the polar polymethacrylates and related compounds (Chapter 11).

20.4.5 TACKINESS AND ANTIMISTING ADDITIVES

Tackiness and antimisting additives are used in several applications. In particular, tackiness is important in maintaining contact between the lubricant and a metal surface. Lubricants can have the tendency to migrate away from the surfaces that need lubrication depending on the lubricant viscosity and the geometry of the equipment. Antimisting is important in terms of reducing the tendency of lubricants to become airborne aerosols or fine mists. The materials that are used to reduce these phenomena are described in Chapter 13.

20.4.6 SEAL SWELL ADDITIVES

Seal swell additives are critical in maintaining contact between rubber or other types of seal materials and the metal surfaces in equipment. These seals keep lubricant where it is needed and away from areas where it is not desired. Seal swell agents are adsorbed by the seal material and prevent the seals from cracking and deteriorating. These additives are described in Chapter 14.

20.5 DYES

Dyes are often used to identify fluids by application. Hydraulic fluids were often dyed red and coolants green during World War II to make it easier for technicians to select the correct lubricant and thus properly maintain equipment. MIL-L-Spec.5605 Red Oil was used as an aircraft hydraulic fluid in World War II in many aircraft. Dyes are also used for product branding and are used to identify that a particular supplier's oil has been used instead of a lower-cost-competitive oil.

20.6 BIOCIDES

Biocides are used to reduce the growth of bacteria in lubricants used in metalworking. These applications by nature use large volumes of lubricants that are exposed to air and the environment and consequently have the tendency to decompose by natural processes. To maintain lubricant quality and performance, biocides are added to these lubricants. These are described in Chapter 15.

20.7 SURFACTANTS

Surfactants are one of the most widely applied and diverse group of materials. They have been applied to lubrication for centuries and form the basis for a combination of performance features that include reducing friction and wear and cooling during lubrication. As these materials can solubilize polar and nonpolar components, surfactants make possible many of the fluids used in metalworking and other areas of lubrication. Surfactants adsorb to the metal surface and provide a *cushion* or molecular boundary between moving surfaces to protect them from wear. The chemistry of surfactants is described in Chapter 16.

20.8 CORROSION INHIBITORS

Corrosion is potentially devastating to industrial equipment that comes in contact with water and other corrosive materials. Even water in the form of atmospheric humidity, that can enter equipment or react with exterior surfaces, can reduce the lifetime of expensive industrial machines. Corrosion inhibitors are summarized in Chapter 17.

20.9 ADDITIVES FOR FOOD-GRADE LUBRICANTS

Lubrication is obviously needed in the food production and the preparation industries for the same reasons as are needed to lubricate machinery in other industries. An additional requirement, however, in the food industry is the need to be certain that the chemistries used are safe in the event that any of the lubricant makes contact with the food product. There are specific additives that are allowed and limiting concentrations of these additives permitted in food-grade additives. Additives for food-grade lubricants are described in detail in Chapter 21.

20.10 MAGNETIC DISK DRIVE ADDITIVES

Magnetic disk drives are a critical component of our modern technology. These components are evolving in terms of the rate or rotation of the magnetic disk, and precision and smaller tolerances in the rotating spindle. Lubricants are designed to provide adequate lubrication, and additives must maintain performance at both the spindle motor and the head–disk interface. Additives protect against oxidation of the base fluid and control conductivity and other properties necessary for long-term performance.

Additives for magnetic disk recording applications are described in Chapter 22.

20.11 ADDITIVES FOR GREASE

Additives for use in grease are in general similar to those used in other industrial lubricants, but their concentrations and combinations can be quite different. These additives are described in Chapter 23.

20.12 ADDITIVES USED IN BIODEGRADABLE LUBRICANTS

Bioderived and biodegradable lubricants are becoming more important due to increased interest in protecting the environment and due to regulations imposed by many governments around the world. For lubricants to meet the environmental criteria of biodegradability and toxicity, the additives must perform needed functions without being toxic themselves. These additives are sometimes the same as those currently in use in other applications, but more and more, they are specifically developed to meet the performance criteria and be nontoxic and biodegradable. The performance of some of these materials is described in Chapter 18. One example of newly synthesized additives directed at biodegradable esters is reported [20]. These additives were reported to form stable lubricating films on the surface of stainless steel balls used in four-ball wear testing.

Additives improve the properties and performance of lubricants by modifying chemical and physical characteristics of the oil. The mechanisms of action of additives depend on the chemical structure of the additive, the chemical structure of the base fluids, the temperature of use, and the mechanical pressures applied to the formulated oil. Many of these mechanisms are well understood and have been described in the literature. Some aspects of the additive chemistry of the more common additives are briefly reviewed in the following section.

20.13 ADDITIVE CHEMISTRY

An understanding of additive chemistry is necessary both for the synthesis of additives and to develop an understanding of how lubricants and additives react, perform, and degrade during use. Beginning in the 1940s, the severe operating conditions of military equipment during World War II led to the investigations of these areas in much greater detail than had previously been done. More severe operating conditions required greater thermal and oxidative stability, less friction, and better wear protection from the lubricants. As lubricant base fluids provide only part of the required properties and performance, the additives used in formulations needed to provide greater performance than ever before.

Research on oxidation mechanisms and oxidation inhibitor additives have been investigated by Ingold [21], Watson [22], Mahoney et al. [23], Chao et al. [24], Jensen et al. [25], Booser et al. [26–28], Dennison and Condit [29] and Zuidema [30], and others.

Antioxidants reduce oxidation by trapping free radicals or by decomposition of hydroperoxides generated during the oxidation process. As discussed earlier, substances containing amines or phenolic groups are effective antioxidants. Antioxidants that contain sulfur and combinations of phosphorus and sulfur are effective against hydroperoxides [31,32]. Some metal-containing compounds such as copper naphthenates can be either prooxidants or affect antioxidants depending on the formulation and the additive concentration [33,34].

A review of the effects of metals and the effect of hard-coated metals on the thermooxidative stability of branched perfluoroalkylether lubricants have also been reported [35,36].

Metal deactivators reduce the effect of metals and their salts on the rate of oxidation of the bulk fluid [37]. Some of these, such as ethylenediaminetetraacetic acid (EDTA), complex with the metal particles suspended in the fluid rendering them inactive.

AW additives form protective films by chemical or physical reaction with the surface [38–42]. They minimize the removal of metal through formation of lower shear strength films that reduce friction, decreasing the contact temperatures or by increasing the contact surface thereby reducing the effective load. The most effective AW additives contain sulfur or phosphorus or both. Studies of the performance and mechanisms of action of tricresyl phosphate (TCP) and ZDDP have been well documented in the literature [43–48].

EP, or more correctly extreme-temperature additives, also contain phosphorus or sulfur compounds. Chlorinated compounds are also effective [49]. Use of phosphorus compounds started around the time of World War I, and addition of sulfur and chlorine to gear oils began in the 1930s [50–53]. EP gear oils in the 1960s and 1970s were formulated using combinations of sulfur-, phosphorus-, and chlorine-containing additives. The use of chlorine-containing AW and EP compounds is gradually declining due to environmental concerns with some suppliers developing new replacement products [54].

Rust and corrosion inhibitors adsorb on the surface forming a barrier hydrocarbon film against water and corrosion-causing materials. These are often basic amine-type compounds that have the ability to neutralize acids. They may also passivate the metal surface reducing the catalytic effect on oxidation of the oil [55,56]. When combined with antioxidants in an additive package, this combination is typically referred to as *rust and oxidation package* or *rust and oxidation oil (R&O)* and generally provides protection to industrial oils that are used under relatively mild operating conditions.

Detergents can neutralize acids produced by oxidation of the oil or, in the case of internal combustion engines, combustion. The combustion products get into the fluid as a result of blowby. Detergents can be phenates, sulfonates, and salicylates [38,57]. Typical dispersants are succinimides, succinates, and Mannich-type reaction products. Dispersants slow the formation of deposits and sludge by dispersing the precursors and insoluble particles in the fluid. These, like detergents, are large molecules with a polar end and a nonpolar portion. Dispersants and detergents are typically used in engine oils and not in industrial oils. These two categories of additives represent the largest category of additives sold. Normally, dispersants and detergents are not required in industrial gear oils, turbine oils, or industrial hydraulic fluids.

Foam inhibitors prevent formation of foam by changing the surface tension that results in the collapse of gas bubbles as they form [58]. The inhibitors are high-molecular-weight polymers that are relatively insoluble in the oils. Antifoam additives are generally used at concentrations measured in parts per million and are usually blended into a more soluble solvent system to facilitate the accuracy of addition of the small quantities required. Some commercial antifoam additives supplied are already diluted in a suitable carrier fluid at concentrations that help to make addition of the material more accurate. Air entrainment is often mistaken for foaming in hydraulic systems. Additives can sometimes help with air entrainment, but usually, mechanical changes

to the system to prevent air entering the system or modifying the base fluid is a better approach. Polydimethylsiloxanes, polydiarylsiloxanes, mixed siloxanes, and polyglycol ethers are examples of these additives.

Friction modifiers are used to lower the energy requirements of a system by reducing the friction of the system. These additives are often long-chain hydrocarbon molecules with one end of the molecule containing a polar group that is adsorbed on the surface [59–61]. Chain length and branching of the carbon chain affect both the surface adsorption of these additives and the packing density on the metal surface. Oleic acid and other organic fatty acids, alcohols, and amides are typical structures of commercial friction modifiers.

In addition to liquids, there are also solids that act as friction modifiers. Graphite or molybdenum compounds are examples of solid friction modifiers. These materials provide reduction in friction and often help reduce wear. These materials are not soluble in hydrocarbon oils and are therefore suspended in the lubricating fluid.

Rheological properties of industrial oils are important performance criteria [62–65].

Viscosity at normal operating temperatures is an important lubricant specification. The lubricant film thickness under operating conditions needs to be considered to mitigate wear and damage to equipment. Viscosity is a function of temperature and pressure (and shear rate for non-Newtonian fluids). VIIIs are used to modify the temperature–viscosity characteristics of an oil. VIIIs are high-molecular-weight polymers that are compact molecules at low temperatures and expand in size as the temperature increases. Styrene-butadienes, acryloids, polymethacrylates, and various copolymers are the main VIIIs used in industrial oils today. Also VIIIs usually increase the viscosity of the lubricant and can be used in formulating a fluid to increase the viscosity of a base fluid.

Low-temperature viscosity is also an important specification for equipment that must start or operate at low ambient temperatures. Paraffinic petroleum-derived base oils become very viscous at low temperatures unless the high wax content is removed. Typically, isoparaffinic and naphthenic base oils are fluid down to temperatures below -40°C . Synthetic fluids generally have excellent low-temperature properties. Natural oils, such as vegetable oils, are solids or become very viscous by $\sim 0^{\circ}\text{C}$.

Pour point depressant additives are often used to improve deficiencies in lubricants based on petroleum-derived paraffinic base fluids. These additives interfere with the wax crystalline network formed in these paraffinic oils at low temperatures. The effectiveness depends on both the type of fluid and the chemical structure of the additive used. Evaluation of concentration levels and fluid blending is required to achieve the maximum low-temperature properties for these additives. Several Group II and Group III base fluids contain high levels of isoparaffinic molecules and have acceptable pour points without the need of pour point depressants. Natural oils, on the contrary, may require blending with synthetic fluids and pour point depressants to achieve the necessary viscosity levels at lower temperatures. Some commercially available additives are effective in mineral oils but have limited or no effect in natural oils. Acceptable pour point depends on the conditions of use. Obviously, fluids to be used in arctic conditions must have fluidity at the lowest temperature of use. Generally, this will be most important at start-up because some frictional heating will help bring a lubricant to a lower viscosity as the equipment continues to run. This is critical for equipment in remote locations such as space applications and remote measuring equipment. However, these fluids are generally designed with synthetic base fluids that have low pour points and low low-temperature viscosities.

System components such as seals and gaskets can shrink, swell, crack, or otherwise deteriorate if they are not compatible with the fluids used. Seal swell control is important to ensure fluid compatibility with the proper seal materials to prevent oil leaks. Organic phosphates have been used; however, the generally accepted approach, especially for synthetic fluids, is to blend the base fluids to achieve the correct degree of seal swell. For example, blending mixtures of synthetic hydrocarbons, such as polyalphaolefins, and esters to achieve desired seal swell results is a common practice.

In the case of water base fluids such as hydraulic, metalworking, water-glycols, antifreeze, and other similar fluids, the use of demulsifiers, emulsifiers, biocides, and corrosion prevention additives are often required.

Metalworking fluids can contain AW, EP, antimist, corrosion inhibitors, biocides, antifungicides, defoamers, couplers, and dyes.

20.14 INDUSTRIAL APPLICATIONS

The preceding Section 20.13 has described the form and function of additives and the chemistry involved in the use of these additives. The areas of industrial application are extremely diverse, both in terms of applications and in the severity of the conditions under which the additives must perform and maintain the integrity and quality of the lubricant.

Following is a list of some of the more important lubricants for industrial applications.

1. Air tool lubricants
2. Bearing lubricants
3. Cable oils
 - a. Hollow cables
 - b. Solid cables
4. Chain lubricants
5. Compressor lubricants
 - a. Air compressors
 - b. Reciprocating compressors
 - c. Rotary screw compressors
 - i. Oil-flooded compressors
 - d. Rotary vane compressors
 - e. Centrifugal compressors
 - f. Axial flow compressors
 - g. Gas compressors
 - i. Natural gas compressors
 - ii. Ethylene compressors
 - iii. Process gas compressors
 - h. Refrigeration compressors
 - i. Reciprocating compressors
 - ii. Rotary screw compressors
6. Condenser oils
7. Conveyor lubricants
8. Drilling fluids
9. Gear lubricants
 - a. AW
 - b. EP
 - c. R&O
10. Grease
11. Heat transfer fluids
12. Hydraulic oils
 - a. Gear pumps
 - b. High-pressure hydraulics
 - c. Piston pumps
 - d. Vane pumps
13. Metalworking fluids
 - a. Continuous casting

- b. Cold forging
 - c. Cutting
 - d. Coolants
 - e. Drawing
 - f. Extrusion
 - g. Grinding
 - h. Honing
 - i. Lapping
 - j. Punching
 - k. Rolling
 - l. Quenching
 - m. Spark erosion oils
14. Mold release agents
 15. Rubber release agents
 16. Shock absorber oils
 17. Switch gear oils
 18. Textile lubricants
 19. Turbines
 - a. Gas turbines
 - i. Aircraft turbines
 - b. Steam turbines
 20. Transformer fluids
 21. Vacuum pump oils
 22. Vibration damping oils
 23. Wire rope protection fluids

Each of these applications has various subsets, and lubricants and the additives used will depend on the properties of the oil and the performance requirements for that oil. Some of these applications require oil-only formulations and, therefore, require oil-soluble additives. Other formulations, especially in some metalworking applications, use oil-in-water emulsions, and these formulations require different additive chemistries. Details on the types of additives that are used in each of these areas can be found in various chapters of this book and in several excellent references [2,3,66].

Essentially all industrial lubricants include some additives, even if only a protective amount of antioxidant or a small amount of AW additive. Bench tests are typically used to screen the performance of additives. This is done because the cost of testing using bench tests is significantly less than the cost of field test or full-scale equipment tests. An additional reason is that tests can be performed using less lubricant, and test times permit more variations to be evaluated than can typically be done in full-scale equipment.

There are countless methods available for evaluating lubricant formulations. These range from measuring physical properties, for example, viscosity, pour point, flash point, fire point, specific gravity, and volatility, to structural analysis using infrared spectroscopy, elemental analysis, aniline point, and carbon residue. Further testing might include corrosion testing, hydrolytic stability, seal compatibility, and seal swell tests. There are also a wide variety of mechanical test methods such as the four-ball wear test and various Falex test methods. Most of the industry-accepted tests are those listed by the Institute of Petroleum, the American Standard Testing Materials (ASTM), the Deutsche Industrie Normung (DIN), the Japan Industrial Standard (JIS), and the Co-ordinating European Council (CEC). A summary of many of these standard test methods can be found in Chapter 27.

In addition to the standard test methods, there are several laboratory test techniques that have been used to evaluate various aspects of lubricant fluids and formulations. Furthermore, there are many unpublished proprietary methods that have been designed and used by various companies in

the lubricant industry. A few examples of analytical techniques that have been applied to lubricant evaluation will be described in the following few paragraphs.

Thermal methods, such as thermogravimetric analysis (TGA) and pressure differential scanning calorimetry (PDSC), have been used to evaluate volatility, oxidation stability, and deposit-forming tendencies [67–74]. Noel and Cranton were among the first to realize the potential of using DSC for characterizing lubricant fluids [67–69].

A method has been developed using DSC to evaluate the remaining useful life of a lubricant. This work showed that one could use the data from DSC to essentially predict when to change the oil in turbine engines resulting in savings in the costs associated with equipment failure by not changing the oil soon enough and the costs associated with changing the oil too soon because of inaccurate data on the quality of the used oil [70].

In-Sik Rhee [71] has reported on the development of a new oxidation stability test method for greases using a PDSC. Advantages to use of PDSC are that only small samples are required, the analyses are rapid and repeatable, and sensitivity is high.

The observation that lubricant base fluids exhibit differences in volatility depending on whether air is present or not has been demonstrated, and this difference has been described as the oxidation-mediated volatility [75]. Others have used DSC to evaluate the thermooxidative stability of formulated lubricants using thermal analytical methods [76].

Standard oxidation tests are routinely used to determine the quality of a lubricant formulation, and the results of these tests are frequently listed in the product specification or on the technical data sheets for the product. Two important industry tests are the rotating pressure vessel oxidation test (RPVOT), ASTM Method D2272, and the oxidation characteristics of inhibited mineral oils, ASTM Method D943. Both of these are examples of bulk oxidation tests [77]. More recently developed oxidation tests are the thin-film oxygen uptake test (TFOUT) and a thermooxidation engine oil simulation test (TEOST). These, in contrast to the previously described tests, are thin-film oxidation tests [78,79]. All of these tests are used to evaluate the thermal and oxidative stability of base fluids and formulations containing additives expected to enhance performance.

Evaluation of friction and wear can be performed on various testers. ASLE (now STLE) in 1976 [80] compiled a list of 234 wear test methods. ASTM lists several friction and wear methods including four four-ball methods—ASTM Methods D2266, D2783, D4172, and D51283 [76]. Variations of the use of the four-ball test as a research tool are reported in the literature [81,82]. The Cameron-Plint and pin-on-disc tests are also widely used for evaluation of materials, friction, and wear [83,84].

20.15 SUMMARY AND CONCLUSIONS

Additives perform a wide variety of functions and represent an important and necessary contribution to the overall properties and performance of industrial lubricants. Without additives, even the best base fluids are deficient in some features. Formulation of a product is always a compromise. There is always the issue of cost/performance. Many times, there is a great amount of research necessary to balance the various effects of the different additives used in combination with the base oils.

The arsenal of lubricant additives is large, and yet, new additives continue to be developed. This will help future lubricants meet the increasingly demanding conditions that equipment manufacturers require. Furthermore, environmental issues will require more benign and environmental-friendly additive design in the future to meet the global regulations that are being proposed and implemented.

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21 Formulation Components for Incidental Food-Contact Lubricants

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21.1 INTRODUCTION

21.1.1 BACKGROUND

Lubricants are used in the food industry during processing, production, manufacture, and packaging of food products. Lubricating oils and greases as well as solid lubricants are used in the food industry. These lubricants are classified into three categories—H1, H2, and direct food-contact lubricants. A fourth category, H3, is generally applied to trolley lubricants. An excellent review of this topic is found in the previous edition of this book [1,2].

By definition, H1 lubricants have to be used in applications where the lubricant is likely to come into contact with food, and as a result, H1 lubricants are called *incidental food-contact lubricants*.

TABLE 21.1
Classification of Lubricants Used in the Food Industry

Lubricant Classification	Application	Compliance
H1	Application where there is possibility of food contact	21CFR Section 178.3570
H2	Application where there is no possibility of food contact	Not defined but generally the lubricants must be free of any toxic heavy metals or ingredients
H3	Trolley oils	None defined

These lubricants are also commonly referred to as food-grade lubricants in the industry, but this term is to some extent misleading in that the end user may be led to believe that the lubricants meet the same safety standards as edible food and food ingredients, which is not the case. In contrast, H2 lubricants can only be used in parts of a food plant where there can be no possibility of contact with food. H1 lubricants can therefore be used in place of H2 lubricants but not the other way around. The distinction between the categories is summarized in Table 21.1.

The finished lubricant and components undergo different levels of scrutiny.

21.1.2 APPROVAL OF COMPONENTS AND BASE OILS

The additive components and base oils used in the formulation of H1 lubricants must belong to specific sections in the *Code of Federal Regulations*, Book 21. These sections include [3]

- Incidental Food-Contact Lubricants (21 CFR Section 178.3570)
- Prior Sanctions List (21 CFR Section 181)
- Generally Recognized as Safe (GRAS, 21 CFR Section 182)

Section 178.3570 specifically contains ingredients that can be used as lubricating additives or base oils for incidental food contact applications. To be listed in this section, the supplier has to petition the Food and Drug Administration (FDA). This review could result in an opinion letter from the FDA (which generally applies to chemical equivalents such as in cases where the sodium salt is listed but the potassium salt is not) or a full review for new ingredients. A full review can be very expensive and time-consuming. A key global supplier of incidental food-contact lubricants has effectively developed, petitioned, and won approval for a large number of additives that are listed in Section 178.3570 and has effectively enabled the development of this category of lubricants. On the base oil side, there are many suppliers who have successfully passed the scrutiny of the FDA.

The prior sanctions list and GRAS list does not specifically list ingredients for use in incidental food-contact lubricants. However, if ingredients on these lists will function as additives, or base oils they may be used in incidental food-contact lubricants. The prior sanctions list does not change as it identifies components that have been grandfathered due to the history of safe use.

The GRAS list is a well-established list that contains numerous ingredients that are mostly of value for food use, but there are some ingredients on the GRAS list that have lubricating properties. For example, vegetable oils would fit this category as they are on the GRAS list and can be used as lubricant base oils. Likewise, lecithin and certain fatty acids are GRAS listed and may be used in lubricants also. To list an ingredient as GRAS, the supplier can either self-affirm its GRAS status or petition the FDA.

As noted later, the National Sanitation Foundation (NSF), Ann Arbor, Michigan, is the entity that registers H1 lubricants [4]. All ingredients and base oils that belong to the 21CFR lists indicated are now categorized as HX-1, whereas the finished lubricants are classified as H1.

21.1.3 REGISTRATION OF THE FULLY FORMULATED (FINISHED) LUBRICANT

Generally, lubricant suppliers to the food industry undertake the exercise of registering their products as H1 or H2 lubricants. Until 2002, the U.S. Department of Agriculture (USDA) offered a program to register H1 or H2 lubricants and granted letters of approval to the manufacturer of the lubricant. The process involved submission of forms that outlined the complete composition (which was held in confidence by the USDA) as well as a label and sample of the lubricant. The USDA provided a letter of approval if the components of the lubricant complied with the 21 CFR sections indicated earlier. The service was free. If there were one or more ingredients not belonging to the sections mentioned earlier, then the USDA sought the opinion of the FDA.

However, the USDA abruptly discontinued this program in 1998. As a result, two organizations, the NSF and the Underwriters Laboratory (UL), entered the fray with proposals to continue and improve the program [1].

As of 2008, the NSF is now the key provider of this registration. More than 350 companies worldwide have now registered their lubricants with the NSF, and the list continues to grow. Growing awareness about the use of H1 lubricants is a key reason for this growth. Also, growth is driven by the fact that the U.S. companies are opening manufacturing facilities in Asia, South America, and other parts of the world. Previously, little consideration was given to the use of H1 lubricants in these areas. But to stay competitive and to be able to export their food production, local companies in these countries are also likely to use H1 lubricants, this is expected to spur further growth in this market.

It must be noted that the NSF certification is not mandatory, and suppliers may self-certify their products.

21.1.4 RELIGIOUS APPROVALS

In addition to approvals that are based on federal government criteria, there are certain approvals associated with religious affiliations that are sought after by manufacturers of components and finished lubricants for incidental food contact.

The two key approvals are kosher and halal. Facilities that make food belonging to these categories expect that the lubricants used in their facilities also meet this qualification. As a consequence, customers may demand kosher and halal certification for lubricants' additives, and finished lubricants.

For kosher and halal, manufacturers of additives base oils or finished lubes must generally meet two distinct levels of compliance. The plant and process where the product is made must be kosher or halal compliant, and the components or finished lubricant itself must be kosher or halal certified. Often, therefore, the two criteria are not mutually exclusive but intertwined, and certification letters may be obtained for the facility and the products.

Jewish dietary laws are termed *kosher* [5]. Although there may be slight differences in interpretation of these laws by various kosher-certifying agencies, the ingredients and the facility must meet the following criteria:

The products cannot mix meat and milk products or contain pork and related products. Also, if there is an animal derived product then the animal must be slaughtered according to Kosher guidelines. From a procedural standpoint no product should be processed on equipment that is processing non-Kosher material. In such cases special cleaning and twenty-four hour wait periods apply.

In the United States, there are about 300 agencies that offer kosher certification. The Orthodox Union in Manhattan, New York, is the largest and certifies about 4500 facilities in 68 countries. The process involves a fee and a mandatory visit to the facilities by a rabbi. To maintain certification, a company must be willing to pay the requisite fee and be amenable to unannounced inspections.

Muslim dietary laws require the imposition of *halal* (meaning lawful versus “*haram*” which means unlawful), which means that the facility and the ingredients must meet the following criteria [6]:

Kosher approvals described above except that for animal products Halal laws must be observed and additionally alcohol must be excluded from any process. The Islamic Food and Nutrition Council of America, Chicago, Illinois issues Halal certificates and the process involves a fee as well as annual inspections.

Neither of these are mandatory, but given the fact that there are about 13 millions Jews and almost 1.6 billion Muslims worldwide, it is something that manufacturers consider to address its potential customer base.

21.1.5 OTHER FACTORS TO CONSIDER FOR INCIDENTAL FOOD-CONTACT LUBRICANTS

In addition to the considerations indicated earlier, the manufacturer may consider using “good manufacturing practices” (GMP) or registration against specific “International Standards Organization” (ISO) standards such as 9001 and 14001.

GMP involves self-established protocols during manufacture, which can range from cleaning protocols to analysis for heavy metals. The ISO standards, which are now common, involve annual audits and fees.

21.1.6 SUMMARY OF CRITERIA FOR INCIDENTAL FOOD-CONTACT LUBRICANTS

The purpose of this section is to summarize the various criteria that are expected for incidental food-contact lubricants (additives and finished fluids or greases). The use of approved components generally leads to automatic qualification for registration of the finished fluid or grease as an H1 lubricant. This may be done by self-affirmation or through the NSF.

However, the implication of these restrictions is that the development of these products is challenging, and the entire process adds cost. This is generally reflected in the higher price of these lubricants when compared to conventional lubricants. An excellent overview of challenges encountered in the development and manufacture of incidental food-contact lubricants has been published recently [7].

Figure 21.1 provides a summary of various criteria that must be met at the ingredient level, the finished fluid or grease level, or at the plant level.

Ingredients Additives Components Base oils	Finished Lubricant Lubricating oil Grease and compounds Solid lubricant	Facility Manufacturing and Packaging Sites
21CFR Sections Incidental Food Contact Lubricants 178.3570 GRAS 182 Prior Sanctions 181 Other NSF HX-1 Kosher Halal	21CFR Sections Incidental Food Contact Lubricants 178.3570 GRAS 182 Prior Sanctions 181 Other NSF H-1 Kosher Halal ISO 21469 OEM approvals	Facility GMP Kosher Halal ISO21469 ISO 9001 ISO

FIGURE 21.1 Summary of criteria for incidental food-contact lubricants.

TABLE 21.2
Typical Properties of Base Oils

Base Oil	ISO Viscosity Range	Pour Point (°C)	Antioxidant Response	Cost Range (\$/lb) ^a
Group II oils				
Technical white mineral oil	32–46	−9	Excellent	0.30–0.35
Group II oils	32–46	−9	Excellent	0.30–0.35
Group IV oils				
PAO	32–46	<−30	Excellent	1.00–2.0
Group V Oils				
Polyisobutylenes	220 to >1000			0.85–1.20
Polyinternal olefins				
PAG	32–46	−12	Good	1–2
Vegetable oils	32 and 220	−15	Moderate	~0.60 to 1.0
Esters	46–1000	−45	Good	~1 to 3
Silicones	46	−50	^b	~2 to 4
Perfluoro oils	32	~−12	^b	~1 to 3

^a Price will vary based on quantity, customers, suppliers, and market conditions.

^b Most additives are not soluble in these base oils.

21.1.7 COMPONENTS USED IN INCIDENTAL FOOD-CONTACT LUBRICANTS

The USDA program classified all qualified additives, base oils and finished lubricants as H1 lubricants as long as the components belonged to 21CFR Section 178.3570, GRAS list, or the prior sanctions list. Since the NSF took over the program, a new category termed HX-1 has been created for components that include additives, thickeners, and base oils, whereas finished lubricants are classified in the H1 category.

21.1.8 BASE OILS FOR INCIDENTAL FOOD-CONTACT LUBRICANTS

Whether the lubricant is an oil or grease, the base oil—usually the main ingredient. For mineral oils to meet the criteria for incidental food contact lubricants, the presence of aromatics in mineral base oils is not tolerated. This limitation led to the approval and use of technical white mineral oil as base oil. Although speculative, it could be argued that Group II oils, polyalphaolefins (PAOs) and polybutenes, were presumably approved due to the fact that they are also free of aromatics. In addition to hydrocarbon base oils, polyalkylene glycols (PAGs) are also approved. More recently, the NSF has approved various esters which enhances formulation flexibility. Additionally, technology is available for vegetable oil-based incidental food-contact lubricants and is covered in a U.S. Patent [8]. Vegetable oils can be used by virtue of their GRAS status. This means that a wide range of base oils are now available to a formulator (Table 21.2).

21.2 ADDITIVES

21.2.1 THICKENERS

The viscosity of a lubricant is dictated by the application. Common viscosity grades for various lubricants are listed in Table 21.3.

Polyisobutylenes (PIBs; Figure 21.2) are effective thickeners for mineral oil lubricants. The thickening efficiency of a commercially available PIB is shown in Figure 21.3 [9]. PIBs are available

TABLE 21.3
**Typical Viscosity Ranges for Incidental
Food-Contact Lubricants**

Fluid Type	Typical ISO Viscosity Range
Hydraulic fluids	32–68
Gear oils	100–460
Air compressor oils	32–100

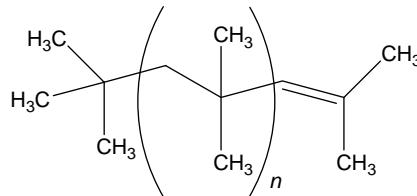


FIGURE 21.2 Chemical structure of polyisobutylenes (increasing n increases the molecular weight of polyisobutylene and its thickening efficiency).

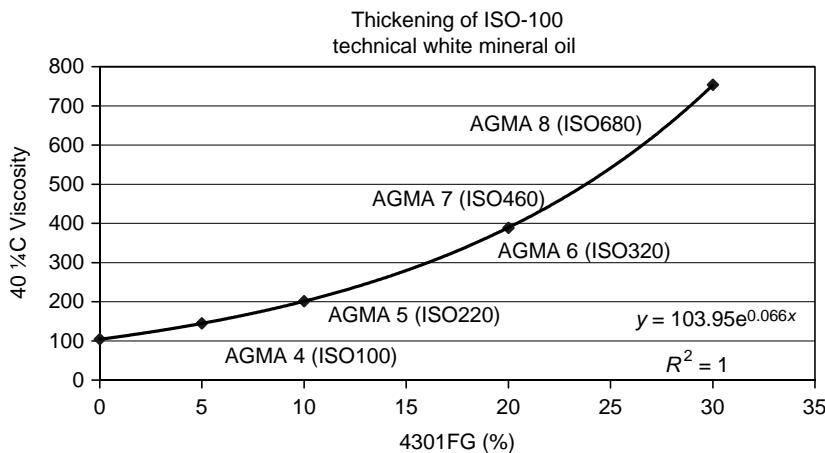


FIGURE 21.3 Increasing the ISO grade of incidental food-contact lubricants.

in various viscosity grades. Special handling of PIBs is required for higher viscosity PIBs. PIBs are soluble in hydrocarbon oils but may be insoluble in water-insoluble PAGs and certain esters. Vegetable oils have a limited viscosity range between ISO 32 and 46, which limits their usage in higher-viscosity applications, and PIB is generally incompatible with vegetable oils.

21.2.2 TACKIFIERS

Tackifiers are used to impart stringiness to a lubricant, which in turn improves its adherence to surfaces. An excellent general review on this topic is available [10]. Tackifiers find use in chain oils used in the food industries. Traditionally, tack has been qualitatively measured and is often tested by the *sticky finger test*. Here, the number of strings between two fingers is counted, and a large number of strings indicate better tack. A recent publication has reported substantial progress toward

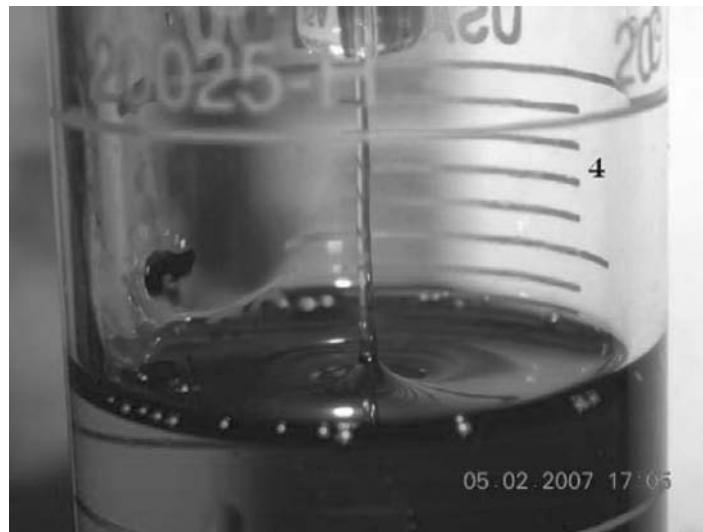


FIGURE 21.4 Free jet length resulting from tack. (Devore, D., Private Communication, Functional Products.)

quantifying tack using an open siphon method that ultimately measures *free jet* length (Figure 21.4), which is correlated to the tackiness [11]. Tack was found to be a result of exudation of solvent from a swollen gel in dilute polymer solutions of the tackifier in oil. Tack depends on the molecular weight (MW) and concentration of the polymer and its viscoelastic properties.

One of the approved HX1 tackifiers are high-molecular-weight polybutene tackifiers. These polymers have the ability to *extend* and are also oxidatively stable due to their low level of unsaturation.

21.2.3 POUR POINT DEPRESSANTS

Although low-temperature properties are important in industrial and off-highway applications, most food manufacturing occurs in controlled conditions of temperature, and low-temperature properties are not as critical. At the time of writing, there is no pour point depressant that is approved for use in incidental food-contact lubricants. The best approach to lower pour points is to blend in low viscosity base oils.

21.2.4 ANTIOXIDANTS

Incidental food-contact lubricants are used in applications such as hydraulic fluids, gear oils, compressor oils, chain oils, and greases. These lubricants are subject to oxidative stresses much like conventional lubricants but also present additional challenges. First, the approved hydrocarbon base oils have very low polarity and solubilizing power due to the removal of the aromatic content in the oil. As a result, by-products of oxidation such as sludge are not easily solubilized, and this can affect equipment performance. Second, these lubricants can be subject to temperatures as high as 350°F in oven chain oils and bearing grease. Fortunately, group II base oils and technical white mineral oils and PAOs, which are commonly used base oils in these applications, respond well to antioxidants because they have very low unsaturation. Many antioxidants are available for incidental food-contact lubricants. These include hindered phenols to substituted amine antioxidants. Some natural antioxidants such as tocopherols may also be used. The structures of some of these antioxidants are shown in Figure 21.5.

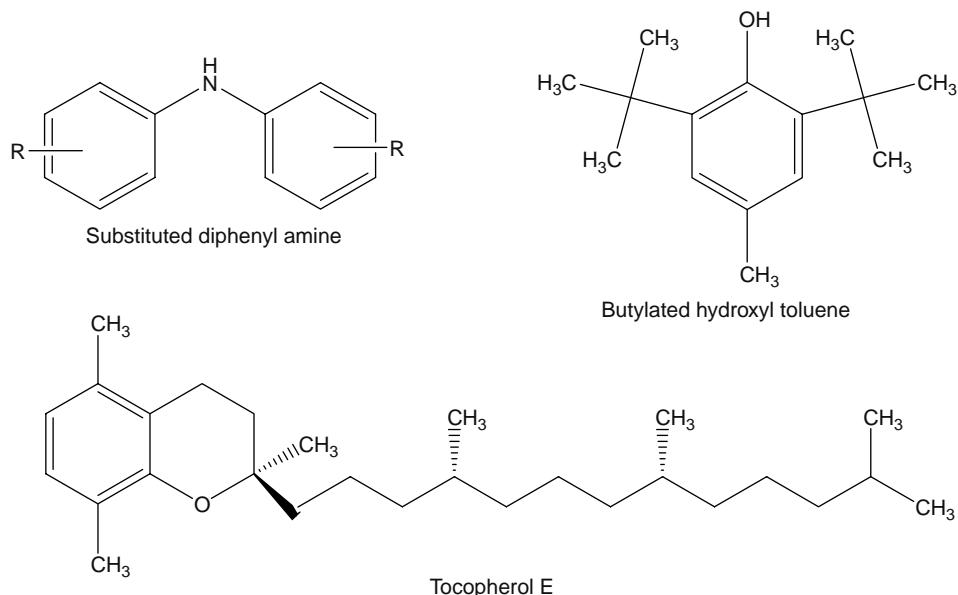
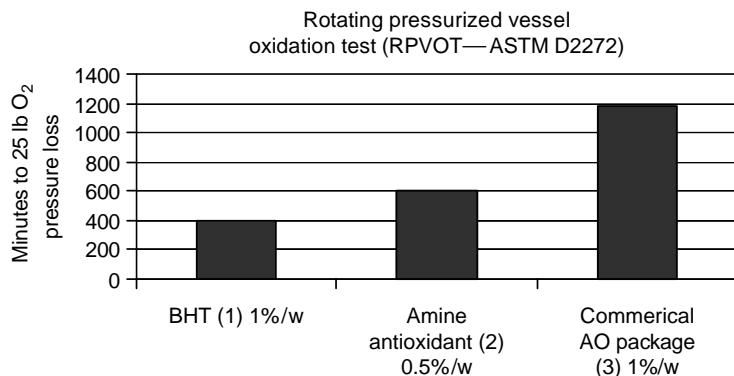


FIGURE 21.5 Chemical structures of antioxidants.



- (1) Shown at treat level comparable to the commercial antioxidant package
- (2) Shown at maximum permitted level
- (3) Shown at half the maximum permitted treat level

FIGURE 21.6 Performance of a commercial antioxidant package. (Devore, D., Private Communication, Functional Products.)

Substituted amine antioxidants are very effective in mineral oils although some darkening may be expected. Hindered phenols such as butylated hydroxyl toluene (BHT) are also very effective and may not cause as much discoloration. However, BHT may be difficult to solubilize in a blend, and therefore, there is a clear need for more soluble antioxidants.

The recent introduction of an antioxidant package offers a product that is in liquid form and is highly effective in various oils. The results of this package in technical white mineral oil are shown in Figure 21.6 [9].

21.2.5 ANTIWEAR AND EXTREME-PRESSURE AGENTS

Antiwear agents are a crucial component of a lubricant. One of the most commonly used antiwear agent in incidental food-contact lubricants is an amine phosphate salt shown in Figure 21.7. The amine phosphate salt also provides a degree of rust protection. Other antiwear agents include glycerol esters as well as certain fatty acids.

A limited number of extreme-pressure (EP) agents are available. One of the most commonly used EP components is triphenyl phosphorothionate (TPPT), which is a white crystalline solid. Soluble versions of this EP agent containing alkyl substitutions on the aromatic rings are also available (Figure 21.8). Very often, Timken OK load values obtained for mineral oil and PAO-based incidental food-contact lubricants are in the 15–25 lb range. Although the approval of ingredients with active sulfur is desirable to obtain conventional EP performance it appears that the industry has quite successfully managed with the use of EP agents shown in Figure 21.8.

21.2.6 RUST AND CORROSION INHIBITORS

Incidental food-contact lubricants can be exposed to high-moisture conditions, which means that it is important that the lubricants have adequate rust and corrosion protection. Oleyl sarcosine (Figure 21.9) is commonly used, and it is highly effective in mineral oils, PAO, and vegetable oils. A consistent pass test result can be obtained with this additive in both parts of the ASTM D665 rust test. The maximum treat rate permitted for this additive is 0.5% by weight.

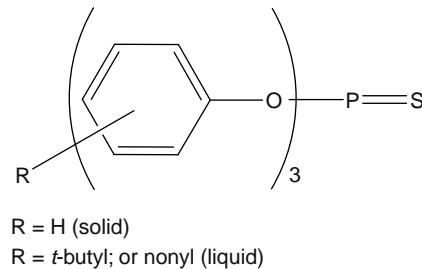
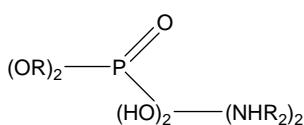
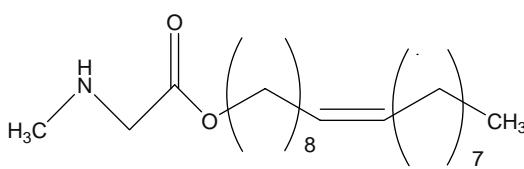
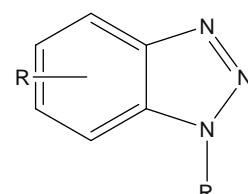


FIGURE 21.7 Chemical structure of a commonly used antiwear agent (phosphoric acid, mono- and dialkylesters, compounds with substituted amines).

FIGURE 21.8 Chemical structure of commonly used EP agent (structure of TPPT).



N-methyl-*N*-(1-oxo-9-octadecynyl) glycine — Oleyl sarcosine



Substituted imidazoline

FIGURE 21.9 Chemical structures of rust inhibitors and metal deactivators.

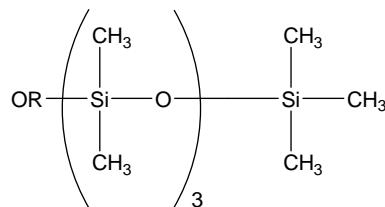


FIGURE 21.10 Chemical structure of a dimethylpolysiloxane defoamer.

21.2.7 DEFOAMERS

Defoamers are used to prevent excessive foaming. Silicon defoamers are approved for use in incidental food-contact lubricants as long as the molecular weight of the defoamers is > 2000 (Figure 21.10). They are generally effective in all approved base oils for this application.

21.2.8 ADDITIVE PACKAGES FOR INCIDENTAL FOOD-CONTACT LUBRICANTS

As in conventional lubricants, additive packages simplify operation and can cut development time. One of the challenges in offering additive packages is to ensure that the limits specified for components must be adhered to. Hydraulic fluid additive packages are now offered by two leading additive suppliers. One of the suppliers offers a product that may be used in hydraulic oils as well as gear oils, thereby providing additional procurement simplicity. Key performance results for this additive package are shown in Table 21.4 and performance tests are shown in Table 21.5 [9].

21.2.9 FORMULATION CHALLENGES FOR INCIDENTAL FOOD-CONTACT LUBRICANTS

The formulation of incidental food-contact lubricants is challenging because the formulator has to abide by many restrictions. These include

- Limited list of approved ingredients—base oils and additives
- Limitations on the amount of additive that can be used
- Limited solubility of additives in technical white mineral oil
- A *fixed* additive database that creates challenges in product differentiation

This is similar to other specialty lubricants that must meet not only performance standards expected out of a conventional lubricant but also additional criteria [12]. A recently published article summarizes “five hurdles to making incidental food-contact lubricants” and addresses some of the aspects related to the formulation and manufacture of incidental food-contact lubricants in more detail [8].

21.2.10 FUTURE OUTLOOK AND DRIVING FORCES FOR COMPONENTS USED IN INCIDENTAL FOOD-CONTACT LUBRICANTS

Incidental food-contact lubricants constitute a growing area in the mature lubricant market. Several factors will continue to drive this growth. In the western hemisphere, there is growing awareness of the need to use this special class of lubricants. Some plants are converting to all H1 lubricants to reduce complexity and operational errors, which can lead to wastage if food gets contaminated by non-H1 lubricants. The growth in population creates direct and increased demand for food. Furthermore, the increasing affluence in China and India has led to an increased demand for processed and packaged food. This has resulted in local companies establishing modern food

TABLE 21.4
Performance of a Commercial Hydraulic and Gear Oil Additive Package

Test Method	Test Method (ASTM or Other)	ISO 46 Hydraulic Fluid (Typical Result)	ISO 220 Gear Oil (Typical Result)
Performance tests			
Air release at 50°C	D3427		
Air bubble separation (in minutes)		2.5	
Oxidation and seal performance			
RBOT (minutes to 25 lb oxygen pressure loss)	D2272	571	623
Seals 168 h/100°C	Hydraulic SRE-NBR28		
% volume/hardness change			4.8/-5
% tensile strength/elongation decrease			1.3/-4
Corrosion and wear performance			
Copper strip	D130		
3 h at 100°C		1B	1A
3 h at 121°C			1B
Rust test—part A/part B	D665	Pass/pass	Pass/pass
4-Ball wear test (167°F, 1200 rpm, 20 kg)			
Scar diameter (mm)		0.30	
Average friction coefficient		0.108	
4-Ball wear test (167°F, 1200 rpm, 40 kg)	D4172		
Scar diameter (mm)		0.37	0.37
Average friction coefficient		0.113	0.117

TABLE 21.5
Pump Test Performance of a Commercial Hydraulic and Gear Oil Package

Test Method	Initial/Final Flow (gpm)	Total Ring and Vane Weight Loss (mg) ^a	Ring Weight Loss (mg) ^a	Vanes Weight Loss (mg) ^a
Eaton-Vickers V104-C 100 h at 150F Conestoga	5.3/5.3	42	39	3
Eaton-Vickers 35VQ (50 h)		52	45	7

^a The values indicated in the tables are typical results and are not intended to be specifications.

manufacturing, processing, and packaging plants and likewise attracted western food companies to establish operations in these countries. To maintain their global quality standard, most of these operations use incidental food-contact lubricants.

On the regulatory front, a key change on the horizon is the introduction of the ISO 21469 standard. Although most of the aspects of this standard pertain to finished lubricants, the standard could potentially increase the types of additives available since the additives may be included in any one of the following [13]:

- Joint FAO/WHO Expert Committee on Food Additives (JECFA)
- Council Directive 95/2/EC on food additives other than colors or sweeteners
- United States CFR 21 part 178.3570: Lubricants with incidental food contact and relevant sections referenced therein

Overall, incidental food contact lubricants are an exiting subset of industrial lubricants. The growing awareness regarding use of these lubricants and the evolution of ISO standards could lead to global harmonization and increased use of incidental food-contact lubricants.

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22 Lubricants for the Disk Drive Industry

Tom E. Karis

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22.1 INTRODUCTION

When thinking of a disk drive, one picture that comes to mind is that of digital data bits stored on a spinning disk housed inside a device such as a computer, digital video recorder, or music player. The outstanding precision and reliability of these high-speed rotating electromechanical devices is, perhaps, the leading example of microelectromechanical systems and nanotechnology at work today. For example, the magnetic recording read/write head floats on an air-lubricated bearing just ~ 5 nm away from the disk surface with a relative velocity that is often more than 10 m/s. That is a shear rate of 2,000,000,000 m/s. As the data track width in the near future is decreased below 200 nm, the spindle motor on which the disks are mounted must have increasing stiffness with diminishing vibration amplitudes that are well below the track width to minimize servo seek time and track following. Ball bearing spindle motors used in the past have reached their limit, and current products incorporate fluid dynamic bearing spindle motors. In addition, when there is a high relative velocity between metallic and insulating components, electrostatic charge generation and dissipation must be controlled. Lubricants play a vital role in fulfilling these requirements for the disk drive industry. Fundamental understanding of the lubrication mechanism and lubricant chemistry is essential to the continued advancement of the technology.

This chapter focuses on lubricants for the magnetic recording disk and the spindle bearing motor. Emphasis is placed on the analytical tools that are common to lubricants in general. Similar techniques are applied to characterize the physical properties of lubricants that influence their performance. Rheological measurements are employed not only to characterize the viscosity, but also to estimate the short-time dynamic response of disk lubricants through time-temperature superposition. Shear rheometry is exploited to characterize the yield stress of grease, as well as the effect of blending on fluid dynamic bearing motor oils. Dielectric spectroscopy is utilized to probe the dipole relaxation of disk lubricant end groups. Dielectric permittivity and conductivity measurements are employed for development of conductivity additives for ferrofluid used in motor seals and to investigate the effects of contamination on ball bearing grease electrochemistry. Another powerful technique that is highlighted in this chapter is Fourier transform infrared (FTIR) spectroscopy. This method can be used to study thin films in reflection or bulk samples in transmission. Examples are shown in which infrared (IR) spectroscopy is also applied to identify reaction products formed during electrochemical oxidation of ball bearing grease. Thermal analysis is employed to measure the vapor pressure of disk lubricants. A model is described that simulates evaporation of polydispersed lubricants from molecular weight distributions measured with gel permeation chromatography (GPC). Surface energy from contact angle measurements is combined with the chemical kinetic model for viscous flow and evaporation to predict the viscosity of molecularly thin films and to understand factors that limit lubricant spin-off from rotating disks. The chemical kinetic model is also employed to combine vapor pressure and viscosity data in the quest for the molecular structure of a fluid bearing motor oil that has both low viscosity and vapor pressure. Not only are the techniques illustrated here with examples from the disk drive industry applicable to the lubrication industry in general, but they will also be particularly useful in adapting these methodologies to the tribology of micro- and nanoelectromechanical systems.

In this revised chapter, nuclear magnetic resonance (NMR) spectra of several fluid dynamic bearing oils are included to highlight the chemical structural differences. As accelerated motor life tests, and even tests on stabilized oils at elevated temperatures take a very long time, a kinetic model that includes the synergistic effects of primary antioxidant (PriAOX) and secondary antioxidant (SecAOX) and metal catalyst on oil oxidation lifetime is presented to help estimate the optimum additive concentrations. Examples of accelerated oil life testing are shown with an aromatic amine PriAOX and an alkyl dithiocarbamate SecAOX as well as the effect of dissolved metal catalyst in isothermal accelerated oil oxidation life tests.

22.2 RECORDING DISK LUBRICANTS

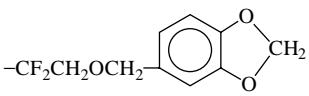
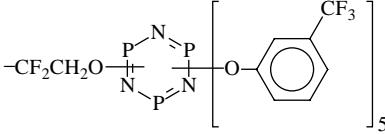
The soft magnetic layers on the magnetic recording disk substrate are typically overcoated with a 3–5 nm thick carbonaceous film. As the overcoat has a relatively high surface energy, a low-surface energy perfluoropolyether (PFPE) lubricant is applied on top of the overcoat. The most widely used PFPEs are those having the Z-type backbone chain. These are random copolymers with the linear backbone chain structure:



where X is the end group and Z the backbone chain with degree of polymerization x_0 .

A wide range of end groups is available to tailor the lubricant for optimum lubrication properties. The end groups for some of the commercially available lubricants are given in Table 22.1 [1]. The adsorption energy of end groups (other than $-CF_3$) on the carbon overcoat surface is higher than that of the backbone chain [2,3]. The X1P type end group on A20H [4,5] is sterically large in comparison to the chain monomers [6], and the X1P end group molecular weight of ~1000 Da is a significant contribution to the molecular weight of commonly used backbone chains of 2000–4000 Da [7]. Lower-molecular-weight end groups, also intended to passivate Lewis acid sites, are derived from Zdol with dipropylamine [8] and referred to as ZDPA.

TABLE 22.1
Molecular Structure for Some of PFPE End Groups on
the Z-Type PFPE Chain

Name	Structure
Z	$-CF_3$
Zdol	$-CF_2CH_2OH$
Ztetraol	$\begin{array}{c} OH \\ \\ -CF_2CH_2OCH_2CHCH_2OH \end{array}$
Zdiac	$-CF_2COOH$
Zdeal	$-CF_2COOCH_3$
Zdol TX	$-CF_2CH_2(OCH_2CH_2)_{1.5}OH$
AM-3001	
A20H	
ZDPA	$\begin{array}{c} CH_2CH_2CH_3 \\ \\ -CF_2CH_2N\backslash \\ \\ CH_2CH_2CH_3 \end{array}$

Note: A20H has one Zdol end group.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

The molecular structures of the D and K series of PFPEs, also considered for magnetic recording disk lubricants at one time, are given in Table 22.2 [1]. The repeat unit of the D chain is perfluoro *n*-propylene oxide. The D series includes Demnum with nonpolar end groups, Demnum SA with a hydroxyl end group, and Demnum SH with a carboxylic acid end group. The repeat unit of the K chain is perfluoro isopropylene oxide. The K series includes Krytox with nonpolar end groups and Krytox COOH with a carboxylic acid end group.

Recently, PFPE magnetic recording disk lubricants have been developed with a multiplicity of hydroxyl end groups to increase their chemisorption to the overcoat (Table 22.3) [1]. Two Zdol chains are linked with epichlorhydrin to form a Zdol multidentate (ZDMD) with one hydroxyl group at each end and one in the middle [9]. Two Ztetraol chains are linked with a fluorinated di-epoxide to form a Ztetraol multidentate (ZTMD) with two hydroxyl groups at each end and four near the middle [10]. A novel three-arm star multidentate PFPE comprising poly perfluoroethylene oxide was derived by direct fluorination of the hydrocarbon ester with one hydroxyl group at the end of each arm (LTA-30) [11,12] (Table 22.3).

22.2.1 PROPERTIES

PFPEs are attractive as magnetic recording disk lubricants because of their low surface energy, low vapor pressure, wide liquid range, transparency, and lack of odor. PFPEs are related to polytetrafluoroethylene, but they have lower glass transition temperatures [13–15]. The first commercially available PFPEs had perfluoromethyl end groups and are referred to as nonpolar PFPEs. More recently, polar PFPEs with hydroxyl, carboxylic acid, and other polar end groups have come

TABLE 22.2
Molecular Structure of D- and K-Type PFPEs

Name	Structure
Demnum S100	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\left(\text{CF}_2\text{CF}_2\text{CF}_2\text{O}\right)_{x_0}\text{CF}_2\text{CF}_3$
Demnum SA	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\left(\text{CF}_2\text{CF}_2\text{CF}_2\text{O}\right)_{x_0}\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$
Demnum DPA	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\left(\text{CF}_2\text{CF}_2\text{CF}_2\text{O}\right)_{x_0}\text{CF}_2\text{CF}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$
Demnum SH	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\left(\text{CF}_2\text{CF}_2\text{CF}_2\text{O}\right)_{x_0}\text{CF}_2\text{CF}_2\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{OH}$
Krytox 143AD	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\left(\overset{\text{CF}_3}{\text{CF}}\text{CF}_2\text{O}\right)_{x_0}\text{CF}_2\text{CF}_3$
Krytox COOH	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}\left(\overset{\text{CF}_3}{\text{CF}}\text{CF}_2\text{O}\right)_{x_0}\overset{\text{CF}_3}{\text{CF}}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

TABLE 22.3
Multidentate Disk Lubricant Structures Derived from Z-Type PFPEs

Name	Structure
ZDMD	$\text{HOCH}_2\text{CF}_2-\text{Z}-\text{OCF}_2\text{CH}_2\text{OCH}_2\overset{\text{CHCH}_2\text{OCH}_2\text{CF}_2-\text{Z}-\text{OCF}_2\text{CH}_2\text{OH}}{\underset{\text{OH}}{\text{OCH}_2\text{CHCH}_2\text{OCH}_2\text{CF}_2-\text{Z}-\text{OCF}_2\text{CH}_2\text{OH}}}$
ZTMD	$\text{HOCH}_2\text{CHCH}_2\text{OCH}_2\text{CF}_2-\text{Z}-\text{OCF}_2\text{CH}_2\text{OCH}_2\overset{\text{CHCH}_2\text{OCH}_2\text{CF}_2-\text{Z}-\text{OCF}_2\text{CH}_2\text{OCH}_2\text{CHCH}_2\text{OH}}{\underset{\text{OH}}{\text{OCH}_2\text{CHCH}_2\text{OCH}_2\text{CF}_2-\text{Z}-\text{OCF}_2\text{CH}_2\text{OCH}_2\text{CHCH}_2\text{OH}}}$
LTA-30	$\text{HO}\overset{\text{CF}_2\text{O}}{\underset{x}{\left[\text{OCF}_2\text{CF}_2\right]}}\overset{\text{OCF}}{\underset{x}{\left[\text{CF}_2\text{O}\right]}}\overset{\text{CF}_2\text{O}}{\underset{x}{\left[\text{CF}_2\text{CF}_2\text{O}\right]}}\text{CF}_2\text{OH}$

Note: The ZDMD is derived from Zdol 1000 or Zdol 2000. The ZTMD is derived from Ztetraol 1000. The LTA-30 has a molecular weight of 3000 Da.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

into widespread use. The polar end group provides an additional means to adjust the fluid properties and the interaction with surfaces. PFPEs with polar end groups are predominantly used to lubricate present day rigid magnetic recording media.

Their versatility has motivated considerable and detailed study of PFPEs. The bulk viscosity and glass transition temperature of the nonpolar PFPEs have been extensively characterized by Sianesi

TABLE 22.4
The Composition of Several PFPEs

Lubricant	<i>m</i>	<i>n</i>	<i>p</i>	<i>q</i>	<i>m/n</i>	O/C	<i>x</i>	<i>M_n</i> (Da)
Z03	0.530	0.405	0.057	0.008	1.31	0.754	73.4	6810
Zdiac	0.508	0.435	0.048	0.008	1.17	0.744	24.4	2310
Zdeal	0.567	0.426	0.003	0.004	1.33	0.782	22.8	2070
Ztetraol 2000	0.485	0.515	0	0	0.94	0.743	23.2	2300
Ztetraol 1000	0.523	0.477	0	0	1.10	0.762	14.2	1270
Ztx	0.475	0.517	0.007	0.001	0.92	0.736	22.7	2230
Zdol4KL819	0.612	0.383	0.003	0.0025	1.60	0.720	46.5	4000
Zdol4KL492	0.568	0.425	0.005	0.002	1.34	0.693	39.1	3600
Zdol4KL990	0.515	0.475	0.005	0.005	1.08	0.666	39.2	3600
Zdol4KBL598	0.492	0.508	0	0	0.97	0.658	47.2	4300
Zdol4KL905	0.469	0.526	0.0025	0.0025	0.89	0.650	41.5	3900
Zdol 2500	0.456	0.544	0	0	0.84	0.728	26.1	2420
Demnum S100	—	—	—	—	—	0.333	31.7	5230
Demnum SA2000	—	—	—	—	—	0.333	12.6	2080
Demnum SA2	—	—	—	—	—	0.333	18.6	3080
Demnum DPA	—	—	—	—	—	0.333	48.4	8100
Demnum SH	—	—	—	—	—	0.333	18.3	3040
Krytox 143 AD	—	—	—	—	—	0.333	39.8	6580
Krytox COOH	—	—	—	—	—	0.333	32.3	5370

Note: The degree of polymerization $x = x_0 + 2$. The Zdol4K series are different batches of Zdol 4000 from the manufacturer.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

et al. [13], Ouano et al. [16], Cantow et al. [17], Marchionni et al. [18–21], Cotts [22], and Ajroldi et al. [23]. Subsequent investigations have begun reporting the properties of PFPEs with polar end groups, for example, Danusso et al. [24], Tieghi et al. [25], Ajroldi et al. [26], and Kono et al. [27].

The composition and molecular weight of several PFPE lubricants, measured by NMR spectroscopy [28], is given in Table 22.4 [1].

22.2.1.1 Viscoelastic (Rheological)

Oscillatory shear and creep measurements were done with a Carri-Med CSL 500 (now TA Instruments) Stress Rheometer with the extended temperature module and a 40 mm diameter parallel plate fixture. The dynamic strain amplitude was 5%, and this was within the range of linear viscoelasticity for these materials. The storage, G' , and loss modulus, G'' , were measured between 1 and 100 rad/s at each temperature. Typically, measurements were done at every 20°C, from –20 to –100°C. Low-temperature measurements were performed to provide the high-frequency properties needed for calculations at the short time scales encountered in asperity contacts. The data measured at low temperature are transformed to high frequency through time–temperature superposition with Williams-Landel-Ferry (WLF) coefficients [29] that are derived from the rheological measurement data. The PFPEs were linearly viscoelastic at these test conditions. The dynamic properties were independent of strain amplitude, and no harmonic distortion of the sinusoidal angular displacement waveform was observed even at the lowest measurement temperatures. Time–temperature superposition was employed to obtain the master curves [30]. Viscosities for the lubricants at each temperature were calculated from the steady-state creep compliance. The glass transition temperatures, T_g , were measured using a modulated differential scanning calorimeter manufactured by TA Instruments model number 2920 MDSC V2.5F. The samples were cooled to –150°C and heated to

TABLE 22.5
The Glass Transition Temperature and the WLF Coefficients
of Several PFPEs

Lubricant	T_g (°C)	C_1	C_2
Z03	-131.8	14.13	24.51
Zdiac	-118.4	18.14	25.90
Zdeal	-120.2	17.25	23.64
Ztetraol 2000	-112.2	23.22	45.81
Ztx	-109.9	15.67	42.75
Zdol4KL819	-126.7	11.73	38.46
Zdol4KL492	-123.3	16.27	49.82
Zdol4KL990	-119.7	15.98	52.22
Zdol4KBL598	-117.2	16.66	37.14
Zdol4KL905	-115.6	10.54	38.05
Zdol 2500	-113.6	13.62	59.72
Demnum S100	-111.2	13.06	62.76
Demnum SA2000	-114.1	13.75	43.89
Demnum SA2	-110.2	13.77	62.11
Demnum DPA	-110.7	12.13	78.52
Demnum SH	-110.1	13.27	63.56
Krytox 143 AD	-66.1	12.22	31.65
Krytox COOH	-61.4	11.97	40.79

Note: The reference temperature for C_1 and C_2 is T_g .

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

20°C at 4°C/min with a 1.5° modulation over a period of 80 s. The differential heat flow and temperature phase shift were measured to determine the reversible and nonreversible components of the heat flow. The glass transition temperatures of several PFPE lubricants are listed in Table 22.5 [1].

The temperature dependence of the viscosity is shown in Figures 22.1 through 22.3 [1] as the ratio of the viscosity to the molecular weight η/M_n plotted as a function of distance from the glass transition temperature $T - T_g$. The ratio η/M_n is proportional to the segmental friction coefficient [30], and shifting the temperature by T_g takes into account the effect of T_g on the relaxation times. The smooth curves are from the regression fit of the shift factors in the WLF equation. A subset of the Z series showing the effects of different end groups is shown in Figure 22.1. Most of the PFPEs shown in Figure 22.1 had an O/C ratio of ~0.65, except for the Zdeal, which had an O/C ratio of 0.694. The segmental friction coefficient was the lowest for nonpolar Z03 and the Zdol4KL905 (and Zdol4KL819 shown in Figure 22.2), and highest for the Ztetraol, with two hydroxyls on each end group. The segmental friction coefficients for Z chains with other types of end groups were in between Z03 and Ztetraol. The friction coefficient for the Zdeal was slightly lower than the Zdiac, because the methyl ester probably blocks some of the hydrogen bonding. The Ztx, Zdiac, and Zdol2500 had nearly the same segmental friction coefficient.

The effect of the O/C ratio on the segmental friction coefficient for the Zdol 4K series is shown in Figure 22.2. The lots with intermediate O/C ratio, Zdol4K L492, 990, and 598, were above Zdol4K L819 with (high) O/C = 0.72 and Zdol4KL905 with (low) O/C = 0.65, which were about the same as one another, even though their T_g are 11° apart. This surprising relationship may arise from a dependence of the segmental friction coefficient on the chain flexibility and the cohesive energy density that is different from the dependence of T_g on these properties.

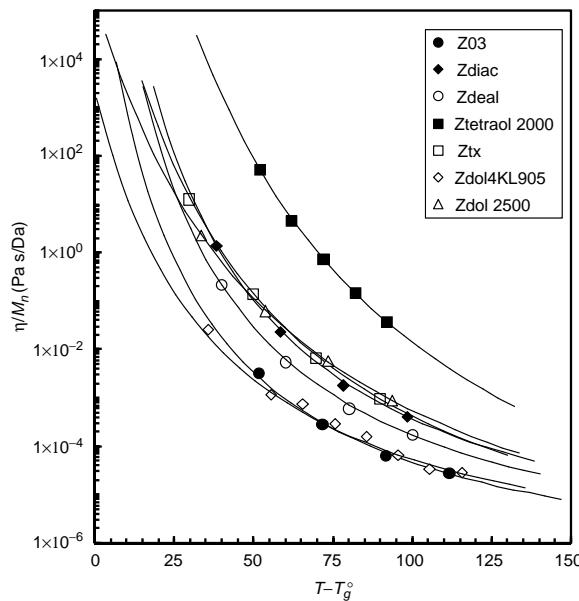


FIGURE 22.1 The ratio of viscosity to molecular weight as a function of distance from the glass transition temperature for the PFPE Z series. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

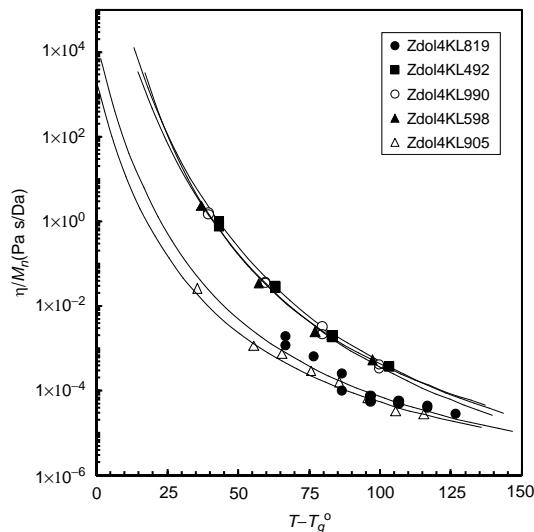


FIGURE 22.2 The ratio of viscosity to molecular weight as a function of distance from the glass transition temperature for the PFPE Zdol4K series, showing the effect of O/C ratio. The smooth curves are from the WLF equation. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

The segmental friction coefficient for the D and K series, shown in Figure 22.3, was within the range of that observed for the Zdol4K series in Figure 22.2. The nonpolar Krytox and the Krytox COOH were nearly the same as one another and were below the Demnum series. All of the Demnum series were nearly the same as one another. The addition of one polar end group had little effect on the segmental friction coefficient of D and K.

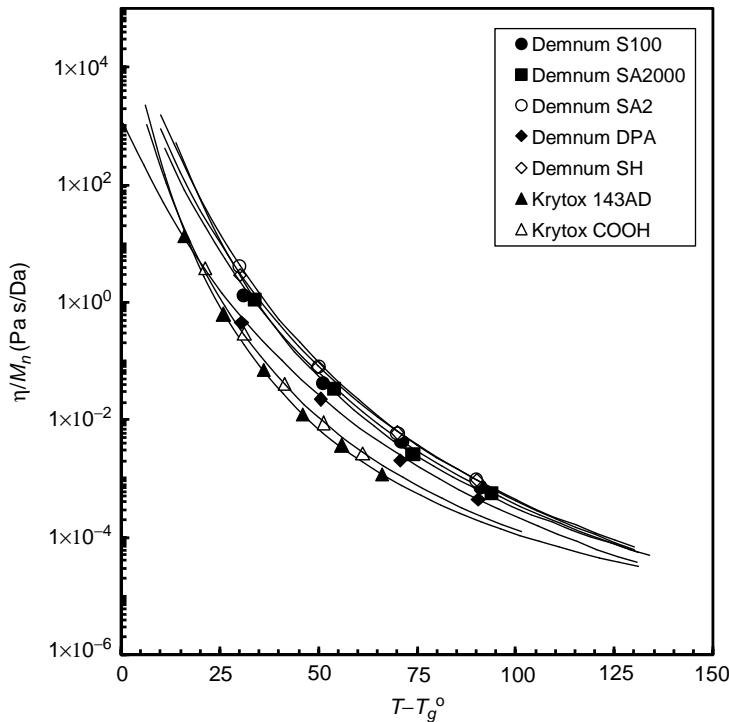


FIGURE 22.3 The ratio of viscosity to molecular weight as a function of distance from the glass transition temperature for the PFPE Demnum and Krytox series. The smooth curves are from the WLF equation. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

The storage and shear moduli, G' and G'' , were measured and shifted along the temperature axis to obtain the master curves. The WLF coefficients [29] were calculated from the shift factors $a_{T_0}(T)$ by nonlinear regression analysis using the functional form

$$\log(a_{T_0}) = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (22.1)$$

where the reference temperature $T_0 = T_g$ and C_1 and C_2 are the WLF coefficients with respect to T_g . The WLF coefficients are listed in Table 22.5. Our range of coefficients $10.5 < C_1 < 23.5$ and $23.5 < C_2 < 79$ is consistent with that for nonpolar PFPEs Y and Z reported by Marchionni et al. [18].

Up to three Maxwell elements were derived from the master curves by nonlinear regression analysis from the linearly viscoelastic shear storage modulus, G' , and loss modulus, G'' :

$$G' = \sum_i \frac{G_i(\omega a_{T_0} \tau_i)^2}{1 + (\omega a_{T_0} \tau_i)^2} \quad (22.2)$$

$$G'' = \sum_i \frac{G_i \omega a_{T_0} \tau_i}{1 + (\omega a_{T_0} \tau_i)^2} \quad (22.3)$$

where ω is the shear strain sinusoidal oscillation frequency.

TABLE 22.6
The Coefficients of the Maxwell Elements from the Master Curves at Reference Temperature T_g

Lubricant	G_1 (kPa)	τ_1 (s)	G_2 (kPa)	τ_2 (s)	G_3 (kPa)	τ_3 (s)	η (-20°C) (Pa s)	
							From Creep	From Dynamic
Z03	49.3	1.11×10^7	—	—	—	—	0.2	0.2
Zdiac	28.4	5.17×10^{10}	5.6	3.09×10^9	—	—	1.0	1.0
Zdeal	31.1	6.31×10^9	4.0	1.44×10^8	—	—	0.4	0.4
Ztetraol 2000	36.6	4.02×10^{13}	8.9	3.86×10^{12}	5.5	3.16×10^{11}	83	70
Ztx	55.6	7.42×10^6	—	—	—	—	2.0	1.6
Zdol4KL819	4.0	3.56×10^5	5.2	7.91×10^4	14.3	8.13×10^3	0.2	0.5
Zdol4KL492	43.4	1.51×10^7	—	—	—	—	1.3	1.1
Zdol4KL990	49.7	5.77×10^6	—	—	—	—	1.3	1.5
Zdol4KBL598	48.4	2.10×10^8	—	—	—	—	2.3	1.4
Zdol4KL905	19.3	2.40×10^3	19.7	2.21×10^2	—	—	0.3	0.2
Zdol 2500	51.9	5.03×10^4	—	—	—	—	2.2	2.0
Demnum S100	11.8	4.52×10^4	38.0	9.91×10^3	3.4	2.84×10^2	3.7	1.5
Demnum SA2000	54.0	4.09×10^5	—	—	—	—	1.1	1.5
Demnum SA2	35.1	5.49×10^4	10.4	6.43×10^3	—	—	2.8	2.1
Demnum DPA	42.0	1.87×10^8	3.38	1.22×10^7	—	—	3.6	2.5
Demnum SH	47.5	2.28×10^4	6.8	1.60×10^3	—	—	2.9	2.8
Krytox 143 AD	55.3	1.35×10^5	3.1	4.30×10^3	1.0	1.16×10^2	81	69
Krytox COOH	44.9	3.08×10^4	4.7	1.21×10^3	2.3	7.17×10^1	220	200

Note: The steady shear viscosity measured in creep, and the zero shear viscosity calculated from the dynamic data at -20°C.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

The shear rigidities G_i and corresponding relaxation times τ_i are listed in Table 22.6 [1]. The WLF coefficients, the shear rigidities, and the relaxation times provide the solid curves in Figures 22.4 through 22.6 [1]. The dynamic response for the Z series with different end groups is shown in Figure 22.4. The polar end group increases the relaxation times. Two relaxation times are observed in the Zdiac, Zdeal, and Zdol4KL905. Three relaxation times are observed in the Ztetraol and Zdol4KBL819. At ambient temperature, the Z03 has nearly the shortest characteristic time, τ_1 , of all the PFPEs even though it has the highest M_n . Ztetraol has the longest τ_1 within the Z series. The response of the Zdol with a range of O/C ratio is shown in Figure 22.5. The O/C ratio has a significant effect on the dynamic response of the Zdol 4K series. The dynamic response of the Demnum and Krytox is shown in Figure 22.6. The τ_1 for the Krytox is much longer than that for the Demnum.

The linear viscoelastic properties zero shear viscosity $\eta = G_1\tau_1$ and the equilibrium recoverable compliance $J_e^0 = \tau_1/\eta$ may be calculated from the dynamic properties listed in Table 22.6. The viscosity or relaxation time can be calculated at an arbitrary temperature T with the ratio of the shift factors from the WLF equation. For example, $\tau_1(T)$ or $\eta(T) = \eta(T_g)a_{T_g}(T)$. The relaxation times for the Z series of lubricants calculated at 50°C is shown in Figure 22.7 [1].

22.2.1.2 Dielectric

The lubricant dielectric properties provide complementary information to the rheological data. The concept is similar in that both energy storage and dissipation are characterized in response to a sinusoidal application of an electric field.

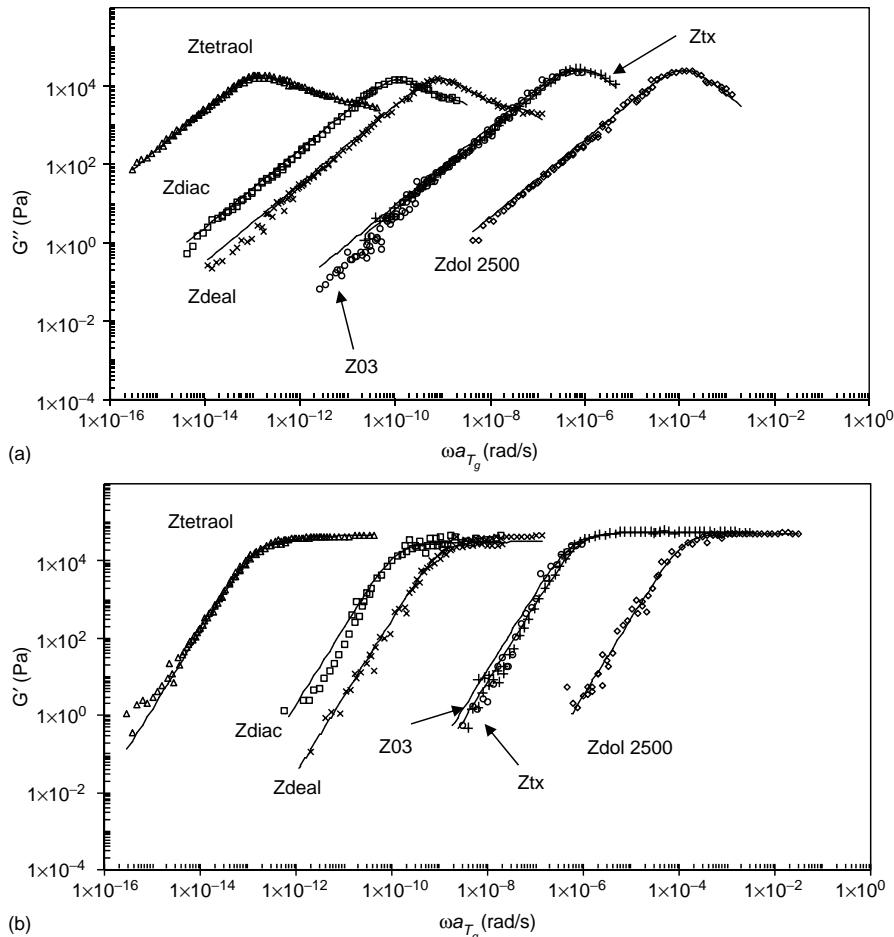


FIGURE 22.4 Shear loss (a) and storage (b) modulus master curves for the Z series. The smooth curves are from the discrete relaxation time series fit to the frequency–temperature shifted data. Reference temperature is T_g . (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

The permittivity and loss factor of the different lubricant samples were measured using a TA Instruments Dielectric Analyzer (DEA) model 2970 with a single-surface ceramic sensor. Measurements were taken at an applied voltage of 1 V. The frequency sweep ranged from 0.1 to 10,000 Hz. Measurements were done at temperatures ranging from -100 to 100°C . The data at the various temperatures were shifted relative to reference temperature $T_0 = 50^\circ\text{C}$ to provide the dielectric master curves for several magnetic recording disk lubricants, shown in Figure 22.8 [1].

The dielectric properties are derived from the master curves with a discrete relaxation time (Debye) model [31] for the dielectric loss factor, ϵ'' , and the dielectric permittivity, ϵ' :

$$\epsilon'' = \frac{\sigma}{\epsilon_0 \omega a_{T_0}} + \sum_i \frac{(\epsilon_{s,i} - \epsilon_\infty) \omega a_{T_0} \tau_i}{1 + (\omega a_{T_0} \tau_i)^2} \quad (22.4)$$

$$\epsilon' = \epsilon_\infty + \sum_i \frac{\epsilon_{s,i} - \epsilon_\infty}{1 + (\omega a_{T_0} \tau_i)^2} \quad (22.5)$$

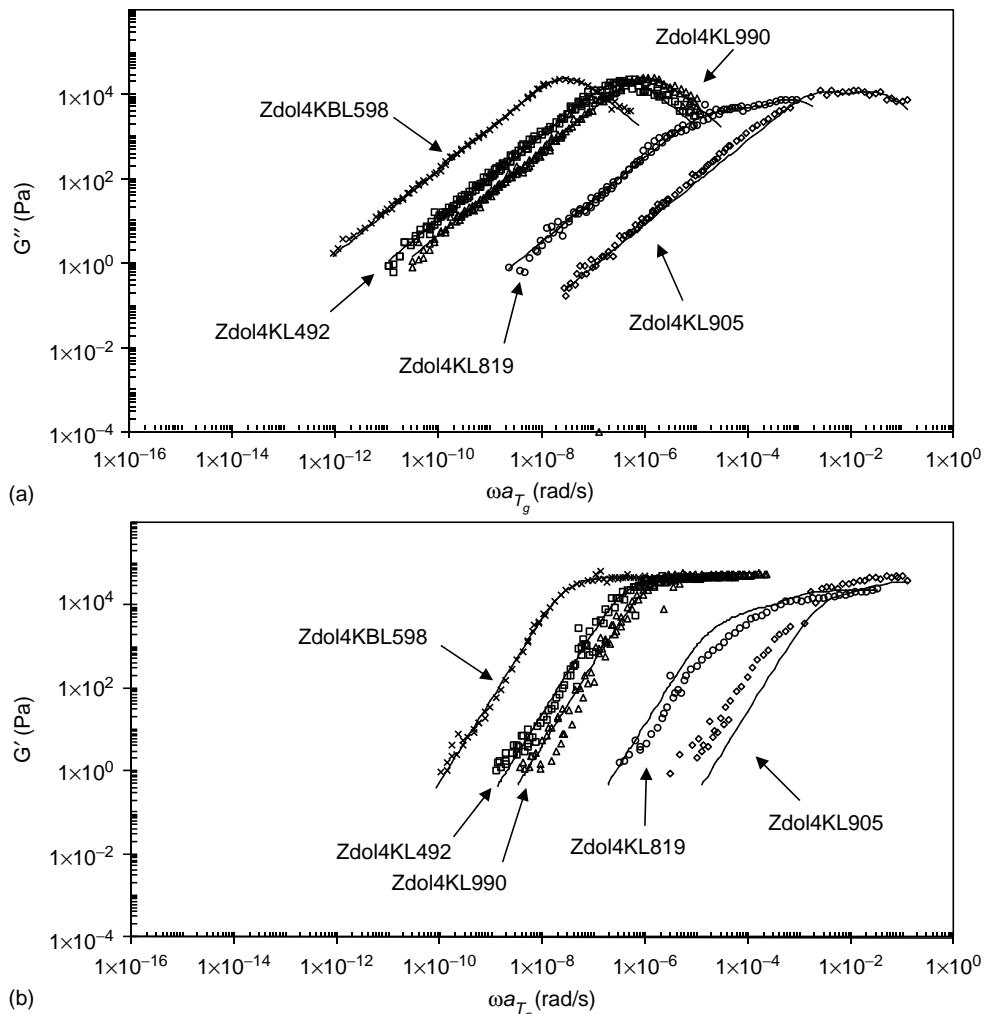


FIGURE 22.5 Shear loss (a) and storage (b) modulus master curves for the Zdol4K series. The smooth curves are from the discrete relaxation time series fit to the frequency–temperature shifted data. Reference temperature is T_g . (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

where

ω = sinusoidal oscillation frequency of the applied voltage

τ_i = dielectric relaxation time

ϵ_0 = absolute permittivity of free space (8.85×10^{-12} F/m)

The parameters in the discrete relaxation time series are determined by a regression fit to the dielectric master curves. There are multiple dielectric relaxation times for Zdol and Ztetraol. Four relaxation times were employed to fit the data in Figure 22.8. These provide estimates for the conductivity, σ , the dc relative permittivity, $\epsilon'(0) = \sum_i \epsilon_{s,i}$, and the limiting high-frequency permittivity, ϵ_∞ . Note that the capacitive energy storage is proportional to the dc relative permittivity, and the refractive index n is related to the high-frequency relative permittivity by the Maxwell relation $n \approx \sqrt{\epsilon_\infty}$. For PFPEs, $n \approx 1.3$ [28], which gives $\epsilon_\infty \approx 1.7$. The dielectric properties and the four relaxation times and static relaxation amplitudes are listed in Table 22.7 [1].

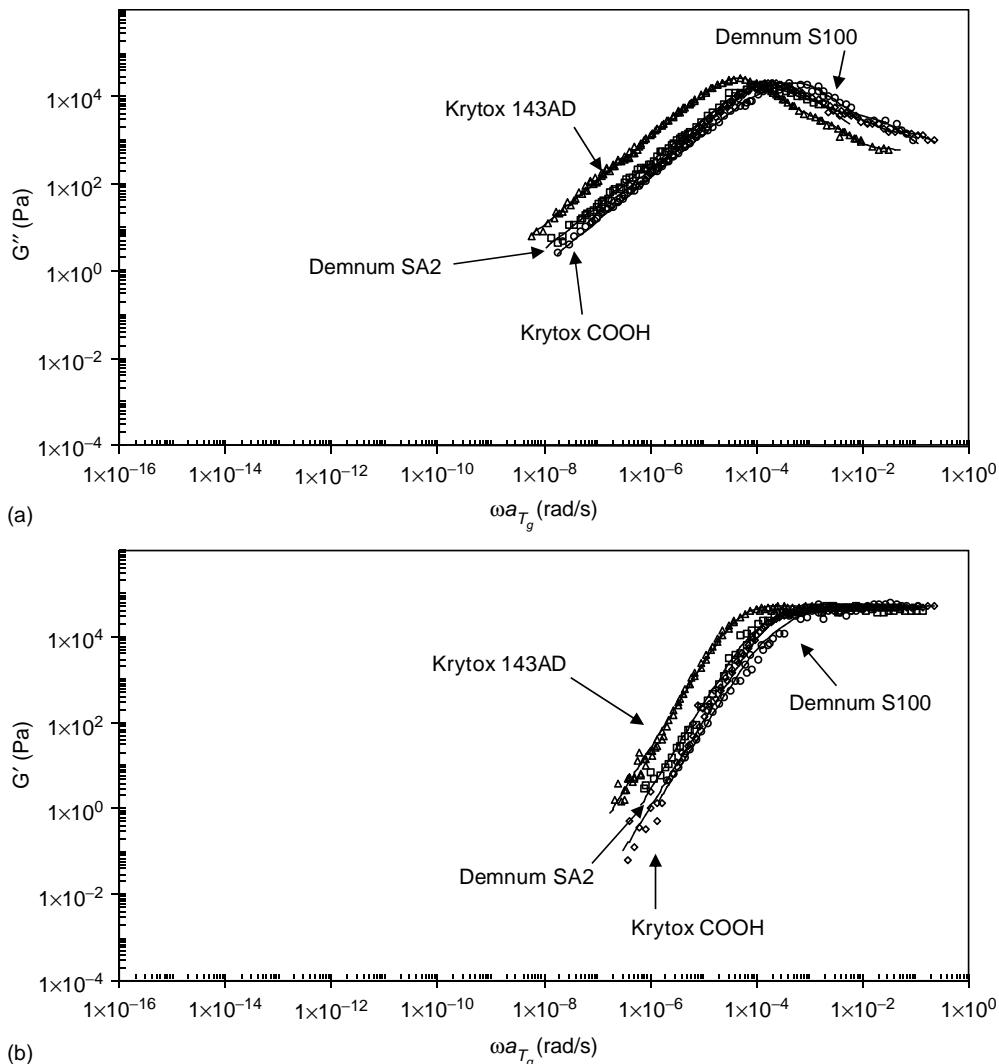


FIGURE 22.6 Shear loss (a) and storage (b) modulus master curves for the Demnum and Krytox series. The smooth curves are from the discrete relaxation time series fit to the frequency–temperature shifted data. Reference temperature is T_g . (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

22.2.1.3 Thin Film Viscosity

The aforementioned results have shown that in bulk PFPE disk lubricants, viscosity increases exponentially as the measurement temperature approaches the glass transition temperature. This is because chain motions are progressively *frozen out* as the thermal energy becomes less than their activation energy. The lubricant viscosity also increases as the lubricant film thickness decreases, which helps to prevent the lubricant from flowing completely off of the magnetic recording disks in the air shear [32]. Viscosity enhancement of thin films arises from a different mechanism than that found with decreasing temperature.

Dispersive interaction has a dramatic effect on the viscosity of the molecular layers closest to the surface, which can be explained in terms of the rate theory for viscous flow. Within the

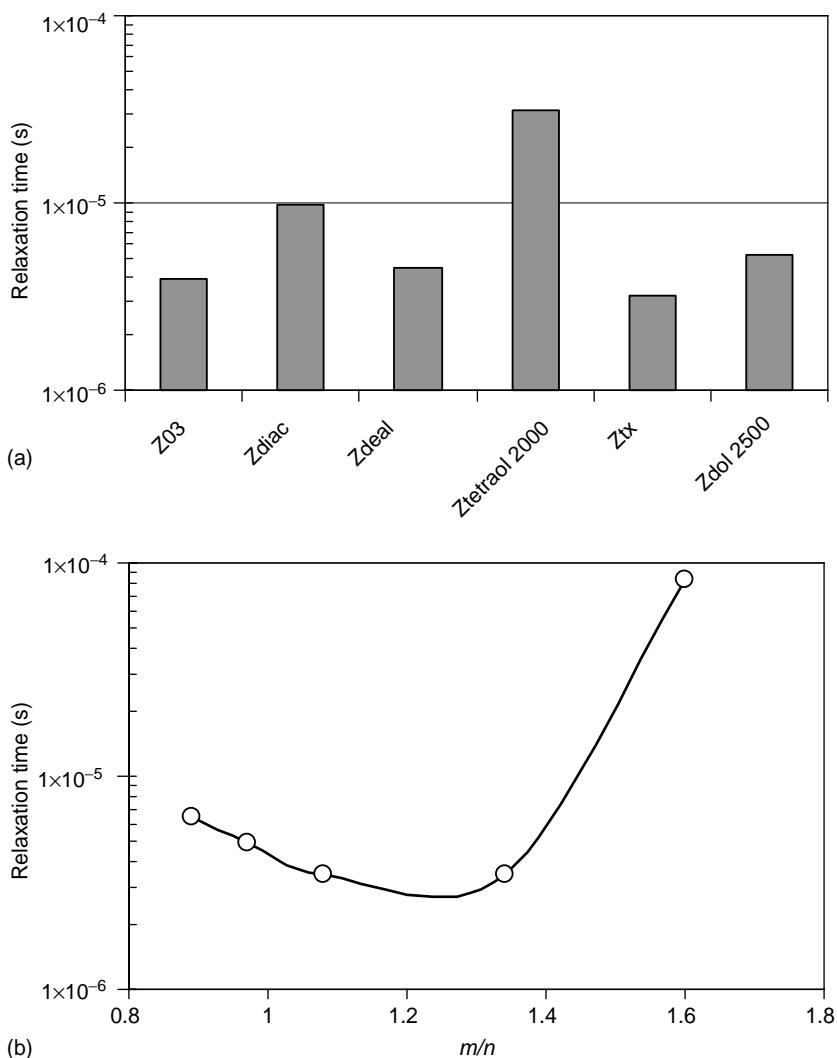


FIGURE 22.7 Longest relaxation time at 50°C for the Z series of lubricants (a) and Zdol4K series with a range of monomer chain composition (b) calculated from the dynamic rheological measurements with time–temperature superposition. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

rate theory, a flow event comprises the transition of a flow unit from its normal or quiescent state, through a flow-activated state, to a region of lower free energy in an external stress field. For small molecules, the flow unit is the whole molecule, whereas for longer chains, the flow unit is a segment of the whole molecule. By analogy with chemical reaction rate theory, there is a flow activation enthalpy, ΔH_{vis} , and entropy, ΔS_{vis} , for transition into the flow-activated state.

A flow unit is approximated by a particle in a box, with the energy being partitioned among rotational and translational degrees of freedom, which govern the transition probability. On this basis, the viscosity $\eta = (Nh_p/V_1) \exp(\Delta G_{\text{vis}}/RT)$, where N is Avogadro's number, h_p the Planck's constant, V_1 the molar volume, R the universal gas constant, T the temperature, and $\Delta G_{\text{vis}} = \Delta H_{\text{vis}} - T\Delta S_{\text{vis}}$ the flow activation Gibbs free energy. The flow activation enthalpy $\Delta H_{\text{vis}} = \Delta E_{\text{vis}} + \Delta(pV)_{\text{vis}}$, where ΔE_{vis} is the flow activation energy and $\Delta(pV)_{\text{vis}}$ the pressure–volume work. At constant pressure, $\Delta(pV) = p\Delta V_{\text{vis}}$. For PFPE Z, the flow activation volume $\Delta V_{\text{vis}} \approx 0.1 \text{ nm}^3$ [17],

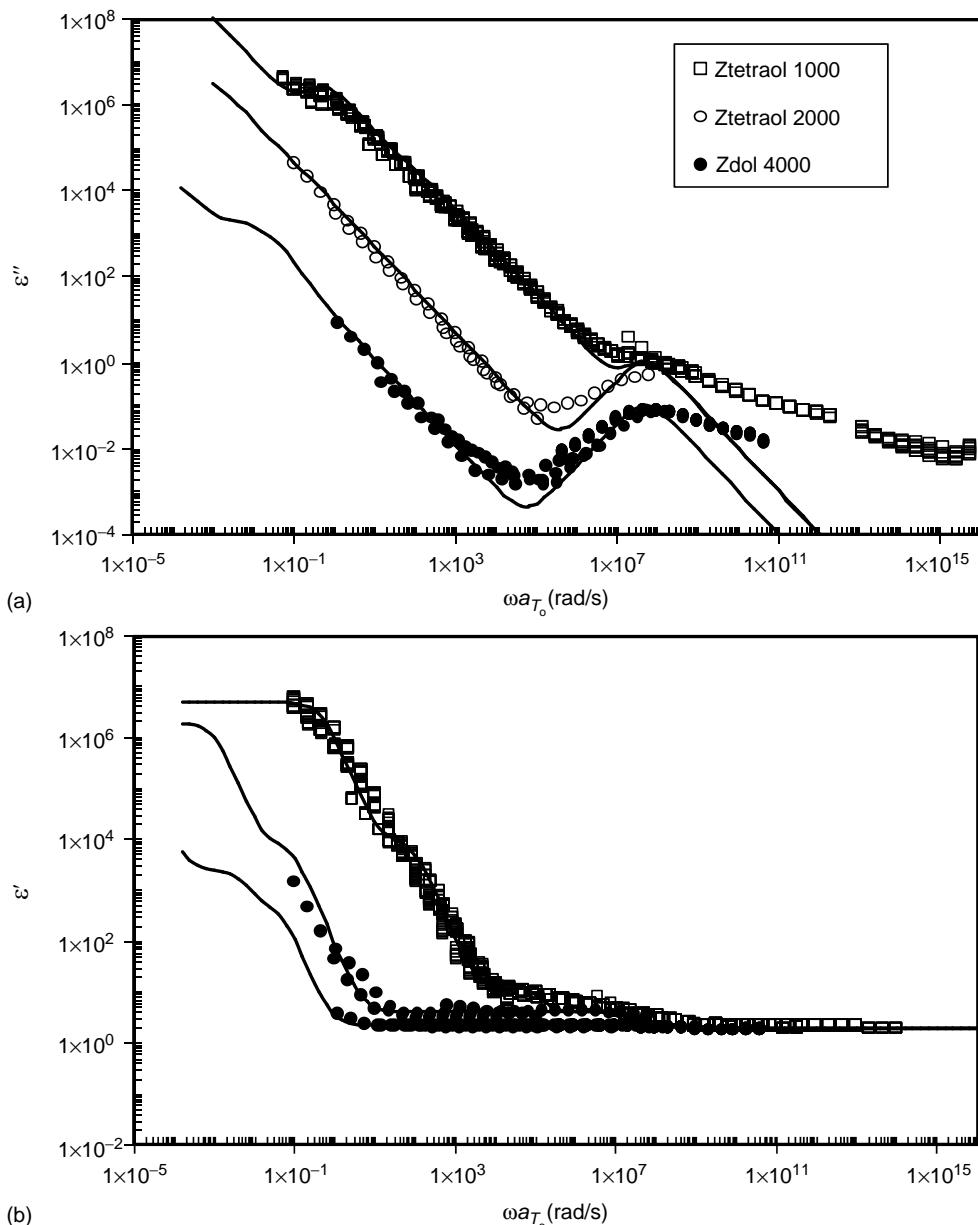


FIGURE 22.8 Dielectric loss factor (a) and relative permittivity (b) master curves for the Ztetraol 2000, Ztetraol 1000, and Zdol 4000. The smooth curves are from the discrete relaxation time series fit to the frequency-temperature shifted data. Reference temperature is $T_0 = 50^\circ\text{C}$. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

which is equivalent to a spherical region ≈ 0.6 nm in diameter. At ambient pressure (100 kPa), $\Delta(pV)_{\text{vis}} \approx 6.2$ J/mol, so that near ambient conditions, $\Delta H_{\text{vis}} \approx \Delta E_{\text{vis}}$. Therefore, the viscosity is given by

$$\eta = \left(\frac{Nh_p}{V_l} \right) \exp \left[\frac{(\Delta E_{\text{vis}} - T\Delta S_{\text{vis}})}{RT} \right] \quad (22.6)$$

TABLE 22.7

The Coefficients of the Debye Equation from the Dielectric Master Curves at Reference Temperature $T_0 = 50^\circ\text{C}$

Parameter	Zdol 4000	Ztetraol 2000	Ztetraol 1000
$\epsilon'(0)$	3.3×10^3	1.1×10^4	1.1×10^7
$\sigma(\text{S/m})$	1×10^{-11}	4×10^{-8}	6×10^{-7}
$\epsilon_{s,1}$	3×10^3	1×10^4	1×10^7
$\tau_1(\text{s})$	500	50	8
$\epsilon_{s,2}$	3×10^2	1×10^3	1×10^6
$\tau_2(\text{s})$	50	5	0.8
$\epsilon_{s,3}$	30	100	100,000
$\tau_3(\text{s})$	5	0.5	0.06
$\epsilon_{s,4}$	2	4	5
$\tau_4(\text{s})$	1×10^{-8}	1×10^{-8}	1×10^{-8}

Note: The high frequency $\epsilon_\infty \approx 1.7$ from the index of refraction.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

A regression fit to the bulk viscosity as a function of temperature [32] provided $\Delta E_{\text{vis}} = 34.7 \text{ kJ/mol}$ and $\Delta S_{\text{vis}} = 9.87 \text{ J/mol K}$. The flow activation energy is close to that reported for bulk Zdol with a molecular weight of 3100 Da in Refs 33 and 34. A positive value for the flow activation entropy of bulk Zdol means that the entropy of the flow unit increases on going into the flow-activated state.

Changes in the lubricant flow activation energy and entropy near the solid surface cause changes in the viscosity with decreasing film thickness. The flow activation energy near a solid surface is estimated from the thin film vaporization energy as follows. In an ideal gas, the chemical potential μ (or partial molar Gibbs free energy) is given by

$$d\mu = RT d \ln P \quad (22.7)$$

where P is the partial pressure of the lubricant in the vapor phase.

The chemical potential energy per unit volume in the lubricant film is $\mu/V_1 = \Pi$. The ratio of the film surface vapor pressure to the vapor pressure of the bulk lubricant, $P^\circ(h)/P^\circ(\infty)$, is derived by integrating Equation 22.7

$$\mu(h) - \mu(\infty) = RT \ln \left[\frac{P^\circ(h)}{P^\circ(\infty)} \right] \quad (22.8)$$

The reference state is taken to be the chemical potential and vapor pressure of the bulk lubricant, $\mu(\infty) = 0$, and $P^\circ(\infty)$ is the vapor pressure of the bulk liquid.

In general, as the surface energy is defined as the free energy per unit area, the total disjoining pressure (Π) for these fluids can be derived from the experimental surface energy (contact angle) data by

$$\Pi = -\frac{\partial}{\partial h} (\gamma^d + \gamma^p) \quad (22.9)$$

Here γ^d and γ^p are the dispersive and polar components of the surface energy, respectively, and h the film thickness.

The regression fit to the surface energy data, shown as smooth curves in Figures 22.9a and 22.9b [1], was numerically differentiated to obtain the disjoining pressure [35,36]. The total disjoining pressure, including the individual contributions from the dispersive and polar components, is shown in Figure 22.10a [1]. Notice that γ^d decreases monotonically with h , which is consistent with Equation 22.10. Below film thicknesses of ~ 0.5 nm, Π at each molecular weight is dominated by γ^d , which increases rapidly with decreasing film thickness and is largely independent of molecular weight. The γ^p , however, oscillates with film thickness and becomes larger in magnitude than γ^d as h increases. Oscillations in γ^p provide an additional contribution to Π for PFPE Zdol that produces alternating regions of stable and unstable film thickness [37]. The sum of the two contributions

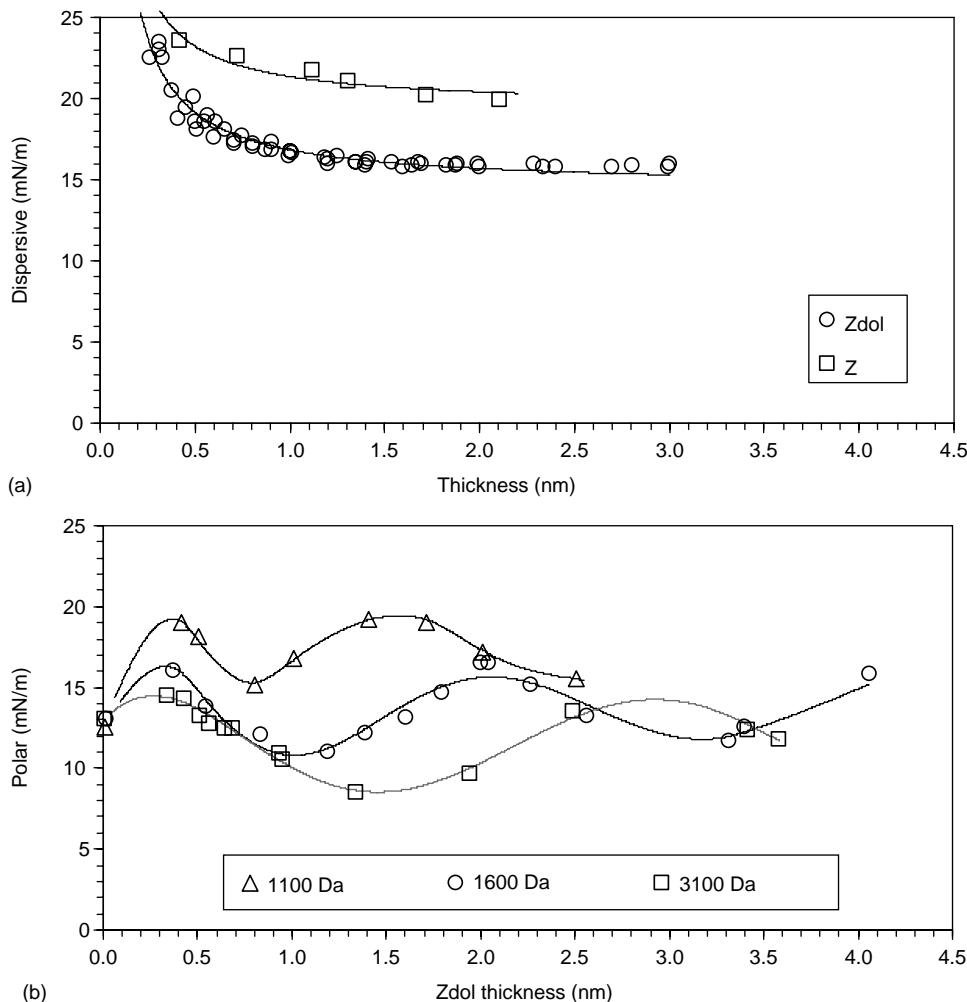


FIGURE 22.9 The components of the surface energy measured on CHx-overcoated thin film magnetic recording media with fractionated Zdol of narrow polydispersity index. (a) The dispersive component of the surface energy for PFPE Z and Zdol. (b) The polar component of the surface energy for PFPE Zdol. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

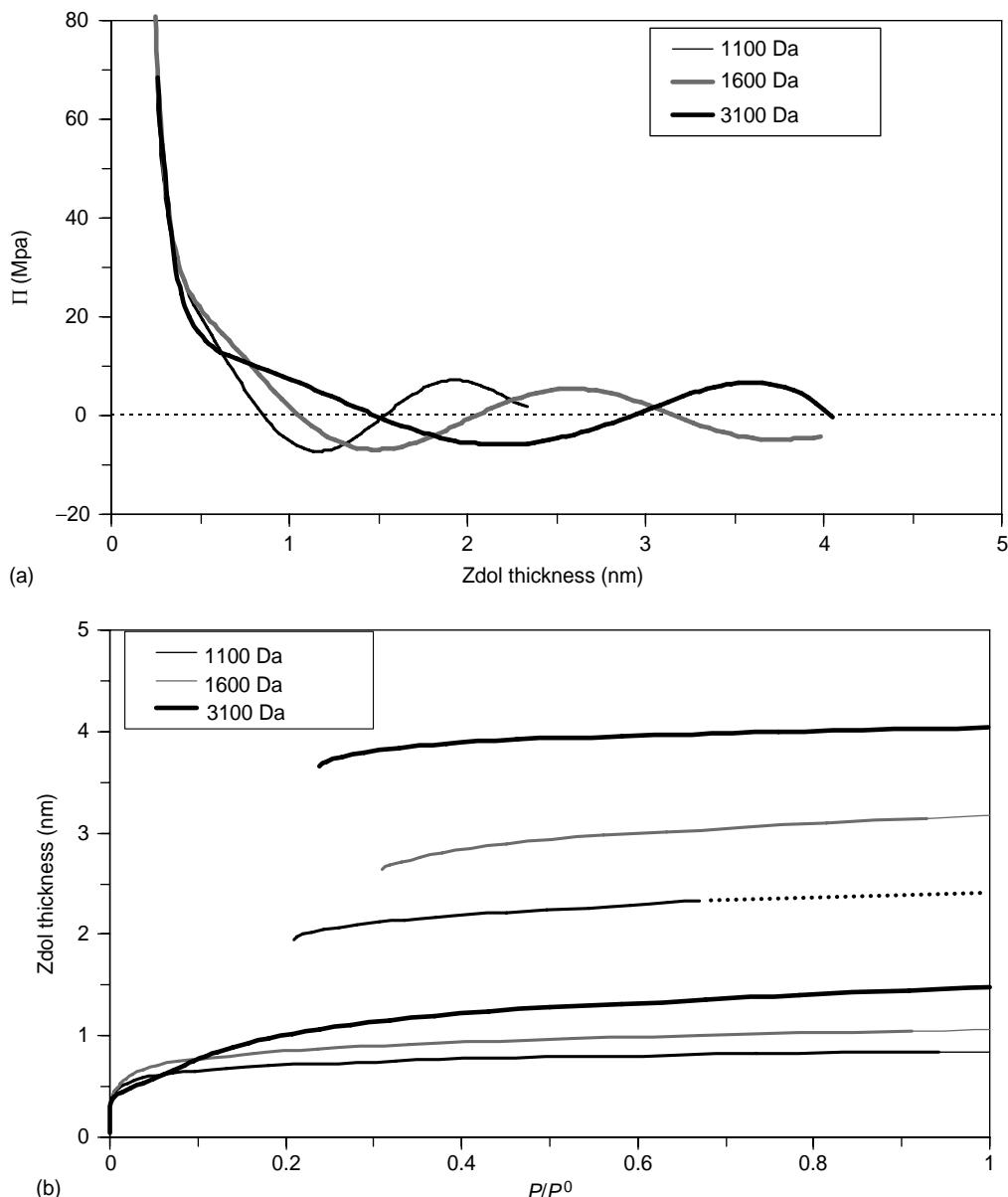


FIGURE 22.10 (a) The disjoining pressure from the fractionated Zdol surface energies in Figure 22.9a and (b) the corresponding Zdol adsorption isotherms at 60°C. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

gives rise to oscillations in the total disjoining pressure. It is remarkable that the disjoining pressure from the surface energies as a function of film thickness, and Equation 22.8 relating the disjoining pressure to the degree of saturation predict the adsorption isotherms for low-molecular-weight Zdols, according to $P/P^0 = \exp(-\Pi V/RT)$, which are shown in Figure 22.10b. There are two thermodynamically stable regions of film thickness for degrees of saturation corresponding to regions where $\Pi > 0$ and $\partial\Pi/\partial h < 0$. For thicknesses in between these regions, condensing Zdol molecules will either reevaporate or form islands at the next higher stable film thickness.

For the purpose of explaining the viscosity increase of thin films, surface chemical potential is approximated by the unretarded atom-slab dispersive interaction energy

$$\mu = -\frac{V_l A}{6\pi h^3} \quad (22.10)$$

The dispersive interaction coefficient A is also referred to as the Hamaker constant and $A = 10^{-19}$ J for Zdol.

As mentioned, the vaporization energy is the energy required to remove a molecule from the liquid without leaving behind a hole, which is the energy needed to form a hole of the size of a molecule in the liquid. The free volume needed for a flow unit to transition into the flow-activated state is less than the size of the entire molecule. It is found that the ratio $n \equiv \Delta E_{\text{vap},\infty}/\Delta E_{\text{vis},\infty} > 3$, where $\Delta E_{\text{vap},\infty}$ and $\Delta E_{\text{vis},\infty}$ are the vaporization and flow activation energies of the bulk liquid, respectively. Thus, the flow activation energy near the surface is given approximately by

$$\Delta E_{\text{vis}} = \Delta E_{\text{vis},\infty} - \frac{\mu}{n} \quad (22.11)$$

For linear chains longer than 5 or 10 carbon atoms, n increases due to the onset of segmental flow. In practice, n is experimentally determined from the measured values of the vaporization and flow activation energy. For PFPE Zdol 4000, $\Delta E_{\text{vap},\infty} = 166$ kJ/mol, giving $n \approx 4.8$. This is consistent with segmental flow.

To calculate the thin film viscosity with Equation 22.6, the flow activation entropy near the surface is also needed. Experimental flow activation entropy is calculated from the spin-off data [32] with Equations 22.6 and 22.11 as follows. The experimental η versus h is determined from dh/dt during air shear-induced flow on a rotating disk. Equation 22.6 is then solved for ΔS_{vis} versus h using Equation 22.11 for ΔE_{vis} .

The flow activation energy and entropy are shown in Figure 22.11a [1]. The flow activation energy suddenly increases below ~ 0.8 nm due to the strong film thickness dependence of the dispersion force. The retarding effect of this increase on flow is compounded by the apparent effect of confinement on restricting the degrees of freedom in the flow transition state, as seen by the negative entropic contribution in Figure 22.11a. Below 2.3 nm, $T\Delta S_{\text{vis}} \approx -1.9$ kJ/mol, which corresponds to the critical configurational entropy change for flow ($-R \ln 2 \approx -5.76$ J/mol °K). The combined effects give rise to the observed increase in viscosity with film thickness shown in Figure 22.11b and enables extrapolation of the viscosity to even thinner films where the spin-off is so slow that it takes years to measure.

The viscosity increases by a large amount with film thickness, which is much greater than the increase with temperatures that might normally be encountered in the disk drive. The bulk viscosity for several PFPE lubricants is shown in Figure 22.12 [1]. As the increase in viscosity with thickness below ~ 0.8 nm is much more than the increase with temperature between 0 and 60°C, the operating temperature of disk drives should have no significant effect on lubricant spin-off from the disk by air shear. That is, excluding air shear force due to the head suspension assembly and the air bearing [38] and dispersion force between the lubricant and a low-flying slider [39].

22.2.1.4 Vapor Pressure

The vapor pressure of PFPE lubricants must be low to prevent evaporation from the disk. A method to measure the vapor pressure was developed as follows. A model was derived to calculate the vapor pressure from the measured Zdol molecular weight distribution and evaporation rate. Molecular weight distributions were measured by GPC, as described in Karis et al. [28]. The vapor pressure of discrete molecular masses was calculated from the evaporation rate measured by isothermal thermogravimetric analysis (TGA) with a stagnant film diffusion model as described by Karis and

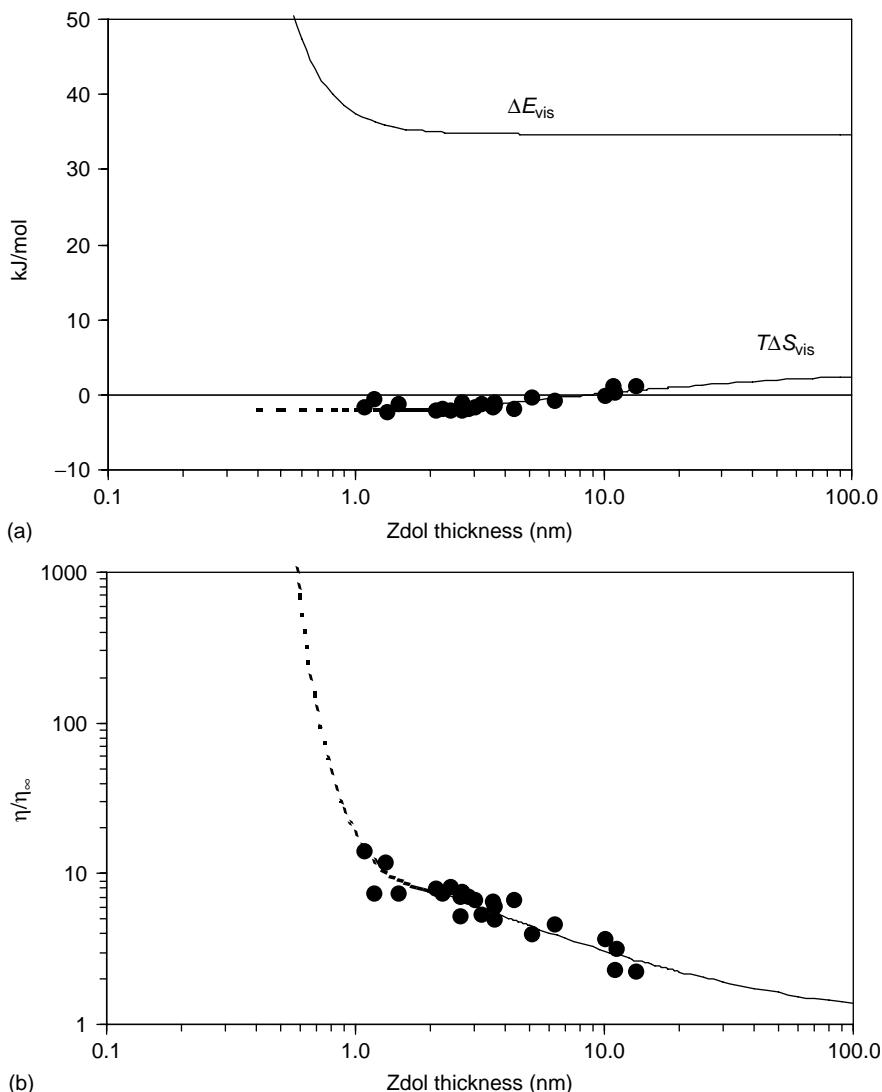


FIGURE 22.11 The vertical axis is defined by the annotations on the curves in (a) Flow activation energy and the entropic component of the flow activation free energy and (b) dispersion-enhanced viscosity as a function of film thickness. The filled symbols are from the spin-off measurements, and the dashed region of the curve was calculated with constant flow activation entropy below 2.3 nm. Fractionated Zdol molecular weight 4500 Da, temperature 50°C. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

Nagaraj [40]. Polymers such as Zdol differ from the low-molecular-weight synthetic hydrocarbon oils in that polymers comprise various different molecular weights. Further considerations must be taken into account in modeling the evaporation of polymers, as described later.

A numerical model was developed to simulate the evaporation of a polymer from an initial molecular weight distribution measured by GPC. The evaporation simulation is written in terms of mass flux and the discrete form of the molecular weight distribution $w_i(t)$ as

$$w_i(t^+) = w_i(t) - \text{flux}_i(t) \left\{ \frac{A}{m_0} \right\} \Delta t \quad (22.12)$$

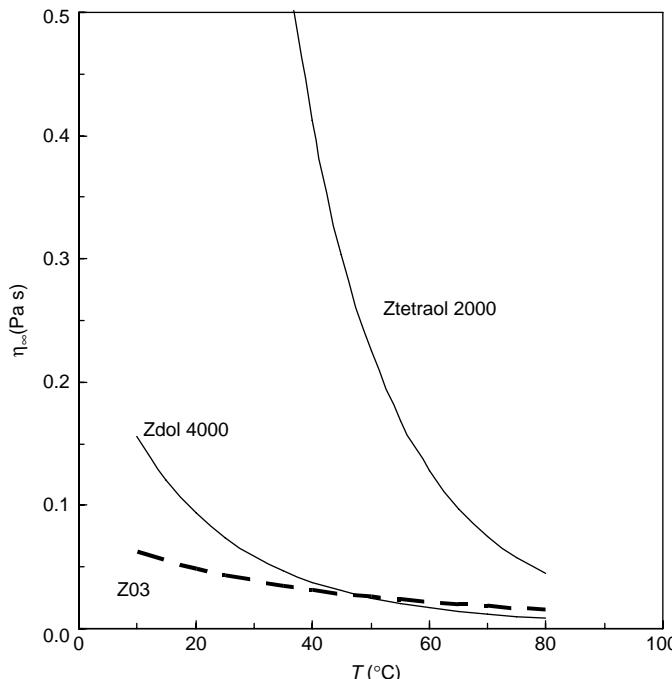


FIGURE 22.12 Bulk viscosity and flow activation energy of several PFPE lubricants as a function of temperature. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

where

A = surface area of the evaporating lubricant

m_0 = initial mass of lubricant

Δt = time step in the simulation

The mass flux of the i th molecular weight fraction M_i is given by stagnant film diffusion:

$$\text{flux}_i(t) = \frac{D_i}{\delta} \left(\frac{M_i}{RT} \right) P_i \quad (22.13)$$

Here D_i is the vapor-phase diffusion coefficient and δ the diffusion length (calculated or measured with a liquid of known vapor pressure).

The mass flux divided by the mass density yields the rate of film thickness change. The solution vapor pressure for the i th molecular fraction was approximated assuming an ideal solution according to Raoult's law $P_i = x_i P_i^0$, where x_i is the mole fraction of the i th molecular fraction.

The Hirschfelder approximation [41] is used for the vapor-phase diffusion coefficient

$$D_i = 1.858 \times 10^{-4} \left(\frac{1}{M_i} + \frac{1}{M_{\text{gas}}} \right)^{1/2} \frac{T^{3/2}}{P \sigma_i^2 \Omega} \quad (22.14)$$

where

M_{gas} = molecular weight of the ambient atmosphere (air or nitrogen to suppress oxidation)

P = ambient pressure

$\sigma_i = (\sigma_{\text{lube}}^i + \sigma_{\text{gas}}^i)/2$ = collision diameter

TABLE 22.8

**The Gas-Phase Molecular Diameter for Ideal Monodisperse Zdol Fractions
Calculated from the Radius of Gyration in Theta Solvent $d = 0.05 \sqrt{M}$**

M (Da)	d (nm)	Degree of Polymerization	Contour Length (nm)	Equilibrium Thickness (nm)
500	1.12	3.54	2.71	0.66
750	1.37	6.29	4.06	0.74
1000	1.58	9.03	5.41	0.82
1350	1.84	12.88	7.29	0.93
1500	1.94	14.53	8.10	0.98
2000	2.24	20.02	10.79	1.14
3000	2.74	31.01	16.18	1.46
4000	3.16	42.00	21.56	1.79
4300	3.28	45.30	23.18	1.88
5400	3.67	57.38	29.10	2.24

Note: Also included are the degree of polymerization, the contour length measured along the chain from one end to the other, and the equilibrium thickness. The equilibrium thickness is the maximum stable film thickness, or dewetting thickness, determined from the first zero crossing of the disjoining pressure with increasing film thickness.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

For nitrogen, $\sigma_{\text{gas}}^i = 0.315$ nm. The vapor-phase molecular diameter of the i th molecular fraction employed in estimating the binary mass diffusion coefficient is approximately given by $\sigma_{\text{lube}}^i = 2 \times R_{g,i} \approx 0.05 \times \sqrt{M_i}$, where the molecular weight M_i is in daltons and the radius of gyration $R_{g,i}$ is in nanometers. This expression was derived from the radius of gyration for Zdol measured in Freon [42,43]. The molecular diameters from this approximation for a range of ideal monodisperse Zdol molecular weights are listed in Table 22.8 [1].

By analogy to hydrocarbon oils, the collision integral Ω for collision between molecules in the gas phase is a function of their binary Lennard-Jones interaction potential. The collision integral between Zdol molecules and nitrogen molecules was taken to be the same as that for collision between hydrocarbon molecules and nitrogen, $\Omega = 1.2$.

The Clapeyron equation is employed to calculate the pure component vapor pressure:

$$P_i^0 = P \exp \left\{ \frac{\Delta S_{\text{vap}}^i}{R} \right\} \exp \{-1\} \exp \left\{ -\frac{\Delta E_{\text{vap}}^i}{RT} \right\} \quad (22.15)$$

where the vaporization entropy $\Delta S_{\text{vap}}^i = S_{\text{vap}}^i - S_{\text{liq}}^i$ is the difference between the entropy in the vapor state and that in the liquid state. The Zdol liquid entropy is assumed to be independent of molecular weight. It was determined along with the activation energy by comparison of the simulated evaporation with isothermal TGA evaporation weight loss data. The liquid entropy for Zdol, $S_{\text{liq}} = 107$ J/mol K, is within the range obtained for the synthetic hydrocarbon oils. The vapor-phase translational entropy for oils is approximated with the Sackur-Tetrode equation:

$$S_{\text{vap,trans}}^i = R \left[\frac{5}{2} + \ln \left\{ \frac{(2\pi)^{3/2}}{h_p^3} \frac{(RT)^{5/2}}{N^4 P} \right\} + \frac{3}{2} \ln(M_i) \right] \quad (22.16)$$

The vapor-phase rotational entropy is given by [44]

$$S_{\text{vap,rot}}^i = R \left[1 + \ln \left\{ \frac{1}{\pi q} \left(\frac{8\pi^3 IRT}{h_p^2} \right)^{a/2} \right\} \right] \quad (22.17)$$

Here

a = number of independent rotation axes

q = degeneracy

I = moment of inertia

An approximation for $S_{\text{vap,rot}}^i$ is given in Ref. 40.

The vaporization entropy also includes the vibrational entropy. The available vibrational states are comparable between liquid and vapor for these high-molecular-weight hydrocarbons or polymeric oil molecules, whereas the translational and rotational states are much more restricted in the liquid phase.

Note that the ideal gas law is employed in deriving Equation 22.15. The vaporization enthalpy $\Delta H_{\text{vap}}^i = \Delta E_{\text{vap}}^i + \Delta(PV)_i$. The pressure volume expansion work term has been replaced by $\Delta(PV)_i = RT$. The vaporization activation energy, ΔE_{vap}^i , also depends on molecular weight because a longer molecule requires more energy to overcome the intermolecular interaction force between itself and its neighbors in the surrounding liquid. Polar end groups contribute a fixed amount to the vaporization energy, which accounts for the intercept in the plot of vaporization energy as a function of molecular weight. As one might expect, there is a linear relation between the activation energy and molecular weight for Zdol [45], $\Delta E_{\text{vap}}^i \approx \Delta E_{\text{int}} + \Delta E_{\text{slope}} \times M_i$. The slope, $\Delta E_{\text{slope}} = 0.029 \text{ kJ/mol/Da}$, and intercept, $\Delta E_{\text{int}} = 50 \text{ kJ/mol}$, of the vaporization activation energy dependence on molecular weight for Zdol were determined by comparing the simulated evaporation data with that measured by isothermal TGA. The thermodynamic properties, vapor-phase diffusion coefficient, and vapor pressure for a range of ideal monodisperse Zdol molecular weights calculated as described earlier are listed in Table 22.9 [1]. The numerical values in Table 22.9 can be used in Equation 22.15 to calculate the vapor pressure of perfectly monodispersed molecular weight fractions.

Actual samples of commercial PFPE lubricant such as Zdol are polydisperse. Consequently, there is a wide range of partial pressures for a given sample, and the lowest molecular weight species in the distribution have the highest vapor pressure. In the case of Zdol 2000, because it is a copolymer of perfluoromethylene and perfluoroethylene oxide, the lowest molecular weight oligomers group together with similar molecular weights, hence similar vapor pressures. Figure 22.13a [1] shows the molecular weight distribution of Zdol 2000 measured by GPC. The oscillations in the molecular weight distribution are visible up through 1000 Da. The mole fraction distribution is also shown, as it plays a key role in determining the actual vapor pressure. Qualitatively, the vapor pressure increases with decreasing molecular weight, but as the molecular weight becomes lower, there are fewer of these molecules in the solution, so Raoult's law acts to partly offset the increase in vapor pressure, causing the vapor pressure to decrease in the limit of low molecular weight. Hence, the shape of the partial pressure distribution superimposed on the distribution in Figure 22.13a, calculated at 50°C. The partial pressure distribution for Zdol is shown with units on an expanded scale in Figure 22.13b. This shows the great detail provided by the GPC method, and also, the partial pressure peaks show the molecular weights that will evaporate with the highest rate or distill out of the distribution. The total vapor pressure of polydisperse Zdol 2000 at 50°C is the sum of the partial pressures of each component, in this case, 0.2 Pa.

There are some other important properties of magnetic recording disk lubricants that will not be covered in this chapter, and several references on these are provided later. Lubricant spin-off and transfer to the slider is minimized by chemisorption to the overcoat [46]. Chemisorption [47], also referred to as bonding, is well described by Tyndall et al. [48]. Disk lubricants also serve to inhibit

TABLE 22.9

Vaporization Entropy ΔS_{vap}^i , Binary Diffusion Coefficient D_i , and Vapor Pressure P_{vap}^i for Perfectly Monodispersed Zdol Fractions Evaporating into Nitrogen at Ambient Pressure (10^5 Pa) at Three Different Temperatures, $S_{\text{liq}} = 107 \text{ J/mol K}$, $\Delta E_{\text{vap}}^i = 50 + 0.029 \times M_i$

M_i (Da)	ΔS_{vap}^i (J/mol K)	D (m ² /s)	P_{vap}^i (Pa)
Temperature 35°C			
500	123	3.16×10^{-6}	1.13×10^0
750	133	2.27×10^{-6}	2.26×10^{-1}
1000	140	1.78×10^{-6}	3.17×10^{-2}
1350	147	1.38×10^{-6}	1.48×10^{-3}
1500	150	1.26×10^{-6}	3.72×10^{-4}
2000	157	9.79×10^{-7}	3.07×10^{-6}
3000	167	6.82×10^{-7}	1.25×10^{-10}
4000	174	5.25×10^{-7}	3.61×10^{-15}
4300	176	4.91×10^{-7}	1.50×10^{-16}
5400	182	3.98×10^{-7}	1.16×10^{-21}
Temperature 45°C			
500	123	3.32×10^{-6}	2.76×10^0
750	133	2.38×10^{-6}	6.01×10^{-1}
1000	141	1.87×10^{-6}	9.19×10^{-2}
1350	148	1.44×10^{-6}	4.87×10^{-3}
1500	151	1.32×10^{-6}	1.29×10^{-3}
2000	158	1.02×10^{-6}	1.27×10^{-5}
3000	168	7.15×10^{-7}	7.44×10^{-10}
4000	175	5.51×10^{-7}	3.05×10^{-14}
4300	177	5.15×10^{-7}	1.41×10^{-15}
5400	183	4.18×10^{-7}	1.61×10^{-20}
Temperature 60°C			
500	124	3.56×10^{-6}	9.51×10^0
750	135	2.55×10^{-6}	2.34×10^0
1000	142	2.00×10^{-6}	4.05×10^{-1}
1350	149	1.55×10^{-6}	2.55×10^{-2}
1500	152	1.41×10^{-6}	7.28×10^{-3}
2000	159	1.10×10^{-6}	9.19×10^{-5}
3000	169	7.66×10^{-7}	8.80×10^{-9}
4000	176	5.90×10^{-7}	5.91×10^{-13}
4300	178	5.52×10^{-7}	3.17×10^{-14}
5400	184	4.48×10^{-7}	6.26×10^{-19}

Note: Other parameters used are given in the text.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

corrosion. The corrosion protection ability of Zol lubricants was related to surface energy by Tyn-dall et al. [48] The most successful disk lubricant additive has been cyclic phosphazines. However, cyclic phosphazine increases the lubricant mobility [49] and decreases the dewetting thickness [37]. More recently, an effort has been made to combine the desirable properties of both by incorporating a cyclic phosphazine end group onto Zdol. This lubricant is referred to as A20H, and it is described by Waltman et al. [5]. The A20H end group is shown in Table 22.1.

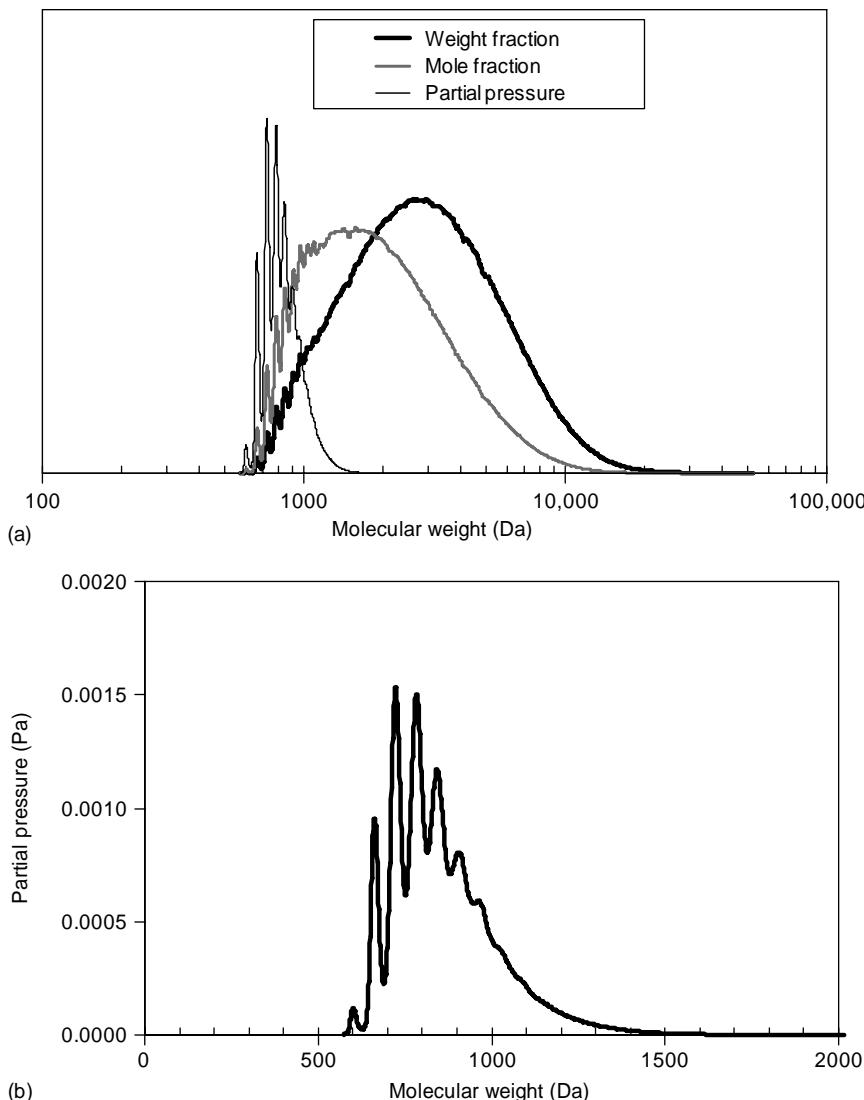


FIGURE 22.13 The molecular weight distribution, mole fraction distribution, and the calculated partial pressure distribution (a), and the partial pressure distribution on an expanded scale with units (b) for Zdol 2000 at 50°C. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

22.3 SPINDLE MOTOR LUBRICANTS

There are ball bearing and fluid dynamic bearing spindle motors (see Ref. 50 for a good overview). The arrangement of the spindle motor and types of spindle motor bearing are shown in Figure 22.14 [1].

22.3.1 BALL BEARING SPINDLE MOTOR BEARING GREASE

Ball bearing spindle motor bearings are typically lubricated with an NLGI grade 2 lithium grease. The grease composition, referred to as SRL, is a lithium grease comprising approximately 10% Li 12-hydroxy stearate, 17% di-2-ethylhexyl sebacate, and 70% pentaerythritol tetraesters, and the rest is a sulfonate rust inhibitor and an amine antioxidant. Lithium soap gel fibers thicken the

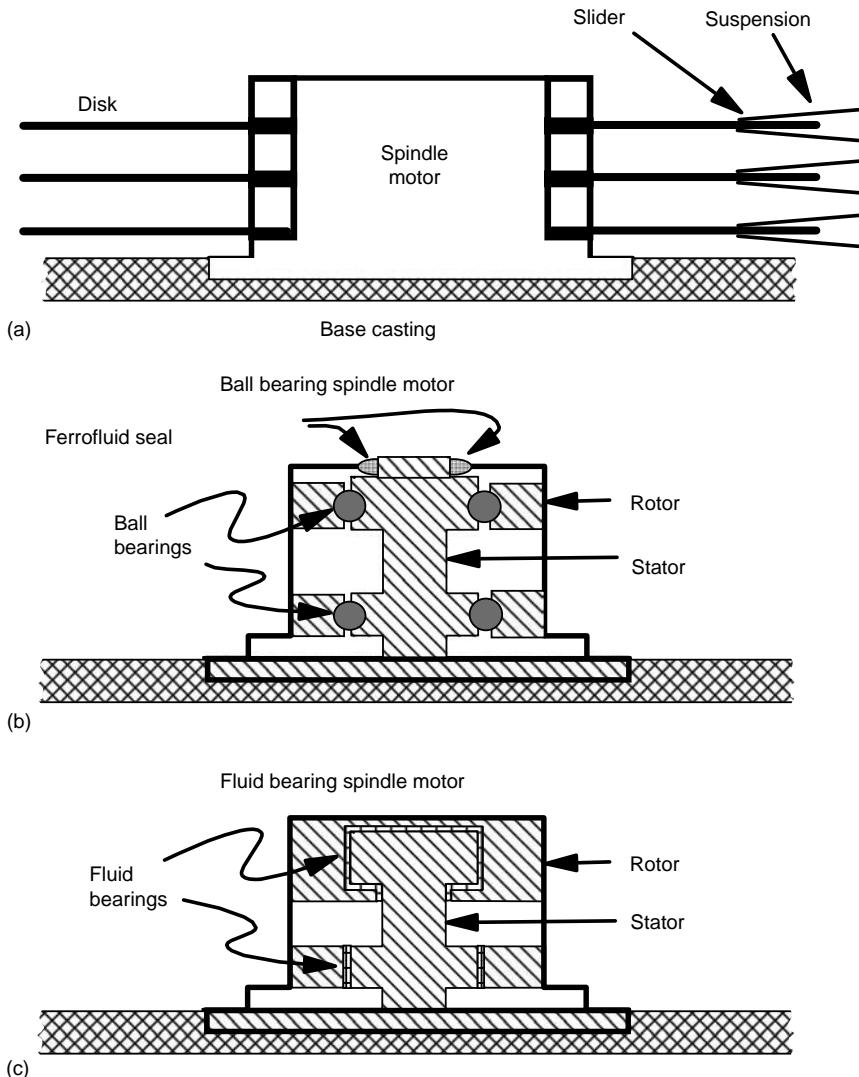


FIGURE 22.14 The arrangement of the magnetic recording disks and head suspension assembly on the spindle motor (a), schematic ball bearing spindle motor (b), and schematic fluid bearing spindle motor (c). (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

grease [51,52]. The grease base oil viscosity at 40°C is 22 mPa s, and the worked penetration is 245. A great variety of greases could potentially be used in these bearings, but in practice, the grease is limited by stringent requirements of low volatility, yield stress at temperature, low torque noise, and good thermal stability.

22.3.1.1 Yield Stress at Temperature

Typical ball bearing spindle motor grease rheological properties and yield stress are described by Karis et al. [53]. For practical purposes, the yield stress is measured by gradually increasing the stress in a stress rheometer with a cone-plate fixture. The yield stress is detected when the cone begins to rotate. For example, the yield stress as a function of temperature for several grease candidates for use in ball bearing spindle motors is shown in Figure 22.15 [1]. There is a general trend

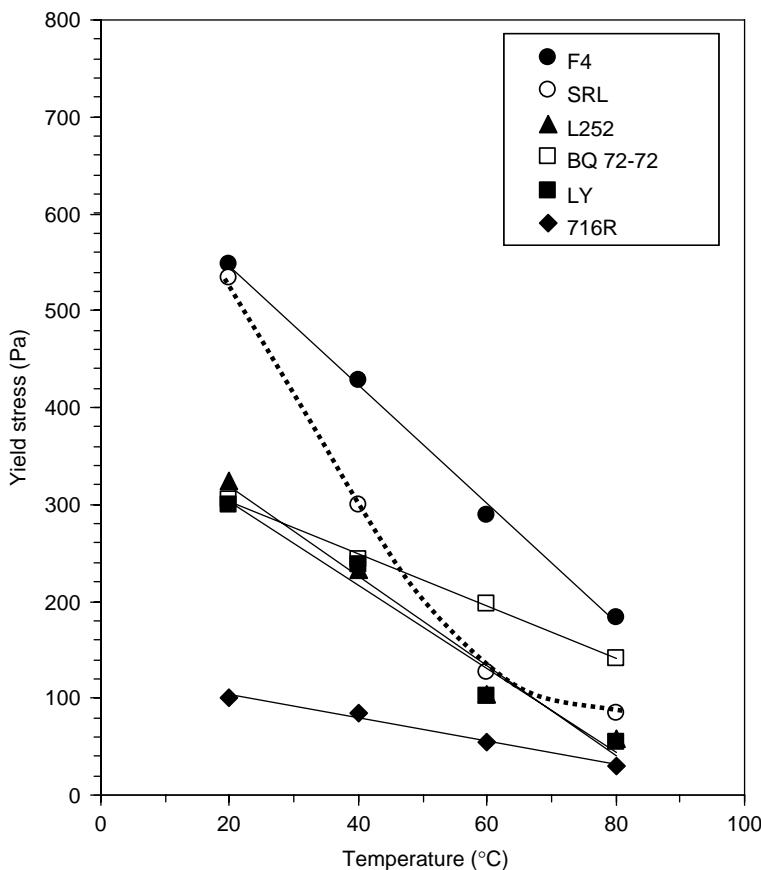


FIGURE 22.15 The yield stress of various candidate greases for ball bearing spindle motors as a function of temperature. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

of decrease with temperature, but all the greases maintain a measurable yield stress up through at least 80°C. The decrease of the yield stress with temperature is much less than that of the grease base oil, as will be shown later.

Diluting the grease with additional base oil, or incorporation of contaminants in the grease, also affects the yield stress. Additional oil is often added to prelubricate the new bearing once it has been filled with grease. This is done to provide a lubrication film during initial start-up of the new bearing, before the base oil from the gel thickener of the grease has had time to diffuse throughout the surfaces of the balls and raceways. The prelube can either be the grease base oil itself or specially formulated prelube oil. Results with two types of prelube are also described here. Prelube oil A is diester oil with a sulfonate rust inhibitor and a hindered phenol antioxidant. Prelube oil B is mostly diester oil with several percent of poly alpha olefin oil, a sulfonate rust inhibitor, and a Zn dialkyldithiocarbamate antiwear additive. Grease may also be exposed to organometallic salts formed from various components within the bearing, bearing shields, or motor. Zn was incorporated as Zn(diacrylate), and Fe was incorporated as iron (III) 2-ethylhexanoate. The Zn(diacrylate) contaminant was intended to model products of bearing corrosion by the incomplete curing of a motor bearing adhesive [54].

Model grease containing prelube or contaminants was prepared in the laboratory by thoroughly mixing them in a custom-built lab-scale grease mill. The grease mill capacity was ~10 g of grease. The mill comprised two 32 mm diameter disks perforated with 35 circular holes,

each 460 μm in diameter, inside a stainless steel tube. The perforated disks were separated by a 3.8 mm wide cavity. Grease was forced back and forth through the holes in the perforated disks by the reciprocating action of two opposing pneumatic cylinders driving Teflon pistons against the perforated plate within the steel tube. Air pressure was alternately applied to the cylinders using a cam and follower arrangement driven by a variable speed gear motor.

The yield stress of these model greases is shown in Figure 22.16 [1]. The yield stress was increased by Zn(diacrylate), whereas prelube oils decreased the yield stress.

For comparison with the yield stress versus temperature, the viscosity and density of the SRL grease base oil and two prelube oils are shown as a function of temperature in Figure 22.17 [1]. The viscosity and density of the base oil are somewhat higher than that of the prelube oils. Blends between the base oil and the prelube oil A or B will have intermediate viscosities. The oil viscosity decreases much more than the yield stress with temperature. This implies that most of the yield stress change with temperature (Figure 22.16) is due to the gel network of the thickener. The reduction in yield stress on blending grease with prelube oil is probably due to dilution of a transient network in the gel thickener.

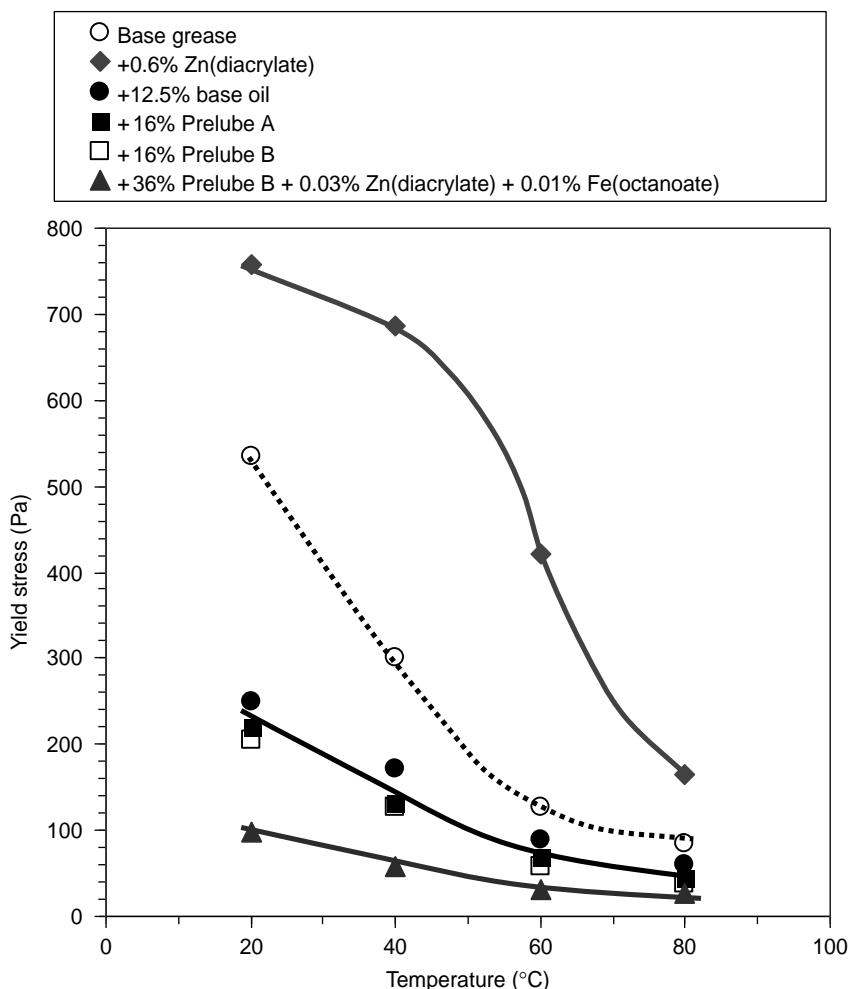


FIGURE 22.16 The yield stress of base grease SRL showing the effect of additional base oil, prelube oils, and organometallic salt contamination on yield stress as a function of temperature. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

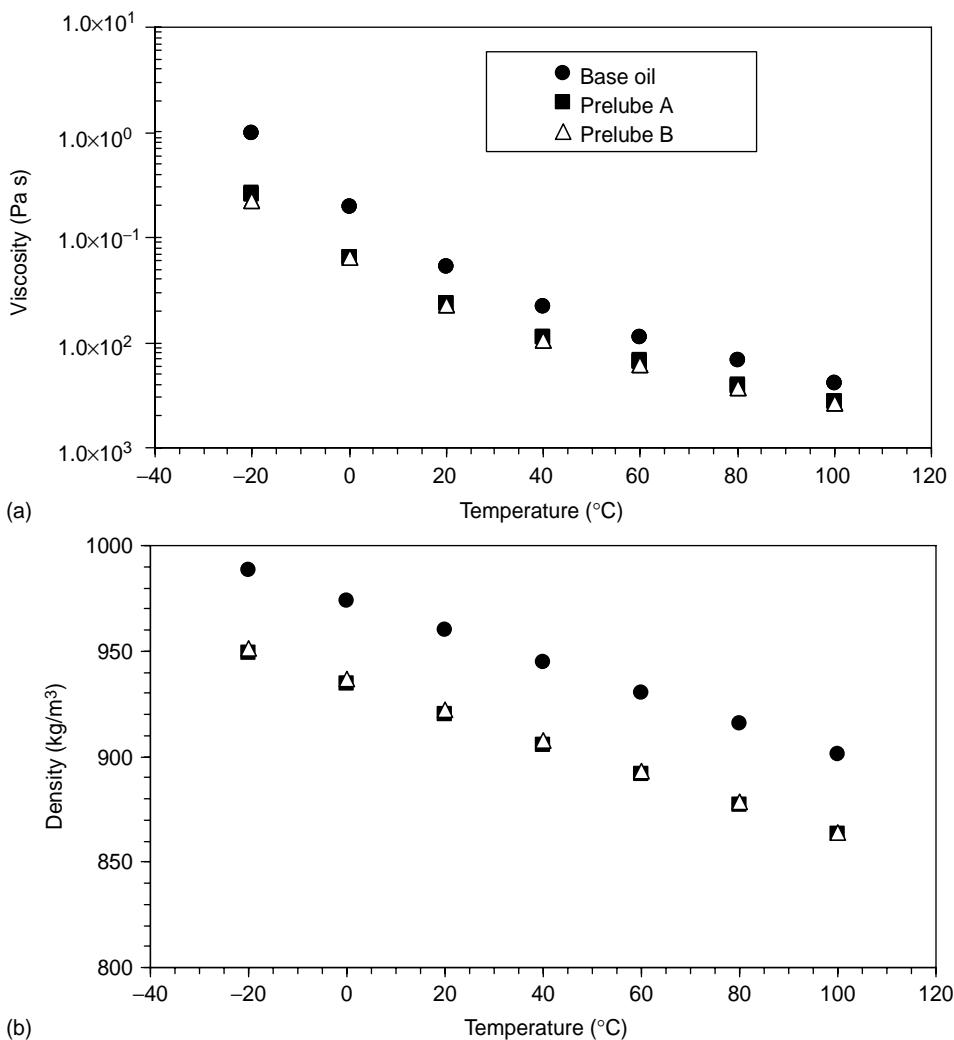


FIGURE 22.17 The viscosity (a) and density (b) of SRL grease base oil and two prelube oils as a function of temperature. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

22.3.1.2 Hydrodynamic Film Thickness

The hydrodynamic film thickness of the oil provided by the grease must be sufficient to clear the asperities on the balls and race during operation at the specified load and velocity. The hydrodynamic film thickness is given by

$$h = k(U\eta_0)^{0.67}(\alpha_p)^{0.53} \quad (22.18)$$

where

h = film thickness

k = material and geometry parameter

U = entrainment velocity

η_0 = viscosity at atmospheric pressure

α_p = pressure-viscosity coefficient [55]

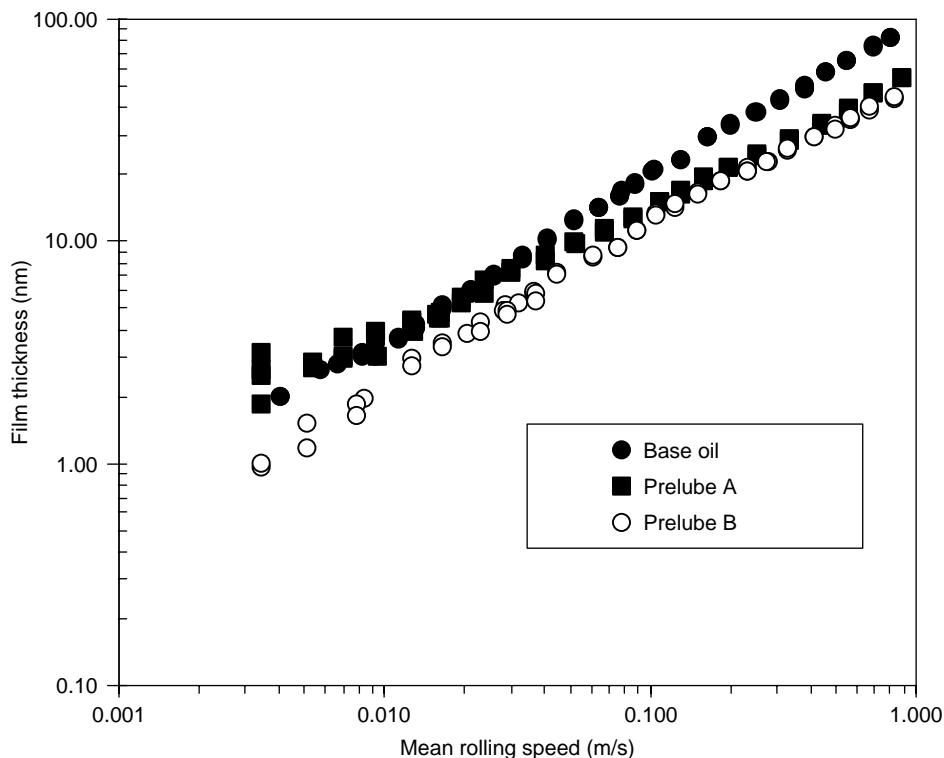


FIGURE 22.18 The film thickness as a function of rolling speed measured by ultrathin-film interferometry. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

The film thickness between a steel ball and a plate by ultrathin-film interferometry [56] was measured by Professor H.A. Spikes, and his students, at Imperial College in London. The film thickness as a function of sliding speed for the grease base oil, and the prelube oils A and B, is shown in Figure 22.18 [1]. There is some variation in the power law slope between the oils, which slightly varies from the coefficients used in Equation 22.18. By comparison with a fluid with a known pressure–viscosity coefficient, they estimated the pressure–viscosity coefficients over a limited speed range between 0.1 and 1 m/s to be ~15 1/GPa for the base oil, 12 1/GPa for prelube oil A, and 10.5 1/GPa for prelube oil B. The difference between prelube oils A and B is probably due to the minor fraction of polyalphaolefin in prelube oil B.

22.3.1.3 Grease Electrochemistry

Some types of high-performance disk drive spindle motors incorporate ball bearings with silicon nitride ceramic balls for higher stiffness and lower vibration. It is critical that the bearings and grease provide smooth rotation so as not to excite resonances of the disk pack (Figure 22.14a). Electrostatic potential generated by bearings can induce a small current flow through the bearing, with a return path through the ferrofluid seal (Figure 22.14b). To investigate the effect of electrochemistry, grease containing various types of contaminants was sandwiched between two steel electrode plates. The plates were made of 25 mm diameter mirror polished 304 stainless steel disks with grease in between them on a 160 μm thick filter paper. The plates were subjected to 25 V to simulate the passage of electrical current through the grease in the bearing. After several hundred hours, the plates were separated and examined for degraded grease as deposits on the plates. Film deposits were characterized by optical microscopy, FTIR spectroscopy in reflection, and x-ray photoelectron spectroscopy (XPS).

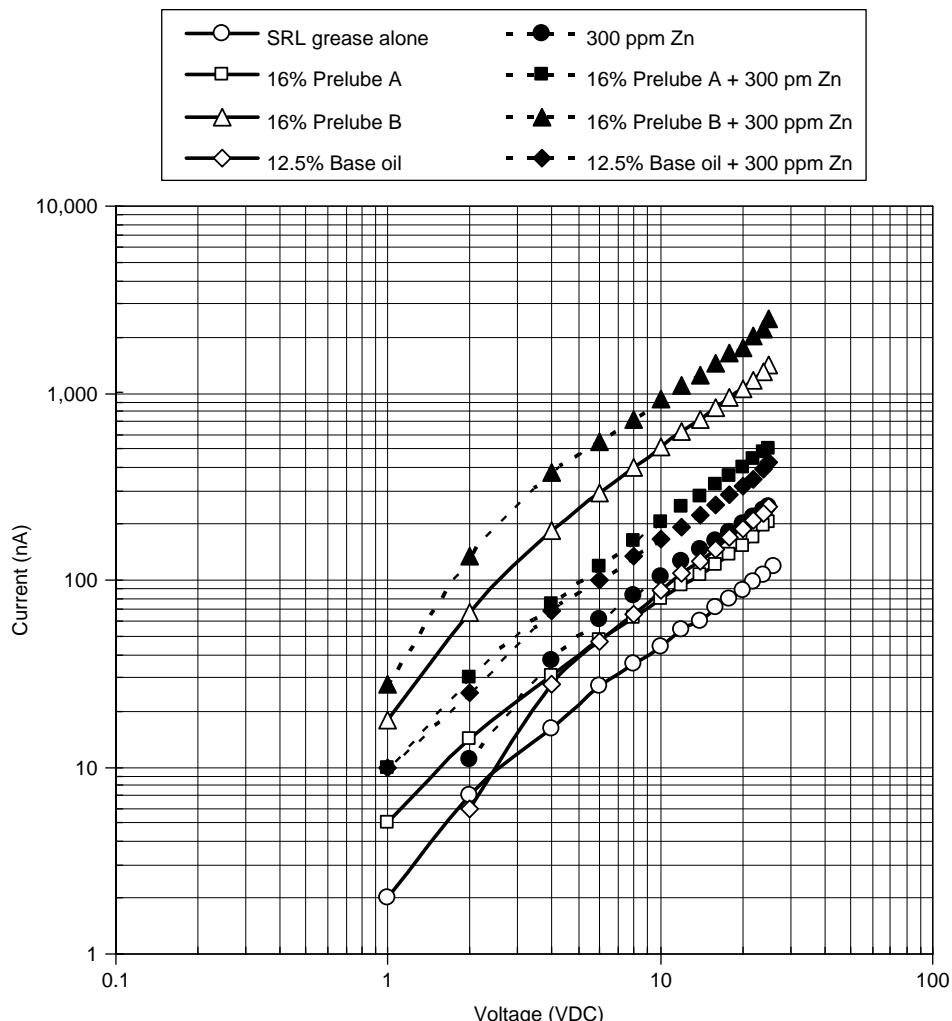


FIGURE 22.19 Initial current–voltage plot for SRL grease alone, and SRL grease with the indicated additives and contaminants measured in the electrochemical cells. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

Figure 22.19 [1] shows the current through the electrode plates plotted as a function of the voltage applied across the grease film with fresh grease between the plates. The conductance of the ferrofluid seal in the motor was ~ 77 nS ($13\text{ M}\Omega$), so that the current through the bearing is typically 30–80 nA. In steady state, the electrochemical cells were operated at 25 V, or between 100 and 3000 nA, depending on the type of grease contamination. The higher voltage was employed in the electrochemical cells to increase the rate of any electrochemical reactions that might take place. The initial conductance of the electrochemical cells, calculated from the linear region of the current–voltage plot, is listed in the second column of Table 22.10 [1]. The lowest conductance was obtained with the SRL grease alone, and SRL grease combined only with an additional 12.5% more of its own base oil. The highest conductances were found with the grease containing 16% prelube oil B and 300 ppm Zn, and grease containing 16% prelube oil B. The grease conductance gradually varied with time during voltage application, as shown for several greases with and without contaminants in Figure 22.20. The pure grease, with no diluents or contaminants, maintained the lowest conductance.

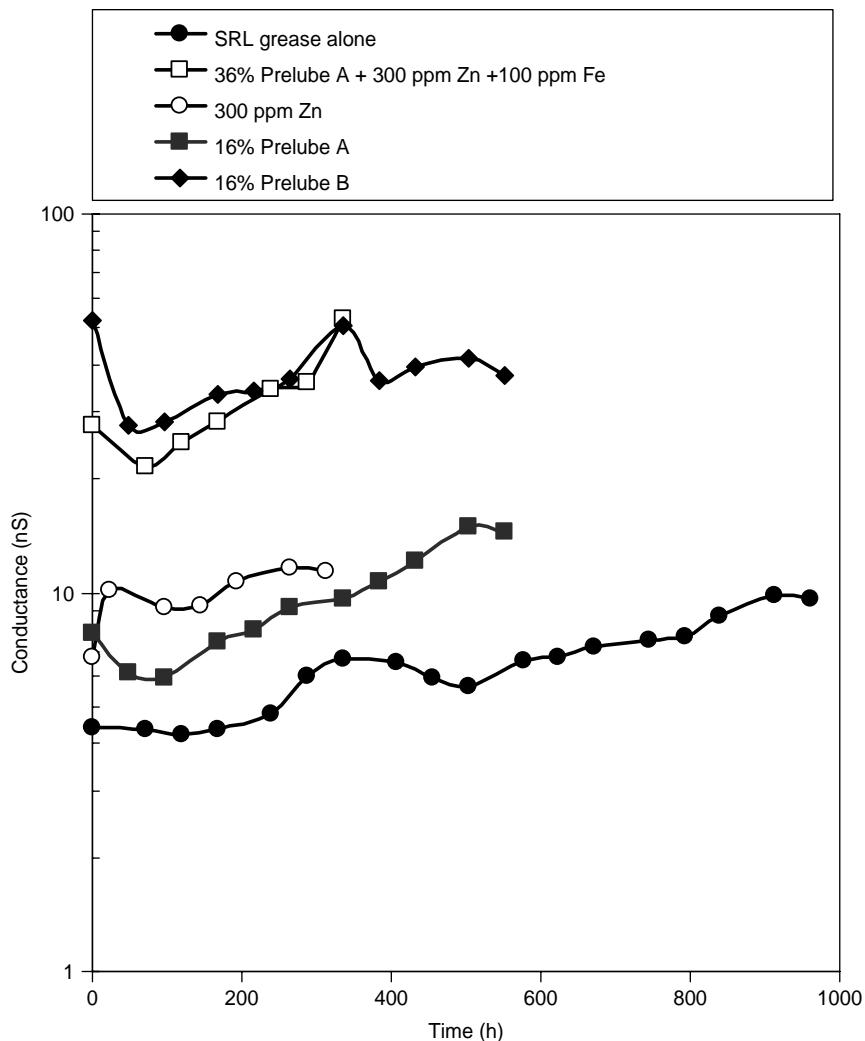


FIGURE 22.20 Conductance–time plot for SRL grease alone, and SRL grease with additives and contaminants measured in the electrochemical cells. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

After several hundred hours, the plates were separated and washed with chloroform by squirting from a pipette. When present, films were observed on the negative electrode plate. Although there was sometimes minor film formation or slight pitting on the positive plate, there was too little to quantify. Micrographs of the film deposits on several of the negative electrode plates are shown in Figure 22.21 [1]. These show the fibrous appearance. The film deposits were highly viscous. Film deposits were qualitatively ranked in terms of their severity, which is referred to as light, medium, and heavy, after the indicated electrolysis time (Table 22.10). The lightest deposits were observed with the virgin grease, and the grease diluted with its own base oil. The heaviest deposit coincided with the highest conductance. However, although they had nearly the lowest conductance, grease contaminated by 300 ppm of Zn as acrylate, or with 16% of the prelube oil A, also formed heavy deposits.

Reflection FTIR was performed on the residue on the plates after each test. Typical FTIR spectra are shown in Figure 22.22 [1]. The IR peaks were assigned to chemical groups according to

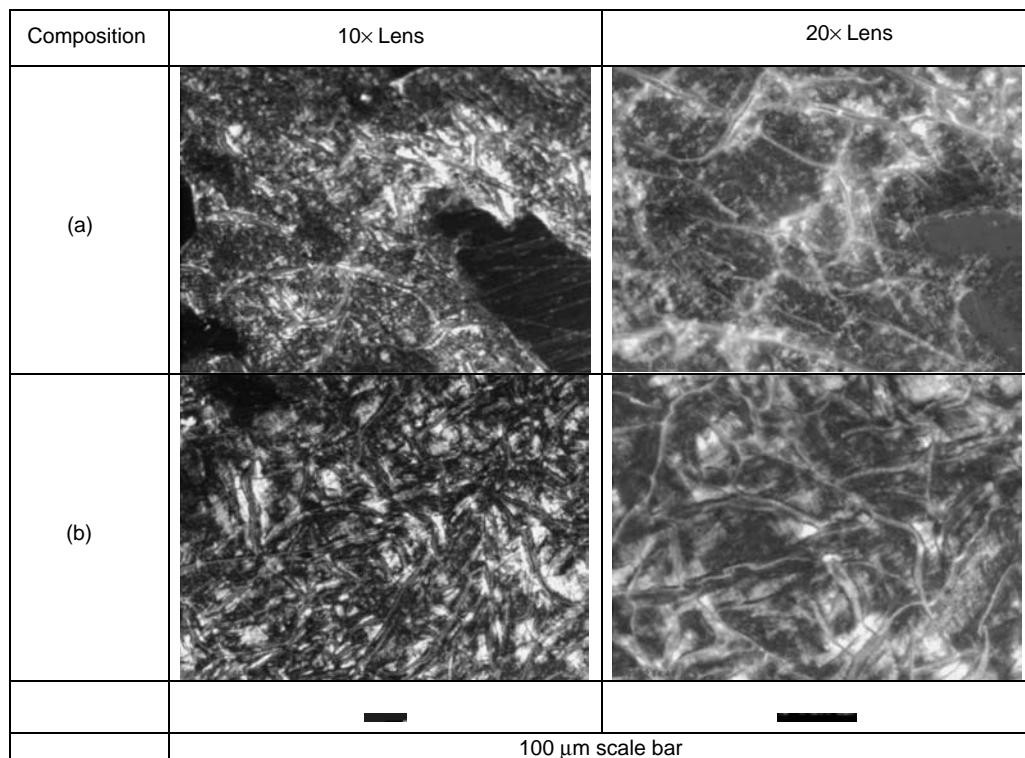


FIGURE 22.21 Optical micrographs showing the film deposits on the negative electrode plate following electrochemical oxidation of contaminated grease at two different levels of magnification. The residue was insoluble in chloroform and isopropanol, whereas the initial grease was easily removed from the plates by rinsing with chloroform. SRL grease + 300 ppm Zn for 336 h (a), and SRL grease + 16% prelube A for 576 h (b). (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

the peak assignments given in Table 22.11 [1]. Similar IR spectra and peak assignments are reported for mechanically stressed grease by Cann et al. [57]. The IR peak assignments, in conjunction with XPS measurements on the residue given in Table 22.12 [1], show electrochemical oxidation of the grease. The ratio of carbonyl groups increased following the electrochemistry. For the pure thickener, the ratio of carbonyl to Li is 1.07, whereas aged grease and electrochemically oxidized grease have increased carbonyl due to oxidation. For black grease from a failed bearing, residue in a noisy bearing and a pin on disk wear test track also show increased carbonyl relative to the original thickener.

In summary, for the longest lifetime and best performance under all conditions, lithium grease should be kept free of metallic impurities and diluents. When electrochemical oxidation does occur, it forms a residue from the soap thickener on the raceway.

22.3.2 BALL BEARING SPINDLE MOTOR FERROFLUID SEAL

As mentioned earlier, the return path from the rotor to the stator for charge generated by the ball bearings is through the ferrofluid seal (Figure 22.14b). The ferrofluid is held in place by magnets in the seal housing, and the primary function of the ferrofluid seal is to prevent airflow through the motor into the disk drive enclosure. The typical ferrofluid is a suspension of 10–30 wt% subdomain magnetite particles 10 nm in diameter in a trimellitic/trimethylol propane ester oil with 10–20 wt% dispersing agent and up to 10 wt% antioxidant.

TABLE 22.10
Grease Electrochemical Cell Test Results for Grease on a 160 μm Thick Filter Paper between 1 in. Diameter Electrode Plates

Sample	Initial Conductance (nS)	Time (h)	Film Deposit
SRL grease alone	4	960	Light
SRL grease + 36% prelube A	28	336	Medium
+ 300 ppm Zn			
+ 100 ppm Fe			
SRL grease + 300 ppm Zn	7	336	Heavy
SRL grease + 16% prelube A	8	576	Heavy
SRL grease + 16% prelube A + 300 ppm Zn	20	336	Light
SRL grease + 16% prelube B	52	576	Light
SRL grease + 16% prelube B + 300 ppm Zn	93	336	Heavy
SRL grease + 12.5% SRL base oil	9	336	Light
SRL grease + 12.5% SRL base oil + 300 ppm Zn	16	336	Heavy

Note: The initial conductance was calculated from the linear region of the current–voltage data measured between 1 and 25 V (Figure 22.19). Prelube is defined in the text. The right-hand column gives the appearance of the film deposit on the negative electrode plate after application of 25 V for the amount of time listed in the third column.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

Ferrofluid is a mature technology, and these fluids are highly stable. The most recent effort to modify the properties of the ferrofluid was intended to increase the electrical conductivity so as to reduce the electrical potential between the rotor and stator of the spindle motor. The development of conductivity additives for ferrofluids is described later.

Additives to increase the conductivity of the carrier oil were investigated. A number of conductivity enhancing compounds were incorporated in a model carrier oil, trioctyltrimellitate (TOTM), and the conductivity was measured by DEA, as described in Section 22.2.1.2. The results of the initial screening are given in Table 22.13 [1]. Most of the additives reduced the conductivity. This probably indicates that the additives were associating with impurities that were the primary charge carriers in the oil. The most promising initial results were obtained with a micellar solution of succinimide and dodecylbenzenesulfonic acid [58]. Variations of the organic acid and the succinimide/acid ratio were explored to optimize the conductivity of the TOTM carrier oil. The results are summarized in Table 22.14 [1]. The mixtures of succinimide and acid provided the highest conductivity to the oil. The most promising conductivity additives based on the tests in the model oil are shown in Figure 22.23 [1]. Even the best combination of conductivity additives in TOTM still had lower conductivity than any of the ferrofluids.

Dielectric spectroscopy was performed to determine the conductivity mechanism of the ferrofluid. The ferrofluid has three dielectric relaxation times: 260, 43, and 6.3 ms. These relaxation

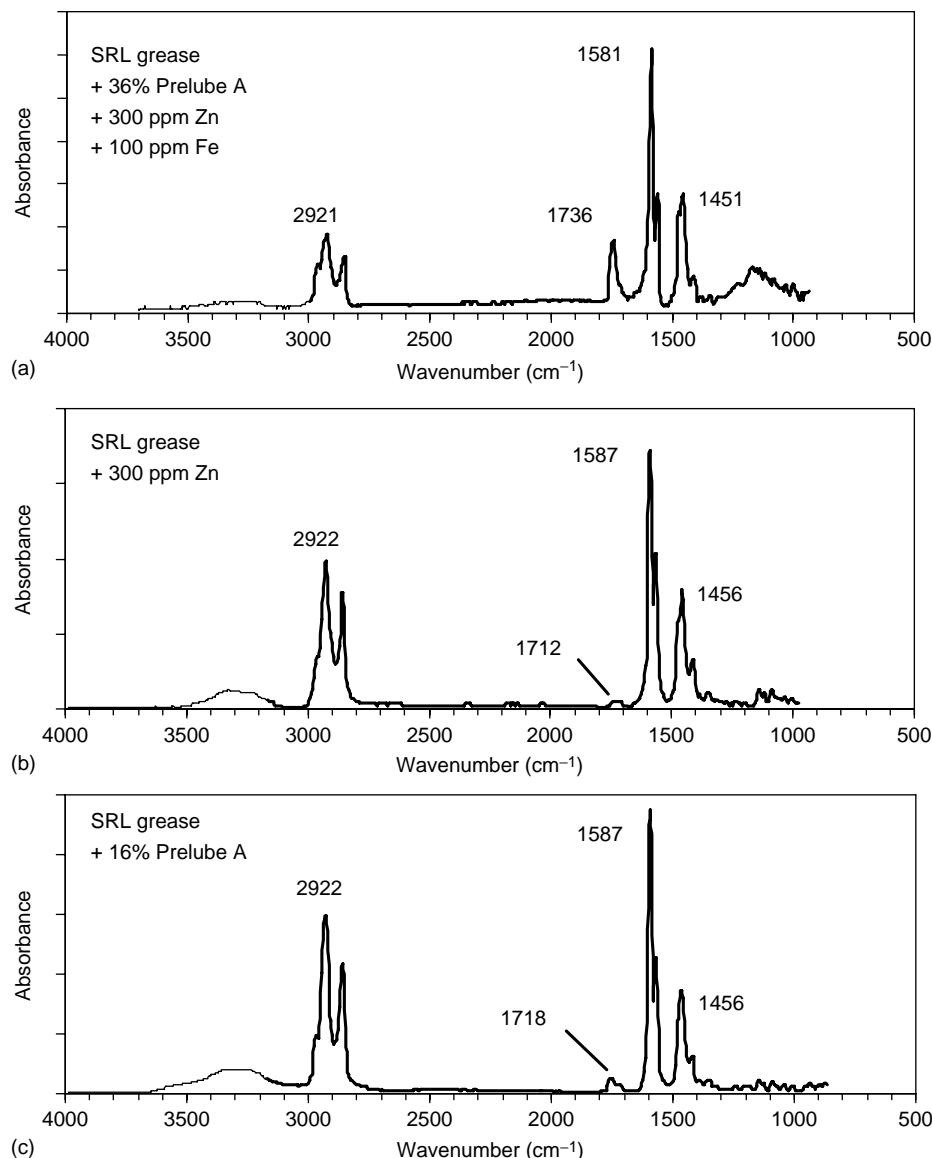


FIGURE 22.22 Reflection FTIR spectra of residue deposited on the negative electrode plates from grease containing various contaminants: (a) Prelube A, Zn, and Fe, (b) Zn, and (c) prelube A. Oil was removed by washing with solvent before measurement. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

modes probably comprise the phoretic motion of the magnetite particles, phoretic motion of ions, and electronic hopping, respectively. The activation energy for conductivity is close to the viscous flow activation energy, so the conductivity of the ferrofluid is mostly due to the phoretic motion of the magnetite particles. The relaxation times were unchanged by the conductivity additives.

As it became apparent that conventional additives used to enhance the conductivity of the carrier oil are of no benefit, or reduce the conductivity of the ferrofluid, a different approach was needed. Ferrofluid is significantly more conductive than the carrier oil, due to the presence of the magnetite particles. The conductivity of a ferrofluid can only be enhanced by improving the efficiency of charge transfer between the suspended magnetite particles. This may be done by incorporating

TABLE 22.11
FTIR Peak Assignments

Absorbance	Wavenumber (cm^{-1})
Broad dimer hydrogen-bonded carbonyl O—H stretch in 12-hydroxy stearic acid	3500–2500
Hydrogen-bonded O—H stretch in alcohol	3500–3200
Asymmetrical methylene C—H stretch	2928–2917
Aliphatic aldehyde or ester C=O stretch	1740
Aliphatic methyl ketone C=O stretch	1730
Aliphatic internal ketone C=O stretch	1725
Carboxylic acid dimer C=O stretch in 12-hydroxy stearic acid	1695
C—O—H in-plane bend in 2-hydroxy stearic acid	1470
Carboxylate anion, asymmetrical stretch	1589–1581
Carboxylate anion, symmetrical stretch	1456–1442
Ester C—C(=O)—O in base oil	1166

Note: The carboxylate anion is formed with Li or Zn and 12-hydroxy stearic acid. The ratio $(\text{C}=\text{O})_{\text{salt}}/\text{C}(\text{—H})_2$ was measured using the carboxylate anion, asymmetrical stretching, and the asymmetrical methylene C—H stretching.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

TABLE 22.12
The Ratio of Carboxylic Acid to Methylene from FTIR, the Ratio of Total Carbonyl Carbon to Methylene Carbon and to Li, and Atomic Percent of Li and Zn from XPS, in Model Compounds, Electrochemically Deposited Films, Inner Race Deposits, and Black Grease from Failed Motor Bearings

Film	FTIR		XPS			
	Hydrogen-Bonded OH	$(\text{C}=\text{O})_{\text{salt}}/\text{C}(\text{—H})_2$	$\text{C}=\text{O}_{\text{total}}/\text{C}(\text{—H})_2$	$\text{C}=\text{O}_{\text{total}}/\text{Li}$	Li (%)	Zn (%)
Li 12-hydroxy stearate	Yes	0.067 (exact)	0.067	1.07	4.3	0.09
Li 12-hydroxy stearate from grease (brown, stored 8 years)	Yes	0.035	0.079	1.5	3.6	—
Zn (12-hydroxy stearate) ₂	—	—	0.063	—	<0.3	3.0
Zn (12-hydroxy stearate) ₂ after 10 min at 130°C	Yes	0.049	—	—	—	—
eChem SRL grease + 36% prelube A + 300 ppm Zn	Yes	0.17, 0.05, 0.054	0.097	1.3	5.1	0.06
+ 100 ppm Fe						
eChem SRL grease + 300 ppm Zn	Yes	0.086, 0.082	0.11	1.4	4.7	0.12
eChem SRL grease + 16% prelube A	Yes	0.072, 0.077	0.11	1.4	5.3	—
Black grease	No	0.076	0.14	0.5	15.8	0.16
In-plane residue	No, yes	0.10, 0.06	—	—	—	—
Ball track residue	No	0.12, 0.20, 0.31, 0.13	—	—	—	—

Note: The extinction coefficient ratio, $\epsilon_{\text{C}(\text{—H})_2}/\epsilon_{\text{C}=\text{O}} = 0.0475$, was calculated from FTIR spectra of methylene C(—H)₂ asymmetric stretch and carboxylic acid (C=O—O) anion asymmetric stretch measured for Li 12-hydroxy stearate and Li stearate. Grease samples were rinsed with solvent to remove the oil. For Li 12 hydroxy stearate, the exact ratio of C=O/C(—H)₂ is 1/15 = 0.067, and the exact ratio of C(=O)/Li is 1, the exact atomic percent of Li = 4.8, and for Zn = 2.4; 300 ppm of Zn corresponds to 0.06 atomic percent of the lithium 12-hydroxy stearate. These results show evidence for electrochemical oxidation of the 12 hydroxy stearate thickener.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

TABLE 22.13**Trial Matrix of Potential Conductivity Additives in Tricycyltrimellitate Model Carrier Oil**

Additive	Concentration (wt%)	Comments	Conductivity (pS/m)
None	—	—	250–300
Disodium sebacate (Ciba DSSG)	1	Milky	5–7
Succinimide (2,5-pyrrolidenedione)	2	Mostly insoluble	80–100
Dodecylbenzenesulfonic acid	2	Clear solution	180–230
Butylated hydroxy toluene (BHT, or Ionol)	2	Clear solution	50–70
Ciba Irgamet 30	2	Clear solution	170–180
Dicyclohexylammonium benzoate	2	Milky	200–260
PMC Cobratec 911S	2	Clear solution	130–150
Mellitic acid	2	Mostly insoluble	8–17
Mixtures			
Succinimide (2,5-pyrrolidenedione)	1.6	Hazy	860–990
Dodecylbenzenesulfonic acid	1	—	—
Succinimide (2,5-pyrrolidenedione)	7.6	Hazy/Gel	3000–5000
Dodecylbenzenesulfonic acid	4.8	—	—

Note: Conductivity measured at 1 Hz and 50°C.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

TABLE 22.14**Optimization Matrix of Succinimide/Sulfonate Conductivity Additives in Tricooctyltrimellitate Model Carrier Oil**

Additive	Concentration (wt%)	Comments	Permittivity (1 Hz)		Conductivity (pS/m)	
			5°C	50°C	5°C	50°C
None	—	—	3.9	6.3	15	250–300
Succinimide	2	Mostly insoluble	—	4.0	—	80–100
DDBSA	2	Clear solution	—	4.0	—	180–230
Succinimide	1.6	Hazy	4.9	6.5	140	860–990
DDBSA	1	—	—	—	—	—
Succinimide	7.6	Hazy/Gel	—	26.0	—	3000–5000
DDBSA	4.8	—	—	—	—	—
Succinimide	1.5	Brownish, hazy	3.0–3.2	4.8–5.6	160–220	4400
DNNSA	1.4	—	—	—	—	—
Succinimide	1.5	Whitish, hazy, looks good	—	2.9–3.2	—	5–8
DNNSDA	0.8	—	—	—	—	—

Note: Succinimide is 2,5-pyrrolidenedione (99.1 g/mol). DDBSA is dodecylbenzenesulfonic acid (326.5 g/mol). DNNSA is dinonyl naphthalenesulfonic acid (460.71 g/mol). DNNSDA is dinonyl naphthalene disulfonic acid (540.79 g/mol). Amounts of DNNSA and DNNSDA adjusted for molecular weight and normality.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

particles coated with conducting polymer, conducting polymer oligomers, or nanowires in the form of multiwall carbon nanotubes. Conducting polymer-coated carbon black particles (Eeonomer, Eeonyx Corp., Pinole, California, United States [59]) and multiwall nanotubes (BU200, Bucky USA, Houston, Texas, United States) were evaluated in the TOTM model oil. As shown in Table 22.15 [1], the Eeonomers and nanotubes increased the oil conductivity by about five orders of magnitude. A stable mixed suspension of the nanotubes could not be adequately dispersed in the ferrofluid.

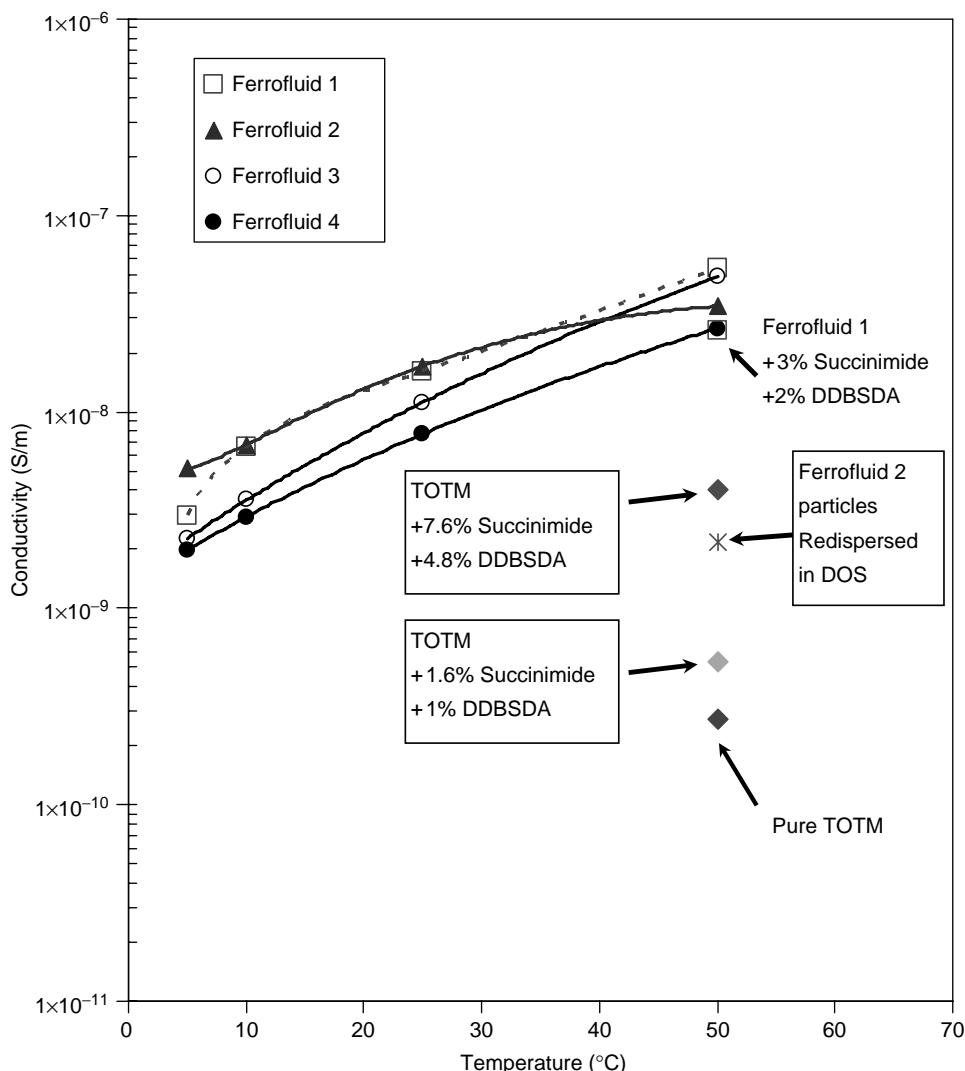


FIGURE 22.23 Conductivity of several types of ferrofluid, conductivity additives in model carrier oil, and ferrofluid 1 combined with one of the most promising conductivity additives. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

The conductivity of the ferrofluid increased with the Eeonomer concentration and was nearly independent of temperature between 5 and 50°C, as shown in Figure 22.24 [1]. The conductivity as a function of temperature for ferrofluid 1 containing Eeonomers is shown in Figure 22.25a [1]. The conduction mechanism seems to be limited by electronic transport through the Eeonomers, rather than by diffusive contacts between the particles, as the product of the conductivity and viscosity of the ferrofluid-containing Eeonomers decreased with temperature (Figure 22.25b). The metallic-like conductivity of the conducting polymer sheath is decreased by scattering because lattice vibrations faster than the transport between particles are increased by Brownian motion with increasing temperature.

Although the Eeonomers appear to be the most effective means to increase the ferrofluid conductivity, the long-term stability may be degraded by reaction of the dodecylbenzenesulfonic acid with the ester carrier oil. Furthermore, the conducting polymer sheath may also be crushed off of the carbon black in milling during the initial dispersion phase of ferrofluid manufacturing.

TABLE 22.15
Conductivity Evaluation of Multiwall Nanotubes and Eeonomers
in TOTM Model Carrier Oil

Additive	Conductivity (σ [S/m])
None	$2.5\text{--}3 \times 10^{-10}$
2% Eeonomer 200F	6.1×10^{-4}
	3.1×10^{-4}
2% Eeonomer 610F	2.0×10^{-4}
	2.3×10^{-4}
1% BS200 multiwall nanotubes	9.0×10^{-4}
	9.0×10^{-4}
10% BU200 multiwall nanotubes	8.8×10^{-4}
	8.6×10^{-4}

Note: The results of two separate measurements are shown for the mixtures.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

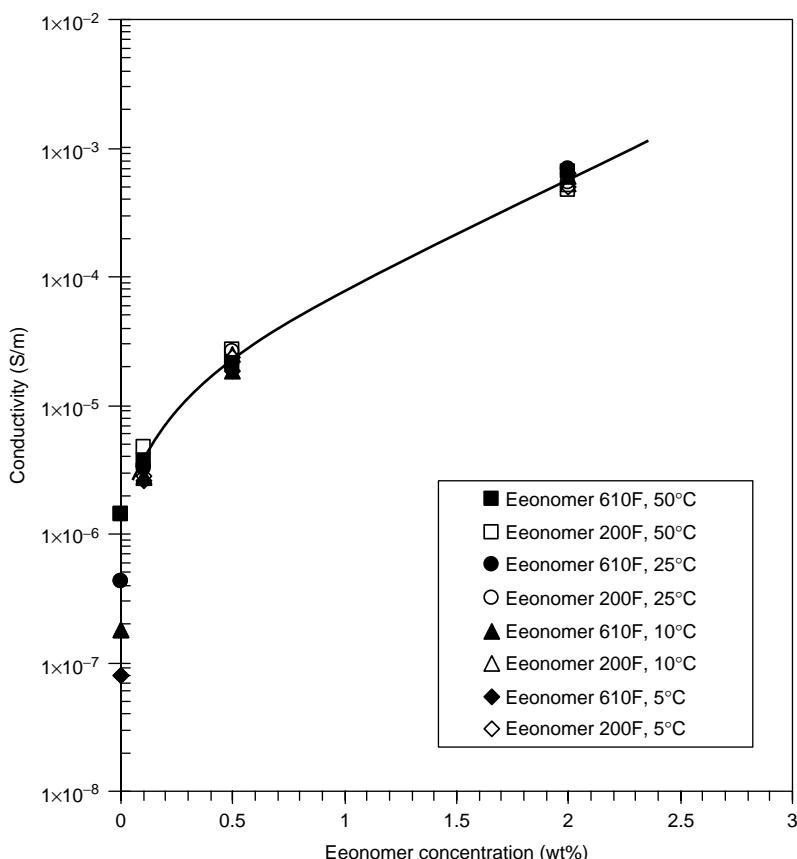


FIGURE 22.24 Conductivity of Eeonomers in ferrofluid 1 as a function of Eeonomer concentration and temperature. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

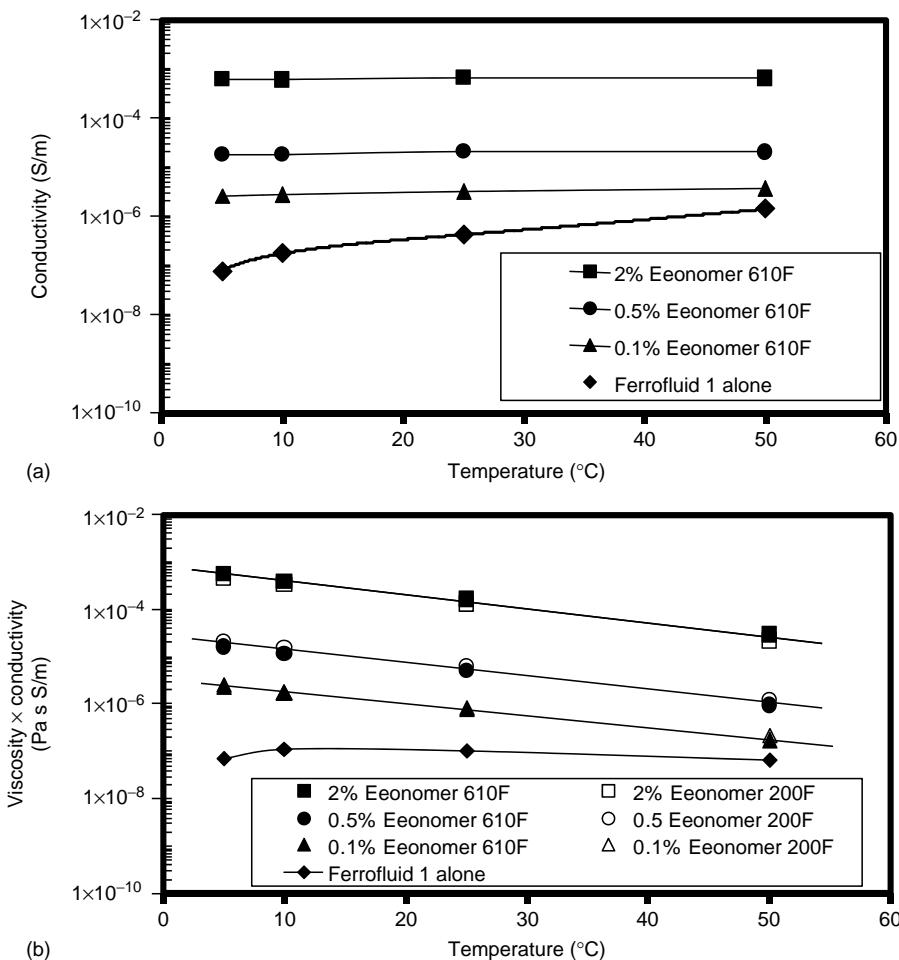


FIGURE 22.25 Conductivity of Eeonomers in ferrofluid 1 as a function of Eeonomer temperature (a) and the product of conductivity and viscosity as a function of temperature (b) with additives in ferrofluid 1. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

22.3.3 FLUID BEARING MOTOR OIL

Disk drive motor bearing dynamics determine the precision of the spindle rotation. As the sleeve spins relative to the stator, the spin axis traces out an orbit. The spin axis motion has a component that is in phase and at the same frequency as the spindle rotation. This is repeatable run out. There is also a component of spin axis motion that is random. This is nonrepeatable run out (NRRO). Increasing computer magnetic recording disk drive data storage density is potentially limited by NRRO. The spindle bearing is the primary contributor to NRRO. Improved NRRO improves the seek time and ability to track follow for a given track pitch and servomechanism. A disk drive with a low-NRRO spindle bearing accommodates higher track density, allowing higher areal density.

Nearly all disk drives are now being built with fluid dynamic bearing motors (Figure 22.14c). These replace ball bearing spindle motors, because their lower NRRO allows the servomechanism to follow narrower data tracks. At the heart of a fluid dynamic bearing are a shaft in a sleeve for radial thrust and a thrust plate and bushing for axial thrust. Embossed on one face of the radial and axial thrust members are grooves that force the oil inward, creating the internal pressure that provides the

bearing stiffness [60]. The fluid dynamic bearing achieves lower levels of NRRO because a relatively thick film of lubricant separates the sleeve and stator. The oil film thickness in high-performance motors for 10–15 krpm is typically 5–10 μm . The film provides viscous damping that attenuates NRRO below that achievable in ball bearings. The forces generated on the sleeve by the fluid dynamic bearing are of a lower frequency and amplitude than with ball bearings. The reduction in the excitation bandwidth and power allows the servo to seek and hold on a higher track density.

However, the bearing must be designed to avoid cavitation [61] and air ingestion [62]; two fundamental requirements of fluid dynamic bearing oil are low viscosity and low vapor pressure. The viscosity must be thin enough to allow for spin-up in a reasonably short period of time at temperatures approaching 0°C. For example, the spin-up time for prototype disk drives with fluid bearing motors is shown in Figure 22.26 [1]. The viscosity dominates the spin-up time when it is higher than ~25 mPa s. For lower viscosities, the spin-up time is limited by inertia of the disk pack and peak motor power.

The oil vapor pressure must be low enough so that there is no appreciable evaporation over the 5 to 7 year lifetime of the motor at its maximum internal operating temperature of ~80°C. In addition, the fluid bearing oil must be sufficiently conductive to dissipate static charge accumulation due to air shear, electrical double-layer shear [63], and work function difference between the slider and disk [64]. The oil must also have a low dc dielectric permittivity to minimize charge storage by ionic separation or dipole orientation. Finally, well-formulated oil should contain antioxidants and other additives to inhibit oxidation and corrosion. Formulation and testing of antioxidants for fluid bearing oil is described in Ref. 50. Oil oxidation kinetics is discussed in Section 22.3.4.

Various model oils were investigated with the goal of providing guidelines for selection of the oil with the lowest possible viscosity and vapor pressure. The oils studied were diesters (Table 22.16) [1], triesters (Table 22.17) [1], and nonpolar hydrocarbons (Table 22.18) [1]. The first five model oils are

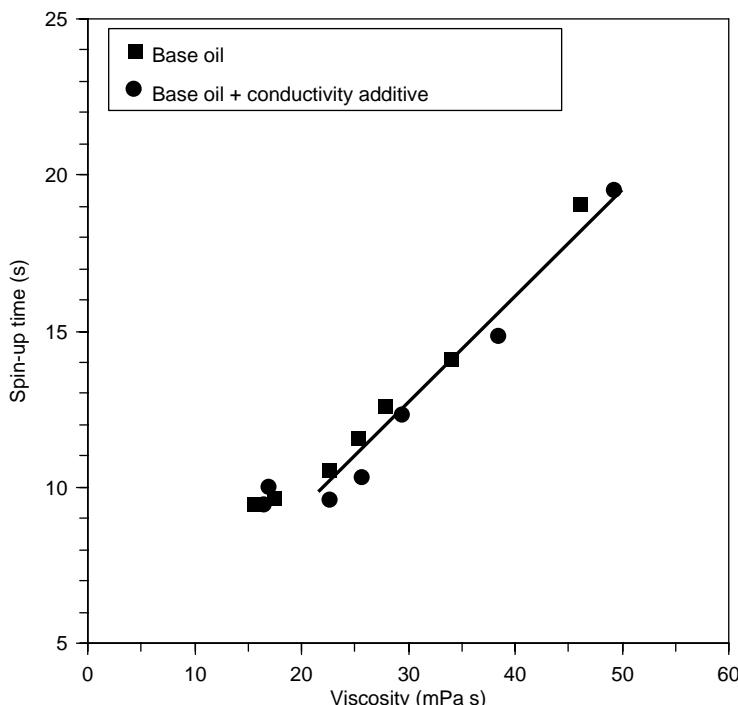
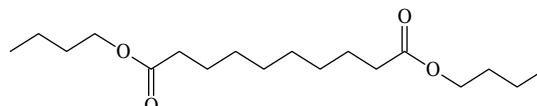
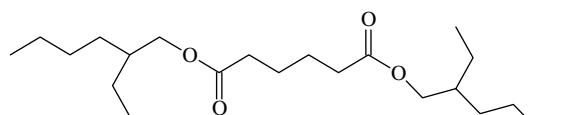
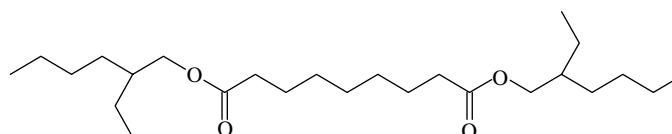
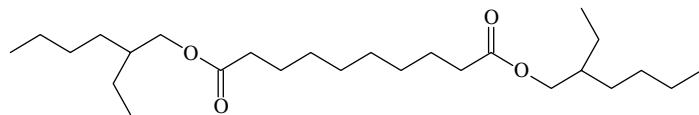
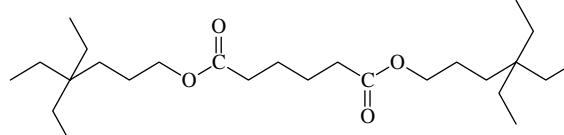


FIGURE 22.26 Spin-up time for prototype disk drives as a function of fluid bearing oil viscosity measured between 1 and 25°C. The conductivity additive was mixed polymers, as described in Ref. 50. The base oil is a commercially available diester. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

TABLE 22.16
Molecular Structures of the Diester Oils Investigated for Fluid Dynamic Bearing Motors

Acronym	Molecular Weight (g/mol)	Structure
DBS	314	
DOA	371	
DOZ	413	
DOS	427	
DIA	427	

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

diesters made from alkanedioic acids and alcohols with a range of diacid chain lengths and several alcohol molecular weights and branched isomers. The di(*n*-butyl)sebacate (DBS), di(2-ethylhexyl)adipate (DOA), and di(2-ethylhexyl)sebacate (DOS) were obtained from Aldrich Chemical Company (Saint Louis, MO, USA). The di(2-ethylhexyl)azelate (DOZ) is Emery 2958 and the di(4,4-diethylhexyl)adipate (DIA) is Emery 2970. The Emery oil samples were provided by Henkel Corporation (Emery Group, Cincinnati, OH, USA). The next four model oils are triesters made from triols and alcanoic acids with a range of acid chain length. The triglycerides, glycerol tributanoate (TRIB), glycerol trihexanoate (TRIH), and glycerol trioctanoate (TRIO) (also referred to as tributyrin, tricaprin, and tricaprylin, respectively) were obtained from Aldrich Chemical Company. About 8% of low-molecular-weight impurities were evaporated from tricaprin by vacuum baking at 6.3 kPa for 96 h. The level of impurities in the other model ester oils was less than 0.2% during vacuum baking at the same conditions and did not show up in the NMR spectra. The trimethylol propane C7 ester, trimethylolpropane triheptanoate (TMP), is Emkarate 1510 from ICI Americas, Inc. (Wilmington, DE, USA). The branched alkane, a low-molecular-weight poly(alphaolefin), was NYE 167A from Nye Lubricants, Inc. (Fairhaven, MA, USA). Some of the oils are isomers, having the same molecular weight and composition but differing only in molecular structure. More details of the oil properties are given in Ref. 40.

TABLE 22.17**Molecular Structures of the Triester Oils Investigated for Fluid Dynamic Bearing Motors**

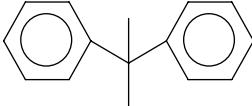
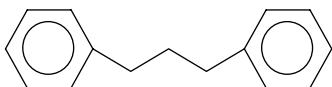
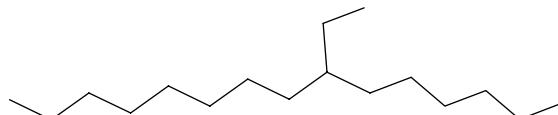
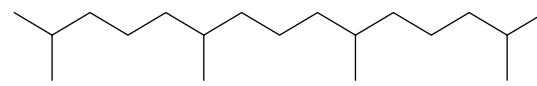
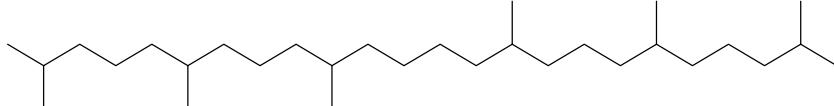
Acronym	Molecular Weight (g/mol)	Structure
TRIB	302	
TRIH	387	
TRIO	471	
TMP	471	

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

Representative proton NMR spectra for the diester oils are shown for DBS and DOS in Figure 22.27. These are most similar to the oils that are widely used in disk drive fluid dynamic bearing spindle motors. The NMR measurements were done on a Bruker Aspect 3000 Nuclear Magnetic Resonance Spectrometer attached to a 250 MHz superconducting magnet with an automatic sample changer. The samples for proton NMR were 10% w/w oil in chloroform-d1. The solution spectra were measured in 5 mm NMR tubes from Kontes Scientific Glassware (Grade 6, 5 pack, #897235). The proton NMR measurements were done using a spectral width of 5 kHz, 45° pulse width of 3.0 μ s, 1 s relaxation delay, and 512 scans.

The proton corresponding to each peak in the NMR spectra in Figure 22.27 [1] is indicated by a letter, and an arrow shows the location of the corresponding proton on the molecular structure. Peak

TABLE 22.18
Molecular Structures of the Nonpolar Oils Investigated for Fluid Dynamic Bearing Motors

Acronym	Molecular Weight (g/mol)	Structure
2,2-DPP	196	
1,3-DPP	196	
PAO	240	
PRS	269	
SQL	423	

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

assignments corresponding to these structures are listed in Table 22.19 [1]. The peak area is proportional to the number of protons at each chemical shift. The peak areas were calculated from the NMR spectra with commercial software (NUTS NMR Data Processing Software, Version 4.27, Acorn NMR, Inc., Fremont, California, United States). The reference peak area (indicated by “a” in the first column of the peak assignment tables) was assigned to the expected area. The rest of the integrated areas are relative to the reference peak area. Both the integrated peak areas and the peak areas expected from the abundance of each type of proton in the model chemical structure agree within 10%. Small changes in the chemical shifts are due to differences in the chemical environment of the protons.

22.3.3.1 Viscosity and Vapor Pressure

Oil viscosity and vapor pressure are thermodynamically interrelated by the dispersion and dipolar forces between the molecules. All of the intermolecular potential energy must be surmounted to evaporate a molecule from the liquid, and part of the intermolecular potential energy must be surmounted for flow. To first order, the dispersion force is proportional to the number and type of atoms, thus to molecular weight. For the relatively low-molecular-weight oils useful in fluid bearings, the flow is mostly by the whole molecule, rather than segments of the molecule. Thus, increasing the molecular weight, or polarity, to reduce the vapor pressure increases the viscosity. The relationship between oil vapor pressure and viscosity is thoroughly investigated with Eyring's chemical reaction rate theory of evaporation and flow (Karis and Nagaraj [40]). The essence of their findings is summarized later.

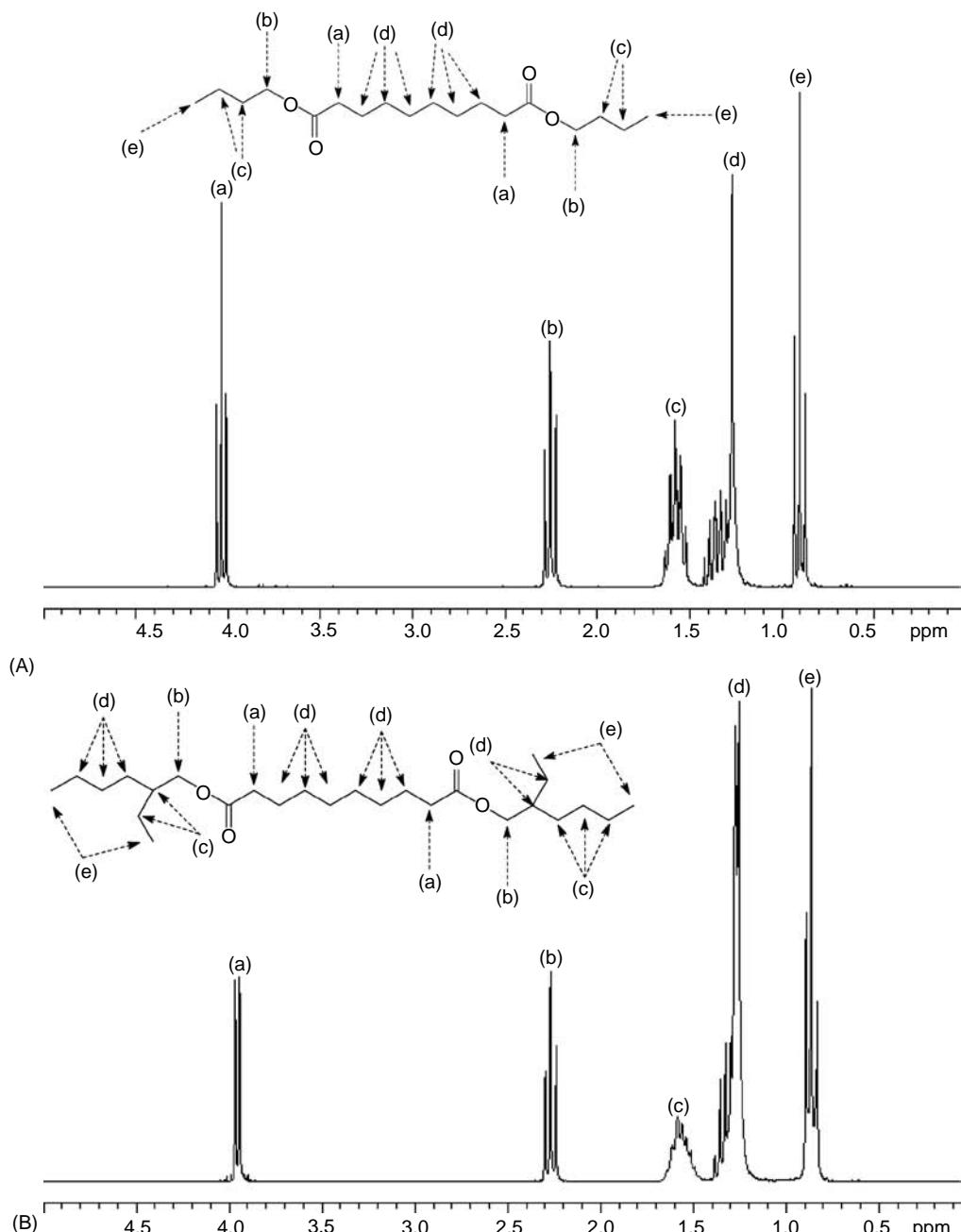


FIGURE 22.27 Proton NMR spectrum of diester fluid dynamic bearing oil (A) DBS and (B) DOS. The peak assignments are indicated on the molecular structures. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

According to the Eyring Equation 22.6, a plot of $\ln(\eta)$ versus $1/T$ is a straight line with slope, $\Delta E_{\text{vis}}/R$ and intercept $\ln(Nh_p/V_l) - \Delta S_{\text{vis}}/R$. The viscosity of several low-molecular-weight ester and hydrocarbon oils is shown plotted as $\ln(\eta)$ versus $1/T$ in Figure 22.28 [1]. There is some systematic deviation from linearity, but overall the general trend is fit by the Eyring equation between -20 and 100°C .

TABLE 22.19
Proton NMR Chemical Shifts and Peak Assignments
for the Spectra in Figure 22.27

Proton	Chemical Shift (ppm)	Measured		Expected Peak Area for DBS
		Measured Peak Area for DBS	Peak Area for DOS	
(a) ^a	4.01	4	4	4
(b)	2.23	4.2	4	
(c)	1.57	8.4	8	
(d)	1.36	12.4	12	
(e)	0.91	6.1	6	

^a Reference peak used as the basis for the other peak areas.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

The flow activation entropy $\Delta S_{\text{vis}} = \Delta S_{\text{vis}}^{\text{trans}} + \Delta S_{\text{vis}}^{\text{rot}}$ is the sum of the translational and rotational contributions. The slope and intercept of the $\ln(\eta)$ versus $1/T$ plot is employed to calculate ΔS_{vis} and ΔE_{vis} for each of the oils. These thermodynamic properties for flow are listed in Table 22.20 [1].

A similar analysis was performed for the vapor pressure of these oils. According to the Claperyron Equation 22.15, a plot of $\ln(P^0)$ versus $1/T$ is a straight line with slope $-\Delta E_{\text{vap}}/R$ and intercept $\ln(P) - 1 + \Delta S_{\text{vap}}/R$. The vapor pressure of several low-molecular-weight ester and hydrocarbon oil is shown plotted as $\ln(P^0)$ versus $1/T$ in Figure 22.29 [1]. The vaporization entropy $\Delta S_{\text{vap}} = \Delta S_{\text{vap}}^{\text{trans}} + \Delta S_{\text{vap}}^{\text{rot}}$ is approximately the sum of the translational and rotational contributions. The intercept of the $\ln(P^0)$ versus $1/T$ plot is then employed to calculate ΔS_{vap} and ΔE_{vap} for each of the oils. The translational component of the vaporization is approximately equal to the vapor-phase entropy given by Equation 22.16, and the rotational component is similarly calculated in the vapor phase with Equation 22.17 [40]. The vaporization entropy and the calculated vapor-phase translational and rotational entropy are employed to estimate the liquid-phase entropy as $S_{\text{liq}} \approx S_{\text{vap}} - \Delta S_{\text{vap}}$. These thermodynamic flow properties for vaporization are listed in Table 22.20.

Further insight into the relationship between the evaporation and flow properties of the potential fluid bearing motor oils is obtained by combining the results together within the framework of thermodynamics and the reaction rate model for evaporation and flow [65,66]. The ratio of the vaporization energy to the flow activation energy $n = \Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ measures the partial decoupling of intermolecular forces between molecules during flow relative to the complete decoupling that takes place upon vaporization [67]. Another thermodynamic quantity that plays a key role in the flow process is the flow activation rotational entropy. The flow activation rotational entropy, $\Delta S_{\text{vis}}^{\text{rot}}$, was calculated from the combined vapor pressure and viscosity versus temperature, given in Karis and Nagaraj [40]. If there is a way to lower the viscosity without increasing the vapor pressure, it seems that it can be done only by increasing the flow activation entropy, ΔS_{vis} . For the oils shown here, ΔS_{vis} is proportional to $\Delta S_{\text{vis}}^{\text{rot}}$, as shown in Figure 22.30a [1]. However, $\Delta S_{\text{vis}}^{\text{rot}}$ decreases with n , as shown in Figure 22.30b. Thus, the flow activation rotational entropy decreases with the amount of decoupling or asymmetry between vaporization and flow. For example, spherical molecules are

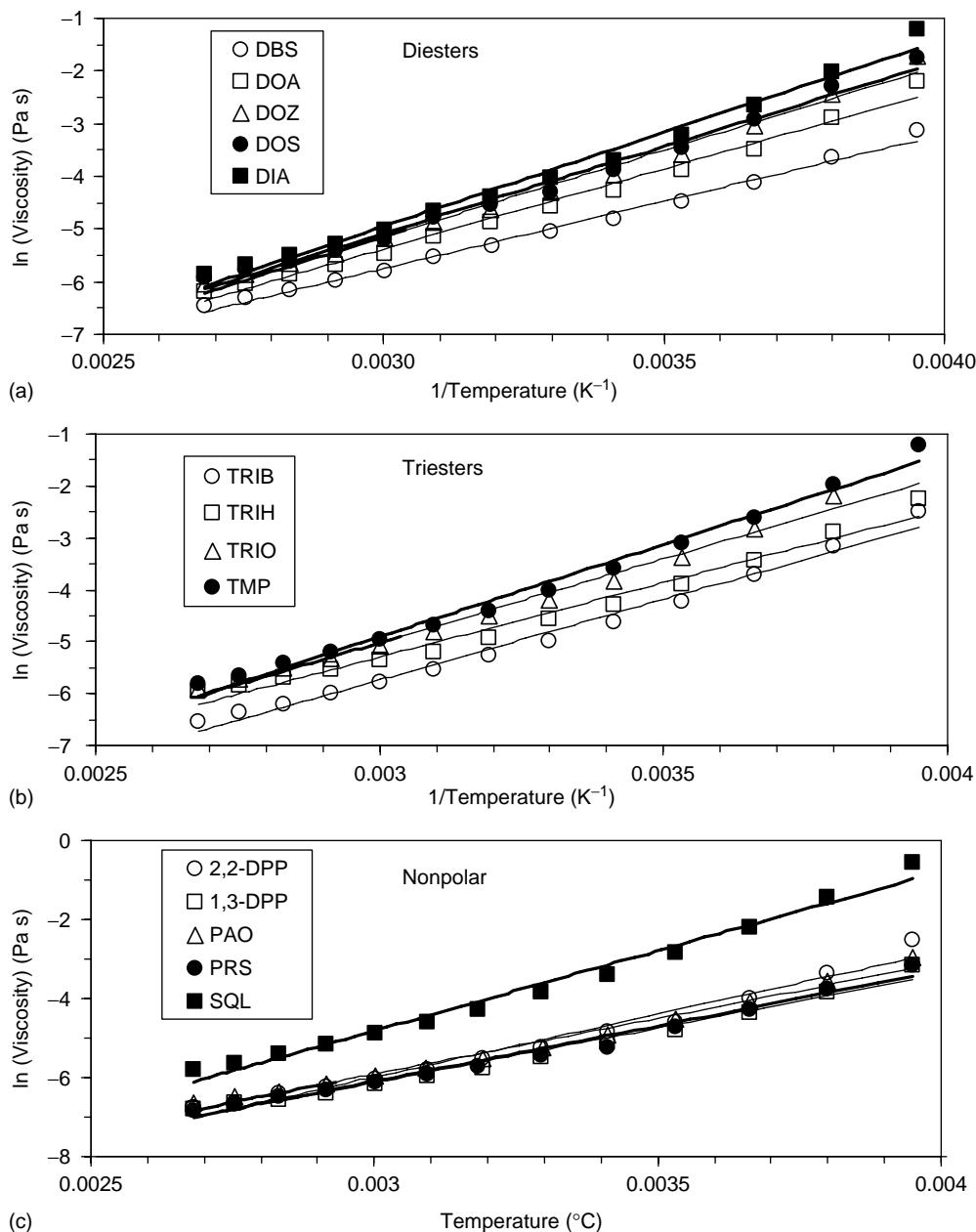


FIGURE 22.28 Natural logarithm of viscosity as a function of inverse temperature of (a) diesters, (b) triesters, and (c) hydrocarbon oils. The line is a fit to the Eyring equation. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

more freely rotating in the flow-activated state, whereas rotation of rod-like molecules becomes less likely in the flow-activated state, as they surmount the energy barrier between adjacent molecules in the surrounding liquid.

Although the preceding discussion shows how the thermodynamic properties of vaporization and flow govern the oil vapor pressure and viscosity, little can be said about specifically what molecular structure and compositions can be synthesized to provide an improved fluid bearing

TABLE 22.20

Evaporation and Flow Thermodynamic Properties Calculated from Vapor Pressure and Viscosity Data for Model Fluid Dynamic Bearing Oils

Oil	Evaporation			Flow				<i>n</i>
	ΔE_{vap} (kJ/mol)	ΔS_{vap} (J/mol K)	S_{liq} (J/mol K)	ΔE_{vis} (kJ/mol)	ΔS_{vis} (J/mol K)	$\Delta S_{\text{vis}}^{\text{rot}}$ (J/mol K)		
DBS	90.7	160	114	20.6	-4.2	-3.1	4.4	
DOA	94.4	160	117	24.7	4.1	6.61	3.8	
DOZ	84.5	125	154	26.7	6.8	19.8	3.2	
DOS	108.6	175	105	26.7	5.8	2.6	4.1	
DIA	94.1	143	137	28.9	11.2	18.1	3.3	
TRIB	81.8	154	163	25.1	10.5	12.5	3.3	
TRIH	93.3	156	167	23.2	-1.5	2.4	4.0	
TRIO	116.3	185	143	26.2	3.5	-1.4	4.4	
TMP	81.0	110	218	28.9	10.4	30.3	2.8	
2,2-DPP	59.1	120	144	25.5	17.0	30.4	2.3	
1,3-DPP	74.2	159	105	22.3	8.4	6.6	3.4	
PAO	89.6	188	80	22.7	4.5	-4.2	3.9	
PRS	78.5	166	104	22.8	4.6	2.6	3.5	
SQL	82.8	124	156	32.9	21.2	36.6	2.5	

Note: Evaporation properties are referenced to 100°C and atmospheric pressure (100 kPa). Flow properties are referenced to 40°C.

Source: Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.

motor. Recent developments on molecular dynamic simulation promise to bridge this gap between molecular structure and thermodynamics. For example, Bair et al. [68] have demonstrated good agreement between high shear viscosity measurements and predictions from a molecular dynamics simulation. Yet, the model requires input of a particular molecular structure, in their case, squalane, and numerically intensive computations that are required to predict the viscosity. Even more complexity is involved if one tries to similarly predict the viscosity of a more complex polar molecule such as diesters.

Oil blends, or viscosity-reducing additives, have also been considered. Blending oils change the pressure–viscosity coefficient [55] and provide an intermediate viscosity [69,70]. The vaporization energy and entropy and flow activation energy and entropy are shown for a blend of polar diester oil in nonpolar poly alpha olefin (PAO) oil in Figure 22.31 [1]. In this case, the vaporization energy of the blend was less than that of the pure components. The entropy of the blend was higher than that of the pure components. The reduction in the vaporization energy outweighed the effect of the increase in liquid entropy, and the vapor pressure of the blend was higher than that of the pure components. There is, however, an interesting dip in the properties near 95% DOS, which was reproducible. The flow activation energy and entropy of the blends are shown in Figures 22.31c and 22.31d. The flow activation energy is approximately given by a linear combination of the weight fractions of blend components. While the blend viscosity is actually less than the linear combination due to an increase in the flow activation entropy near 50%. Taking the analysis one step further, the flow activation rotational entropy has a sharp maximum near 95% DOS in Figure 22.32a. The ratio $n = \Delta E_{\text{vap}} / \Delta E_{\text{vis}}$ has a sharp minimum near 95% DOS (Figure 22.32b). This unusual behavior near 95% DOS suggests that synergistic effects are possible in oil blends. These probably arise from clustering of the nonpolar oil with the aliphatic chains of the diester. Perhaps, this type of effect could be exploited to develop viscosity-reducing additives that have a lower vapor pressure than the base oil.

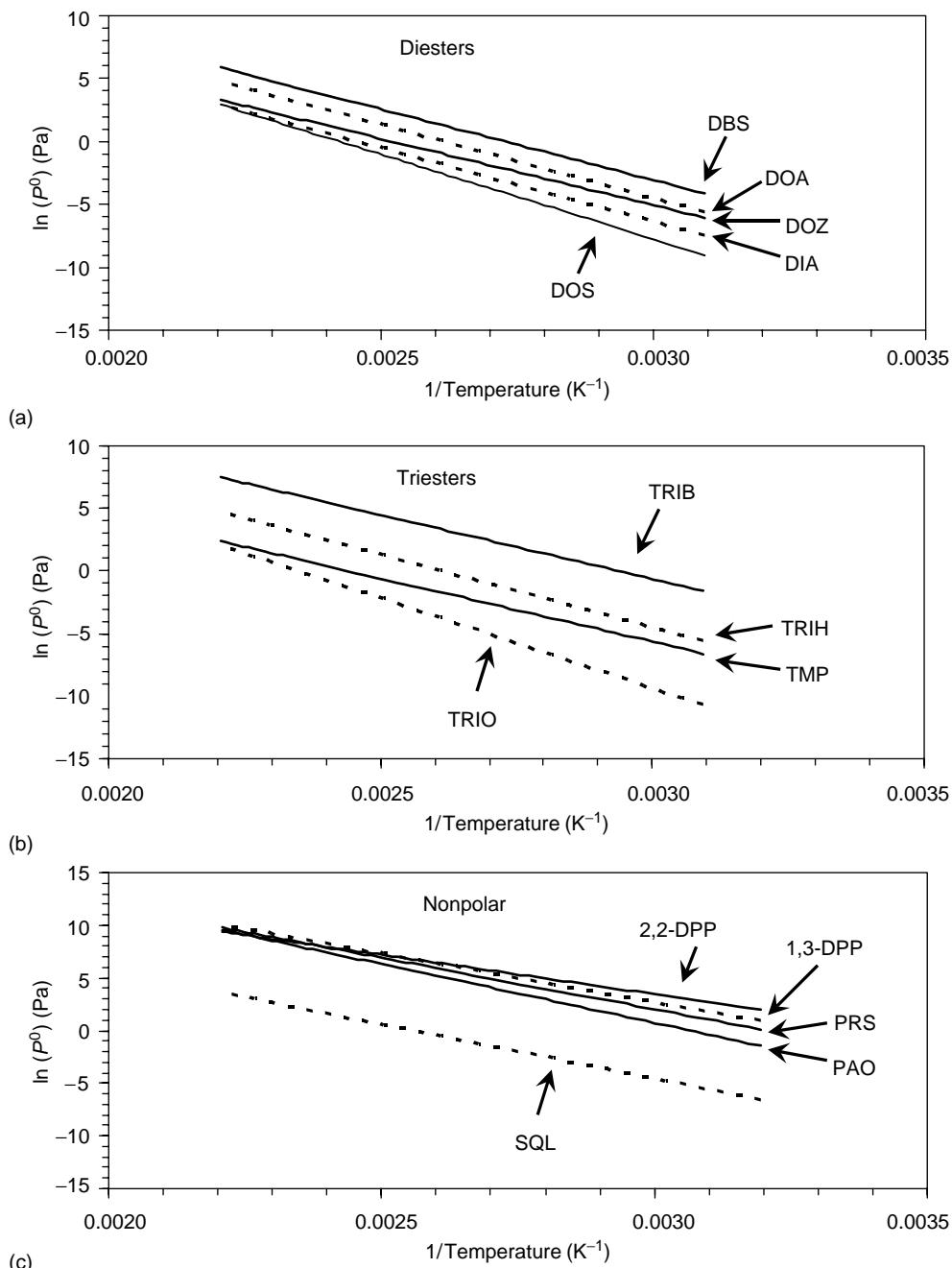


FIGURE 22.29 Natural logarithm of vapor pressure as a function of inverse temperature of (a) diesters, (b) triesters, and (c) hydrocarbon oils. The line is a fit to the Clapeyron equation. Ambient pressure $P = 100 \text{ kPa}$. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

However, for a blend to be useful, it would also need to be capable of forming an azeotrope, and then it could only be used in motors at the azeotropic composition. Otherwise, the evaporation of the oil component with the highest vapor pressure would gradually change the oil blend viscosity and vapor pressure with time.

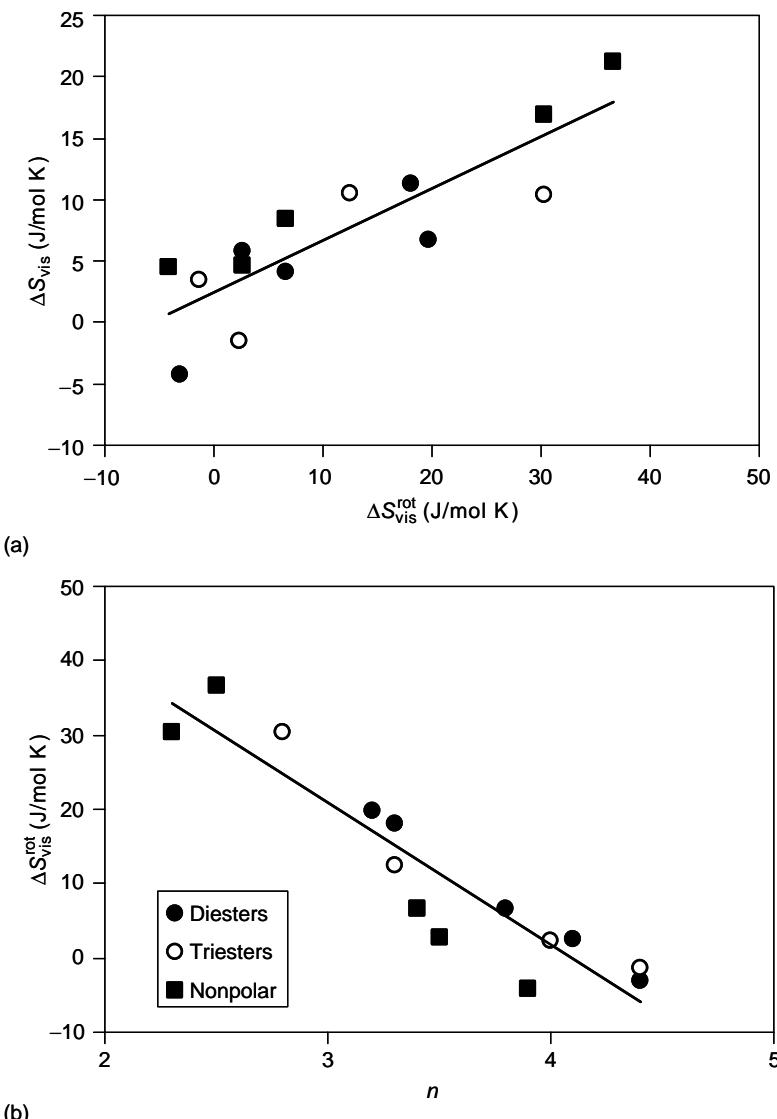


FIGURE 22.30 Flow activation entropy versus flow activation rotational entropy (a) and the flow activation rotational entropy versus the ratio of the vaporization energy to the flow activation energy (b) for the oils listed in Tables 22.16 through 22.18. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

22.3.4 OIL FORMULATION CHEMISTRY

Thermal stability is imparted to grease and oil through formulation with additives. Over the past two decades, we employed the principles of oil oxidation chemistry in developing formulations for ball bearing grease [71] and fluid dynamic bearing [72] spindle motors at the leading edge of the industry in our laboratory. The general outline of the chemical mechanisms for oxidation and stabilization, potential additives, and accelerated test results is published in Ref. 50. Here, we summarize the low-temperature elementary reactions for each type of oxidation pathway including inhibition by antioxidants. The rate equations are solved numerically in nondimensional form, and the model results are compared with thermal oxidation life test data to illustrate the synergistic effects of primary antioxidant PriAOX and secondary antioxidant SecAOX and metal catalysis.

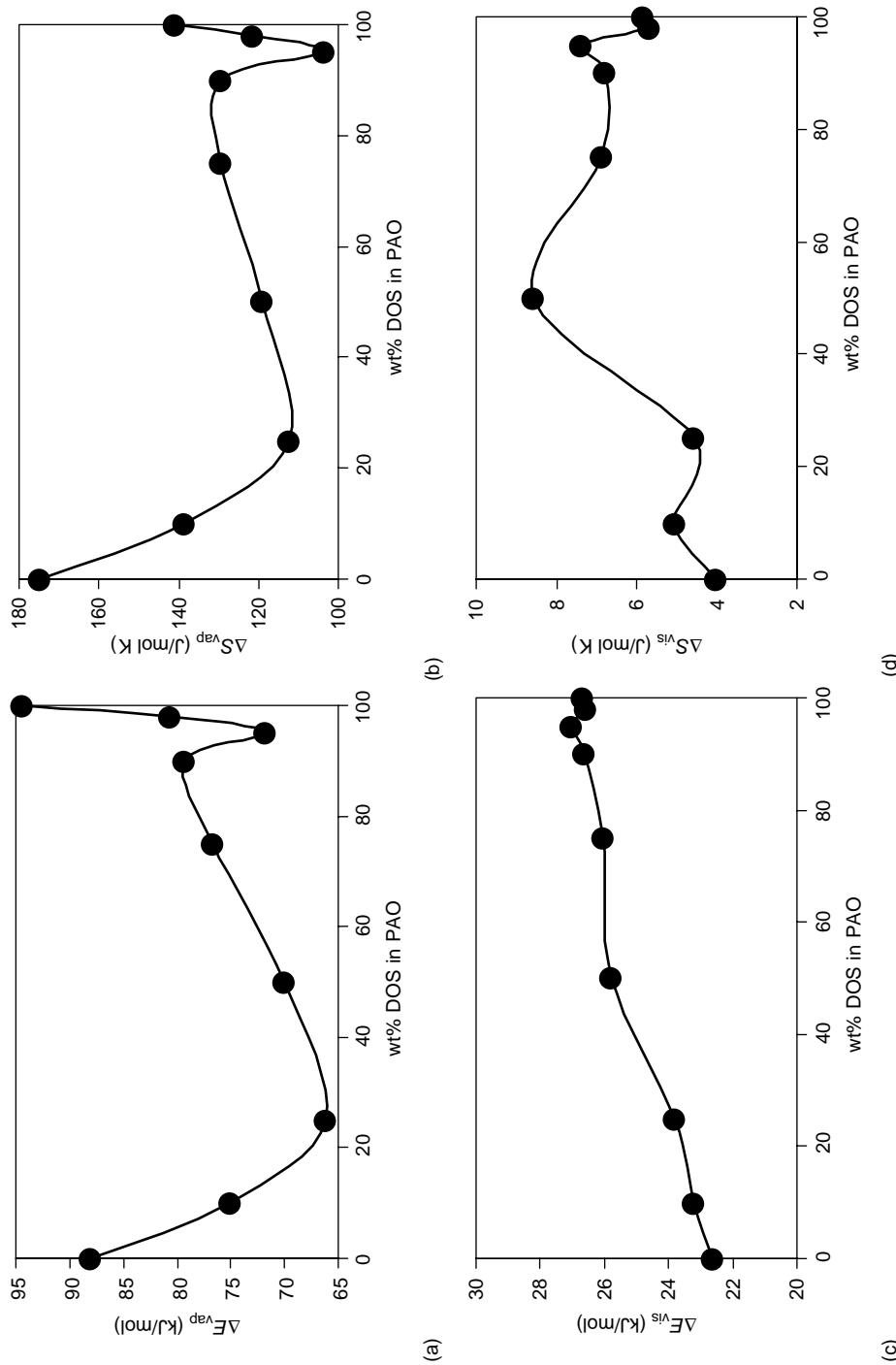


FIGURE 22.31 Vaporization activation energy and entropy change (a, b) and flow activation and entropy change (c, d) for blends of DOS in PAO. (Adapted from Rudnick, L.R. (ed.), *Synthetics, Mineral Oils, and Bio-Based Lubricants Chemistry and Technology*, Chapter 38, CRC Press, Taylor & Francis Group, Boca Raton, FL, 2006.)

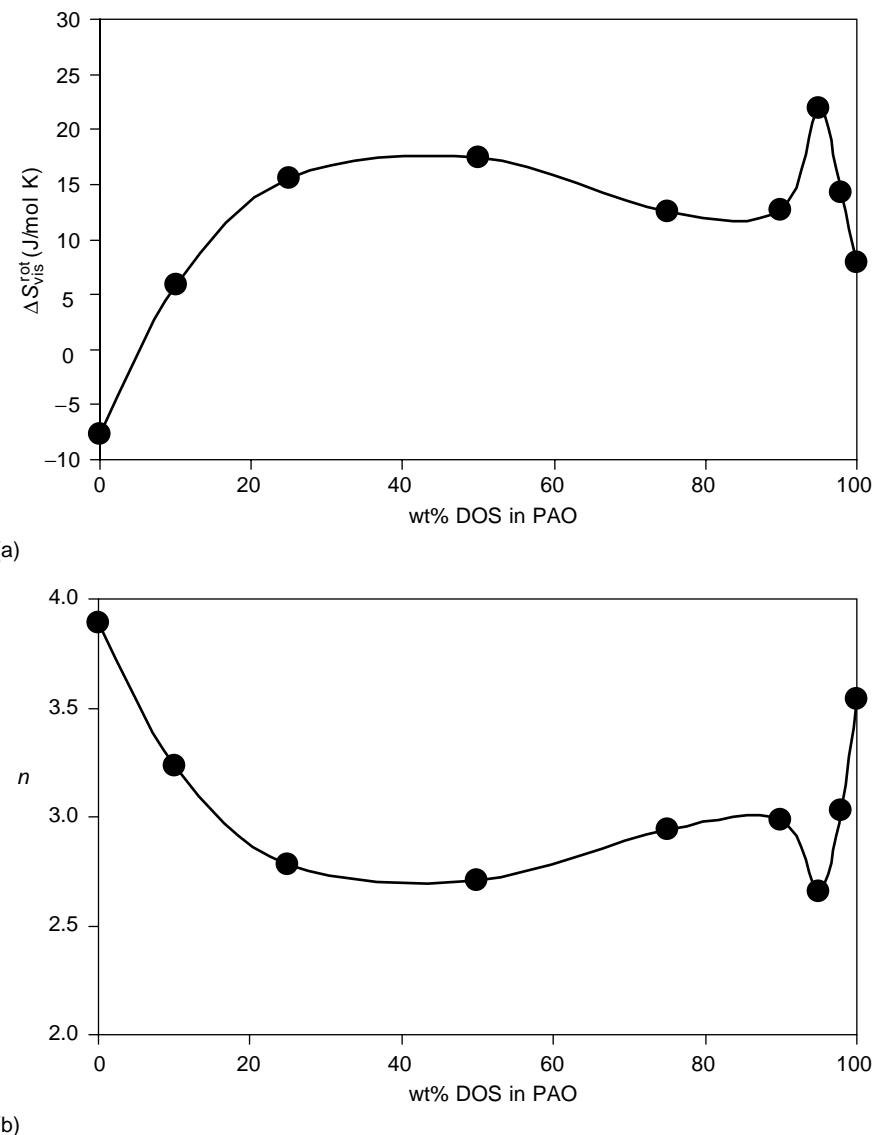
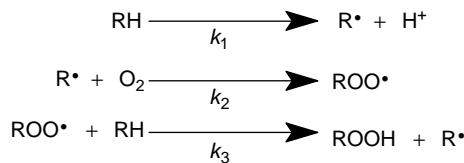


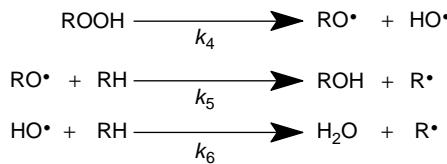
FIGURE 22.32 The rotational component of the flow activation entropy (a) and the ratio of the vaporization energy to the flow activation energy, n , (b) for blends of DOS in PAO.

The following sets of elementary reactions, derived from schemes in Refs 50 and 73, are employed to model the data. Intrachain proton abstraction and self-termination are not included. Some of the non-rate-controlling reactants and products are not shown. The initiation reactions and the propagation reactions are shown in Figures 22.33a and 22.33b, respectively. The dot denotes a carbon radical. Only interchain proton abstraction (no cleavage reaction) is considered because this is the dominant reaction pathway that we observed with ester oils. Proton abstraction from RH by thermal or mechanical excitation is the rate-limiting step in the initiation mechanism. Decomposition of the hydroperoxide ROOH is the rate-limiting step in the propagation mechanism.

PriAOX protonates radicals, as shown in Figure 22.34a. Examples of PriAOX are butylated hydroxy toluene (BHT), dioctyldiphenyl amine (DDA), and phenyl naphthylamine (PNA). SecAOX decomposes hydroperoxide, as shown in Figure 22.34b. Examples of SecAOX are zinc

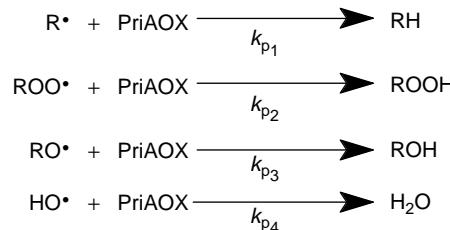


(a)

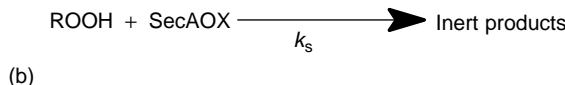


(b)

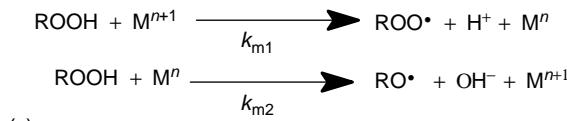
FIGURE 22.33 Oil oxidation initiation (a) and propagation (b) elementary reactions. RH stands for the hydrocarbon oil. H is a proton and R the rest of the molecule.



(a)



(b)



(c)

FIGURE 22.34 Oxidation inhibition by PriAOX (a), SecAOX (b), and metal M catalysis of hydroperoxide decomposition (c).

dialkyldithiophosphate (ZDDP) and zinc dialkyldithiocarbamate (ZDTC). The products of hydroperoxide decomposition by these SecAOXs form an antiwear film on metal surfaces [74]. Dissolved catalytic metal ions M^n and M^{n+1} decompose hydroperoxide in a charge shuttle reaction [75] as shown in Figure 22.34c. The superscripts refer to the valence state of the metal ion. The rate constants in the elementary reactions were estimated by approximating isothermal oil oxidation life test results on a pentaerythritol tetraester oil [73] (Figure 22.35a). The values of the model rate constants are given in Table 22.21. Unless stated otherwise, model calculations and isothermal measurements were performed at 150°C. As the activation energies for the individual elementary reactions are unknown, the activation energies for nonmetal-catalyzed reactions were approximated by the overall activation energy of 120 kJ/mol determined from the measured lifetimes of oil with and without antioxidants. The activation energy for metal-catalyzed elementary reactions was set to

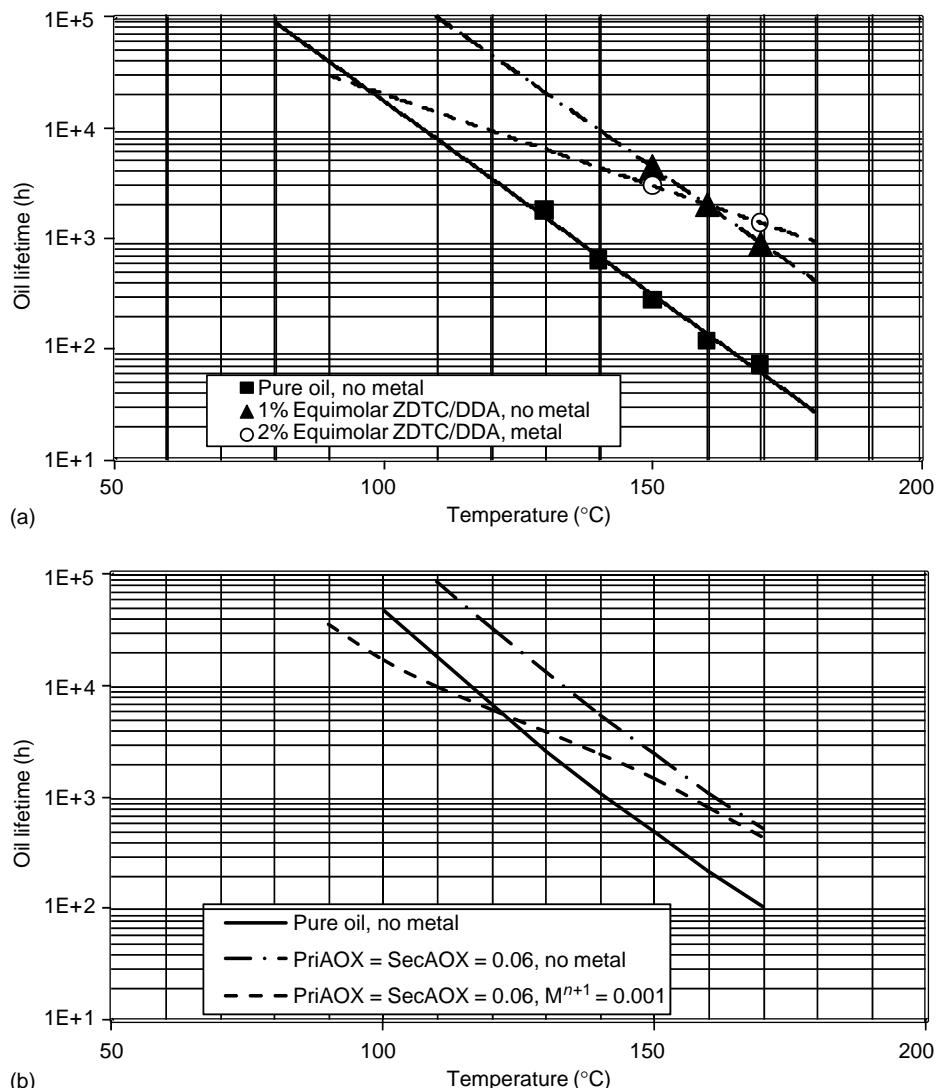


FIGURE 22.35 Isothermal oxidation lifetime of a pentaerythritol tetraester oil and oil containing equimolar amounts of primary and secondary and metal catalyst (included as ball bearings) (a) and model-calculated oil oxidation lifetime for equimolar PriAOX and SecAOX concentrations showing the qualitative effect of metal catalyst (b).

10 kJ/mol to fit the overall activation energy of 70 kJ/mol determined from the measured lifetimes of oil containing antioxidant and catalytic metal ions.

Model-calculated oil lifetime is taken to be the peak in the ROOH concentration (Figure 22.36), which corresponds to the sudden consumption of oil molecules RH shown in Figure 22.36a. Note that the radical products actually continue on to further reactions, which are not included in the present model. Low-molecular-weight products and water evaporate at elevated temperature. Hydroxyl groups form hydrogen bonding, which increases the oil viscosity.

The model-calculated oil lifetime curves from the abovementioned rate constants and activation energies are shown in Figure 22.35b. The slopes of the curves with pure oil and oil containing antioxidants are in reasonable agreement with the experimental data in Figure 22.35a. A more complicated temperature dependence is predicted for the oil containing PriAOX and SecAOX

TABLE 22.21
Elementary Reaction Rate Constants for the Reactions
in Figures 22.33 and 22.34

Rate Constant	Value
k_1	1×10^{-10}
k_2	5
k_3	1
k_4	0.05
k_5	1
k_6	5
k_{p1}	10
k_{p2}	1
k_{p3}	1
k_{p4}	1
k_s	0.3
k_{m1}	10
k_{m2}	10

Note: The units are nondimensional based on initial nondimensional oil proton concentration of RH = 1 and nondimensional dissolved oxygen concentration of 0.5. The rate constants were determined to provide qualitative agreement with oil oxidation life in hours at 150°C.

and metal catalyst. The increase in the hydroperoxide decomposition rate by metal catalyst [75] is apparently more significant at lower temperatures [76].

Model-calculated depletion of PriAOX and SecAOX is shown in Figure 22.36b. The end of life for the oil corresponds to the simultaneous depletion of both the PriAOX and the SecAOX. This suggests that oil life could be extended by replenishing the antioxidant before the end of oil lifetime. The qualitative ability of the model to match the experimental effect of increasing metal ion concentration on the PriAOX depletion with time in oil containing PriAOX and SecAOX is shown in Figure 22.37. Dissolved catalytic metal ions decrease the oil life by increasing the rate of antioxidant consumption, hence decreasing the induction period of time until the onset of rapid oil oxidation.

As PriAOX and SecAOX interact with the complex oxidation mechanism in distinctly different ways, and depending on the values of the elementary reaction rate constants k_{pi} and k_s , there may be synergistic effects between the two. For example, the maximum inhibition of oxidation could be achieved when the peroxy radicals react with PriAOX to form hydroperoxide (Figure 22.34a) before they can abstract a proton (Figure 22.33a), and the hydroperoxide is decomposed into inert products by SecAOX (Figure 22.34b) before the hydroperoxide decomposes into alkoxy and hydroxy radicals (Figure 22.33b). Synergistic effect of PriAOX and SecAOX in oil containing ball bearings is shown in Figure 22.38a. The optimum mole ratio of primary/(primary + secondary) antioxidant for maximum oil oxidation lifetime is close to 0.2, or when 20 mol% of the antioxidant is primary and 80 mol% of the antioxidant is secondary. The model calculation for the effect of the ratio on oil life is shown in Figure 22.38b. There is a maximum (synergistic) oil life predicted both with and without catalytic metals in the oil. The optimum ratio is closer to 50 mol% of PriAOX and SecAOX. The presence of catalytic metal ions diminishes the benefit of the synergistic effect. Further refinement of the individual rate constants and possibly incorporation of more detailed elementary reactions could improve the model fit to the measured oil life.

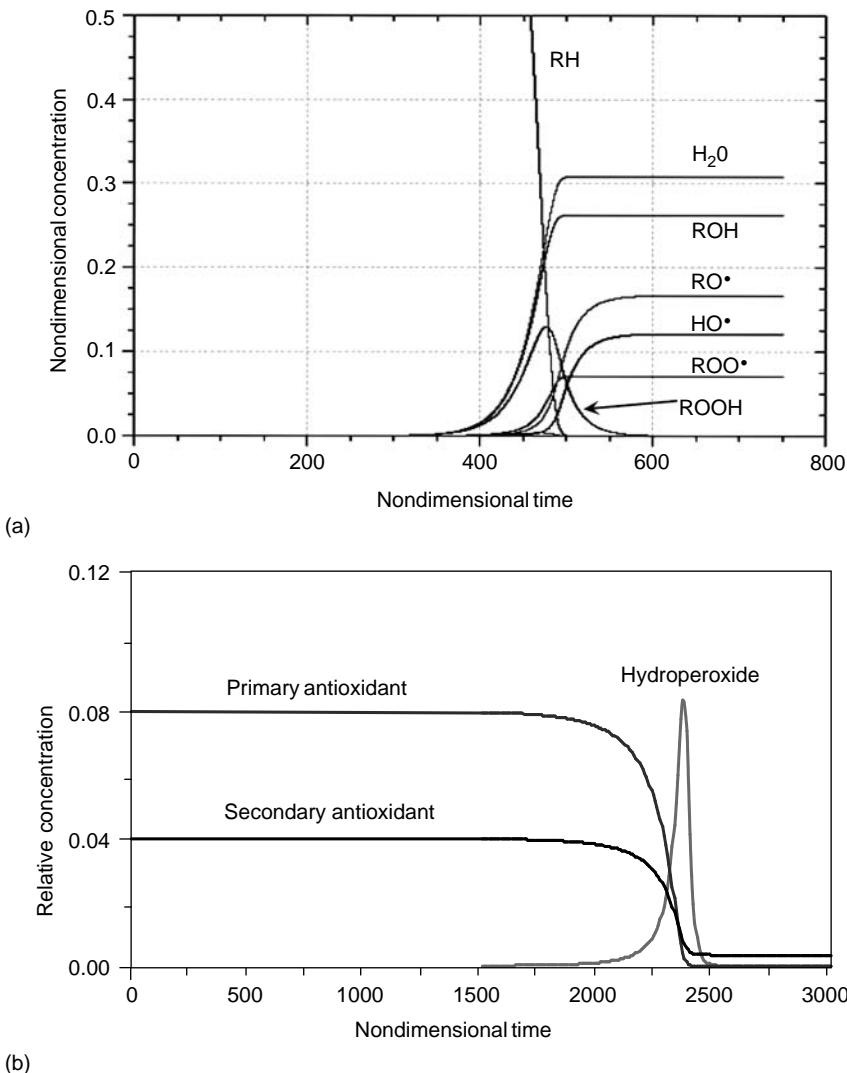


FIGURE 22.36 Oil oxidation products and reaction intermediates during the model isothermal oxidation of pure base oil (a) and the change of PriAOX and SecAOX and the hydroperoxide concentration peak with time (PriAOX + SecAOX) = 0.12 and PriAOX/(PriAOX + SecAOX) = 0.67 (b).

The kinetic model also qualitatively predicts the oxygen consumption during oil oxidation, the effects of antioxidant concentration, oxygen pressure on induction time in isothermal pressure differential scanning calorimetry, exothermal peak temperature in nonisothermal pressure differential scanning calorimetry, and the effect of heating rate on the exotherm temperature. These will be covered in a subsequent publication.

22.4 CONCLUSIONS AND FUTURE OUTLOOK

Magnetic recording disk drives employ the state-of-the-art lubrication in lubrication science and technology to achieve unparalleled reliability. Continued growth in storage capacity relies more than ever before on fundamental understanding to provide key advancements in the critical areas of lubrication: nanolubrication of the head disk interface and fluid bearing motor lubricants.

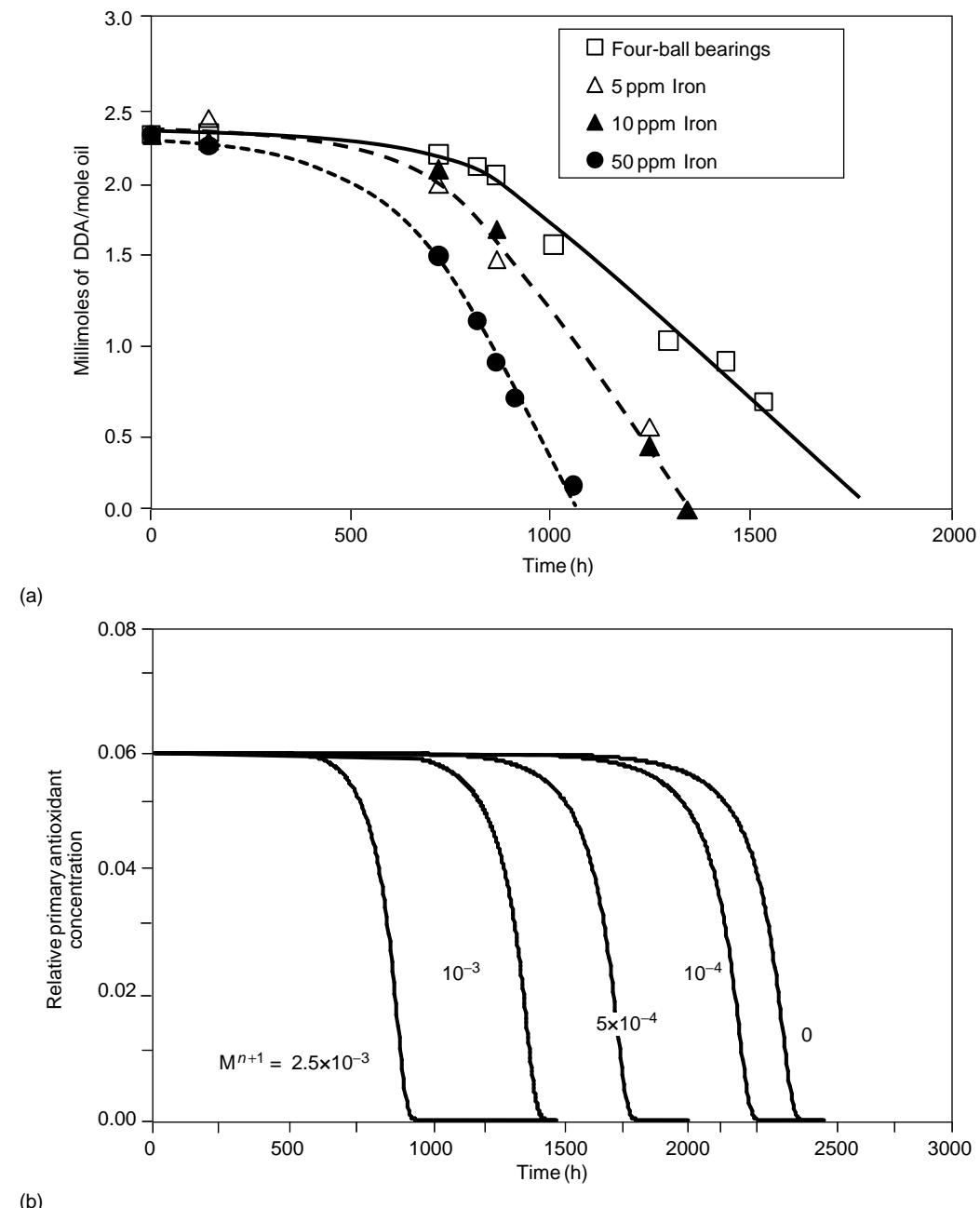


FIGURE 22.37 The effect of dissolved metal catalyst on PriAOX concentration during aging at 150°C in air measured by NMR spectroscopy with 1 wt% (ZDTC + DDA) in the ratio DDA/(ZDTC + DDA) = 0.57 in a pentaerythritol tetraester oil (a) and model calculated relative PriAOX concentration at various nondimensional initial amounts of dissolved metal ion M^{n+1} where nondimensional PriAOX + SecAOX = 0.12 and the ratio PriAOX/(PriAOX + SecAOX) = 0.5 (b).

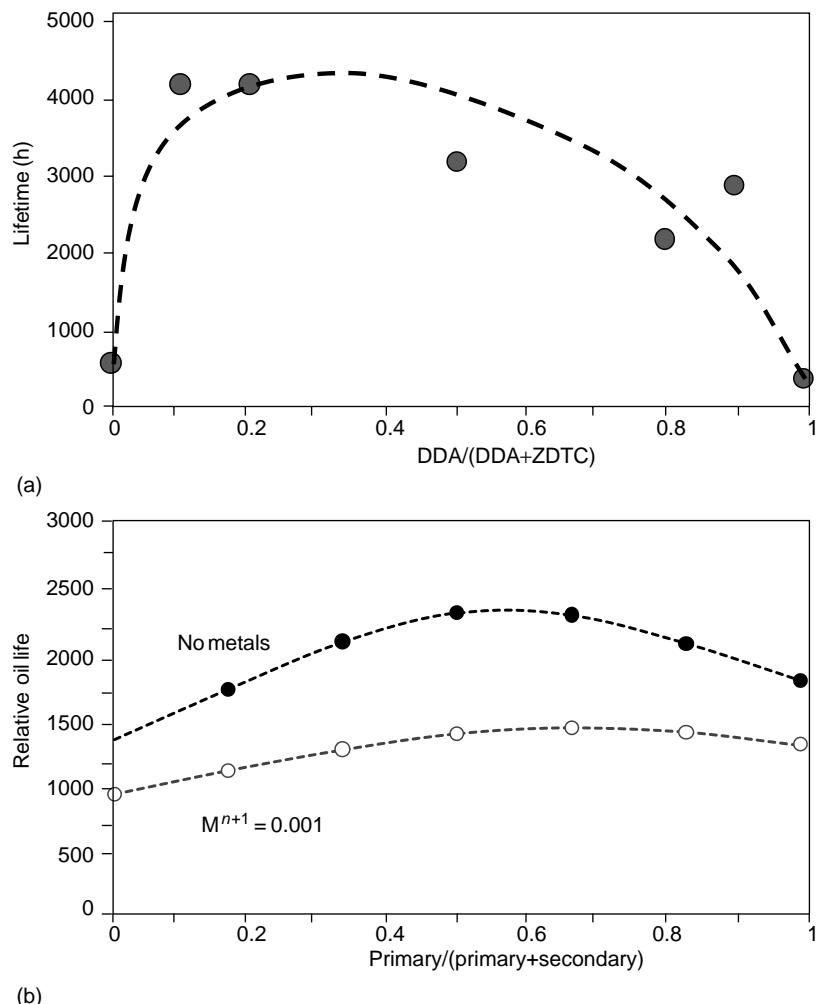


FIGURE 22.38 Oil oxidation lifetime as a function of the molar ratio of primary + secondary antioxidant measured at 170°C in pentaerythritol tetraester oil containing ball bearings with total antioxidant amount 1 wt% (a) and calculated from the kinetic model with PriAOX + SecAOX = 0.12 with and without catalytic metals (b).

The physical properties of the PFPE disk lubricants were described here. The bulk and thin film properties, in combination with polar end groups, provide many years of lubrication by virtue of viscosity enhancement and vapor pressure reduction of molecularly thin films. Advanced disk lubricants are being designed to fulfill increasingly stringent requirements of environmental variations [77,78] and friction at low flying height [79,80]. Currently, advanced lubricants are being developed with a high-level chemisorptive attachment to the disk overcoat to prevent transfer of liquid lubricant to the slider and to enable reduced element spacing to the magnetic layer before the onset of adhesive interaction.

Grease-lubricated ball bearing spindle motors reached their pinnacle with 10,000 rpm drives. Over the course of developing sophisticated channeling greases for these high-performance, low-vibration, long-life bearings, much was learned about grease chemistry, physical properties, and the effects of contamination. Herein was described a comprehensive overview of grease yield stress and the effects of grease contamination on yield stress and electrochemical oxidation of an ester

oil-based grease with a lithium soap thickener. The same principles apply to grease in general, therefore may potentially be useful in wide ranging fields of application where smooth high-speed rotation is needed.

Spindle motors have evolved to fluid dynamic bearings, which provide much smoother rotation with comparable or better stiffness than ball bearings. Stiffness is provided by the relative motion between a shaft and a sleeve, one of which contains a pattern of grooves on its surface. The grooves pressurize a several micron thick film of oil. This chapter highlighted two key properties of the fluid bearing oil—viscosity and vapor pressure. Present fluid bearing oils have a low enough vapor pressure so that the evaporation loss of oil is small over the lifetime of the drive. However, there is a trade-off between the vapor pressure and oil viscosity such that the lowest operating temperature of the drive is limited by the maximum power of the motor and oil viscosity. Attempts to use lower-viscosity oils result in oils with a higher vapor pressure, and this appears to be a physical constraint of oils in general. Detailed thermodynamic analysis of the relationship between oil vapor pressure and viscosity was reviewed. The flow and vaporization activation energies are linked to one another by interaction forces between the oil molecules. There is, however, in principle, some chance of reducing the viscosity without altering the activation energies if a molecular structure that has a large positive rotational component of the flow activation entropy could be found. Molecular structures examined have so far provided limited insight into how this may be accomplished. Another approach is to develop a blend of two different oils—combining mixtures of polar and nonpolar molecules. There is the potential to develop an oil blend that forms an azeotrope and also has a lower viscosity and vapor pressure than the pure component oils. Much fruitful work remains to be done here in the quest for a lower-viscosity and vapor pressure fluid bearing motor oil. The reward for success will be a reduction in spin-up time at cold temperature and a lower minimum operating temperature for drives with fluid bearing motors. Current work on advanced fluid bearing oil formulation is aimed at suppression of evaporation, aerosolization, and air ingestion at the air–oil interface meniscus and to suppress cavitation in the oil film between the rotor and stator.

Thermally stable oil and grease additive packages were developed with the assistance of a chemical kinetic model. The model provides interpretation of thermally accelerated oil oxidation life tests and predicts the interaction between primary antioxidant and secondary antioxidant and dissolved catalytic metal ions. Oil oxidation tests at low temperature take a long time, whereas certain tests such as isothermal and nonisothermal pressure differential scanning calorimetry can be done in a short period of time. The kinetic model links the short-time high-temperature test results with the long-time low-temperature tests and enables the test data to be used to predict ideal oil oxidation life at the use temperature.

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23 Additives for Grease Applications

Robert Silverstein and Leslie R. Rudnick

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23.1 INTRODUCTION

Greases are one of the oldest forms of lubricating materials, and in fact, the first greases can be considered environmentally-friendly and biodegradable by our modern conventions. Ancient Egyptians about 1400 BC made crude greases to lubricate the wheels of their chariots. These early greases

consisted of both mutton- and beef fat, which were sometimes mixed with lime. In fact, the word “grease” is derived from *crassus*, the Latin word for fat. As time progressed, there was only minimal improvement in grease performance until about the eighteenth century. During the eighteenth and nineteenth centuries and the Industrial Revolution, society created a greater variety of new machines. This modern technology that developed during and after the Industrial Revolution required lubricants to handle greater loads and to operate under more severe conditions. New grease technology was needed to improve the performance of equipment and the lifetime of machine components.

Grease is a semisolid or solid lubricant composed of a thickening agent dispersed in a liquid lubricant or in a combination of lubricants. The principal advantage of choosing grease over conventional lubricating oil in certain applications is the grease’s ability to remain in contact with the desired moving surfaces. Greases will generally not leak away from the point of application. Thickeners in the grease are designed to reduce any migration caused by gravity, pressure, or centrifugal action. Grease is best thought of as thickened oil.

There are at least three instances where grease is chosen over oil as a lubricant. In applications

- Where leakage of oil would occur
- Where the natural sealing action of grease is needed
- When greater film thickness is necessary

The liquid lubricant or base oil in grease usually accounts for 70–95% of the grease. The base oil may be mineral oil, synthetic oil, or natural oil such as a vegetable oil. Oils from animal sources are generally not used today. Generally, thickening agents constitute between 5 and 25% of the grease composition. The most common thickeners in use today are metallic soaps, particularly lithium soaps, which account for >60% of the grease market. Silica, expanded graphite [1], or clays (bentonite or hectorite) are sometimes used as thickeners. Clay thickeners represent ~5 to 10% of the grease market.

Additives, required to improve certain properties of the grease such as oxidative stability, wear protection, and corrosion inhibition are used in 0.5–10% of the grease depending on the grease type and application. When grease is to be used under more severe conditions, it generally contains a more enhanced additive package. These additives are often the same additives used in liquid lubricants. Exceptions are solid additives such as graphite and molybdenum disulfide, which are typically used as antifriction and extreme-pressure (EP) additives.

Further research will continue to provide newer and more effective components that will serve as thickeners and additives in the field of lubrications. These future materials are expected to provide greases and liquid lubricants with properties and performance capabilities exceeding those possible today.

In addition to the resistance to flow that maintains grease at the point of application, the primary performance features are to reduce friction and wear. Some of the main factors that affect grease properties and performance are

- Type and amount of thickener
- Consistency or hardness
- Dropping point
- Antioxidant additives
- EP additives
- Pumpability
- Volatility
- Environmental considerations as toxicity and biodegradability

Soaps, used as thickeners, can be considered additive in greases, although they generally comprise a large percentage of the grease composition. Thickeners are, in fact, what make grease

and what differentiate grease from conventional lubricating fluid. This chapter does not consider soaps, because they have been previously described by Klamann [2] and Boner [3]. Functionalized soaps have also been used to impart EP and antiwear (AW) performance to grease [2].

The purpose of this chapter is to serve as a review of some of the important additives used in greases and present various additive testing results that demonstrate their performance benefits. Because final grease formulations are a function of particular performance needs, application data described herein are focused on base oil/thickener/additive affects and not on fully formulated greases, many of which are proprietary.

23.2 WORLDWIDE USE OF GREASES

On a global basis, the regions that consume the largest percentage of the world's grease are North America (545 MM lb), Peoples Republic of China (510 MM lb), and Europe (414 MM lb). India and the Indian subcontinent (182 MM lb), Japan (184 MM lb), Pacific and Southeast Asia (113 MM lb), Caribbean, Central and South America (99 MM), and Africa and the Middle East (71 MM) represent the remaining bulk of the global grease production [4]. Each of the world's different regions requires different grease products.

The National Lubricating Grease Institute (NLGI) Grease Production Survey Report for the year 2006 reports a grand total of £2.1 billion of lubricating grease manufactured worldwide. Of this, conventional lithium soap and lithium complex were ~59 and 15% of the total, respectively. In the United States and Canada, conventional lithium and lithium complex greases represent 32 and 36%, respectively, of the £545 million of grease produced in 2006 [4].

Highly refined, chemically modified mineral oils (CMMO) or synthetic base oils are used in high-performance complex soap greases, in more demanding applications that cannot be met with commodity greases [5]. Industrial applications compare the majority of grease used worldwide; the largest application areas are found in railroad lubrication, steel production, mining, and general manufacturing. Automotive applications include trucks, buses, agricultural and off-road construction equipment, and passenger cars [5].

23.3 PRODUCTION OF GREASES

Soap-thickened greases are manufactured using three basic sequential process steps. First, the soap is formed by the saponification of various fats. Then the soap is dehydrated and further optimized in properties. Finally, milling disperses the soap, base fluid, and additives to provide a consistent dispersion of all components. Milling is a process of shearing the grease to disperse all components. Brown et al. [6] have demonstrated how the process of shearing during milling orients the soap fibers. Dispersion and orientation can harden greases by 100 penetration units [7].

Grease is produced using a kettle process, a contactor process, or a continuous process. These processes differ in terms of the rate of grease production, the quantity of grease to be produced, and the initial investment in equipment. The kettle and contactor processes are both batch processes. The contactor process utilizes pressure to reduce reaction time.

When grease is prepared using a batch process, the base oil is heated together with the additives and thickening agents. If saponification of the fat is required to form soap, the reaction mixture is brought to a higher temperature to complete the reaction and fully disperse all components. A typical batch kettle reaction will take 8–24 h and can range in scale from 2 to 50,000 lb. They are typically cylindrical in shape with a height-to-diameter ratio of 1–1.5. They can have dished or conical bottoms and flat or dished tops. Because the principal objective in making grease is the dispersion of components, kettles may have either one set of rotating paddles or an arrangement of stationary and rotating paddles so as to more efficiently mix the components. Scrapers are sometimes used to remove material adhering to the kettle walls.

TABLE 23.1
Comparison of Continuous and Kettle Grease Processing

	Continuous Process	Kettle Process
Investment cost factor	1.0	1.2
Manufacturing cost factor	1.0	4.1
Heat load (Btu/h)	1,500,000	3,000,000
Cooling water (gal/main)	75	200
Electrical use (kW/h)	120	380

Note: Values are based on a £10 million/year output of lithium, calcium, and sodium greases.

The advantages of the contactor process are reduced heating and reaction time. For example, a typical 20,000 lb batch of lithium grease may take 20 h in a kettle process, but only 5–7 h in a contactor process [8,9]. In the contactor process, fatty acids or glycerides such as hydrogenated castor oil, tallow, vegetable oil, and lithium hydroxide are added at the top. Base fluid is added and water may also be added. The contactor is pressurized, which accelerates the process of saponification. Other process steps include cooling after reaction, adding additional finishing oil, and pumping the grease to a finishing kettle.

There are three main sections in a continuous grease reactor: the soap reactor section, a dehydration section, and a finishing section. Saponification occurs in the reactor section, where the fatty component, alkali, and base fluids are added. The grease components are transferred to the dehydration section, which operates under vacuum to remove volatiles. The product at this stage is a dehydrated soap base. The product of the dehydration section is moved to the finishing section, where additional base fluid and additives are combined and dispersed [10]. A comparison of the continuous and kettle processes is summarized in Table 23.1 [8].

Many chemical and manufacturing factors can affect the properties and performance of greases. For example, several factors that affect the manufacture of lithium complex greases include the base fluid, fatty acid concentration, temperature, moisture, and additive chemistry [11]. Several features of the various manufacturing processes need to be considered in preparing greases. These include the yield of the grease product, any energy requirements to prepare the grease, production time, and capital investment along with associated maintenance costs.

For applications in extreme environments, such as aerospace and military, specialized lubricating greases are necessary. These greases must be able to perform reliably under conditions that most other greases never experience. These materials must have excellent thermal stability, low volatility, and be able to function under very-low and very-high-temperature regimes. The base fluid and all additive components must meet these criteria. For example, high-performance greases have been made that incorporate multiply alkylated cyclopentanes (MACs) as the base fluid [12]. Other specialized base fluids have been studied, including those containing fluorine and other heteroatoms.

23.4 GREASE COMPOSITION AND PROPERTIES

23.4.1 COMPOSITION

Base fluids used in conventional grease are of three types: mineral (petroleum-derived), synthetic (synthesized from discrete chemical components), and natural (plant- and animal-derived). Mineral oils can be paraffinic or naphthenic. Synthetic base fluids commonly used include polyalphaolefins (PAOs), esters, polyglycols, and silicones. Natural oils can be derived from soybean, rapeseed, and other plant oils and high oleic acid versions of these oils.

Base fluid viscosity, in general, directly affects the viscosity characteristics of the resultant grease. Base fluids used in grease formulation generally range from 150 to 600 N oils and may also include bright stock. High-viscosity base fluids are typically used for high-temperature, heavy-duty applications. Alternatively, high-speed applications generally require low-viscosity oils. Lubricating greases are also classified according to thickener type [13].

There are many different types of grease thickeners; however, a few major types are generally employed throughout the industry, depending on the application. Alkali components include lithium hydroxide, calcium hydroxide, sodium hydroxide, and aluminum hydroxide. These alkalis are reacted with materials from animal, marine, and vegetable sources. Nonsoap thickeners can also be used. These include silica, clays, urea, polyurea, and Teflon®.

Grease stability, oxidation resistance, effects of water, maximum operating temperature, and other properties have been summarized by Wills [13].

23.4.2 PROPERTIES

Grease is generally classified and evaluated for properties and performance using tests in the following categories:

- Consistency
- Stability
- EP/AW
- Pumpability
- Corrosion
- Water tolerance
- Bench performance tests

23.4.3 CONSISTENCY

One of the most important properties of grease is its consistency. Just as lubricating oils are available in different viscosity grades, greases are specified in terms of their consistency, as measured by their American Society for Testing and Materials (ASTM) *worked penetration*. *Worked penetration* means that the grease is *worked* for 60 strokes in a standard manner before measurement. Penetration is measured by distance, in tenths of millimeters, that a standard cone will penetrate a grease sample when a standard force is applied. The standard method of measurement is Standard Test Methods for Cone Penetration of Lubricating Grease ASTM D 217 [7]. However, a special procedure, ASTM D 1403, has been designed to utilize one-quarter and one-half scale cones for smaller samples [14]. Equations have been developed to convert the results to compare ASTM D 217 results.

In these tests, which are performed at a constant temperature of 25°C (77°F), a harder grease will exhibit a lower penetration number than a softer grease. The NLGI classification system (see Table 23.2) ranks grease hardness based on this test.

Other tests include apparent viscosity (ASTM D 1092) and evaporative loss (ASTM D 972 and D 2595).

23.4.4 STABILITY

23.4.4.1 Dropping Point

The hardness of grease is a function of temperature. Greases act as thickened lubricants only to a point, and then at some temperature, they become fluid. A standard measure of the resistance of a grease to flow as temperature is increased is the dropping point (ASTM D 2265) [15]. In essence, the dropping point is the measure of the heat resistance of the grease. In the dropping point test, a grease sample is packed into a standard test cup with a small opening. The sample is heated by

TABLE 23.2
NLGI Classification System for Penetration of Greases

NLGI Grade	Worked Penetration
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

TABLE 23.3
General Temperature Properties of Various Thickened Greases

Thickener	Dropping Point (°F)	Maximum Usable Service Temperature (°F)
Aluminum soap	230	175
Calcium soap	270–290	250
Sodium soap	340–350	250
Lithium soap	390	275
Calcium complex	>500	350
Lithium complex	>500	350
Aluminum complex	>500	325
Polyurea (nonsoap)	>450	350
Organoclay (nonsoap)	>500	350

introducing the sample into a preheated aluminum block. The sample temperature added with one-third of the difference between that temperature and the block temperature when the first drop of fluid leaves the cup is defined as the dropping point. Guidelines for the maximum usable service temperature and ranges for dropping points of greases made with various thickeners are summarized in Table 23.3 [16,17]. The self-diffusion of oil in lubricating greases has been studied using nuclear magnetic resonance spectroscopy at temperatures between 23 and 90°C. Greases based on naphthenic mineral oils and PAO synthetic oils were measured. It was shown in this temperature range (40–90°C) that, using the same base fluid, the concentration of the thickener affected diffusion [18].

Other measures of high-temperature stability include high-temperature bleed (ASTM D 1742), trident probe (ASTM D 3232), cone bleed (FTM 791B), evaporation (ASTM D 972 and D 2595), rolling stability (ASTM D 1831), oxidative stability (ASTM D 942), and a high-bearing test (ASTM D 3336).

23.4.5 EXTREME PRESSURE/ANTIWEAR

23.4.5.1 Four-Ball Wear

ASTM D 2266 describes a test method using three hard steel balls in locked position and coated with lubricating grease. A fourth ball is rotated against the three stationary balls, producing a wear scar on each of the three balls, which is reported as the average scar diameter. This test is run at light loads; thus, seizure or welding does not occur [19].

23.4.5.2 Four-Ball Extreme Pressure

ASTM D 2296 describes a test method similar to ASTM D 2266 except that the loads are much higher. At a certain load, the four balls will weld together; this is referred to as the weld load. The weld load can be used to assess whether lubricating grease has a low, medium, or high level of load-carrying ability. The ASTM defines the load wear index (or the load-carrying property of the lubricant) as an index of the ability of a lubricant to prevent wear at applied loads. Under the test conditions, specific loadings in Newtons (kilogram force) having intervals of ~0.1 logarithmic units are applied to the three stationary balls for 10 runs before welding. The load wear index is the average of the corrected loads determined or of the 10 applied loads immediately preceding the weld point [20].

Fretting wear is measured using ASTM D 3704, and load-carrying capacity can be evaluated using Timken O. K. load (ASTM D 2509).

23.4.6 PUMPABILITY

Pumpability can be evaluated using a United States Steel (USS) low-temperature mobility test. It is largely a function of thickener type and concentration and is not significantly affected by additives.

23.4.7 CORROSION

Three common tests for corrosion are a copper corrosion test (ASTM D 130) modified for grease, a bearing rust test (ASTM D 1743), and the Emcor rust test.

23.4.8 WATER TOLERANCE

Water washout is measured using ATSM D 1264. Water spray-off is measured using ASTM D 4049. The wet roll stability of grease is evaluated using a modified ASTM D 1831 test.

23.4.9 BENCH PERFORMANCE TESTS

Several bench performance tests are used in the grease industry to evaluate greases before field evaluation. Some of these include a high-temperature wheel bearing test (ASTM D 3527), an SKF R2F test that simulates paper mill applications, the FE-8 test, CEM electric motor test, and a General Electric (GE) electric motor test. Low-temperature torque is evaluated using ASTM D 1478 and ASTM D 4693 at a temperature of -54°C .

23.5 GREASE THICKENERS

Most grease is made from metal-salt soaps that serve as the thickeners for the base fluid. Metal-salt soap thickeners are prepared from alkali base and a fat or fatty acids. The fatty materials may be derived from animal, marine, or vegetable fatty acids or fats. Fatty acids from these sources are generally even-numbered, straight-chain carboxylic acids containing zero or one double bond. A common fat used for making grease is hydrogenated castor oil, which yields lithium 12-hydroxy stearate upon saponification. Lithium hydroxide, calcium hydroxide, aluminum hydroxide, and sodium hydroxide are frequently used as the alkali materials. Sample reactions for the formation of some of these soaps are shown in Figure 23.1 [2].

In modern greases, simple soaps and complex soaps are used. A simple soap is prepared from one fatty acid and one metal hydroxide. NLGI defines complex grease as soap wherein the soap crystal or fiber is formed by cocrystallization of two or more compounds: the normal soap and the complexing agent [21]. The normal soap is the metallic salt of a long-chain fatty acid similar to a regular soap thickener, for example, calcium stearate and lithium 12-hydroxy stearate. The complexing agent can be the metallic salt of a short-chain organic acid, for example, acetic acid.

In summary, grease thickeners are generally one of the following types:

- Aluminum
- Aluminum complex
- Calcium
- Calcium complex
- Lithium
- Lithium complex
- Polyurea
- Clay

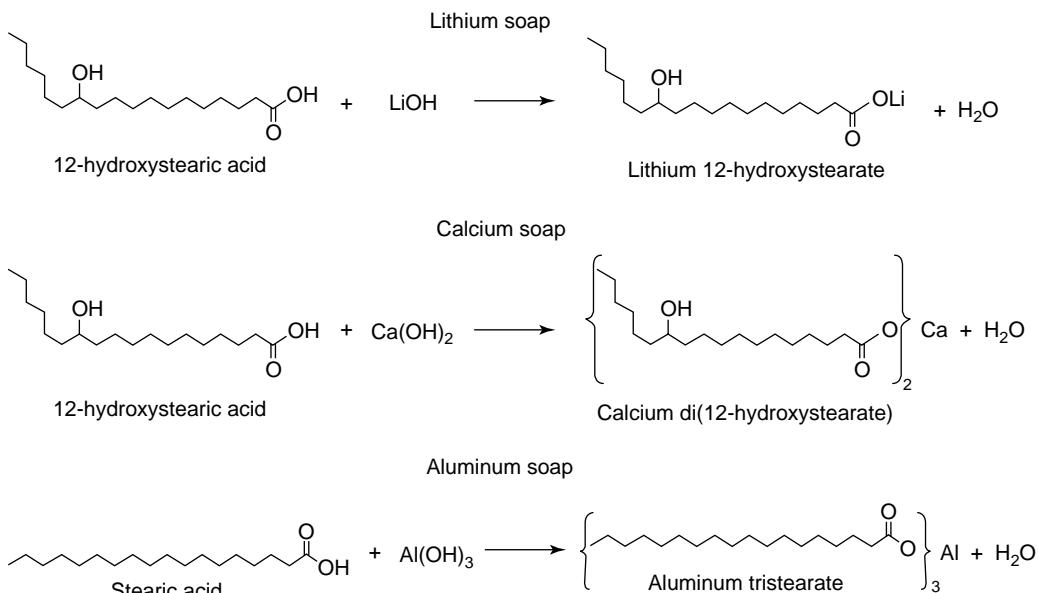


FIGURE 23.1 Chemical reactions for the preparation of grease thickeners.

The properties of complex soap greases depend on the following [22]:

- Metal type (lithium, calcium, etc.)
- Normal soap type (metallic stearate, metallic 12-hydroxystearate, etc.)
- Complexing agent type (metallic acetate, benzoate, carbonate, chloride, etc.)
- Normal soap to complexing agent ratio
- Manufacturing conditions

Complex greases can be used over a greater temperature range because they have higher dropping points than normal greases.

The structure of grease thickeners directly affects the properties and performance characteristics of fully formulated grease. Thickeners range in structure from linear soaplike structures to more complex circular structures. Physically, they may be needles, platelets, or spherical and can vary significantly in dimension. Soaps form microscopic fibers, which form a matrix to hold the base fluid. Fibrous sodium soap structures can be $1 \times 100 \mu\text{m}$, whereas short-fibered lithium soap might be on the order of $0.2 \times 2 \mu\text{m}$. Aluminum soaps might have a diameter of only $0.1 \mu\text{m}$ [23]. Boner [24] has reported that the rheological properties of lithium-based grease depend on the different fiber dimensions of the soap molecules. Fiber structure and the surface area to volume ratio of the fibers tend to vary with different soaps. It has been reported that a thin strip is the most effective shape for a thickener molecule. With increase in the surface area to volume ratio of the thickener molecules, the grease structure is strengthened as indicated by lower penetration [25]. Wilson [26] has reported that lithium soap fibers are long, flat strips. In general, sodium soap fibers range in size from 1.5 to $100 \mu\text{m}$, and lithium soap fibers from 2 to $25 \mu\text{m}$. Aluminum soap fibers are essentially spherical on the order of $0.1 \mu\text{m}$. Calcium soap fibers are short, generally $\sim 1 \mu\text{m}$ long. Organophilic bentonite is $\sim 0.1 \times 0.5 \mu\text{m}$.

In general, it is safe to conclude that greases made with different grease thickeners should not be mixed in the same application. This could result in poorer performance of the mixed greases relative to that expected from either individual grease. Incompatibility and poorer performance could also result in equipment malfunction. For example, it is generally cautioned that lithium and sodium greases are incompatible. There are always two sides to every story, and Meade, in an extensive study, tested more than 1200 grease combinations and found 75% of them to be compatible [27].

The type and structure of the grease thickener affect the stability of the grease during and after shear forces are applied. In bench tests, lithium-thickened greases have been shown to have the least reduction in shear stress and film thickness. Less structural resistance was found for calcium-, sodium-, and bentonite- (clay-) thickened greases [28]. Performance features and application of greases as a function of the types of thickener are summarized in Table 23.4 [2].

Greases are like other lubricants in that they exhibit limited useful lifetimes. The length of time that the grease maintains the property and performance criteria for which it was designed depends on all the factors affecting other lubricants. In addition, grease structure is affected by the thermal, mechanical, and oxidative stresses related to the thickener structure. As grease ages, it may become dry and brittle under the conditions of the application and, therefore, will not exhibit the lubricating properties and performance for which the grease was originally designed.

The general performance and properties of grease as a function of thickener are as follows:

1. An aluminum soap-thickened grease generally exhibits excellent water resistance, poor mechanical stability, excellent oxidative stability, good oil separation, poor pumpability, and in general can be used to a maximum application temperature of 175°F (79.5°C).
2. A calcium soap-thickened grease generally exhibits excellent water resistance, fair mechanical stability, poor oxidative stability, excellent antirust performance, fair pumpability, and in general can be used to a maximum application temperature of 250°F (121°C).
3. A lithium soap-thickened grease generally exhibits good water resistance, excellent mechanical stability, good to excellent oxidative stability, poor to excellent antirust performance depending on the formulation, fair to excellent pumpability, and in general can be used to a maximum application temperature of 275°F (135°C).
4. An aluminum complex soap-thickened grease generally exhibits excellent water resistance, good to excellent mechanical stability, good pumpability, and in general can be used to a maximum application temperature of 350°F (177°C).

TABLE 23.4
Performance Features and Applications of Greases as a Function of Thickener

Thickener	Performance Features	Applications
Aluminum soap	Low dropping point, excellent water resistance	Low-speed bearings, wet applications
Calcium soap	Low dropping point, excellent water resistance	Bearings in wet applications, railroad rail lubricants
Sodium soap	Poor water resistance, good adhesive properties	Older industrial equipment requiring frequent relubrication
Lithium soap	Higher dropping point, resistance to softening and leakage, moderate water resistance	Automotive chassis, automotive wheel bearings, general industrial grease
Calcium complex	Excellent water resistance, inherent EP/load-carrying capability	High-temperature industrial and automotive bearing applications
Lithium complex	Resistance to softening and leakage, moderate water resistance	Automotive wheel bearings, high-temperature industrial rolling-element applications
Aluminum complex	Excellent water resistance, resistance to softening, good pumpability, reversibility	Steel mill roll neck bearings, rolling-element and plain bearings, high-temperature industrial applications, food processing machinery
Polyurea (nonsoap)	Good water resistance, oxidation resistant, less resistance to softening and leakage	Industrial rolling-element bearings, automotive constant velocity joints
Organoclay (nonsoap)	Resistance to leakage, good water resistance, thickener has no melting point	High-temperature bearing with frequent relubrication

5. A calcium complex soap-thickened grease generally exhibits excellent oil separation, good mechanical stability, and in general can be used to a maximum application temperature of 350°F (177°C). The thickener in this case provides a degree of AW and EP protection.
6. A lithium complex soap-thickened grease generally exhibits excellent oil separation, moderate water resistance, and in general can be used to a maximum application temperature of 350°F (177°C).
7. Clay-thickened grease has good to excellent water resistance, good pumpability, excellent oil separation, and in general can be used at maximum application temperatures >350°F (177°C).
8. Polyurea-thickened grease has excellent oxidative stability, excellent pumpability, and excellent oil separation, but has poor worked stability and fair to modest antirust performance. These greases can be used at a maximum application temperature of 350°F (177°C). Polyurea greases soften easily but are reversible.

Chemical and physical processes caused by thermal and shear stresses degrade greases [29]. These authors demonstrated that thermally aged lithium hydroxystearate greases were affected in terms of oil film thickness and oil release in a rolling contact under starved conditions.

23.6 OXIDATION INHIBITORS

The mechanism of hydrocarbon oxidation, because of its importance to lubricant chemistry and performance, has been well studied and is reviewed in Chapter 1.

Hydrocarbons react with oxygen to initially produce peroxides and hydroperoxides, which further react to give alcohols, aldehydes, ketones, and carboxylic acids. These oxidation reactions proceed through free radical chain processes. Grease, which is basically soap-thickened hydrocarbon, is also susceptible to oxidation. In addition, the metals of the metal soaps can catalyze oxidation.

Examples of classes of antioxidants used in grease are

- Hindered phenols, for example, 2,6-di-*t*-butyl phenol and 2,6-di-*t*-butyl-*p*-cresol
- Aromatic amines, for example, diarylamines, di-octyldiphenylamine
- Metal dialkyldithiophosphates, for example, zinc dithiophosphate
- Metal dialkyldithiocarbamates, for example, zinc and molybdenum dithiocarbamates
- Ashless dialkyldithiocarbamates
- Sulfurized phenols, for example, phenolic thioesters, and phenolic thioethers
- Phenothiazine
- Disulfides, for example, diaryl disulfides
- Trialkyl and triaryl phosphates and phosphites, for example, tris(di-*t*-butyl phenyl phosphite)

Alkylated phenol antioxidants are most effective at low temperatures. Secondary aromatic amines such as phenyl alpha-naphthylamine (PANA), phenyl beta-naphthylamine (PBNA), di-octyldiphenylamine, and phenothiazines are most useful at high temperatures [5]. In practice, grease is generally formulated to include a combination of alkylated or secondary amine- and phenol-type antioxidants to provide performance over as wide a temperature range as possible.

In some cases, the combination of antioxidants (or other additives) provides an additive effect, whereas in other cases, synergy is observed when both a hindered phenolic and an aryl amine antioxidant are used together in the same formulation.

23.7 FRICTION AND WEAR

Friction is the force required to cause the motion of two surfaces or bodies in contact with each other. Lubricants are used to reduce the frictional forces. High friction results in heat and because more force or power is necessary to move the parts relative to one another, this friction reduces operating

efficiency. When the lubricant film is insufficient to protect the metal surfaces, there is wear on one or both the components. Wear is material loss directly caused by the interaction of asperities on the two surfaces while in relative motion to each other. As wear results in the loss of material and the scarring changes the size and shape of the machined components, wear reduces the useful life of the components. Extreme wear can result in failure of the equipment and in safety issues. There are three general types of wear: abrasive, adhesive, and corrosive. These are generally addressed by formulating a grease using additives designed to protect against these phenomena. When a lubricant is applied between the rubbing surfaces, the friction and wear can be minimized. Three lubrication regimes are defined depending on the amount of lubricant film separating the surfaces. These are

- Boundary lubrication
- Elastohydrodynamic lubrication
- Hydrodynamic lubrication

These three lubrication regimes are indicated on a Stribeck curve shown in Figure 23.2 [30]. Approximate thickness of films in each regime and how they are related to the size of asperities and sliding wear debris in the boundary regime are shown in Table 23.5 [31].

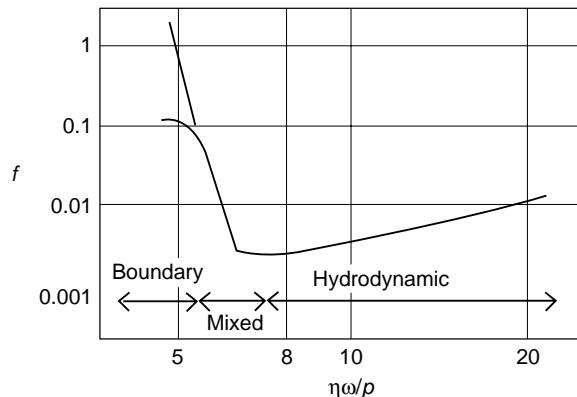


FIGURE 23.2 Stribeck curve for a journal bearing.

TABLE 23.5
Dimensions of Films, Asperities, and Debris Related to Boundary Lubrication

	Approximate Size Range (μm)
Monomolecular layer	0.002–0.2
Sliding wear debris	0.002–0.1
Boundary film	0.002–3
Elastohydrodynamic film	0.01–5
Asperity height	0.01–5
Rolling wear debris	0.07–10
Hydrodynamic film	2–100
Asperity tip radius	10–1000
Concentrated contact width	30–500

Hydrodynamic lubrication is a regime where the moving surfaces are essentially separated from each other. In this regime, the viscosity of the oil in combination with the motion of the mechanical components can produce a fluid pressure high enough to completely separate the two surfaces.

Elastohydrodynamic lubrication is a regime where the film thickness is insufficient to completely separate the surfaces. In this regime, the surface asperities make contact, which leads to wear. The lubricant in the contact area is continually replenished at the front of the contact [32]. The film thickness in the elastohydrodynamic regime is larger than that in the boundary lubrication but smaller than that in the hydrodynamic regime.

Boundary lubrication is a regime where film thickness between the moving surfaces is only a few molecules thick. In this regime, because of the closeness of the moving surfaces, friction and wear are determined by properties of both the surfaces and the lubricant. Boundary films form because they reduce the surface energy and, therefore, are thermodynamically favored [33]. These films form by molecules that contain polar functional groups. Because of this, they orient onto the surface by either chemical or physical adsorption. Even oxidation products derived from the breakdown of the lubricating fluid can adsorb onto metal parts and into contact areas that are being lubricated. Boundary lubrication can range from mild to severe conditions.

Physical adsorption is a reversible process in which molecules adsorb and desorb from a surface without chemical change. Additives that provide protection by physical adsorption are polar structures. This is because at least two phenomena must occur: the molecule must have a preferential affinity for the surface and it should have a preferred orientation on the surface, so that a more closely packed arrangement can be achieved. Alcohols, acids, and amines are examples of long-chain molecules with functional groups at the end. Molecules that can pack tightly and orient in a closely packed arrangement relative to the surface provide improved film strength. Because the forces involved in physical adsorption are relatively weak, these films are effective at low to moderate temperatures. New molecules from the bulk lubricant are constantly available to replace those that physically desorb or are mechanically removed from the surface.

Chemical adsorption, however, is an irreversible process in which a lubricant fluid molecule or additive component reacts with the surface to form a low shear strength protective layer. As this new low shear strength material is worn away, additional additive reacts to form a new protective layer. Protection from chemical adsorption occurs at higher temperatures because chemical reactions are required to generate the actual species that form the surface films. EP additives can protect lubricated surfaces at temperatures as high as 400°C.

Wear protection and friction reduction over a wide temperature range can be achieved by combining additives that function by physical and chemical adsorption. Between the low-temperature physically adsorbed layer and the high-temperature chemically adsorbed layer can be a temperature range over which there is poorer protection. This has been experimentally demonstrated where oleic acid was used as the normal wear additive and a chlorinated additive provided EP protection at higher temperatures [34].

23.8 EXTREME-PRESSURE AND ANTIWEAR AGENTS

EP and AW additives are used to reduce friction and prevent wear under moderate to more severe boundary lubrication conditions. Reactive compounds containing sulfur, phosphorus, or chlorine, metals, or combinations are known to provide EP protection.

Under high loads, opposing metal surfaces contact each other, and as a result, high local temperatures develop, enabling an EP agent to react with the metal surfaces, forming a surface film, preventing the welding of opposing asperities [35].

Some of the major group materials that have been used as EP and AW additives are as follows:

- Sulfurized olefins, fats, and esters
- Chlorinated paraffins

- Metal dialkyldithiophosphates, including antimony and zinc
- Phosphate and thiophosphate esters, for example, tricresyl phosphate, di-*n*-octyl phosphite, isodecyl diphenyl phosphite
- Ammonium salts of phosphate esters
- Borate esters
- Metal dithiocarbamates, including antimony
- Metal naphthenates, including bismuth and lead
- Metal soaps, including lead
- Sulfides and disulfides, for example, diaryldisulfides
- High-molecular-weight complex esters

23.8.1 SOLID ADDITIVES

Solid additives are organic or polymeric solid materials or inorganic compounds used to impart EP and friction reduction properties to the grease and protection in case of lubricant loss. A more detailed description of solid additives can be found in Chapter 6. Examples include the following:

- Bismuth has recently been reported as being more environmentally-friendly than lead for application as an EP additive [36,37]
- Boron-containing additives—boric acid, borax, and metal borates
- Boron nitride
- Molybdenum disulfide
- Inorganic-sulfur-phosphorus additive—patented blend of phosphate and thiosulfate [38]
- Fluorinated polymers, for example, perfluorinated polyolefins
- Graphite—in various forms. The merits of expanded graphite have been reported [39]
- Calcium acetate, carbonate, and phosphate, cerium fluoride
- Zinc stearate, zinc oxide
- Copper powder
- Nickel powder
- Phosphate glasses

EP properties and the mechanism of phosphate glasses in lubricating greases have been studied where the authors compared phosphate glasses to molybdenum disulfide, graphite, molybdenum dithiocarbamate, polytrifluoroethylene, and boron nitride [40]. Improvement in the load-carrying capacity of greases using phosphate glass—a white, relatively inexpensive powder compared with other solid additives—has been reported to provide very effective wear protection under severe conditions [41,42]. Under light loads, the finely divided phosphate glass particles were found to maintain their original round shape. The particles were performing as micro ball bearings under these low-load conditions. At very high loads, the phosphate glass particles compressed and formed a thick protective film on the wear surface.

Greases find a place in space applications, where these lubricants need to demonstrate long-term use in situations involving vacuum. Additives used in these greases must have low volatility and excellent lubricity. Greases for these applications have included perfluoropolyalkylether (PFPAE) fluids for many years. Studies using deep-groove ball bearings filled with PFPAE-based grease have been reported with long-run periods in vacuum of 10^{-4} – 10^{-5} Pa at 2000 rpm [43].

23.9 RUST AND CORROSION INHIBITORS

Rust is a form of corrosion formed by electrochemical interaction between iron and atmospheric oxygen and is accelerated in the presence of moisture due to the catalytic action of water [44]. Rusting of iron and steel surfaces can reduce operating efficiencies and cause part and equipment damage.

The electrochemical oxidation of the surfaces of iron or steel can be prevented by the addition of specific water-blocking additives to lubricating grease that inhibit the formation of rust (or iron oxides). Rust inhibitors are typically highly polar surface-active oil-soluble compounds, which attach to metal surfaces by physical adsorption.

Rust inhibitors incorporated into lubricating grease provide a protective film against the effects of moisture, water, and air. Corrosion inhibitors work by neutralizing corrosive acids formed by the degradation of base fluids and lubricant additives.

Examples of various chemical classes of rust and corrosion inhibitors used in grease are

- Carboxylic acids, including fatty acids, for example, alkyl succinic acid half ester, and nonyl phenoxy acetic acid
- Salts of fatty acids and amines, for example, disodium sebacate
- Succinates, for example, alkyl succinic acid half ester
- Fatty amines and amides
- Metal sulfonates, including ammonium, barium, and sodium
- Metal naphthenates, including bismuth, lead, and zinc
- Metal phenolates
- Nitrogen-containing heterocyclic compounds, for example, substituted imidazolines
- Amine phosphates
- Salts of phosphates esters

23.9.1 METAL DEACTIVATORS

These materials reduce the catalytic effect of metal on the rate of oxidation. They act by forming an inactive film on metal surfaces by complexing with metallic ions. Several classes of materials have been reported to be effective:

- Organic complexes containing nitrogen or sulfur, amines, sulfides, and phosphates
- Derivates of 2,5-dimercapto-1,3,4-thiadiazole
- Triazoles, benzotriazoles, and tolyltriazoles
- Di-salicylidene-propanediamine

23.9.2 TACKINESS ADDITIVES

Grease may be formulated to withstand the heavy impact common in heavy-equipment applications. The adhesive and cohesive properties of grease can be improved to resist throw off from bearings and fittings, while providing extra cushioning to reduce shock and noise through the use of tackiness agents. The water resistance of such grease can also be significantly improved through the use of tackiness additives.

High-molecular-weight polymers such as polyisobutylene (PIB), polybutene, ethylene-propylene copolymer, olefin copolymer (OCP) and latex compounds are typical examples of tackiness additives. Like all long-chain polymers, tackiness additives are susceptible to breakdown when exposed to high rates of shear. A further discussion of these interesting materials is described in Chapter 13.

23.10 ENVIRONMENTALLY FRIENDLY GREASE

Fully formulated grease that combines needed high-performance features with environmental safety and compliance has been developed not only for civilian industrial and automotive applications but also for the military [45].

The goal of environmentally friendly lubricants is to minimize or eliminate any potential harm or damage to humans, wildlife, soil, or water. Depending on the nature of the application, the use

of environmentally friendly (or “green”) lubricants will enable industry to reduce some of, and perhaps even eliminate, the costs associated with the remediation and disposal of nonbiodegradable and toxic lubricants.

One key raw material used in formulating biodegradable grease is vegetable oil. Vegetable oils are obtained from renewable sources and are biodegradable and, as such, are more environmentally friendly than conventional mineral oil-based lubricants [46].

A special class of vegetable oils, containing a high oleic content ($\geq 75\%$ oleic) and a low polyunsaturated fatty acid content (linoleic or linolenic), displays good oxidative stability with acceptable low-temperature properties. This makes them well suited for use in greases compared to conventional vegetable oils [46].

In addition to the lubricating fluids, the toxicity and biodegradability of additive components is important. Over the years, many of the additives that were originally based on fractions cut from petroleum or coal-derived liquids are now synthetic and, therefore, are of much higher purity. Linear side chain hydrocarbon groups have in many instances replaced branched and aromatic functional groups. This results in greater potential biodegradability. Toxicity of additives is related to metals in many cases. Current trends are to replace metal-containing additives with ashless varieties having similar or greater performance features. This will result in a lower pollutant load on the environment. Even military formulations are moving toward more environmentally friendly versions.

Environmentally friendly grease is used in applications such as agriculture, construction, forestry, marine, mining, and railroad. Specific applications include tramway tracks and railway switches, wheel flange lubricant for railways, and farm tractors.

23.11 SUMMARY

In summary, grease finds applications where fluid lubricants may drip or leak from the point of application. Grease reduces the need to frequently lubricate a particular site, because the grease structure serves as a lubricant reservoir. Grease is very effective where lubricant is needed on a vertical machine component or at positions that are difficult to reach. Grease acts as a physical barrier that is effective in sealing out external contaminants and provides better protection when contaminated than does a liquid lubricant. Grease can also provide noise reduction in certain applications and is effective in protecting equipment at high temperatures and pressures and under conditions where there is shock loading in the lubricated components.

The formulation of grease can be considered as art or science depending on the researcher questioned, but certain guidelines are generally useful.

For low-temperature applications, grease can use low- and high-viscosity index (VI) lubricating fluids with a relatively low thickener content. The fluid lubricant should have a low pour point and good pumpability and rust protection. Grease for high-temperature applications will typically have a higher-viscosity lubricating fluid and high-temperature complex thickener. This will result in grease with a higher dropping point. This type of grease will also find application where low flammability and, therefore, low volatility are design requirements.

Grease for applications where water contamination is an issue should be designed with a water-resistant thickener and generally a high-viscosity lubricating fluid. The grease should have low water washout and low waster spray-off, which can be improved by incorporating a tackiness additive. Any application in a wet environment requires that the grease has excellent rust and corrosion protection. Careful formulation to balance the chemistries of the needed additives is critical in achieving the described performance where surface protection is so important to machine life. Where shock or heavy loads are applied, grease is formulated using high-viscosity lubricating fluids and should include higher concentrations of AW and EP additives. This combination will provide both thicker lubricant film and appropriate additive chemistry to protect the metal surfaces.

Grease used in a centralized system needs to have a low to moderate thickener concentration and a relatively low-viscosity lubricating fluid, so that the grease exhibits a lower apparent viscosity and can be readily pumped throughout the system.

23.12 EFFECTS OF INDIVIDUAL ADDITIVES AND GREASE SOAPS

This section includes a sample of application data in which various grease additives were employed to modify the performance of various greases. The first section describes the use of individual additives with a particular type of grease. The second section demonstrates some synergistic effects of combining two or more additives that individually may not provide all the performance benefits needed.

An excellent general review of the fundamental characteristics of synthetic lubricating greases has been published [47]. This review describes the very wide range of potential synthetic greases in terms of properties and performance capabilities but also cautions that some of these higher-performance capabilities are not always needed, and thus, the higher cost of synthetics may not always be justified. Previously published chapters on greases can be found in earlier books [48,49].

These application data are meant to serve as a guideline, not as a recipe for greases. The actual combination of all the components of grease, including the base oil, thickener, each additive, and the order of addition, will affect the properties and performance of a final grease formulation, and thus, these issues are left for the formulator. A list of additive components is summarized in Table 23.6.

The data in Table 23.7 show the results of wear experiments on aluminum complex grease using four organo-molybdenum-containing additives at the same concentration. Molyvan A is a powder, and any heterogeneity in the lubricant might result in the observed higher wear scars in grease made with this additive.

Comparison of aluminum complex and lithium complex grease with one level of Vanlube 829 showed improvement in both four-ball EP weld load and four-ball wear scar in the lithium complex grease (Table 23.8). It should be noted that the weld load difference in these results is within experimental error, but the combined improvement in weld load and wear scar is directionally desirable.

TABLE 23.6
Grease Additives—Chemical Components

Molyvan L: Molybdenum di(2-ethylhexyl) phosphorodithioate
Molyvan 822: Molybdenum dialkyldithiocarbamate in oil
Molyvan 855: Organo-molybdenum complex
Molyvan A: Molybdenum di- <i>n</i> -butyldithiocarbamate
Vanlube 829: 5,5-Dithio-bis(1,3,4-thiadiazole-2)3H-thione
Vanlube 73: Antimony tri(dialkyldithiocarbamate) in oil
Vanlube 7723: Methylene bis(dibutylthiocarbamate)
Vanlube 622: Antimony <i>o,o</i> -dialkylphosphorodithioate in oil
Vanlube 8610: Antimony dithiocarbamate/sulfurized olefin blend
Vanlube NA: Alkylated diphenylamines
Desilube 88: Blend of phosphate and thiosulfate
Irgalube 63: Ashless dithiophosphate
Irgalube TPPT: Triphenyl phosphorothionate
Lubrizol 1395: Zinc dialkyldithiophosphate
Lubrizol 5235: Sulfur-phosphorus-zinc additive package
Lubrizol 5034A: Sulfur-phosphorus industrial gear oil additive package
Amine O: Substituted imidazoline
Sarkosyl O: <i>N</i> -oleyl sarcosine
Na-Sul ZS-HT: Zinc dinonylnaphthalene sulfonate/carboxylate complex
MoS ₂ : Molybdenum disulfide

TABLE 23.7
Organo-Molybdenum Compounds in Aluminum Complex Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Molyvan L	3.0	200	0.48
Molyvan 822	3.0	250	0.60
Molyvan 855	3.0	250	0.58
Molyvan A	3.0	250	0.76

TABLE 23.8
Thiadiazole Compound in Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Aluminum complex base grease (900 SUS paraffinic base oil blend)	—	140	0.59
Lithium complex base grease (600 SUS paraffinic base oil)	—	180	0.61
Vanlube 829 in aluminum complex	3.0	620	0.66
Vanlube 829 in lithium complex	3.0	800 kg pass	0.50

TABLE 23.9
Effect of Antimony Compounds in Aluminum Complex Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Aluminum complex base grease (980 SUS paraffinic base oil blend)	—	126	0.68
Vanlube 73	3.0	315	0.84
Vanlube 7723	3.0	315	0.81
Vanlube 622	3.0	500	0.46

The data in Table 23.9 show the improved performance of an aluminum complex grease containing Vanlube 622 over the grease containing a similar amount of Vanlube 73 or Vanlube 7723. There should be concern over the high sulfur content of Vanlube 622 and its effect on copper corrosion for applications where the grease will be in contact with copper-containing components.

Comparison of two antimony-containing EP/AW additives in aluminum complex grease showed improved EP performance and lower wear scar diameter for the sulfurized antimony dithiocarbamate (DTC) (Vanlube 8610; Table 23.10). Comparison of two sulfur–phosphorus EP additives in aluminum complex and lithium complex grease shows extremely high four-ball EP performance using Desilube 88 compared with Irgalube 63 (Table 23.11).

TABLE 23.10
Antimony DTC and Antimony DTC/Sulfurized Olefin in Aluminum Complex

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Aluminum complex base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Vanlube 73	3.0	315	0.84
Vanlube 8610	3.0	400	0.74

TABLE 23.11
Sulfur–Phosphorus Compounds in Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Aluminum complex base grease (900 SUS paraffinic base oil blend)	—	140	0.59
Lithium complex base grease (600 SUS paraffinic base oil blend)	—	180	0.61
Desilube 88 in aluminum complex	3.0	500	0.76
Desilube 88 in lithium complex	3.0	620	0.88
Irgalube 63 in aluminum complex	3.0	250	0.60
Irgalube 63 in lithium complex	3.0	315	0.55

23.12.1 FOOD-GRADE GREASES

Food-grade greases are a special class of grease, which require nontoxic components approved for this particular application. Additional discussion and details can be found in Chapter 22.

The data in Table 23.12 demonstrate the better balance of EP and wear protection by the addition of calcium carbonate when compared to Desilube 88 alone. Rust protection is demonstrated by the synergistic effect of the two corrosion inhibitors using ASTM D1743. The individual additives are not effective in providing sufficient EP and wear protection in this formulation.

23.12.2 SYNERGISTIC ADDITIVE EFFECTS

Frequently, combinations of two or more additives show enhanced performance over that of the individual components. The occurrence and magnitude of synergistic behavior involving specific compounds very likely depend on the nature of the base grease, including the base oil and the thickener.

The use of Vanlube 829 in combination with Irgalube 63 showed improvement in the four-ball wear scar compared with Vanlube 829 in combination with Irgalube TPPT (Table 23.13). These combinations were each better in EP performance than formulations containing only Irgalube 63 or Irgalube TIPPT in the absence of Vanlube 829. Desilube 88 and MoS₂ showed significant improvement in EP and wear performance for aluminum complex grease when compared with lithium complex grease (Table 23.14).

TABLE 23.12
Food-Grade Aluminum Complex Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)	Rust Test ASTM D1743
Aluminum complex base grease (500 SUS technical white mineral oil)	—	140	0.62	Fail
Calcium carbonate	4.0	315	0.49	—
Calcium carbonate	4.0	315	0.55	Pass
Amine O	0.5			
Sarkosyl O	0.5			
Amine O	0.5	160	0.80	Pass
Desilube 88	3.0	500	1.04	—

TABLE 23.13
Synergistic Compounds in Aluminum Complex Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Aluminum complex base grease (880 SUS paraffinic base oil blend)	—	126	0.68
Vanlube 829	1.0	400	0.88
Irgalube TPPT	3.0		
Vanlube 829	1.0	400	0.60
Irgalube 63	3.0		
Irgalube 63	3.0	250	0.50
Irgalube TPPT	3.0	200	0.55

TABLE 23.14
Addition of MoS₂ in Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
MoS ₂ in lithium complex (600 SUS paraffinic base oil)	3.0	500	0.72
MoS ₂ in aluminum complex (900 SUS paraffinic base oil blend)	3.0	400	0.90
MoS ₂	1.3	500	1.0
Desilube 88 in lithium complex	3.0		
MoS ₂	1.3	800	0.80
Desilube 88 in aluminum complex	3.0		

A sulfonate rust inhibitor can enhance the four-ball wear performance of a lithium 12-hydroxy stearate grease in combination with an EP additive, which by itself does not show reduced wear at low loads [50] (Table 23.15). A widely used AW additive, zinc dialkyldithiophosphate (ZDDP) exhibits moderate EP performance and low wear scars in both aluminum and lithium complex greases compared with the base greases alone (Table 23.16).

A multifunctional additive package specifically designed for greases provides good EP and AW performance. In general, this additive package also provides antioxidant and anticorrosion properties and copper metal deactivation (Table 23.17). EP additives can sometimes be detrimental to the oxidative stability of the grease. The addition of an amine antioxidant can improve the oxidation stability of EP-containing organoclay grease, as shown in Table 23.18.

Because gear oils can require good EP and AW properties, they are sometimes used in grease formulations. A sulfur–phosphorus industrial gear oil additive package exhibited good EP and wear performance in both aluminum complex and lithium complex greases (Table 23.19).

TABLE 23.15
Effect of a Sulfonate Additive in Lithium 12-OH Stearate Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Vanlube 73	3.0	250	0.73
Vanlube 73	3.0	250	0.47
Na-Sul ZS-HT	1.0		

TABLE 23.16
ZDDP Component in Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Aluminum complex base grease (900 SUS paraffinic base oil blend)	—	140	0.59
Lithium complex base grease (600 SUS paraffinic base oil)	—	180	0.61
Lubrizol 1395 in lithium complex	3.0	315	0.47
Lubrizol 1395 in aluminum complex	3.0	250	0.55

TABLE 23.17
S-P-Zn-N Additive Package in Aluminum Complex Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Lubrizol 5235 in aluminum complex (900 SUS paraffinic base oil blend)	3.0	250	0.57
Lubrizol 5235 in lithium complex (600 SUS paraffinic base oil)	3.0	315	0.50

TABLE 23.18
Oxidation Stability in Organoclay Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)	Oxidation Stability psi Loss at 500 h, ASTM D 942
Organoclay base grease (600 SUS paraffinic base oil)	—	140	0.61	13.0
Molyvan A in organoclay	1.4	200	0.52	17.0
Molyvan A	1.4	200	—	12.0
Vanlube NA in organoclay	0.5			

TABLE 23.19
S-P Gear Oil Package in Grease

Additive	Wt%	Four-Ball EP Weld Load (kg)	Four-Ball Wear Scar Diameter (mm)
Lubrizol 5034A in aluminum complex (900 SUS paraffinic base oil blend)	3.0	250	0.45
Lubrizol 5034A in lithium complex (600 SUS paraffinic base oil)	3.0	315	0.50

Note: Additional additives such as rust and corrosion inhibitors and antioxidants are usually added to the aforementioned examples to provide fully formulated grease. The four-ball EP test has a repeatability and reproducibility of one loading. The four-ball wear test has a repeatability of 0.2 mm wear scar diameter and a reproducibility of 0.37 mm.

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Part 7

Trends

24 Long-Term Trends in Industrial Lubricant Additives

*Fay Linn Lee and John W. Harris**

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* In memory of John W. Harris, his Shell colleagues—Howard B. Mead (United Kingdom), Cliff Henderson, and Fay Linn Lee (United States)—have contributed this chapter update on behalf of John. In the technical field of industrial lubricants and greases, John was recognized as an international expert by Shell Oil colleagues and by his peers in professional technical societies including the American Society for Testing and Materials (ASTM), the National Lubricating Grease Institute (NLGI), the European Lubricating Grease Institute, and the Society of Tribologists and Lubrication Engineers. He wrote and presented numerous technical papers and patents and contributed to the first edition of this book. As a technical advisor in Shell Global Solutions, John was known as Dr. AeroShell Grease for his contributions in developing and patenting aircraft lubricants. Dr. John W. Harris passed away on November 21, 2005.

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24.1 INTRODUCTION

The formulation of the various types of lubricating oils used in industry varies significantly depending on their application. The types of industrial oil lubricants considered in this chapter, in decreasing order of volumes consumed by industry, are as follows:

1. Circulating oils, including turbine oils
2. Hydraulic oils
3. Gear oils
4. Compressor oils

Trends in lubricating grease formulations are also considered.

TABLE 24.1
Performance Requirements for Industrial Oils

Type of Oil	Performance Property				
	Rust and Oxidation Inhibition	Ability to Resist Foaming	Ability to Separate Water	Antiwear Properties	EP
Circulating and turbine oils	X	X	X	—	—
Hydraulic oils	X	X	X	X	—
Compressor oils	X	X	X	X	—
Gear oil	X	X	X	X	X
Lubricating grease	X	—	—	X	X

Performance requirements relevant to each type of lubricant are listed in Table 24.1. As may be expected, the greater the number of performance properties required of a lubricant, the more complex the formulation.

24.2 ADDITIVES FOR CIRCULATING OILS AND TURBINE OILS

24.2.1 PERFORMANCE REQUIREMENTS FOR CIRCULATING OILS AND TURBINE OILS

The following performance requirements are typically required for circulating oils and, in particular, steam and gas turbine oils:

1. Provide bearing lubrication
2. Remove heat through circulation
3. Serve as hydraulic fluid for governor and other control equipment
4. Lubricate reducing gears
5. Protect against corrosion
6. Allow rapid separation of water
7. Resist foaming
8. Resist oxidation and sludge formation

As gas turbine oils typically operate at higher temperatures than steam turbine oils, requirement 8 is even more critical for gas turbine oils.

Various military and civilian agencies and turbine builders issue specifications for turbine oils [1,2]. Performance tests that usually appear in these specifications are listed in Table 24.2.

24.2.2 ADDITIVES

The types of additives commonly used in turbine oils are listed in Table 24.2 with the performance properties they impart and the related test methods.

24.2.2.1 Antioxidants

Antioxidants are used to inhibit the attack of turbine oil by oxygen and to reduce the formation of adverse oxidation products such as corrosive organic acids and insoluble sludge. In turbine oils, this is often accomplished with synergistic blends of hindered phenols and diaryl amines, which inhibit oxidation by donating a hydrogen atom to reactive peroxy radical intermediates formed during the oxidation process, thus terminating a chain reaction that would otherwise propagate the degradation of more oil molecules [3–7]. Antioxidants that deactivate peroxy radicals are termed *primary antioxidants*. Volatile antioxidants are generally avoided because they can be depleted by evaporation during use.

Another type of antioxidant inhibits oil oxidation by decomposing reactive hydroperoxide intermediates to less-reactive chemical species. Otherwise, these hydroperoxides would decompose to reactive radicals, resulting in the propagation of the oxidation process. Antioxidants that act as peroxide decomposers are termed *secondary antioxidants* [5]. Types of additives that fall into this class include thioethers, zinc dialkyldithiophosphates (ZDDPs), zinc dialkyldithiocarbamates, and organic phosphites.

Industrial oil formulators exploit synergistic relationship between hindered phenols and diaryl amines and between primary antioxidants and secondary antioxidants [8]. Manufacturers of antioxidants have also developed additives that contain both the phenol moiety and the thioether moiety in the same molecule so that one additive can potentially act as both primary antioxidant and secondary antioxidant [5].

TABLE 24.2
Additives Used in Turbine Oils

Additive Function	Types of Additives	Related Performance Tests
Antioxidant	Diaryl amines Hindered phenols Organic sulfides	ASTM ^a D 943, Standard test method for oxidation characteristics of inhibited mineral oils ASTM D 2272, Standard test method for oxidation stability of steam turbine oils by rotating pressure vessel ASTM D 4310, Standard test method for the determination of sludging and corrosion tendencies of inhibited mineral oils ASTM D 6186, Standard test method for oxidation induction time of lubricating oils by pressure differential scanning calorimetry (PDSC)
Rust inhibitor	Alkylsuccinic acid derivatives Ethoxylated phenols Imidazoline derivatives	ASTM D 665, Standard test method for rust-preventing characteristics of inhibited mineral oil in the presence of water
Foam inhibitor	Polydimethylsiloxanes Polyacrylates	ASTM D 892, Standard test method for foaming characteristics of lubricating oils
Metal deactivator	Triazoles Benzotriazoles 2-Mercaptobenzothiazoles Tolatriazole derivatives	ASTM D 130, Standard test method for detection of copper corrosion from petroleum products by the copper strip tarnish test
Mild antiwear/EP additive	Alkylphosphoric acid esters and salts	ASTM D 4172, Standard test method for wear preventive characteristics of lubricating fluid (four-ball method) ASTM D 5182, Standard test method for evaluating the scuffing load capacity of oils (FZG visual method)
Demulsifier	Polyalkoxylated phenols Polyalkoxylated polyols Polyalkoxylated polyamines	ASTM D 1401, Standard test method for water separability of petroleum oils and synthetic fluids

^a American Society for Testing and Materials, *Annual Book of ASTM Standards: Petroleum Products, Lubricants and Fossil Fuels*, Volumes 5.01–5.04, issued annually.

24.2.2.2 Rust Inhibitors

Turbine oils are formulated to prevent rust in areas in contact with the oil. Typical turbine oil specifications require that the oil pass corrosion tests using both demineralized water and saltwater, ASTM D 665, procedures A and B, respectively. Anticorrosion additives are generally polar in nature and preferentially form water-resistant films on iron or steel surfaces [5]. Such additives should not be readily leached from the turbine oil by water entrained in the circulating oil and should not adversely affect other desirable performance properties such as fast water separation and low-foaming tendencies. Types of rust inhibitors that may be used in turbine oils are listed in Table 24.2.

Rust inhibitor-related compatibility problems can occur if certain turbine oils are contaminated with industrial oils that contain organometallic performance additives. For example, antiwear hydraulic oils may contain zinc-based antiwear additives and metal sulfonate rust inhibitors, and interactions between acidic rust inhibitors in the turbine oil and metal-containing additives in the antiwear hydraulic oil can result in the formation of insoluble salts, which can plug filters. Similarly,

if a new turbine component is installed in a unit and metal sulfonate rust preservatives on the component parts have not been completely washed off, a similar filter-plugging situation can occur.

24.2.2.3 Metal Deactivators

Metal deactivators prevent corrosion of copper and copper alloys such as bronze and brass. They function by preferentially adsorbing onto the surface of copper alloys, forming a protective layer that inhibits attack by acids formed during oxidation of the bulk lubricant [5,9]. Conversely, the metal deactivator can act as a copper passivator protect the oil from the catalytic effects of the copper alloy, which could accelerate bulk oil oxidation. Table 24.2 lists the types of metal deactivators that may be used in turbine oils.

24.2.2.4 Foam Inhibitor

Antifoam additives of the type listed in Table 24.2 are added to turbine oils to control foaming tendencies. One method for measuring foaming tendencies is ASTM D 892. Antifoam additives are not completely soluble in oil and form dispersions of tiny droplets of low surface tension, which accelerate the coalescence of air bubbles in oil. Typical dose rates for silicone antifoam additives are in the 10–20 ppm range, whereas typical dose rates for polyacrylates are in the 50–200 ppm range. Because antifoam additives are only partially soluble in oil, they can eventually separate from the oil, resulting in decreased foam control.

It is important that the antifoam additives do not adversely affect the air release properties of the turbine oil, or otherwise, air entrainment in the oil can result in sluggish operation of hydraulic systems and other problems. Air release is measured by the method ASTM D 3427. Typically, values of less than 5–10 min are desirable. Overdosing with antifoam additive can adversely affect air release properties.

24.2.2.5 Demulsifiers

Demulsifiers facilitate water separation from oil. They concentrate at the water–oil interface and promote coalescence of water droplets, resulting in faster separation of water so that it can settle to the bottom of the oil reservoir and be drained off. Types of demulsifiers are listed in Table 24.2.

24.2.3 TURBINE OIL MONITORING

Despite the use of performance additives, turbine oil properties may deteriorate in use, and guidelines for condemnation values for various physical properties of turbine oils have been developed. Such guidelines are described in ASTM D 4378. Turbine manufacturers may also have their own set of monitoring guidelines for turbine oils.

24.2.4 BASE OIL EFFECTS ON ADDITIVES

Modern engine oil requirements have driven changes in the mineral oil base stocks available for formulating lubricants, including industrial lubricants. Three of the types of base oils defined by the American Petroleum Institute (API) are described as follows [10]:

1. Group I base stocks contain less than 90% saturates and greater than 0.03% sulfur and have a viscosity index (VI) greater than or equal to 80 and less than 120.
2. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a VI greater than or equal to 80 and less than 120.
3. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a VI greater than or equal to 120.

A step-change improvement in the oxidation performance of mineral oil-based turbine oils has been achieved by using group II base oils in place of group I base oils. Group II base oils contain significantly lower levels of aromatic compounds, which are susceptible to oxidation, than group I base oils. However, group II base oils also contain lower levels of sulfur components, some of which can act as secondary oxidation inhibitors. It has been reported that the oxidation resistance of group II base oil blends can be further enhanced by adding sulfur-containing secondary oxidation inhibitors along with optimized combinations of hindered phenols and diaryl amine primary antioxidants [8]. Owing to the lower solvency of group II base oils, resulting from the lower levels of aromatic compounds, not all the additive formulations that performed satisfactorily in group I base stocks display adequate solubility in group II base stocks [11].

24.2.5 ENVIRONMENTAL EFFECTS OF TURBINE OILS

As turbine oil additives are metal-free and are used at low rates, typically less than 1%, the environmental impact of turbine oil additives is generally fairly minimal. In some cases, local wastewater treatment requirements may be such that turbine oil users prefer turbine oils free from detectable phenolic antioxidants.

24.2.6 TURBINE OIL TRENDS

As the oxidation life of turbine oils is extended, new test methods will be needed to evaluate field performance. New turbine oils formulated with group II base oils typically have ASTM D 943 lives between 10,000 and 30,000 h, making them impractical to characterize by this method. The ASTM D 943 method primarily monitors acid formation as the results of oxidation. As sludge formation can affect the operation of critical equipment, such as servo-valves, more emphasis will be placed on measuring the tendency of turbine oils to form sludge and varnish and on choosing additives that minimize the formation of insoluble oxidation products. Wider availability of group III base oils in the future may lead to the development of turbine oil formulations with even longer performance lives.

24.3 ADDITIVES FOR HYDRAULIC OILS

24.3.1 PERFORMANCE REQUIREMENTS

There are three basic types of hydraulic pumps: gear pumps, vane pumps, and piston pumps. Each is designed to perform specific tasks. Generally, vane pumps operating under high pressure have the greatest requirements for wear protection by hydraulic fluids [12].

The main functions of hydraulic oils are as follows:

1. Transmit power
2. Protect and lubricate system components
3. Remove heat through circulation
4. Protect the component parts from oxidation and corrosion
5. Provide wear protection
6. Provide mild extreme-pressure (EP) performance

Hydraulic oils are expected to meet the following performance requirements:

1. Consistent performance and appropriate viscosity and compressibility
2. Corrosion protection
3. Wear protection and oxidation and thermal stability
4. Hydrolytic stability
5. Long life

6. Filterability
7. Compatibility with system components
8. Good demulsibility or emulsibility, depending on application

The ASTM has issued a standard specification for mineral oil hydraulic oil, ASTM D 6158. Many pump manufacturers have issued hydraulic oil specifications, which include satisfactory pump performance under severe conditions. A number of these specifications have been summarized in the literature [13], as have military specifications for hydraulic oils [2]. Performance tests that often appear in hydraulic oil specifications are listed in Table 24.3.

24.3.2 ADDITIVES

The types of additives commonly used in hydraulic oils are listed in Table 24.3.

24.3.2.1 Antioxidants

In addition to the types of antioxidants described previously for turbine oils, hydraulic oils may use organometallic antioxidants such as ZDDP [15,16] additives. The ZDDP additives are multifunctional, acting as secondary antioxidants and antiwear additives. The types of antioxidants that can be used in hydraulic oils are listed in Table 24.3.

24.3.2.2 Rust Inhibitors

Rust inhibitors used in hydraulic oils may contain metals, such as metal sulfonates, and may be overbased to provide the capability to neutralize acidic oxidation products. Various rust inhibitors that may be used in hydraulic oils are listed in Table 24.3.

24.3.2.3 Antiwear Additives

Antiwear additives are needed to inhibit frictional wear of moving parts such as the sliding vanes of vane pumps. These additives react with metal surfaces, forming sacrificial films with lower shear strength than the metal itself. The sacrificial films help to reduce friction, and although a small amount of metal is removed with the sacrificial film as it is rubbed off by the moving parts, the rate of metal removal is much lower than if the sacrificial film was not present.

The types of antiwear additives used in hydraulic oils are listed in Table 24.3. Most hydraulic oil formulations contain ZDDP antiwear additives. The composition of the films that ZDDP additives deposit on metal surfaces has been studied and determined to be complex [17]. The popularity of these antiwear additives is due to their cost-effectiveness as they are multifunctional, acting both as antiwear additives and as antioxidants. Although ZDDP additives provide excellent antiwear properties, they can also cause corrosion and deposit formation under conditions that promote their hydrolysis or thermal decomposition. By judicious selection of the types of alcohols used to form the phosphate ester portion of the ZDDP molecule, additive developers can maximize hydrolytic and thermal stability while maintaining good antiwear properties. For example, ZDDP antiwear additives derived from primary alcohols have better thermal stability than the corresponding ZDDP antiwear additives derived from secondary alcohols.

Environmentally aware hydraulic oils are formulated with zinc-free, ashless antiwear additives [12,18]. These additives are generally organic compounds containing sulfur and phosphorus. As with the ZDDP antiwear additives, the ashless antiwear additives must be designed in such a way as to maximize hydrolytic and thermal stability as well as improve antiwear performance. It has been claimed that ashless antiwear oils can exhibit better filterability properties than antiwear oils containing ZDDP [12,19]. Because the possibility exists that ashless and zinc-containing antiwear oils may be inadvertently mixed in commercial applications, it is best to formulate ashless antiwear

TABLE 24.3
Additives Used in Industrial Hydraulic Oils

Additive Function	Types of Additives	Related Performance Tests
Antioxidant	Hindered phenols Diaryl amines Phenothiazine Metal dialkyldithiocarbamates Ashless dialkyldithiophosphates Metal dialkyldithiophosphates	ASTM D 943, Standard test method for oxidation characteristics of inhibited mineral oils
Rust inhibitor	Alkylsuccinic acid derivatives Ethoxylated phenols Fatty amines Salts of fatty acids and amines Salts of phosphate esters and amines Metal sulfonates Ammonium sulfonates Imidazoline derivatives	ASTM D 2272, Standard test method for oxidation stability of steam turbine oils by rotating pressure vessel ASTM D 4310, Standard test method for the determination of the sludging and corrosion tendencies of inhibited mineral oils ASTM D 6186, Standard test method for oxidation induction time of lubricating oils by pressure differential scanning calorimetry (PDSC) ASTM D 665, Standard test method for rust-preventing characteristics of inhibited mineral oil in presence of water
Metal deactivator	Benzotriazoles 2-Mercaptobenzothiazoles Thiadiazoles Tolutriazole derivatives	ASTM 130, Standard test method for detection of copper corrosion from petroleum products by the copper strip tarnish test
Antiwear additive	Alkylphosphoric acid esters and salts Dialkyldithiophosphates Metal dialkyldithiocarbamates [14] Phosphate esters Dithiophosphate esters Derivatives of 2,5-dimercapto-1,3,4-thiadiazoles Molybdenum carboxylates	ASTM D 4172, Standard test method for wear preventive characteristics of lubricating fluid (four-ball method) ASTM D 7043, Standard test method for indicating wear characteristics of non-petroleum and petroleum hydraulic fluids in a constant volume vane pump various pump tests as specified by pump manufacturers ASTM D 5182, Standard test method for evaluating the scuffing load capacity of oils (FZG visual method)
Demulsifiers	Polyalkoxylated phenols Polyalkoxylated polyols Polyalkoxylated polyamines	ASTM D 1401, Standard test method for water separability of petroleum oils and synthetic fluids ASTM D 2711, standard test method for demulsibility characteristics of lubricating oils
PPDs	Poly(alkylmethacrylates)	ASTM D 97, Standard test method for pour point of petroleum product ASTM D 5949, Standard test method for pour point of petroleum products ASMT D 892, Standard test method for foaming characteristics of lubricating oils
Foam inhibitors	Polydimethylsiloxanes	ASTM D 5621, Standard test method for sonic shear stability of hydraulic fluids
Shear stable VI improvers	Poly(alkyl methacrylates) Olefin copolymers Styrene diene copolymers	

oils in such a way that they will be compatible with antiwear additives containing ZDDP so that no precipitates that could plug filters are formed [12].

Test methods have been developed to evaluate the thermal and hydrolytic stability of antiwear hydraulic oils. Test method ASTM D 2070 evaluates the thermal stability of an oil by heating the test oil in the presence of copper and iron rods for 168 h at 135°C. At the end of the test, the metal rods are rated by visual examination and the sludge is isolated by filtration and weighed. Test method ASTM D 2619 evaluates hydrolytic stability by heating and agitating the test oil with water and a copper strip in a sealed glass bottle for 48 h at 93°C. At the end of the test, the viscosity change of the oil and the acidity changes of the oil and the water phases are measured, the weight loss of the copper strip is determined, and any resulting insoluble material is isolated and weighed.

24.3.2.4 Metal Deactivators

Owing to the potential corrosiveness of the decomposition products of the antiwear additives, the presence of an effective metal deactivator is even more important in antiwear hydraulic oils than in turbine oils. Table 24.3 lists the types of metal deactivators that can be used in hydraulic oils.

24.3.2.5 Foam Inhibitor

Because air is compressible, foam or entrained air interferes with the primary function of a hydraulic oil, which is to transfer power. Therefore, the type and amount of silicone or polyacrylate antifoam additive must be carefully chosen to maximize foam inhibition while maintaining good air release properties. Some original equipment manufacturers are extremely concerned about the presence of silicone materials in their plants as it is believed that even a trace of silicone on a metal surface can affect paint coating properties. Therefore, these manufacturers require that only nonsilicone antifoam additives be used in lubricating oils employed in their plants.

The choice of antifoam additive may also be affected by the practice of hydraulic oil condition monitoring. Often, optical particle counters based on light scattering techniques are used to monitor oil cleanliness. As antifoam additives are finely dispersed, partially insoluble fluids in oil, they can falsely be registered as particles by some optical particle counters. In the future, one criterion for choosing antifoam additives may be their ability to disperse sufficiently so as not to interfere with the function of optical particle counters.

24.3.2.6 Viscosity Index Improver

VI improvers are used to widen the useful operating temperature range of hydraulic oils. They are long-chain polymers that function by uncoiling or dissociating at elevated temperatures, resulting in thickening of the oil. Owing to this property, oils containing VI improvers will display higher measured kinetic viscosities at elevated temperatures than comparable oils that have the same 40°C oil viscosity but do not contain VI improver. The types of polymers used as VI improvers are listed in Table 24.3.

An important property of VI improvers for hydraulic oils is shear stability. If a VI improver lacks shear stability, it will quickly be degraded by the hydraulic pump and will lose its ability to increase the viscosity of the base oil at elevated temperatures. This will result in less-than-optimum lubricant film thickness and accelerated pump wear. Generally, the shear stability of VI improvers increases as the molecular weight decreases. However, the thickening capability of the VI improver also decreases as the molecular weight decreases. A trend in the industry is to use VI improvers with better shear stability for better pump protection. Therefore, lower-molecular-weight VI improvers are used although they must be used at higher percentages by weight.

One method for determining the shear stability of hydraulic oil containing a VI improver, ASTM D 5621, is based on sonic irradiation. In this method, a sample of test oil is irradiated in a sonic oscillator for a specified time interval and the change in viscosity after shear is determined. It is claimed that the amount of shear measured by this method is similar to the amount of shear imparted to a hydraulic oil in a hydraulic vane pump test [20].

24.3.2.7 Pour Point Depressants

Pour point depressant (PPD) additives are chemicals that help mineral oil-based hydraulic oils remain pumpable at low temperatures by lowering the pour point of the oil. The PPD additives are polymers that interfere with the crystallization of wax from mineral oil at low temperatures. By retarding the formation of a wax crystal network in oil at low temperatures, PPDs can reduce the pour points of some paraffinic oils by as much as 30–40°C. The effect is less marked in nonparaffinic oils, which have lower wax contents.

24.3.3 ENVIRONMENTAL CONCERNs

Hydraulic oils have received considerable attention regarding their impact on the environment. Hydraulic oil lines carry oil under moderate to high pressure; therefore, rupture of a line in a forest or near a waterway can result in the release of a significant amount of hydraulic fluid into an environmentally sensitive area. Many agencies have drafted methods for evaluating the environmental impact of hydraulic oils and for defining what can be classified as a rapidly biodegradable hydraulic oil. For example, the ASTM has issued the following standards and methods related to the evaluation of the impact of hydraulic oils on the environment:

1. D 5864, Standard Test Method for Determining the Aerobic Aquatic Biodegradation of Lubricants or Their Components
2. D 6006, Standard Guide for Assessing Biodegradability of Hydraulic Fluids
3. D 6046, Standard Classification of Hydraulic Fluids for Environmental Impact
4. D 6081, Standard Practice for Aquatic Toxicity Testing of Lubricants: Sample Preparation and Results Interpretation

Generally, biodegradable hydraulic oils are based on natural or synthetic esters. Additives that are effective with these types of oils [21] and that are environmentally aware must be chosen. Regulations governing environmentally aware hydraulic oils generally require that they be metal-free, readily biodegradable, display low ecotoxicity in water and soil, and exhibit a low tendency for bioaccumulation [22,23]. This necessitates that the additives used to formulate such hydraulic oils meet most of the same requirements.

24.3.4 FUTURE TRENDS

An ongoing trend toward reducing the cost of hydraulic equipment by making it smaller obviates the need for oils that function at higher temperatures and with shorter oil sump residence times. Also, an environmentally driven trend to minimize waste oil disposal will require lubricating oils with longer functional lives. These trends will require oils with improved oxidation resistance, water separation, and air release properties. Some of these improvements will be accomplished by upgrading base oil quality, first from group I to group II base oils and then to group III base oils. The remainder of the improved performance will be accomplished with improved additives that are also environmentally friendly. As base oils are upgraded, changes in additives may also be required to ensure additive–base oil compatibility.

24.4 ADDITIVES FOR GEAR OILS

24.4.1 PERFORMANCE REQUIREMENTS FOR GEAR OILS

Most industrial operations use equipment driven by one type of gear or other, for example, rock drills, crushers, hoists, mobile equipment, grinders, mixers, and speed increases/reducers.

There are many combinations of gear types and materials; therefore, the requirements for gear oils are varied [24,25]. Some of the common types of gears are listed in Table 24.4 and illustrated

TABLE 24.4
Common Gear Types

Gear Type	Configuration of Gear	Comments
Spur gear (Figure 24.1)	Straight teeth cut parallel to the axis of the gear	For moderate loads and moderate speeds
Helical gear (Figure 24.2)	Teeth cut at an angle to the axis of the gear	For higher speeds and higher loads than spur gears Produce axial thrust
Herringbone gear (Figure 24.3)	Teeth cut in a "V" shape	Similar to helical gear, but the "V" shape of the gears eliminates the axial load
Straight bevel gear (Figure 24.4)	Straight teeth cut on an angular surface of a truncated one	For transfer of motion of shafts where shaft centerlines intersect and shafts are at right angles to each other
Spiral bevel gear (Figure 24.5)	Similar to straight bevel gear except the teeth are cut at an angle on a radial line	For moderate loads and moderate speeds
Hypoid gear (Figure 24.6)	Similar to spiral bevel gear, but teeth cut to accommodate shaft centerlines on different planes	For higher speeds and higher loads than straight bevel gear Quieter operation than straight bevel gear For high loads and quiet running Interaction of meshing gear teeth is strictly sliding
Worm gear (Figure 24.7)	Gear wheel turning at right angles to an offset worm (screw) gear	Tooth loads can be high, requiring gear oil with good EP performance Interaction of meshing gear teeth is strictly sliding Tooth loads can be kept low with proper gear tooth design

in Figures 24.1 through 24.7. The relative amount of sliding and rolling motion between interacting gears can be quite different between gear types. For example, worm gears interact by a predominantly sliding motion, whereas spur gears operate by a combination of rolling and sliding interactions. For straight gears, such as spur gears, only one tooth from each gear supports load at one time. Angled and curved gears are designed to allow more than one gear tooth on each gear to simultaneously support load, resulting in greater load-carrying capacity.

Because the amount of sliding and rolling action and the load-carrying capacity of the various gear types can vary significantly, their gear oil performance requirements can vary substantially. For example, lightly loaded spur gears require an oil with only rust and oxidation inhibitors, whereas heavily loaded hypoid gears require oils with high levels of EP additives. In the case of worm gears, their action is almost all sliding, the teeth are generally not heavily loaded, and the smaller worm gears may be made of bronze for better sliding wear resistance. For these types of gears, an oil compounded with a friction modifier, such as acidless tallow, may be sufficient.

The American Gear Manufacturers Association (AGMA) provides a series of gear oil specifications for industrial enclosed gear drives and industrial open gearing. The AGMA classifications provide for three types of oil in various viscosity grades. Oils are classified as those containing rust and oxidation inhibitors only, those that also contain EP additives, and those containing fatty material along with rust and oxidation inhibitors. The fatty material, such as acidless tallow, provides mild EP and friction reduction for predominantly sliding applications such as worm gears. The types of performance tests that appear in gear oil specifications are listed in Table 24.5.

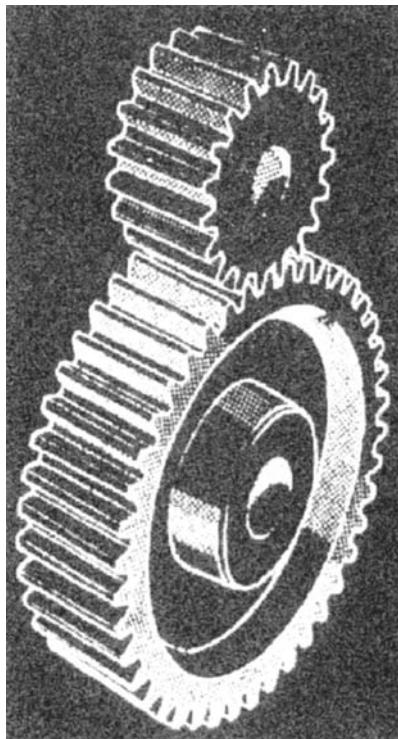


FIGURE 24.1 Spur gears. (Courtesy of Lubrizol Corp.)

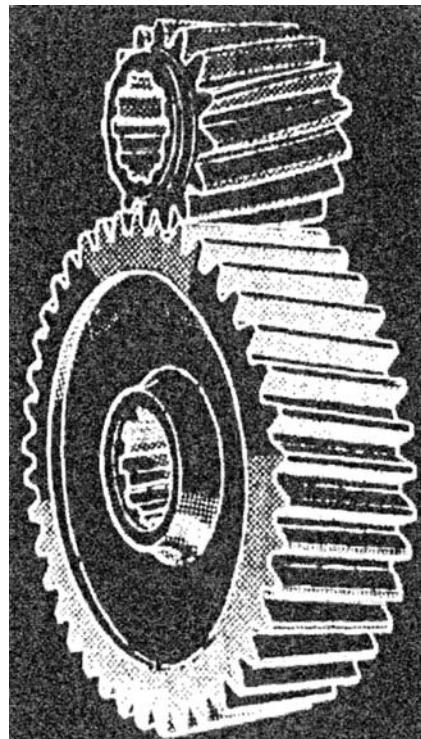


FIGURE 24.2 Helical gear. (Courtesy of Lubrizol Corp.)



FIGURE 24.3 Herringbone gears (double helical). (Courtesy of Lubrizol Corp.)

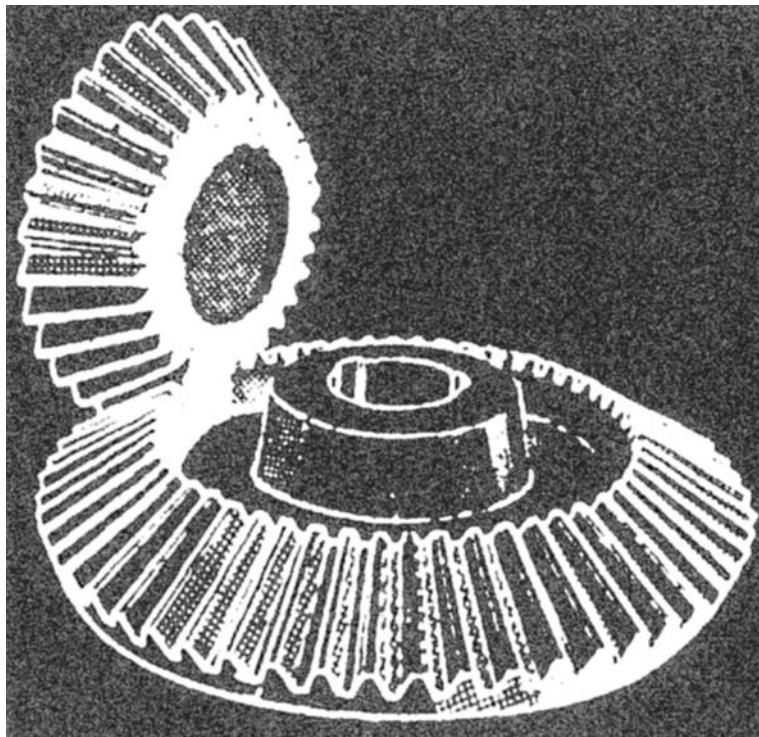


FIGURE 24.4 Straight bevel gears. (Courtesy of Lubrizol Corp.)

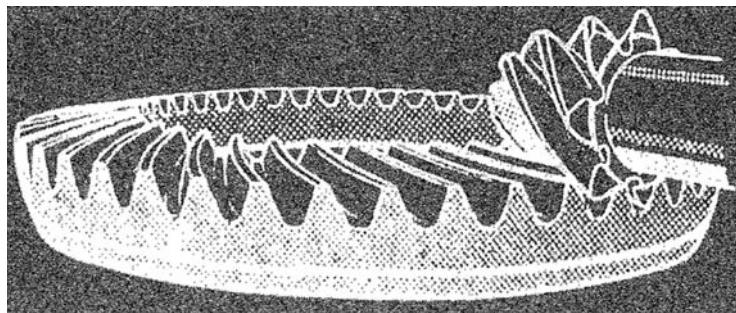


FIGURE 24.5 Spiral bevel gears. (Courtesy of Lubrizol Corp.)

24.4.2 ADDITIVES FOR GEAR OILS

The types of additives used in industrial gear oils are listed in Table 24.5.

Many of the types of additives used in hydraulic oils are also used in gear oils. Additives that differ from those used in hydraulic oils are discussed next.

24.4.2.1 Extreme-Pressure Additives

Organic sulfur and phosphorous compounds and inorganic borates are primary components in gear oil EP additives [33]. The roles of these various elements in gear oil packages have been studied and reviewed [34]. The phosphorus in sulfur/phosphorus EP additives yields low wear rates under normal operating conditions, whereas the sulfur prevents seizure under high loads. Modern gear

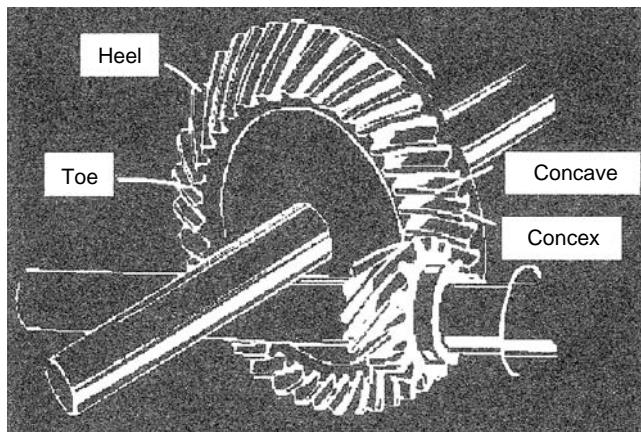


FIGURE 24.6 Hypoid gears. (Courtesy of Lubrizol Corp.)

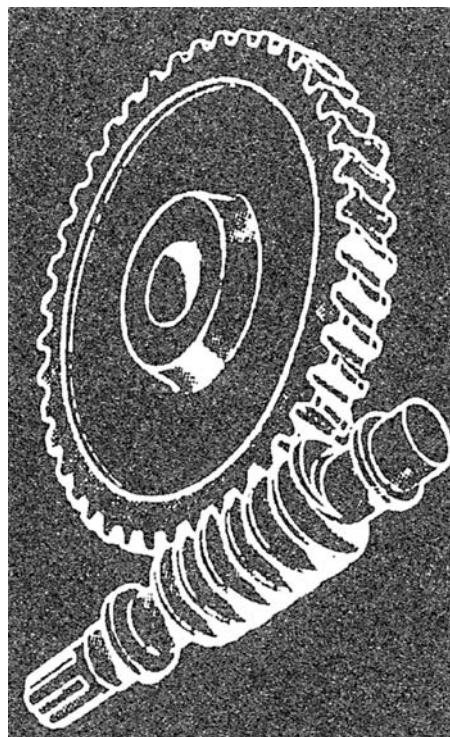


FIGURE 24.7 Worm gears. (Courtesy of Lubrizol Corp.)

oils often contain borates as well. Finely divided inorganic borates dispersed in gear oil can further enhance load-carrying capacities at high and low speeds, possibly by forming a chemically bound borate film on the iron surfaces [34].

Combinations of organic phosphorus- and chlorine-containing compounds have also been used as EP additives for gear oils. However, it is believed that low melt temperatures of iron chlorides is a limiting factor as well as the potential for organic chlorides to decompose in the presence of water and yield hydrochloric acid [34].

TABLE 24.5
Additives Used in Industrial Gear Oils

Additive Function	Types of Additives	Related Performance Tests
Antioxidant	Hindered phenols	ASTM D 6186, Standard test method for oxidation induction time of lubricating oils by pressure differential scanning calorimetry (PDSC)
	Diaryl amines	ASTM D 2893, Standard test method for oxidation characteristics of extreme pressure lubricating oils
	Phenothiazine	ASTM D 665, Standard test method for rust-preventing characteristics of inhibited mineral oil in presence of water
	Metal dialkylthiocarbamates	
	Ashless dialkylthiocarbamates	
	Metal dialkyl/dithiophosphates	
	Alkylsuccinic acid derivatives	
	Ethoxylated phenols	
	Fatty amines	
	Salts of fatty acids and amines	
Rust inhibitor	Salts of phosphate esters and amines	
	Metal sulfonates	
	Ammonium sulfonates	
	Substituted imidazolines	ASTM D 130, Standard test method for detection of copper corrosion from petroleum products by the copper strips tarnish test
	Benzotriazoles	
	2-Mercaptobenzothiazoles	
	Thiadiazoles	
	Toltriazole derivatives	
	Alkylphosphoric acid esters and salts	ASTM D 4172, Standard test method for wear preventive characteristics of lubricating fluid (four-ball method)
	Dialkylthiophosphates	
Metal deactivator	Metal dialkylthiocarbamates	
	Phosphate esters	
	Dithiophosphate esters	
	Derivatives of	
	2,5-dimercapto-1,3,4-thiadiazoles	
Antiwear additive	Molybdenum carboxylates	
		(continued)

TABLE 24.5 (Continued)

Additive Function	Types of Additives	Related Performance Tests
Soluble EP additive	Sulfurized esters [26] Sulfurized olefins [26]	ASTM D 5182, Standard test method for evaluating the scuffing load capacity of oils (FZG visual method)
	Diaryl disulfides [26]	ASTM D 2782, Standard test method for measurement of extreme-pressure properties of lubricating fluids (timken method)
	Dialkyldithiophosphate esters	ASTM D 2783, Standard test method for measurement of extreme-pressure properties of lubricating fluids (four-ball method)
	Lead naphthenate	
	Bismuth naphthenate [27]	
	Antimony dialkylidithiocarbonamate	
	Antimony dialkylidithiophosphate	
	Ammonium salts of phosphate esters	
	Chlorinated waxes	
	High-molecular-weight complex esters [28]	
Borate esters [29]		
Solid EP additive	Molybdenum disulfide	See the above test method for EP properties and wear preventive properties
Tackifier	Graphite	No ASTM standard test method
Demulsifiers	Polyisobutylenes	ASTM D 1401, Standard test method for water separability of petroleum oils and synthetic fluids
	Polyalkoxylated phenols	ASTM D 2711, Standard test method for demulsibility characteristics of lubricating oils
	Polyalkoxylated polyols	
	Polyalkoxylated polyamines	
	Acidless tallow	ASTM D 5183, Standard test method for determination of coefficient of friction of lubricants using the four-ball wear test machine
PPDs	Poly (alkylmethacrylates)	ASTM D 97, Standard test method for pour point of petroleum products
Foam inhibitors	Polydimethylsiloxanes	ASTM D 5949, Standard test method for pour point of petroleum products
	Poly(alkylmethacrylates)	ASTM D 822, Standard test method for foaming characteristics of lubricating oils
	Olefin copolymers	Severe shear tests are under development
	Styrene diene copolymers	
	Polyisobutylenes [30–32]	
Antimisting additives		ASTM D 3705, Standard test method for misting properties of lubricating fluids

24.4.2.2 Friction Modifiers

For applications involving primarily sliding contact, such as worm gears, friction modifiers such as acidless tallow may be used. In these applications, friction modifiers can be more effective than sulfur-containing EP additives, which might promote corrosion of bronze worm gears.

24.4.2.3 Viscosity Index Improvers

Because gear oils can be subjected to even greater mechanical shear than hydraulic oils, the polymers used in VI improvers in gear oils must possess exceptional shear stability. It is preferable to use low-molecular-weight VI improvers in gear oils as low-molecular-weight polymers display greater shear stability than high-molecular-weight polymers. The use of lower-molecular-weight VI improvers increases formulation costs as they must be used at higher percentages than high-molecular-weight VI improvers to achieve the same VI increase. Despite the higher costs associated with the use of lower-molecular-weight VI improvers, this approach is necessary to maintain gear oil viscosity grade and lubricating film thickness during operation.

24.4.2.4 Antimisting Additives

Mist lubrication is an effective means of lubricating gears and other elements; however, care must be taken to minimize stray mist, which could cause health problems for those working in the vicinity. Polymeric additives, such as polyisobutenes, can be used to promote coalescence of oil drops and reduce the formation of stray mist [30–32].

24.4.3 ADDITIVES FOR OPEN GEAR LUBRICANTS

For large, slow-moving gears that cannot practically be enclosed in oil-tight casings, an adhesive, high-viscosity material is required to stick to the gears. Such open gear lubricants are generally applied by spraying or brushing. In cold climates, a synthetic base oil may be required to provide a high-viscosity base fluid that can be sprayed at low temperatures [35,36]. Such lubricants generally contain the following core components:

1. High-viscosity base oil
2. Oil-soluble EP additives
3. Solid EP additives
4. Tackifier
5. Anticorrosion additive

24.4.4 ENVIRONMENTAL CONCERNs

In the past, gear oils have contained organic derivatives of lead for EP performance, and open gear lubricants have contained chlorinated solvents to improve pumpability. Over the last decade, environmental considerations have essentially resulted in the elimination of these components. Newer open gear lubricant formulations also tend to avoid the use of asphalt on the basis of environmental and performance considerations [35,36].

For applications in which industrial gear oils are used in environmentally sensitive areas such as forests and near waterways, biodegradable gear oils based on natural and synthetic esters have been developed [37].

24.4.5 FUTURE TRENDS

A failure phenomenon known as micropitting has surfaced as a problem in certain applications such as wind turbine gearboxes [38]. Although the failure mode is not completely understood, it is

believed to be related to the surface finish of the gears. Test methods have been developed to measure the ability of gear oils to protect against micropitting [39]. There is more to learn in terms of understanding micropitting and minimizing its occurrence.

As in the case of hydraulic pumps, gearbox efficiencies are improved to provide lower operating costs for the end users. This will result in higher gear speeds and loads and higher oil operating temperatures. The challenge for gear oil formulators will be to use base oils and additives that provide

1. Improved thermal stability and cleanliness
2. Improved high-temperature EP performance
3. Improved oxidation resistance
4. Extended demulsibility life
5. Lower friction
6. Improved foam resistance
7. Improved surface fatigue protection

24.5 ADDITIVES FOR COMPRESSOR OILS

24.5.1 PERFORMANCE REQUIREMENTS FOR COMPRESSOR OILS

It is difficult to generalize the lubrication requirements of compressors as requirements depend on a number of parameters such as the type of compressor, the properties of the gas being compressed, and designed discharge temperatures and pressures [40,41].

Compressors can be classified into two types, positive displacement and dynamic, depending on the process by which they compress gas. Compressors based on positive displacement trap the gas, reduce its volume, and then discharge the compressed gas. Dynamic compressors accelerate the gas and convert velocity to increased pressure. Positive-displacement compressors are useful for high-pressure applications with one limiting factor being the discharge gas temperature. Dynamic compressors are useful for high-volume, low-pressure applications.

Positive-displacement compressors can be further classified into reciprocating and rotary compressors. Reciprocating compressors utilize single- or double-acting pistons. Rotary types include rotary vane and rotary screw compressors.

Principal sites for lubrication in reciprocating compressors include the crankshaft and associated bearings, connecting rods, wrist pins, pistons, cylinders, piston rings, and valves. Rotary screw compressor lubrication sites include the rotors, bearings, and shaft seals. Rotary vane compressors require lubrication of bearings and shafts [41].

Dynamic centrifugal compressors require lubrication of bearings, gear reducers, and seals [41]. Critical lubrication requirements of the various types of compressors include the following:

1. Oxidation resistance
2. Thermal stability
3. Low carbon deposits at high temperatures (high-pressure reciprocating compressor)
4. Compatibility with gas being compressed
5. Viscosity retention (resistance to dilution by gas being compressed)
6. Antiwear properties (rotary vane)
7. Gas seal provided
8. General lubrication
9. Heat removal
10. Corrosion prevention
11. Compatibility with compressor components
12. Good demulsibility

13. General cleanliness
14. Low-foaming tendencies
15. Low flammability

24.5.2 COMPRESSOR OIL FORMULATION

High-pressure reciprocating compressors require that lubricants should be stable at high temperatures because discharge temperatures can range from 350 to 500°F. Lubricants for such reciprocating compressors must not generate heavy carbon deposits at hot valve areas as this increases the risk for fires and explosions. Consequently, lubricants for these applications are usually based on synthetic base oils with low carbon-forming tendencies such as diesters and polyol esters.

Although the requirements for compressor oils vary significantly depending on a number of parameters and a substantial portion of compressor oils are based on synthetic fluids, many formulations still rely on the types of additives listed in Tables 24.2 and 24.3 for turbine oils and hydraulic oils. Rotary vane compressors require lubricants that minimize vane wear and vane-sticking problems. In addition to the types of additives already mentioned for turbine and hydraulic oils, detergent additives may be used in some rotary vane compressor oils to help prevent deposit formation and vane sticking.

The formulations of compressor oils can vary significantly depending on the type of compressor and the type of gas being compressed. For example, mineral oils are generally not used for compressing natural gas because natural gas is soluble in mineral oil. Dilution of mineral oil-based compressor oil with natural gas would decrease the viscosity of the oil below an effective lubricating level. In this case, a polyglycol-based oil with limited solubility for natural gas is more suitable.

24.5.3 COMPRESSOR OIL TRENDS

Although mineral oil-based lubricants may be suitable for normal duty with nonreactive gases, a variety of synthetic-based lubricants are used for severe-duty, high-temperature, and high-pressure applications and for gases that are reactive with mineral oils. As a general trend, ester-based compressor lubricants are often used for reciprocating compressors in severe service duty due to their lower tendency to form carbon deposits that can lead to fires in reciprocating compressors. For rotary screw and rotary vane compressors, synthetic polyalphaolefins are growing in popularity due to their good thermal stability and lower cost relative to ester-based fluids. The formulation of compressors oils for severe service is so dependent on equipment design and the chemical nature of the gas being compressed that the compressor manufacturers generally designate the compressor oil formulations that are suitable for their equipment.

24.6 ADDITIVES FOR LUBRICATING GREASES

24.6.1 PERFORMANCE REQUIREMENTS FOR LUBRICATING GREASES

A lubricating grease consists of a lubricating oil, performance additives, and a thickener, which is a fine dispersion of an insoluble solid that is capable of forming a matrix that retains the oil in a semisolid state. Owing to their semisolid consistency, lubricating greases hold some advantages over lubricating oils. A grease is more easily sealed into a bearing than an oil; a grease does not require a circulating system; and in wet or dusty environments, a grease can act as a seal against contaminants. For these reasons, greases are often the preferred lubricant for ball and roller bearings in electric motors, household appliances, mobile equipment wheel and chassis lubrication, and some industrial plain and roller bearings.

Owing to the wide variety of applications in which a lubricating grease may be used, there are many different specifications for lubricating greases. Many multipurpose greases meet the LB-GC requirements of ASTM D 4950, Standard Classification and Specification for Automotive Service

Greases, which is a classification system that was developed by a cooperative effort of the ASTM, the NLGI, and the Society of Automotive Engineers (SAE). The ASTM D 4950 specification covers lubricating greases suitable for the periodic relubrication of chassis systems and wheel bearings of passenger cars, trucks, and other vehicles. In the ASTM D 4950 classification system, the letters LB signify service typical of lubrication of chassis components and universal joints in passenger cars, trucks, and other vehicles under mild to severe duty. The letters GC signify service typical of lubrication of wheel bearings operating in passenger cars, trucks, and other vehicles under mild to severe duty. It is possible to formulate lubricating greases that meet both the LB and GC specifications, and such greases may display the NLGI GC-LB certification mark [42].

Many military grease specifications have been written [2], and greases meeting particular military specifications have been designated for critical applications such as aviation applications. Additionally, many original equipment manufacturers, such as automobile manufacturers, issue specifications for greases that are specific for the equipment that they build.

The main ingredient that differentiates a grease from an oil is the grease thickener. Most grease thickeners are soaps composed of the reaction product of a fatty acid derivative and a metallic hydroxide. Other salts may be combined with the soap thickeners to impart higher grease dropping points (temperature at which the grease liquefies). Such greases are called *complex greases*. A smaller proportion of lubricating greases are manufactured with nonsoap thickeners such as organoclays or polyurea compounds. Some of the more common thickeners are as follows:

1. Lithium salt of hydrogenated castor oil fatty acid
2. Calcium stearate (hydrous)
3. Calcium stearate (anhydrous)
4. Lithium complex
5. Aluminum complex
6. Calcium complex
7. Organoclay
8. Polyurea
9. Silica

24.6.2 ADDITIVE

Performance additives for greases are similar to those used in lubricating oils; however, it is important that the grease additives also be compatible with the grease thickener. Lack of compatibility between an additive and a grease thickener could lead to disruption of the thickener matrix that holds the oil in a semisolid state. This would result in an uncontrolled softening or hardening of the grease or a decrease in the grease dropping point.

Various grease thickeners behave differently with respect to their compatibility with performance additives. Generally, lithium soap thickener is compatible with a much wider variety of grease additives than organoclay thickener. Consequently, an anticorrosion additive such as calcium sulfonate may perform quite well in a lithium soap-thickened grease, whereas it could cause significant softening of an organoclay-thickened grease. Therefore, performance additives must be carefully matched with the type of grease thickener.

The levels at which additives are used in lubricating greases are generally higher than in lubricating oils. Several factors can contribute to the need for higher additive addition rates in lubricating greases as compared with lubricating oils.

1. The grease thickener may compete with the performance additive for adsorption sites on the metal surfaces.
2. The grease thickener may adsorb additive so that less is available for performing the desired additive function.

3. Compared with lubrication by circulating oil, grease lubrication does not provide a mechanism for heat removal, and the reserve of lubricant is much less.

Another difference between lubricating oils and greases, in terms of additive use, is that lubricating greases can more readily utilize solid additives. Although attempts have been made to suspend various dispersions of solid additives in lubricating oils, such lubricants generally suffer from a tendency to separate or plug filters. However, the semisolid consistency of greases is such that they can easily keep fine solid lubricants, such as graphite and molybdenum disulfide, suspended indefinitely.

The types of additives used in greases are listed in Table 24.6 along with corresponding test methods used to evaluate the performance properties these additives impart to the grease. Some of the additives mentioned in Table 24.6 are used much less frequently than in the past with the increasing HSE concerns over the use of heavy metals, chlorinated compounds, and components that may react to give potential carcinogens. National Health Safety and Environment (HSE) regulations as well as equipment manufacturer requirements are making the selection and treat rate of additive components a challenging process. See Section 24.6.3 for more details.

24.6.2.1 Rust and Oxidation Inhibitors

Greases for lightly loaded and high-speed applications rely on elastohydrodynamic lubrication and generally require only rust and oxidation inhibitors and antiwear additives. The types of additives used to achieve these performance properties are similar to those used in lubricating oils (Table 24.6). As mentioned earlier, the additives may be used at higher percentages in lubricating grease than are typically used in lubricating oils.

Unlike oil formulators, grease formulators are not restricted to performance additives that give clear and bright solutions in oil. Even insoluble additives, such as sodium nitrite and sodium sebacate, have been used as rust inhibitors in greases. A drawback of solid additives is that they can contribute to higher noise levels in grease-lubricated bearings [51].

24.6.2.2 Antiwear and Extreme-Pressure Additives

For mobile equipment and industrial bearings in which heavier loads are involved and the oil film may not be sufficient to prevent metal-to-metal contact, EP and antiwear additives, such as those listed in Table 24.6, are used. These additives include most of the types used in EP gear oil formulations.

As indicated by the EP test methods listed in Table 24.6, there are several methods for measuring the EP properties of greases. These test methods differ in the way that they evaluate antiwear and EP performance, and, therefore, it is desirable to develop grease formulations that perform well in all these test methods when designing multipurpose industrial greases. This is usually accomplished by using more than one additive and taking advantage of synergistic effects between the additives [52]. It has been reported that the performance of some EP additives may be affected by the temperature at which they are added to the grease. For example, the Timken OK load (ASTM D 2509) of a lithium base grease appeared to increase from 35 to 55 lb when the temperature of addition of the sulfurized olefin EP additive was raised from 90 to 120°C [53].

Applications in which shock loading may occur, such as the bearings of large shovels and certain conveyor bearings, the rapid application of load could cause scoring of metal surfaces before soluble EP additives could react to form a sacrificial layer. Solid lubricants are used in such applications to provide a physical separation of metal surfaces during shock loading. Such lubricants are usually finely dispersed solids, which have the ability to form films on metal surfaces that decrease sliding friction. Various solid lubricants that have been used in lubricating greases are listed in Table 24.6. Perhaps, the two most commonly used solid lubricants in greases are graphite and molybdenum disulfide. Synergistic EP effects between these two solid lubricants have been exploited in greases and open gear lubricants for a number of years [54]. It has also been claimed that the EP/antiwear performance of graphite can be enhanced by the treatment of graphite with polar agents such as

TABLE 24.6
Additives Used in Lubricating Greases

Additive Function	Types of Additives	Related Performance Tests
Antioxidant	Hindered phenols	ASTM D 5483, Standard test method for oxidation induction time of lubricating greases by pressure differential scanning calorimetry
	Diaryl amines	ASTM D 942, Standard test method for oxidation stability of lubricating grease by the oxygen pressure vessel method
	Phenothiazine	
	Oligomers of trimethylidihydroquinoline	
	Metal dialkyldithiocarbamates	
	Ashless dialkyldithiocarbamates	
Rust inhibitor	Metal dialkyldithiophosphates	ASTM D 1743, Standard test method for corrosion preventive properties of lubricating greases
	Alkylsuccinic acid derivatives	ASTM D 5969, Standard test method for corrosion preventive properties of lubricating greases in the presence of dilute synthetic sea water environments
	Ethoxylated phenols	
	Nitrogen-containing heterocyclic compounds	
	Fatty amines	ASTM D 6138, Standard test method for determination of corrosion preventive properties of lubricating grease under dynamic wet conditions (Emcor test)
	Salts of fatty acids and amines	
Metal deactivator	Salts of phosphate esters and amines	
	Metal sulfonates [43,44]	
	Ammonium sulfonates	ASTM D 4048, Standard test method for detection of copper corrosion from lubricating greases
	Substituted imidazolines	
	Lead naphthenate	
	Bismuth naphthenate	
Anticorrosion	Sodium nitrite	
	Sodium sebacate	
	Disalicylideneepropanediamine	
	Derivatives of 2,5-dimercapto-1,3,4-thiadizole	
	Alkylphosphoric acid esters and salts	ASTM D 5707, Standard test method for measuring friction and wear properties of lubricating grease using a high-frequency, linear-oscillating (SRV) test machine
	Dialkyldithiocarbamates	ASTM D 2266, Standard test method for wear preventive characteristics of lubricating grease (four-ball method)
Anticavitation	Phosphate esters	
	Dithiophosphate esters	
	Derivatives of 2,5-dimercapto-1,3,4-thiadiazoles	
	Molybdenum carboxylates	
Antifriction		

Soluble EP additive	Sulfurized esters [26] Sulfurized olefins [26] Daryl disulfides [26] Organic sulfur/phosphorus compounds Lead naphthenate Bismuth naphthenate [27,45] Antimony dialkylthiocarbamate Antimony dialkylthiophosphate Ammonium salts of phosphate esters Chlorinated waxes High-molecular-weight complex esters Chlorinated waxes High-molecular-weight complex esters Borate esters [46]	ASTM D 5706, Standard test method for determining extreme properties of lubricating greases using a high-frequency, linear-oscillation (SRV) test machine ASTM D 2596, Standard test method for measurement of extreme pressure properties of lubricating grease (four-ball method) ASTM D 2509, Standard test method for measurement of load-carrying capacity of lubricating grease (timken method)
Solid EP additive	Metal borates Molybdenum disulfide [47] Perfluorinated polyolefins Graphite [48] Calcium carbonate Calcium phosphate Calcium acetate Boron nitride Boric acid Metal powders Phosphate glasses [49] Polyisobutylenes Atactic polypropylene Polyethylene Functionalized polyolefins [50] Alkylsuccinimides Polyisobutenes Styrene–butadiene block copolymers	See the above test methods for EP properties and friction and wear properties
Tackifier	No standard test method	
Polymers for water resistance	ASTM D 4049, Standard test method for determining the resistance of lubricating grease to water spray	

alkali molybdates and tungstates and alkali earth sulfates and phosphates. Treatment of graphite with these polar inorganic materials helps the graphite to adhere to metal surfaces more strongly, even in the absence of trace water, which is normally necessary for untreated graphite to adhere to metal, and act as a friction-reducing lubricant [55].

Specialized semifluid grease containing solid lubricants have been developed for the lubrication of open gears that cannot be lubricated by means of an oil reservoir [56]. These greases are required to produce a sturdy protective film on heavily loaded gears that may also be subjected to shock loading. The grease is usually applied at intervals through a spray nozzle and therefore must be readily pumpable and sprayable. In the past, pumpability has been achieved by the addition of a solvent such as 1,1,1-trichloroethane or a hydrocarbon solvent. More recently, solvent-free open gear greases have been developed using synthetic base oils to achieve low-temperature performance and pumpability [56]. Open gear greases generally contain combinations of soluble EP additives and solid lubricants to achieve high EP performance. These lubricants may also contain high levels of polymers to promote adhesion and water resistance. Open gear greases are usually gray to black in color due to the presence of graphite and molybdenum disulfide; however, light-colored open gear greases have been developed through the use of colorless solid lubricants such as phosphate glass [49]. With the increasing cost of raw materials, alternatives to molybdenum disulfide are used where technically suitable.

Thread compounds are another example of specialty greases that contain high levels of solid lubricants. These compounds are generally composed of grease combined with a very high level of metal powder and other solid lubricants. For example, API Bulletin 5A2 [57] describes a thread compound composed of 36 wt% grease, 30.5 wt% lead powder, 12.2 wt% zinc powder, 3.3 wt% copper powder, and 18 wt% natural graphite. Thread compounds may also be formulated with anti-corrosion additive to protect pipe threads during storage.

24.6.2.3 Polymers for Water Resistance

Mobile equipment is often used in applications in which grease-lubricated bearings may be subjected to water, as are bearings in certain industrial applications such as in steel and paper mills. It has been found that the addition of various polymers to lubricating greases improves their water resistance. Some of the types of polymers that have been used to impart water resistance to lubricating greases are listed in Table 24.6. Although most of these polymers improve water resistance by raising the grease base fluid viscosity, at least one functionalized polymer actually reacts with alkali during the formation of the soap thickener and becomes a part of the grease thickener matrix [58].

24.6.2.4 Grease Thickeners as Performance Additives

A recent development in the evolution of lubricating grease technology has been the use of solids that act both as grease thickeners and as performance additives. For example, a number of patents have been written concerning the preparation and use of calcium sulfonate complex greases in which calcium carbonate dispersed by calcium sulfonate acts as a thickener, an anticorrosion additive, and an EP additive [59,60]. Similar multifunctional claims have been made for greases thickened with specially designed titanium complex thickeners [61,62].

24.6.3 ENVIRONMENTAL CONCERNs

Environmental concerns and regulations have influenced modern grease formulations, and this trend will likely accelerate in the future. The disposal of lubricants that contain restricted substances is onerous and expensive. Therefore, there has been a shift away from additives that appear on restricted substance lists or that may appear on future restricted substance lists.

Examples of formulation changes instigated primarily by environmental concerns include the following:

1. Substitution of alternative EP and anticorrosion additives to replace lead naphthenates and lead dialkyldithiocarbamates.
2. Removal of heavy-metal powders from thread compounds [63–65].
3. Removal of chlorinated solvents from open gear lubricants and greases [56].
4. Substitution of alternative EP and antiwear additives to replace chlorinated paraffins [28,66].
5. Substitution of alternative anticorrosion additives to replace sodium nitrite.

Concern was raised in California over the possible toxicity of the solid lubricant molybdenum disulfide. This could have been a problem for the disposal of used grease containing molybdenum disulfide. However, after toxicological review, the California Department of Toxic Substances Control ruled that wastes containing molybdenum in the form of molybdenum disulfide are excluded from identification as hazardous waste [67].

With the increasingly global nature of the lubricant business, regulations such as those in the European Union covering Registration, Evaluation, and Authorisation of Chemicals (REACH) are affecting the lubricants and additive industries worldwide. The European Union's new chemical legislation came into effect on June 1, 2007. Although the details of its implementation are still to be finalized, it is likely to have a significant impact on suppliers, producers, and consumers of more than 30,000 chemicals.

Various original equipment manufacturers, such as automobile manufacturers, provide long lists of restricted substances that are not allowed in materials, such as lubricants, which they purchase. There is not much doubt that the list of restricted substances will grow in the future. Concerns about environmental persistence will likely increase the demand for biodegradable greases. Although the market for this type of grease is currently quite modest, the U.S. Army has written a specification for biodegradable multipurpose grease that should help to advance the technology [68]. Such greases usually contain natural or synthetic ester base oils that are biodegradable and additives of low toxicity that, if not readily biodegradable themselves, at least do not impede the ability of microorganisms to ultimately biodegrade organic portions of the grease to carbon dioxide, water, and biomass. Studies have been performed to determine the effectiveness of various grease additives in these types of base greases [69,70].

24.6.4 LUBRICATING GREASE TRENDS

As in the case of other industrial lubricants, the trend for lubricating greases is to develop products with improved high-temperature performance leading to longer bearing lives. Grease formulators are also searching for anticorrosion additives that provide better protection against saltwater corrosion and that do not significantly affect the performance of the grease thickener [44].

Because interaction of grease additives and grease thickener must be considered for the development of optimum grease formulations, it follows that the importance of various grease additives may change as the popularity of the various grease thickeners changes. Although the versatility of lithium soap and lithium complex greases causes them to be the most widely used grease types, polyurea greases are growing in popularity as they tend to give significantly longer bearing lives in certain sealed bearing applications. It is expected that the popularity of polyurea- and diurea-thickened greases will continue to grow, and, as they do, more emphasis will be placed on developing additives that perform optimally with these types of thickeners.

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25 Long-Term Additive Trends in Aerospace Applications

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25.1 UNIQUE REQUIREMENTS FOR AEROSPACE APPLICATIONS

Aerospace, especially military aerospace systems, requires faster, highly maneuverable, and higher-temperature systems. The higher temperatures typically experienced in aerospace applications are common for all lubricants, but we use hydraulic fluids as an example. The high temperatures experienced in aerospace hydraulic systems are the result of three related factors. First, for military aircraft, the operational requirements for the aircraft (e.g., high speed and high degree of maneuverability) impose more severe demands on the hydraulic systems. Second, weight is always a critical issue for aircraft that drives hydraulic system components that are small and operate under more strenuous conditions (e.g., higher speed and higher loads) and that impose more severe operating conditions on the hydraulic fluid (e.g., higher temperatures and higher shear rates). Third, the high emphasis on weight savings for aircraft applications results in smaller fluid volume systems. All these factors result in higher temperatures being imposed on the hydraulic fluids. Although high maneuverability is usually not an issue for commercial aerospace applications, the other two factors are equally important for commercial as well as military applications. In addition to the higher temperatures imposed on aerospace hydraulic fluids, they must also be capable of operating at extremely low temperatures. Aircraft hydraulic and lubrication systems are required to operate at temperatures as low as -54°C . Typical operational temperature ranges for the hydraulic fluids used in aerospace are shown in Figure 25.1. Similar factors make unique demands on other aerospace lubricants such as gas turbine engine oils and greases. Aerospace applications include both spacecraft and aircraft applications. The major emphasis of this chapter is aircraft applications. Hydraulic fluids and gas turbine engine oils are discussed in this chapter because they represent the larger volume usage, but similar factors and issues exist for the other aerospace lubricants and fluids such as greases and coolants. Liquid and grease lubricants for space applications are also discussed because the space environment creates some unique and challenging problems for lubricant additives. Often, the customary additives are not adequate for aerospace applications, and more development is needed to make acceptable aerospace lubricants [1–8].

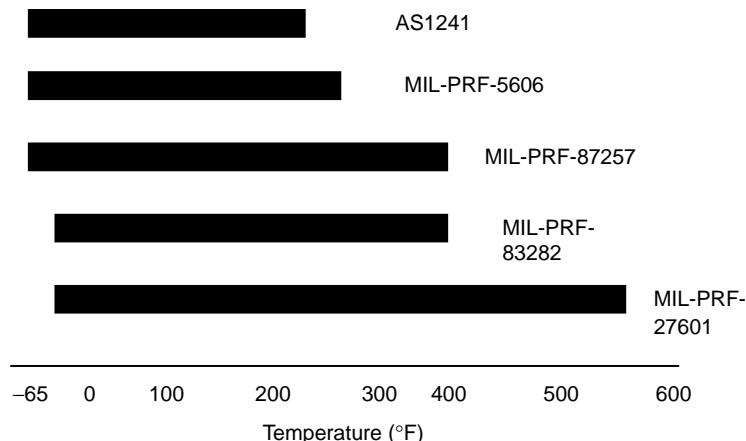


FIGURE 25.1 Temperature ranges for aerospace hydraulic fluids.

25.2 WHY ARE ADDITIVES NEEDED?

Additives are required for aerospace fluids and lubricants to enhance or impart a required operational capability to a specific fluid or lubricant not provided by the base fluid alone. When a lubricant (lubricating oil, hydraulic fluid, grease, etc.) is stressed in its operating environment, it can degrade such that the performance of the system or components in which it is used is adversely affected. To enhance the performance of a lubricant or to mitigate its degradation during use, additives are required. Some of the additive types used in aerospace applications are listed in Table 25.1. Depending on the application, a formulation may contain one or more of these and other additives:

1. Boundary lubrication additives (antiwear, lubricity, extreme pressure)
2. Antioxidants
3. Anticorrosion additives
4. Metal deactivators
5. Viscosity index (VI) improvers

A lubricant has to be effective in both the fluid-film lubrication and the boundary lubrication regimes. In fluid-film lubrication, a fluid film separates the interacting surfaces, whereas in boundary lubrication, more direct contact occurs between the two surfaces. Fluid-film lubrication can be further divided into two broad categories—hydrodynamic lubrication and elastohydrodynamic lubrication. In fluid-film lubrication, the physical properties of the lubricant such as viscosity, pressure viscosity, and traction determine the performance of the lubricated contact. Although fluid-film lubrication is the desired mode of operation, the boundary lubrication regime cannot be avoided. Even in fluid-film lubrication, boundary lubrication occurs during the start-up and shutdown and occasional asperity interaction during operation. Therefore, the material (both the surface and the lubricant) properties important for the boundary lubrication regime are equally important for the fluid-film lubrication. Boundary lubrication additives are generally needed for reducing friction and wear of the components [9].

Antioxidants are required to prolong the useful life of fluids and lubricants. Most fluids and lubricants are hydrocarbon-based and are susceptible to oxidative degradation through a free-radical mechanism. Antioxidants react with the initially produced free radicals to prevent the oxidation process from proceeding from the slow initiation phase of the process to the rapid autocatalytic phase.

Corrosion inhibitors are usually synonymous with rust inhibitors for most lubricants. However, as we go to more exotic metals and with the emergence of halogenated lubricants, corrosion

TABLE 25.1
Typical Additives Used in Aerospace Fluids and Lubricants

Fluid	Gas Turbine Engine Oil	Hydraulic Fluid		Space Lubricant	
		Hydrocarbon	Phosphate Ester	Hydrocarbon	PFPAE
Additive antioxidant	Aromatic amines, for example, PANA ^a	Hindered phenol	Proprietary	Hindered phenol	Experimental
Lubricity/antiwear	Aryl phosphate	Aryl phosphate	Proprietary	Aryl phosphate	Experimental
Viscosity Index	N/A	Polymethyl Methacrylate	Proprietary	N/A	
Rust Inhibitor	Metal sulfonate or metal Organic acid	Sulfonate	Proprietary	N/A	NaNO ₂ ^b
Antifoam	Silicone	Silicone	Proprietary	N/A	N/A
Metal deactivator	Benzotriazole	Benzotriazole	Proprietary	N/A	N/A

^a Phenylalphanaphthylamine.

^b Greases only.

Note: N/A, not typically used for this application.

can occur with nonferrous metals and by attack of very aggressive fluid degradation products. For example, degradation products from perfluorinated polyalkylethers react with various metals to cause what one could call corrosion [10,11]. A better definition of corrosion inhibitors would be additives that inhibit the reaction of moisture or fluid degradation products with metals. They are widely used for that function in many classes of fluids and lubricants.

Metal deactivators are additives that passivate the surface of metals. The passivation can result in either reducing the metal's catalytic effect on lubricant degradation or reducing the effect of the lubricant on the surface of the metal. They are widely used in hydraulic fluids and lubricants.

VI improving additives are discussed in Section 25.5.

25.3 HOW ADDITIVES WORK

In general, certain performance-improving additives are optimized for specific base oils, but in some instances, the same additive can be effective in various classes of base fluids. However, in some cases, additives that have been effective at improving a specific property or performance parameter in one or several classes of base fluids are not effective in others. For example, substituted aryl phosphates have been very effective antiwear additives for steel-on-steel rubbing contacts in a large number of chemical base stocks, for example, mineral oils, synthetic hydrocarbons, esters, and even more exotic base fluids such as the polyphenyl ethers and the silahydrocarbons. They are not effective additives, however, for steel-on-steel contacts in polydimethyl siloxanes or chlorotrifluoroethylene lubricants. The reason for specificity of some additives is beyond the scope of this chapter, but it is important to recognize this phenomenon as we consider future trends for additive applications. As we attempt to develop advanced lubricants using new and novel base oils, we must recognize that new additive technology may be required. How different additives enhance the performance of a lubricant is discussed throughout the rest of the chapter.

In boundary lubrication, the interacting surfaces react with the lubricant components to form protective physisorbed, chemisorbed, or reaction films [12]. When metal-to-metal contact occurs between two surfaces in a lubricated contact, the asperities on the surfaces shear, thereby exposing a fresh metal surface. The appropriate lubricant component reacts with the exposed fresh metal to form protective surface films. The surface films thus formed are generally low-friction and wear-resistant and protect the surfaces from early failure/wear. During operation, these surface films

can wear off and regenerate. Antiwear or lubricity additives are generally added to the base oil to enhance the formation of the protective surface films during boundary lubrication. Thus, in boundary lubrication, the chemistry of the lubricant along with the material properties of the interacting surfaces determines the performance of the lubricated contact.

Many researchers have expended significant effort at determining the detailed mechanism by which specific additives work. In some cases, for example, the free-radical interceptor mechanism of most effective antioxidants, the mechanisms have been intensively studied, worked out, and generally well understood [13]. In other cases, however, although extensive research has been conducted, for example, the mechanism of action of tricresyl phosphate, there are a number of theories, many of which are supported by chemical data, but no one theory is universally accepted.

When one reviews the published data and, in the case of many researchers, their unpublished data, a few common facts can be found for many types of performance-improving additives. First, most additives appear to be effective through a *competitive reaction* mechanism. In other words, the additive is reacting with some undesirable species that occurs in the lubrication system that, if unchecked, will lead to premature failure of the lubricant or component. In the case of an antioxidant in a hydrocarbon lubricant, the additive is reacting with the initial free radicals formed early in the oxidation process to retard or prevent their attack on the lubricant molecules in an autocatalytic process that results in rapid deterioration of the lubricant. In the case of the antiwear additives in hydrocarbon lubricants, the additive reacts with the newly formed high-energy, fresh metal surfaces formed by metal-to-metal contact, thereby passivating these surfaces by forming, in most cases, lubricious reaction products that prevent the catastrophic wear of the component. The chemistry of that reaction product will vary depending on the chemistry of the additive and the surface. The mechanism of wear protection, however, may vary with lubricants and surfaces of different chemistries, especially as discussed per perfluoropolyalkylethers (PFPAEs) in 25.4.

Another common factor with many is that the additives are generally unreactive and stable during the *normal* functioning of the lubricant and only become effective and reactive on demand. For example, antioxidants in hydrocarbons become effective and reactive only when free radicals are formed in the lubricant due to oxidation of the lubricant molecules. Similarly, effective antiwear additives in hydrocarbon lubricants generally do not react until the fresh metal surfaces are formed. Whether this reaction is induced by the reactivity of the fresh metal surface or the momentary high temperatures that occur during the metal-to-metal contact is an issue still under debate, but it is generally accepted that the additive, until this reactivity is triggered by a specific event, is inactive and stable. Something occurs to lower the activation energy and allows the additive to be effective.

Other additives are less affected by *events* that trigger their action. For example, VI improvers [14] and rust inhibitors are generally effective during the entire life of the lubricants and do not require some specific (unusual) event to trigger their actions. But as we consider future additive requirements for future classes of base fluids and surfaces requiring lubrication, new additive technology must be developed.

An additive may work by more than one mechanism. For example, many metal-alkylated sulfonate rust inhibitors form a physical barrier on metal surfaces. The polar portions of the molecules are adsorbed on the metal, effectively blocking water from the corrosion-prone surfaces [8]. The molecules also form micelles or groups of molecules loosely in rings with their polar portions toward the center. These act as little water traps to surround and tie up water molecules and, again, to prevent them from getting to the metal surfaces.

25.4 ADDITIVES FOR SPACE APPLICATIONS

Lubricants for outer space applications are particularly challenging. First, the volume of space lubricants used is so small that major oil companies have little interest in investing in research, development, and commercialization, even if the lubricants command a high price. Fortunately, several companies deal with specialty lubricants and are willing to supply to this niche market.

The most important additive for a space lubricant is an antiwear additive [7]. Spacecraft mechanisms generally operate on a very small quantity of lubricant. With lubricant depletion due primarily to evaporation or lubricant creep, the lubricated components experience a higher degree of boundary lubrication. Effective antiwear additives are required for prolonged life of these components. As a general rule, perfluoropolyalkylether (PFPAE) lubricants are not used in applications where the bearing contact stress is >100,000 psi because they may undergo tribocorrosion-induced failure. An antioxidant is often used to protect a spacecraft hydrocarbon oil and its antiwear additive for the time the formulation is on Earth, waiting for launch, but is not essential in space, where little oxygen is available.

The major technical challenges for spacecraft lubricant additives are low volatility and good solubility. Spacecraft lubricants were originally mineral oils/greases, but these are gradually being replaced with synthetics including hydrocarbon polyalphaolefins (PAOs) and multialkylated cyclopentane (MAC; Pennzane[®]) and PFPAEs. Even lower volatility and improved low-temperature viscosity silahydrocarbon fluids are in development for spacecraft [15]. Soluble and effective additives are readily available for terrestrial hydrocarbon oils and, with some looking, commercially available low-volatility additives may also be found. In greases, solubility is less important, but it is generally believed that at least partially soluble additives are advantageous in grease performance over nonsoluble additives.

For many years, there were no soluble additives for PFPAE lubricants. Conventional additives are not soluble in PFPAE fluids. Solubilizing substituents, similar to the backbone structure of PFPAE fluids, are required in the additive structure to make it soluble in PFPAE fluids. However, PFPAE manufacturers have recently offered soluble additives for their fluids. These additives are made for use in the manufacturers' own product lines and are not available for purchase to use in formulations in products produced by other companies. The U.S. Air Force has conducted research and development of soluble additives for PFPAE fluids as part of a high-performance turbine program [16]. Additives are needed for PFPAE fluids because of their unique behavior especially in boundary lubrication in low-humidity environments [17]. A phenomenon called *tribocorrosion* can occur, which is a combination of fluid decomposition and wear metal corrosion. This happens at much lower temperatures than are predicted by static, nonwear stability tests. The additives act to interrupt the cycle of fluid decomposition and metal interaction, thereby minimizing the tribocorrosion and improving wear performance [18].

Besides antiwear additives, antirust additives are needed to prevent steel components from rusting when used with PFPAE fluids or greases. Conventional hydrocarbon lubricants tend to leave a protective film on the surface of steels, whereas PFPAE fluids do not, thus leaving low-chrome steel components prone to rusting after use with a PFPAE fluid. This is due to the high solubility of oxygen into the PFPAE fluids, which allows oxygen to get to the iron surfaces, leading to rust.

Several important new classes of additives were developed in the Air Force program [16], most notably a perfluoroalkyldiphenylether (DPE), a perfluoroalkyltriphenylether (TPE), and a tri(perfluoropolyalkyletherphenyl)phosphine (PH3) [19]. These provide improved antiwear and high-temperature stability to the PFPAE fluids by interacting with and neutralizing fluid decomposition products that, without the additives, attack metal surfaces and cause an autocatalytic decomposition of the fluid.

As the molecular weight of any lubricant increases, the solubility for polar additives decreases. This is especially true for the very nonpolar PAOs. Long-chain alkyl groups on the additives improve additive solubility but often reduce effectiveness. Additives, in general, are polar compounds, which is what makes them effective. All of this makes for a very short list of effective, soluble, and low-volatility additives for spacecraft.

The spacecraft lubricant additives do not need to be especially thermally stable as the spacecraft mechanisms do not operate at high temperatures. They may, however, operate at extreme cold temperatures, and the additives must stay in solution in oils.

Test methods for spacecraft lubricants are not well standardized and often are peculiar to a particular satellite company. Because there are few second chances in spacecraft lubricants once

in operation, usually a “life test” is conducted for years on Earth under high vacuum to simulate actual operation.

25.5 ADDITIVES FOR HYDRAULIC FLUIDS

Hydraulic fluids are operated in closed systems, although the fluid reservoir may be open to air. Hydraulic fluid additives may include antioxidant, antiwear, rubber swell, VI improver, and minor amounts of metal deactivator and dye. (This is a simpler list than that of engine oil, where thermal-oxidative stability is critical.) The application temperature often dictates the additives used. Hydraulic fluids for military applications are defined by the military specifications including MIL-PRF-5606H [20] (mineral oil-based fluid), MIL-PRF-83282D [21], and MIL-PRF-87257 [22] (both synthetic hydrogenated PAO-based fluids). Hydraulic fluids for commercial aircraft, which are phosphate ester based, are defined by SAE AS 1241 [23].

Antioxidants are usually ashless (containing no metals) and are believed to serve primarily to protect the fluid in storage rather than in an application. A test such as ASTM D4636, corrosiveness and oxidation stability to aircraft turbine engine lubricants, and other highly refined oils is often used to evaluate the antioxidant effectiveness.

Arylphosphate antiwear additives in hydraulic fluids are widely used and are very effective for steel-on-steel rubbing surfaces. The ASTM D4172, wear preventive characteristics of lubricating fluids (four-ball wear method), is widely used to evaluate antiwear additives, but other methods are also used.

Rubber swell additives are used with synthetics such as PAOs that, by themselves, provide little swell or even shrinkage to nitrile seals, the most widely used seal material in military aircraft. Nitrile seals were originally developed to swell an appropriate volume with naphthenic mineral oil. When synthetic PAOs were introduced, they had to be adjusted to be a drain-and-fill replacement for mineral oils, so rubber swell additives were added to the synthetic formulations. Rubber swell additives are usually polar esters actually adsorbed into the elastomeric compounds, creating a positive seal to the hydraulic system. Seal tests may include swell per FED-STD-791 method 3603 and other physical property determinations.

VI improvers are used mainly with naphthenic mineral and phosphate ester oils to increase the VI (lower the amount of change in viscosity with temperature). They are long-chain polymers such as polymethylmethacrylates, but other chemical classes are also used. In theory, they are coiled at low temperature and strung out at higher temperature and therefore impede flow less at lower temperatures but more at higher temperatures. The VI improvers do impede flow in bulk, such as past seals, and provide additional fluid-film thickness in low-shear environments, but do little to improve the fluid-film thickness in the elastohydrodynamic regime in bearings [14]. VI improvers are broken into smaller pieces in high-shear and high-stress environments, present in both elastohydrodynamic and boundary lubrication regimes, and therefore become less effective. A shear stability test, for example, as in the MIL-PRF-5606 hydraulic fluid specification [20], is used to determine a formulation’s resistance to shear under a specific set of conditions, but this test does not duplicate the severity of real lubricated contacts.

A minor amount (0.05%) of metal deactivator is needed with PAO-based hydraulic fluids for them to pass all the metal weight changes in ASTM D4636. A small amount of dye is used in hydraulic fluids for leak detection. Hydrocarbon hydraulic fluids are usually dyed red, whereas phosphate ester hydraulic fluids are dyed purple.

25.6 ADDITIVES FOR GAS TURBINE ENGINE OILS

Aircraft engine oils must have a critical balance of performance-improving additives, especially if used at high temperatures. Engine oils are often sprayed onto hot bearings with considerable airflow

present to help cool the bearing. This gives rise to hot spots and thin oil films with lots of contact with oxygen. Coking of the fluid and additives, when they oxidize and turn to carbonaceous deposits, is detrimental to the cooling efficiency of the engine. Also, coke can clog the breathing and oil delivery tubes in an engine.

Engine oils are oxidatively very stable polyol ester-based with one or more antioxidant, and antiwear, antifoam, and metal deactivator additives. All the additives must have a low propensity to form coke. Often the optimized oil represents a compromise between low cooking and optimum performance as provided by specific additives. For example, different aryl phosphate antiwear additives exhibit various degrees of effectiveness, and it may not be possible to select the best antiwear additive because its presence in the oil causes too much coke formation. As a rule, the coking tendencies of formulations are greater with more effective aryl phosphates and with higher percentages of additive.

An antifoam additive, a specific molecular-weight-range dimethyl silicone, may be used. The following tests are generally used to evaluate the effectiveness of the additives:

1. Oxidative stability: ASTM D4636
2. Antiwear performance: ASTM D1947, Ryder Gear Test and Modified ASTM D5182, FZG Test
3. Anticoking performance: Fed-Std 791, Method 3450, Bearing Deposition
4. Foaming: Fed-Std 791, Method 3213, Foaming Characteristics of Aircraft Turbine Engine Oils (Static Foam Test)

In addition to these tests, each new engine oil qualified to a military specification must pass an actual engine test as described in the specifications.

25.7 FUTURE TRENDS

Three major factors will drive the need for new additive research and development for aerospace applications. The first, which has been discussed in detail in Section 25.1, is the need for additives effective over a wide temperature range, from as low as -54°C to $>300^{\circ}\text{C}$. The second has already been discussed to some extent, and that is the new class of the base oils developed to meet new, more demanding requirements. The class discussed earlier, the PFPAEs, sometimes called perfluoroethers or perfluoropolyethers, is one of the examples. Another class that demonstrated unique requirements is the chlorofluorocarbon oligomers that served as the base fluid for a -54 to 175°C nonflammable aerospace hydraulic fluid. Although most additives typically used in hydrocarbon-based lubricants are quite soluble in the chlorofluorocarbon base stock, most of them have no beneficial effect. The successful development of an effective formulation using that unique base fluid required years of research. The final formulation that met the Military Specification MIL-H-53119 [24] utilized a carefully balanced additive package composed of a lubricity additive and a rust-inhibiting additive. Although these are two new and unique base fluids with which the authors have firsthand experience, other new base stocks could be developed for future applications that also require new additive research and development.

The third factor that will prompt the development of new performance-improving additives for future lubricating systems is the change in the chemistry of the surfaces with which the lubricants will come into contact and be expected to lubricate and provide long life. The main type of additive influenced by this factor is the lubricity additive. Two examples are new metal alloys and surface modifications such as hard coatings. In both the cases, the metal atoms, which in the past have been available to interact with the additive, are not available or are not readily available.

The chemical reactions that activate the additive are halted. However, the surface modifications may provide a barrier for any undesirable interaction between the lubricant and the substrate

material. New bearing materials such as Cronidur-30[®], Rex20[®] (CRU20[®]), and CCS42L[®] [25] have been developed that are more corrosion resistant and harder than the traditional tool—steel bearing materials such as M50 and 52100. Higher hardness of these new bearing materials gives them higher load-carrying capability. For high-speed precision bearings, hybrid bearings, utilizing the lower-density silicon nitride rolling elements, are gaining popularity.

The lack of reactivity of these materials with the environment (including the lubricant/additive system) that makes them effective at corrosion resistance also inhibits the formation of the beneficial surface films for enhanced boundary lubrication performance. The state-of-the-art boundary additives such as tricresylphosphate are not optimized for the newer chemical composition bearing steels. To completely realize the benefits of the new corrosion-resistant/harder bearing steels, new additives are currently being developed under U.S. Air Force sponsorship through a program involving oil companies, engine companies, and contractors. Similar additive development will be required for optimized performance of bearings utilizing hard coatings on the balls and races. These hard, wear-resistant coatings such as titanium carbonitride (TiCN)- [26] and titanium carbide (TiC)-coated balls have been shown to extend the lifetime of bearings in critical applications, but in most cases, they have been used either with no liquid-grease lubricant or with lubricants optimized for steel-to-steel contacts. Again, the chemistry of the lubricity additives was optimized to react with fresh steel (iron) asperities caused by contact in boundary lubrications. With the changed chemistry of the surface of the bearing material from iron-based alloys to a hard coating, the typical lubricity additives may not effectively provide the significant increase in lifetime as is typically experienced with the steel bearings. In many cases, improved lifetimes are experienced with hybrid bearings that incorporate a coated or ceramic ball and a standard steel race. However, with a fully ceramic bearing or one that uses coated surfaces on both the ball and the race, the maximum enhancement in performance cannot be experienced unless new additives are developed. These new additives will beneficially interact with these new bearing surfaces to produce the lubricious coatings that are believed to be the main mechanism resulting in the currently experienced wear improvement in steel bearings with the state-of-the-art lubricity additives.

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26 Eco Requirements for Lubricant Additives

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26.1 BIOLUBRICANTS

Amidst increasing public awareness, the Intergovernmental Panel on Climate Change (IPCC) has recently finalized its Fourth Assessment Report “Climate Change 2007.” The report states that it is *very likely* that human activities are the main cause of global warming in the past 50 years. One reason for this is that global greenhouse gas (GHG) emissions have grown since preindustrial times, with an increase of 70% between 1970 and 2004 [1].

Tribology by nature can play an important role in the reduction of greenhouse gas emissions. The use of a suitable lubricant to reduce friction and prevent wear decreases the necessary energy consumption and therefore has a direct impact on greenhouse gas emissions. In this sense, every lubricant could be considered as *environmentally friendly* or as a *biolubricant*. This signifies how

difficult it is to define the term *biolubricant* and is the only reason why there is not a single, generally accepted definition by the industry or by legislation. Biolubricants therefore tend to be characterized by *soft* descriptions such as environmentally friendly, environmentally acceptable, environmentally suitable, or more concrete claims such as possessing a high degree of biodegradability, produced from renewable sources, and having a reasonable ecological and toxicological profile.

The use of biodegradable and ecologically acceptable lubricants has traditionally been more prevalent in industries such as agriculture, forestry, water treatment, and water management and in areas of environmental interest such as national parks, tourist areas, and waterways.

In regard to the greenhouse gas emissions, renewability of a lubricant is an important factor. Making a lubricant from biologically produced carbon-containing materials rather than using mineral oils enables to reduce the amount of new carbon released into the atmosphere. For this reason, the use of *biobased* lubricants has a positive impact on the environment.

Våg et al. [2] undertook a comparative life cycle assessment study into base oils used in the manufacture of hydraulic fluids and calculated that the energy consumption per functional unit during the production of a mineral oil-based fluid (45,000 MJ) is greater than that for a synthetic ester (22,000 MJ).

The use of biobased material is also recommended to conserve the limited resources of mineral oil. To quantify the term *biobased*, methods such as ASTM D 6866-4 [3] using radiocarbon and isotope ratio mass spectrometry analysis to determine the biobased content are used.

However, the greenhouse gas balance might not be the most important impact of a lubricant for the environment. According to literature reports, at present ~50% of all lubricants sold worldwide end up into the environment through total loss applications, spills, volatility, or various other ways [4]. Estimates for the loss of hydraulic fluids are as high as 70–80% [5,6]. These lubricants can contaminate the soil, the surface- and groundwater, as well as the air. To protect the environment against the pollution by lubricants, the best approach would be, of course, first to prevent the loss of the lubricant. If this is not possible, *environmentally acceptable* fluids have to be used. *Environmentally acceptable* or *environmentally friendly* lubricants are described as those that are rapidly biodegradable, have a low ecotoxicity, and do not harm water. Of course, these fluids could also be biobased, but this is not mandatory—in principle, some products derived from petrochemicals could achieve the aforementioned environmental criteria.

The situation is made even more complex by the fact that terms such as *being biodegradable* are not described by one single definition. Biodegradation can be measured in a number of ways and is usually undertaken indirectly by the measurement of the amount of oxygen consumed or the amount of carbon dioxide produced by microorganisms. Typically, tests according to the Organisation for Economic Co-operation and Development (OECD) are used, such as the following:

301: Ready Biodegradability

- A: Dissolved Organic Carbon (DOC) Die-Away Test
- B: CO₂ Evolution Test
- C: Modified Ministry of International Trade and Industry (MITI), Japan Test (I)
- D: Closed Bottle Test
- E: Modified OECD Screening Test
- F: Manometric Respirometry Test

302A: Inherent Biodegradability: Modified Semi-continuous Activated Sludge (SCAS) Test

302B: Inherent Biodegradability: Zahn-Wellens/Eidgenössische Materialprüfungs-und Versuchsanstalt für Industrie, Bauwesen und Gewerbe (EMPA) Test

302C: Inherent Biodegradability: Modified MITI Test (II)

303: Simulation Test—Aerobic Sewage Treatment

- A: Activated
- B: Biofilms

304A: Inherent Biodegradability in Soil

- 305: Bioconcentration: Flow-through Fish Test
- 306: Biodegradability in Seawater
- 307: Aerobic and Anaerobic Transformation in Soil
- 308: Aerobic and Anaerobic Transformation in Aquatic Sediment Systems
- 309: Aerobic Mineralization in Surface Water—Simulation Biodegradation Test
- 310: Ready Biodegradability—CO₂ in Sealed Vessels (Headspace Test)
- 311: Anaerobic Biodegradation of Organic Compounds in Digested Sludge—Method by Measurement of Gas Production
- 312: Leaching in Soil Columns [7]

The determination of the ecotoxicity is normally based on the extrapolation of results obtained for aquatic organisms (algae, daphnia, and fish) using defined assessment factors. Such an evaluation results in a concentration limit. A tested substance is then believed to have no negative impact on an ecosystem, as long as the concentration of the substance is below the set limit. Additionally, in some countries such as Germany, the so-called water hazard classes exist [8]. According to their potential for being hazardous to waters, substances are classified into three different categories: from class 1 (water hazardous class, WGK 1 = slightly hazardous to water) to class 3 (WGK 3 = severely hazardous to water) [9].

With different definitions applicable for a biolubricant, it is important to clarify the exact requirements and specifications to be met before starting to formulate such a fluid. A good biolubricant must not only comply with the environmental requirements but also has to meet necessary technical requirements for the intended application. Ideally, a biolubricant should have at least the same technical performance compared with a mineral oil-based fluid and should meet all relevant original equipment manufacturer (OEM) specifications and national and international norms.

26.2 DRIVERS FOR THE USE OF BIOLUBRICANTS

For many years, the raw materials for biolubricants have been relatively expensive compared with mineral-based fluids. Moreover, the first generation of biolubricants was found to be deficient in performance and acquired a poor reputation among end users. As cost and performance have been, and still are, the major market drivers for lubricants, the success of biolubricants in the market was retarded. On the contrary, many politically motivated initiatives have been undertaken to increase the market share of environmentally friendly lubricants. These initiatives have become one of the dominant market drivers for biolubricants. In general, these biolubricant initiatives can be roughly distinguished into three main groups: legislation, market introduction programs, and national or international labeling schemes.

26.2.1 LEGISLATION

With legislation, government regulates the use of certain ingredients positively or negatively—either there is an obligation or mandate to use special components or a ban on some ingredients or chemical classes. To enforce the use of biolubricants by law, however, is still somewhat of an exception, more common being the *obligation to use*. The first obligation to use biodegradable lubricants was mandated in Portugal in 1991 [10]. This obligation required for outboard two-stroke engine oils a degree of biodegradability of 66% (according to CEC-L-33-T-82 [11]), but stopped short of further specifying the base fluid to be used. Austria made another approach in 1992, when it banned mineral oil-based chainsaw oils and mandated to end users the use of oils that are at least 90% biodegradable [12]. In Sweden, the Swedish Standard is mandatory, for example, for hydraulic equipment in forestry application [13]. As the Swedish Standard also provides a labeling scheme, it will be described in more detail in Section 26.2.3.2.

26.2.2 MARKET INTRODUCTION PROGRAMS

To promote the use of biolubricants, governments introduce programs in which, for example, the expenses for the oil itself and the labor costs required to change to biolubricants, are subsidized. A successful establishment of such market introduction programs has taken place in Germany (German MIP Biobased Fuels and Lubricants [14]). The current funding to the market introduction program (MIP) in Germany equates to ~10 million euros every year [15]. In the framework of this program, the government attempts to negate the price difference between mineral bases and biobased lubricants, with end users being able to apply for funds to compensate for the additional costs. Lubricants eligible for this program—of which qualifying categories are hydraulic fluids, multifunctional oils, gear oils, engine oils, and total loss lubricants—are declared on a positive list [14]. Qualifying lubricants on the positive list must be made at least from 50% of renewable resources, being at least 60% readily biodegradable according to OECD 301 B, C, D, or F, and as ecotoxicological criteria, a classification of WGK 1 (low hazardous to water) is required. According to H. Theissen, ~90% of the subventions are requested for applications in hydraulic equipment (H. Theissen, Personal Information).

In the United States, the U.S. Farm Bill [16] has been introduced to strengthen the farm economy over the long term [16], the main focus of which is to ensure a high degree of renewability of used components. In the United States, a biobased product describes a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials), or forestry materials [17].

The American program requires differing biobased content, depending on the application [18,19]:

Mobile equipment hydraulic fluids: 44%

Penetrating lubricants: 68%

Cutting, drilling, and tapping oils: 64%

Firearm lubricants: 49%

To support the use of ecological products and services, the U.S. government also passed the Federal Bio-based Product Preferred Procurement Program [20], also known as FB4P [20], which creates a federal market for biobased products. This type of green procurement requires federal agencies to buy preferentially biobased products, provided the same technical performance can be achieved in comparison with conventional products. A test tool was developed, called Building for Environmental and Economic Sustainability (BEES [21]), which measures environmental performance, economic performance, and human health aspects. BEES also provides a computer program [22], which will calculate a score to aid selection of the correct biolubricant, as shown in Figure 26.1. Aspects such as aquatic toxicity, content of dangerous components, CO₂ balance, and life cycle analysis are also considered using BEES.

In the BEES calculation model, the environmental performance score results from a combination of product performances, across 12 different environmental impacts on a single score—the lower the score, the better is the product's overall environmental performance. BEES scores economic performance on the basis of a product's life cycle cost—all cost from purchase to disposal. The lower the life cycle cost, the better is the product's overall economic performance [23].

The United States currently does not have a biobased product labeling program, in the sense of being awarded with a special label (Jessica Riedl, Center for Industrial Research and Service (CIRAS), Private Communication, e-mail, July 3, 2007).

26.2.3 NATIONAL OR INTERNATIONAL LABELING SCHEMES

Companies can apply at different, mostly nongovernmental, organizations to have their products and services certified with a specially created label for environmental friendly lubricants (European Eco-label, German Blue Angel, Nordic Swan, Swedish Standard, etc.). The labeling schemes are not

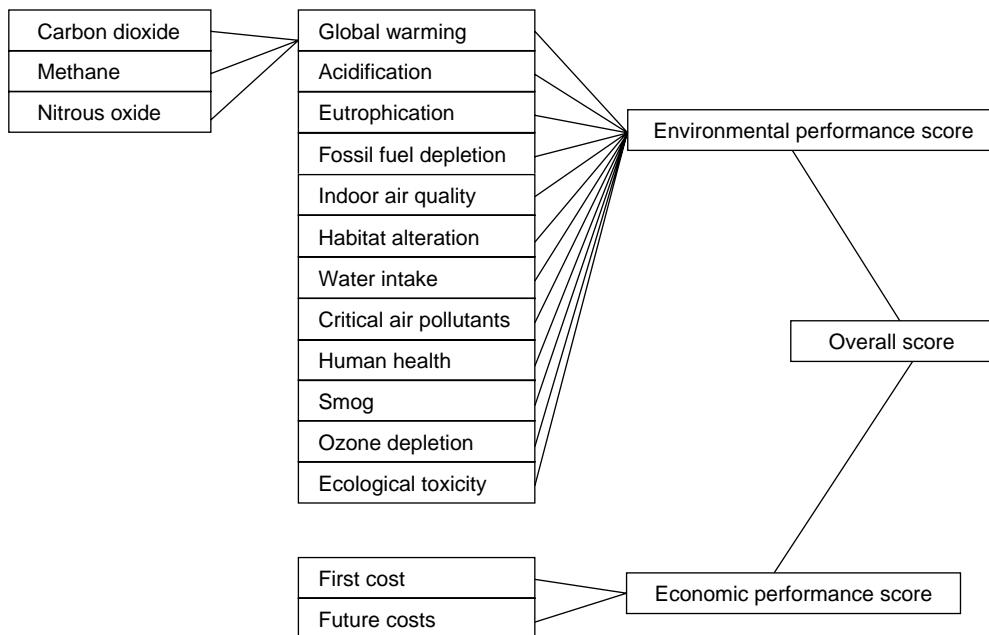


FIGURE 26.1 Impacts on environmental and economic performance score. (Based on <http://www.bfrl.nist.gov/oae/software/bees/model.html>.)

intended to grant subsidies, but to provide a commonly recognized promotional tool and to increase public awareness and create sensitivity for environmentally friendly products and services. Currently, several such labels exist worldwide.

26.2.3.1 German Blue Angel

The general Blue Angel label was founded in 1977/1978 [24], and the first voluntary environmental standard specifically for lubricants (RAL-UZ 48 [25]) came into effect in 1988. The German Eco-label Blue Angel now contains three standards for the use of lubricants:

RAL-UZ 48 Readily Biodegradable Chain Lubricants for Power Saws [25]

RAL-UZ 64 Readily Biodegradable Lubricants and Forming Oils [26]

RAL-UZ 79 Readily Biodegradable Hydraulic Fluids [27]

According to VDMA 24568 [28], not only technical performance requirements, but also the environmental effect of the used lubricants play an important role. As can be deduced from the naming of the standards or norms, biodegradability plays an important role for this label. For example, hydraulic fluids must have a biodegradability of 70% according to OECD 301—B, C, D, or F [27]. In addition, hydraulic fluids must not contain among others, any substances that are listed in Annex I to Directive 67/548/EEC [29] and that are classified according to Section 4a, Gefahrstoffverordnung [30] (Ordinance on Hazardous Substances) as *very toxic* (T+) or *toxic* (T) and which according to Annexes III and VI to Directive 67/548/EEC have to be marked with the following risk phrases: R 45 (may cause cancer), R 46 (may cause heritable genetic damage), R 48 (danger of serious damage to health by prolonged exposure), and R 68 (possible risk of irreversible effects). Furthermore, they must not be water-hazardous (Water Hazard Class 3). An additional point is that the German label explicitly includes technical performance requirements. To be awarded, the hydraulic fluids are required to fulfill at least the minimum technical requirements under ISO 15380 [29,31].

Broadly, this German Eco-label focuses on aquatic toxicity, biodegradation, bioaccumulation, content of dangerous components, and technical performance for the different categories of lubricants. Other characteristics such as renewability, CO₂ balance, or life cycle analysis are not considered in detail. Nevertheless, it can be stated that the Blue Angel requirements are much harsher than the requirements of the German Market Introduction Program. This can also be derived from the fact that only 14% of the lubricants currently listed on the MIP positive list also bear the Blue Angel label.

26.2.3.2 Swedish Standard

The Swedish standard [13] has been developed from a starting point of an environmental project in the city of Gothenburg [32]. Since then, two standards—SS 155434 for hydraulic fluids and SS 155470 for greases—have been put into place. The environmental requirements in both standards are focused on individual chemical substances regarding sensitizing properties, acute toxicity, and biodegradability [33]. The Swedish standard SS 155434 is a legal requirement for hydraulic equipment in forestry application. Version 4 of SS 155434, which came into effect in July 2000, introduced new and more stringent ecological requirements. Depending on the applicable method, the biodegradability of the base fluid must meet at least 60% (ISO 9439 [34], ISO 9408 [35], ISO 10707 [36], ISO 10708 [37]) or more than 70% (ISO 7827 [38]). The biodegradability of the oil and the toxicity of the oils and the additives are considered. To be awarded with this label, technical application requirements—that is, to offer nearly the same performance as mineral oil-based lubricants—must be fulfilled. According to Willing [39], only products that are listed on a *positive list* and then automatically fulfill diverse requirements are allowed to be marketed. In addition, in certain Scandinavian countries, a tax exemption on biolubricants is in place [40].

26.2.3.3 Nordic Swan

Another well-known European Eco-label is the Nordic Swan [41], which is awarded by Norway, Sweden, Finland, Iceland, and Denmark. These countries decided to introduce a neutral, independent, and the world's first multinational label with the intention of assisting consumers in the selection of environmentally friendly and nonhazardous products (see Ref. 42, p. 139). Beginning in the late 1970s, the first biodegradable outboard marine engine oils were developed for the Scandinavian and the North American markets, for use not only in boats but also in snowmobiles and golf carts.

The Nordic Swan itself was introduced as a voluntary Eco-label in 1989 and can be awarded for chain oil, mold oil, hydraulic oil, two-stroke oil, lubricating grease, metal cutting fluid, and transmission/gear oil. For chain oils, mold oils, hydraulic oils, lubricating greases, and two-stroke oils, a certain percentage of renewable raw materials is imposed.

As base fluids, virgin mineral oil, white oil, severely hydrotreated oil, synthetic oil, synthetic esters, polyalphaolefins (PAO), dibasic acid esters, polyol esters, alkylated aromatics, polyalkylene glycols, phosphate esters, vegetable oil, animal oil, and re-refined mineral oil, as well as mixtures of these oils are all potential options.

"The eco-labelling criteria acknowledge that lubricating oils must function satisfactorily and that for this purpose, some lubricant types might need to contain higher levels of potentially hazardous components" [43]. Conversely, products labeled with the Nordic Swan are not allowed to represent a hazard to the environment or to the health, must function satisfactorily, and must have a minimum content of renewable resources. The requirements are listed in Table 26.1.

In accordance with OECD 201 and 202 or equivalent methods, aquatic toxicity must be measured [7]. Short- and medium-chained chloroparaffins and alkylphenolethyoxylates and other known endocrine disrupters must not be present in the product. Aerosol products must not contain halogen hydrocarbon [43].

TABLE 26.1
Environmental Criteria by Type of Lubricating Oil to Meet Nordic Swan Requirements

Amount of Renewable Substances in the Product (%)	Amount of Refined Substances in the Product	Base Oil Fulfilling R50, R51/53, R52/53, R53 (%)	Additives Classified with Risk Phrase R50 or R50/53 (%)	Additives Classified with Risk Phrase R51/53 (%)	Additives Classified with Risk Phrase R52/53 or R53 (%)
Chain oil	Minimum 85	No requirement	0.0	Maximum 1.0	Maximum 3.0
Mold oil	Minimum 85	No requirement	0.0	Maximum 1.0	Maximum 3.0
Hydraulic oil	Minimum 65	No requirement	0.0	Maximum 2.0	Maximum 3.0
Lubricating grease	Minimum 65	No requirement	0.0	Maximum 1.0	Maximum 2.0
Two-stroke oil	Minimum 50	No requirement	0.0	Maximum 1.0	Maximum 1.5
Metal cutting fluid	Minimum 65 or minimum 65%	No requirement	Maximum 2.0	Maximum 2.0	Maximum 5.0
Gear/transmission fluid	Minimum 65 or minimum 65%	No requirement	No requirement	No requirement	No requirement

26.2.3.4 Canadian Eco-Label—EcoLogo^M

If manufacturers, suppliers importers, or dealers of environmentally preferable products and services participate in the Environmental Choice Program (ECP), they can be awarded with the Canadian Eco-label EcoLogo^M [44] if guidelines for different product categories are fulfilled. These categories include, among others, automotive engine oil (recycled), bicycle chain oil (biodegradable), chainsaw lubricants (biodegradable and nontoxic), engine oil marine (inboard and outboard), and industrial lubricants (re-refined oil, synthetic, and vegetable oil-based). For each category, a different set of criteria must be fulfilled to qualify for the Canadian EcoLogo. For example, for *synthetic industrial lubricants*, biodegradability according to CEC-L33-T82 is required. The lubricant should not contain more than 0.1% petroleum oil (or additives containing petroleum oil) and any of the following metals—lead, zinc, chromium, magnesium, and vanadium [45]. In addition, the lubricant shall not be subject to be labeled according to Class D, poisonous and infectious material [46]. Technical performance is tested with various ASTM test methods—for example, ASTM D97 for pour point, ASTM D 665 for rust, ASTM D525 for oxidation stability, and ASTM D-892 for foam [45].

In general, the Canadian EcoLogo concentrates on aquatic toxicity and biodegradability and technical performance, while the CO₂ balance and renewability are focused marginally. The Canadian EcoLogo is one of the few labels that includes a life cycle analysis in its considerations for awarding products.

26.2.3.5 European Eco-Label

In 1992, the European Union introduced a generally accepted label to help the consumer identify environmental friendly products and services [47]. It represents a voluntary scheme with a clear objective to market more environmental friendly products and services and has been developed in cooperation with industry and nongovernmental organizations (NGOs). After 13 years of existence of the common label, it was decided by the European Commission on April 26, 2005 to establish the category of the European Eco-label Lubricants (EEL) [48].

The newly established label covers the fields of hydraulic fluids, greases, chainsaw oils, and total loss lubricants such as two-stroke oils and concrete release agents. The label is valid for private consumers and professional users. Lubricants qualifying for the EEL should meet requirements for technical performance and should have limited aquatic toxicity, high biodegradability, high bioaccumulation, a limited content of dangerous components, and a positive CO₂ balance. According to Mang and Dresel, ecological criteria for a product group are normally established for a period of 3 years. This period allows for improvements in the technology used, and changes in the market can be reflected when the criteria are revised (see Ref. 42, p. 137).

Additives must be evaluated under ecotoxicological perspectives, and additional components must be proven for acceptability with respect to the following criteria:

- R-clauses and impact on formulation
- Aquatic toxicity (daphnia and algae)
- Biodegradability/bioaccumulation
- Not listed on Oslo-Paris-Konvention, Organization for the protection of the Marine Environment of the North-East Atlantic (OSPAR) [49]

R-clauses have an important impact on the allowed treat levels of additives and have to be seen cumulatively according to Directive 1999/45/EC [50], the finished product not being permitted to carry any R-clause. Evaluation of aquatic toxicity, biodegradation, bioaccumulation, and so on must be undertaken for all ingredients separately, or for the finished formulation. This implies that for all additives, a fully documented toxicological dossier has to be submitted to meet the requirements stated by the European Eco-label. The technical performance requirements depend on the intended application; hydraulic fluids, for example, should fulfill ISO 15380 [31].

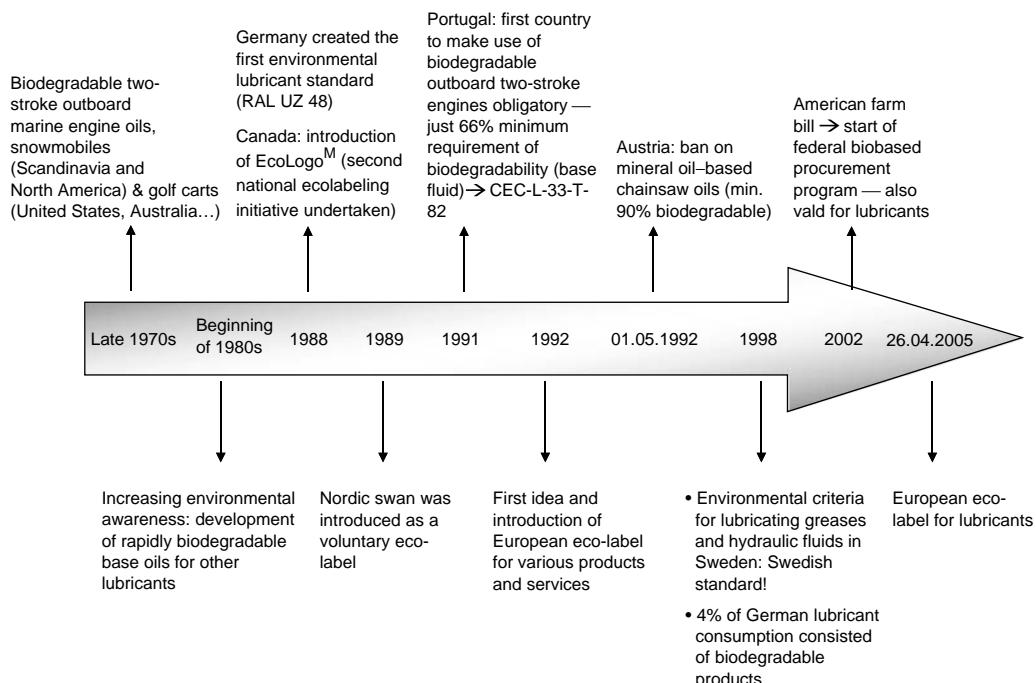


FIGURE 26.2 Historical development of biolubricants and corresponding eco-labels.

In practice, this means that tests such as the Baader test (DIN 51554-3), the steel corrosion test (ASTM D 665 A), the copper corrosion test (ASTM D 130), and the Forschungsstelle für zahnräder und Getriebbau (Technical University Munich) (FZG) test (DIN 51354-2) must be passed. Some criteria only have to be reported or can be agreed with the end user—for example, the dry TOST test (ASTM D 943 modified). As ISO 15380 [31] differentiates technical performance according to different base oil types, lubricants with differing qualities may be developed.

So far, many of the new European members still have their own label with their individual specifications, but many of these countries have declared their intention of adapting the relevant criteria of the European Eco-label to their national label. For example, Hungary and Czech Republic intend to harmonize their national label with the European Eco-label. Some countries will only award the EEL in future, some will award their national label with the specifications of the EEL, and it is estimated that only a minority will still have only their national label with their own specifications.

Figure 26.2 gives a schematic representation of some of the key developments in the biolubricant market and the development of various Eco-label schemes, market implementation programs, and legislation.

Overall, it can be seen that the general requirements of the various eco-label schemes are quite similar, as can be also seen in Table 26.2.

However, looking into the details, there are still some disparities, but with the institution of the European Eco-label, a first step toward harmonization has been taken. Only the future will tell if this will simplify the area of eco-labels or add to the complexity.

An important driver in the development of any market, and in this respect the biolubricant market is no different to any other, is the economic consideration. Typically, the price level for biolubricants can be 1.5–5 times (depending on the base fluid chosen) the price of a similar mineral oil-based formulation, although this is partially offset by lower costs for disposal and those incurred as a consequence of accidental leakages and spills. This cost differential may in time

TABLE 26.2
Comparison of Relevant Parameters of European Eco-Label, German Blue Angel, Canadian EcoLogo, and U.S. Farm Bill

Eco-Label	Applications/Valid for	Biodegradation	Aquatic Toxicity	Health Hazards	Renewability	Technical Performance
German Blue Angel	Chain lubricants for power saws; lubricants and forming oils; hydraulic fluids	++	++	++	-	++
Swedish Standard	Hydraulic fluids; greases	++	++	++	+/- ^a	-
Nordic Swan	Chain oil; mould oil; hydraulic oil; two-stroke oil; lubricating grease, metal cutting fluid and transmission/gear oil	++	++	+	++	+
Canadian EcoLogo	General-purpose industrial lubricants; marine propeller lubricants; engine oils: marine inboard/outboard; chainsaw lubricants; bicycle chain lubricants; automotive engine oil recycled; marine oil absorbent; hydrocarbon ab(d)sorbents	+	++	+	-	+
European Eco-Label	Hydraulic fluids; greases; chainsaw oils; two-stroke oils; concrete release agents	++	++	++	++	++

^a Greases: consideration of renewability aspects; Hydraulics: no consideration.

Note: ++, major focus; +, consideration; -, no consideration.

reduce, if trends in the price of mineral oil continue, and of course, any accurate analysis of economical factors should take into account all costs incurred over the lifetime of the lubricant, including but not limited to purchase cost, disposal cost, effects on energy consumption, and servicing and maintenance costs.

Health and safety considerations make the adoption of biolubricants favorable; typically, higher flashpoints at similar viscosities lead to a lower flammability risk, and with lower hazard ratings, the potential for harm to the person from inhalation or skin contact is reduced.

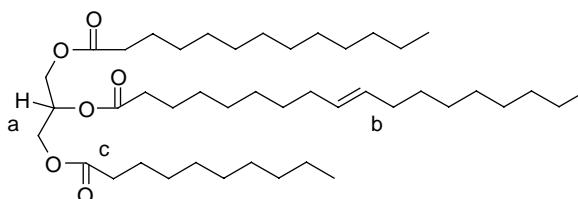
26.3 BASE FLUIDS FOR BIOLUBRICANTS

The broad variety of definitions for biolubricants is also reflected by the large number of suitable base fluids. A good example to illustrate this is the international standard ISO 6743-4 [51]. In this norm, the group of hydraulic fluids in which environmentally acceptable fluids are requested is divided into four base fluid categories: triglycerides, polyglycols, synthetic esters and PAOs, and related hydrocarbon products. Clearly, good understanding of the different characteristics of these base fluids is needed to develop and formulate biolubricants.

26.3.1 TRIGLYCERIDES

Triglycerides are the main components of fats and oils found in plants and animals. Chemically spoken triglycerides are esters composed of glycerin and three (typically natural) fatty acids. The most important fatty acids contained in such oils are the saturated acids—palmitic acid (C16:0) and stearic acid (C18:0)—as well as the unsaturated acids—oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3). The exact fatty acid composition of natural oil depends very much on the source from whence it is derived. The main fatty acid in a rapeseed oil, for example, is oleic acid (C18:1), and in a soybean oil, linoleic acid (C18:2) is dominant. Modern agricultural technology such as breeding new plants or the use of genetically modified organisms (GMOs) allows further possibilities to tailor the fatty acid composition. A typical example is the development of new sunflower oils containing a high amount of oleic acid (C18:1).

Triglycerides have three drawbacks in regard to the technical performance as a lubricant.



First, due to the hydrogen atom in a β position (a), triglycerides can decompose relatively easily through a low-energy, six-membered ring intermediate. The thermal stability of natural esters is hence very low. Second, the presence of unsaturated double bonds (b) in the fatty acid moiety negatively affects the oxidation stability of these compounds. Typically, the bonding energy of a hydrogen atom in an allylic position is much lower ($\Delta H_{(C-H)} = 345 \pm 5 \text{ kJ/mol}$), compared with a hydrogen atom in a fully saturated hydrocarbon ($\Delta H_{(C-H)} = 411 \pm 2 \text{ kJ/mol}$) [52].

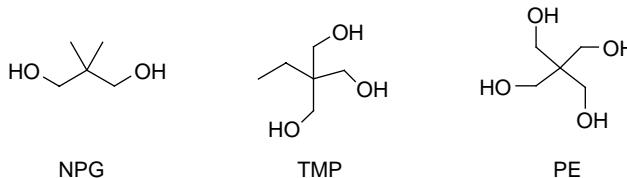
A hydrogen atom in an allylic position can therefore be abstracted easily in a radical reaction initiating the oxidation process. Even worse is the oxidative stability of polyunsaturated fatty acids. According to Falk and Meyer-Pittroff [53], the difference in the reactivity of oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) is approximately 1:10:100.

The third drawback of a triglyceride is the low sterical demand of the ester groups (c) when glycerin is used as an alcohol. This allows water to attack the carbonyl group and hydrolyze the ester, releasing free fatty acids.

Despite the fact that unsaturated fatty acids are prone to oxidation, the unsaturation also provides a benefit to the natural oils with respect to their low-temperature flow properties. As a rule of thumb, it can be stated that a natural triglyceride needs at least one *cis* configured double bond to show a suitable low-temperature performance. A fully saturated triglyceride would be a solid fat at room temperature and not be usable for a lubricant formulation.

26.3.2 SYNTHETIC ESTERS

To overcome some deficits of natural esters, the glycerol moiety can be replaced. By using sterically demanding alcohols not bearing a hydrogen atom in β position for such a transesterification process,



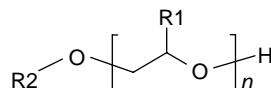


FIGURE 26.3 R1 and R2 are typically hydrogen, methyl, or ethyl groups.

products with considerably greater stability are obtained. Usually alcohols such as trimethylpropane (TMP), neopentyl glycol (NPG), or pentaerythritol are used [54–56].

The obtained polyol esters show improved hydrolytic and thermal stability, the oxidation stability however being equal to the used starting material and only dependent on the degree of saturation. Such esters can be classified as semisynthetic, and they still have a high degree of biobased material, as the alcohol part is typically derived from petrochemicals, whereas the fatty acid part can stem from natural resources.

Synthetic esters are made from synthetic alcohols and fatty acids and can hence be tailored to the expected or required performance. The use of branched alcohols or fatty acids allows, for example, for the production of esters with a good oxidative stability, without compromising on low-temperature performance. A high degree of branching also has a positive effect on the seal compatibility of such products. Stemming from petrochemicals, such esters would of course not meet *biobased* requirements anymore but could still have good biodegradability and a good eco-toxicological profile.

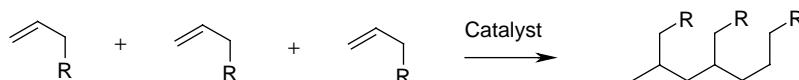
26.3.3 POLYGLYCOLS

Polyglycols are synthesized technically from petrochemical starting materials such as ethylene oxide and propylene oxide yielding a polymeric structure (Figure 26.3).

Depending on the used starting material, polyalkylene glycols can be either water-soluble (polyethylene glycols) or oil-soluble (polypropylene glycols), but using copolymerization, this property can be further adjusted to the performance requirements. Polyalkylene glycols are biodegradable, especially water-soluble polyglycols, whereas oil-soluble polyglycols have a typically lower biodegradability. However, a high water solubility could be seen as an environmental disadvantage; in the case of a fluid getting into the environment, water-soluble fluids would migrate rather quickly into waterways causing an instant contamination. Currently, as polyalkylene glycols are produced from petrochemicals, they do not meet a *biobased* requirement. Theoretically, it would also be possible to produce polyalkylene glycols from natural resources such as lactic acid or sugar, but these are not yet common industrial processes.

26.3.4 POLYALPHAOLEFINS

PAOs and related hydrocarbons are produced from petrochemical resources and are hence not bio-based; however, they can have a good biodegradability. PAOs are polymerized from olefins, in which the double bonds are in α position. For lubricants, typical starting materials used are 1-decen and 1-dodecen and, despite the name, only oligomers such as trimers and tetramers are used [57].



The technical performance of PAO is good, especially in regard to the oxidative stability. As PAOs are very nonpolar, the additive solubility can be a concern, and therefore, PAOs are often used in mixtures with polar esters to overcome this deficiency. Such mixtures can have very good technical performance, but the variabilities and permutations are so wide that in-depth description would be out of the scope of this chapter.

TABLE 26.3
Comparison of Selected Parameters for Environmentally Acceptable Fluids

Parameter	Triglyceride	Synthetic Ester	PAG	PAO
Renewability content	High	Variable	Not	Not
Biodegradability	Good	Good	Moderate	Moderate
Water solubility	Low solubility	Low solubility	Compatible	Low solubility
Low-temperature performance	Weak	Good	Good	Good
Oxidation resistance	Weak	Good	Good	Good
Hydrolytic stability	Low	Medium	Good	Good
Seal material compatibility	Good	Limited	Limited	Good
Paint and varnish compatibility	Good	Good	Limited	Good
Additive solubility	Good	Good	Moderate	Limited
Lubricity of base oil	Good	Good	Good	Limited
Corrosion resistance	Poor	Limited	Limited	Good

To formulate a biolubricant, the choice of the correct base fluid is critical, and depending on the specific requirements, each of the described fluids could be optimally selected. The advantages and disadvantages should be balanced and matched with the lubrication needs of the application (Table 26.3).

Future trends for base fluids used for biolubricants are difficult to predict. One possible trend could be the so-called second generation of biolubricants—using biogas to produce liquid hydrocarbons: biogas to liquid (BTL). If such technology is developed to an industrially feasible process, this would enable the exploitation of the biomass of complete plants and a wide range of feedstock such as wood and waste plants. Utilizing gasification and Fischer–Tropsch technology, all kinds of hydrocarbons could be produced. Similar to triglycerides, the products of this technology for use in lubricants are in strong competition to their demands as fuels; hence, it cannot be predicted when such technologies could have a substantial impact on the biolubricant market.

26.4 ADDITIVES FOR BIOLUBRICANTS

The performance of a finished lubricant depends collectively on the base oil, additives, and formulation; and for biolubricants, the selection of base oils and additives is limited by ecological regulations. The selection of the right additives and their combination has to be seen integrally. First, it should be established what type of biolubricant is to be formulated and what criteria it should meet. If the target is to stabilize a *biobased* fluid without any further requirements, practically all additives known could be used. However, if the fluid has to be environmentally acceptable, as a rule of thumb, the formulation has to be ashless (not containing metals) and only ecotoxicologically harmless additives can be used. Whereas the first requirement is relatively easy to achieve, as a broad variety of ashless additives exists on the market, the latter can be a problem. Currently there are only a limited number of additives available, in which the full ecotoxicological data have been assessed and disclosed from additive suppliers. For harsh criteria such as demanded from the European Eco-label, only a few additives are currently approved (van der Sijp, SMK list, Private Communication, 2007). In addition, the nonmineral base oils used for biolubricants very often need different additives and treat rates to achieve the performance known from classical formulations.

26.4.1 ANTIOXIDANTS

In practice, the oxidative aging of the lubricant is the dominating process, which influences the lifetime of a lubricant significantly [42]. The oxidative degradation can cause the formation of acids, varnish, deposits, sludge, and an increase in the viscosity. It is generally accepted that the oxidative degradation is following a cyclic, free radical mechanism through alkyl and peroxide radicals, as shown in Figure 26.4.

To prevent oxidation, antioxidants are included in the formulation. Radical scavengers, which inhibit the propagation of the radical chain mechanism, are described as primary antioxidants. Sterically hindered phenols and secondary aromatic amines are typical examples of primary antioxidants.

Despite the fact that aminic and phenolic antioxidants stabilize a lubricant through similar reaction mechanisms, it has been found that both antioxidant classes act synergistically [58]. Hence, often, combinations of aminics and phenolics are applied. Unlike phenolic antioxidants, aminic antioxidants are active at higher temperatures ($>120^{\circ}\text{C}$) [59]; therefore, it is essential to know the operation temperature of the intended application. A chemically unmodified vegetable oil, which is used typically only in low-temperature applications, preferably would be stabilized with a high amount of phenolic antioxidants ($>1\%$), whereas for a high-temperature application, for example, a PAO-based base fluid, would be optimized with the addition of a synergistic mixture of aminic and phenolic antioxidants. As primary antioxidants can be regenerated, they are catalytically active in the stabilization of a lubricant.

Secondary antioxidants react stoichiometrically with peroxides and deactivate these aggressive chemical intermediates. Examples of secondary antioxidants are phosphorus- and sulfur-containing compounds, in which the heteroatom has a lower valence state, thus it still can be readily oxidized. As secondary antioxidants deactivate peroxides, they prevent the chain propagation reaction initiated when a peroxide is divided into two radicals. A standard secondary antioxidant would be zinc dialkyldithiophosphates (ZDTPs); however, as zinc compounds are classified to be eco-toxic, and labelled “N” based on toxicity to algae [60], this chemistry could not be used to formulate

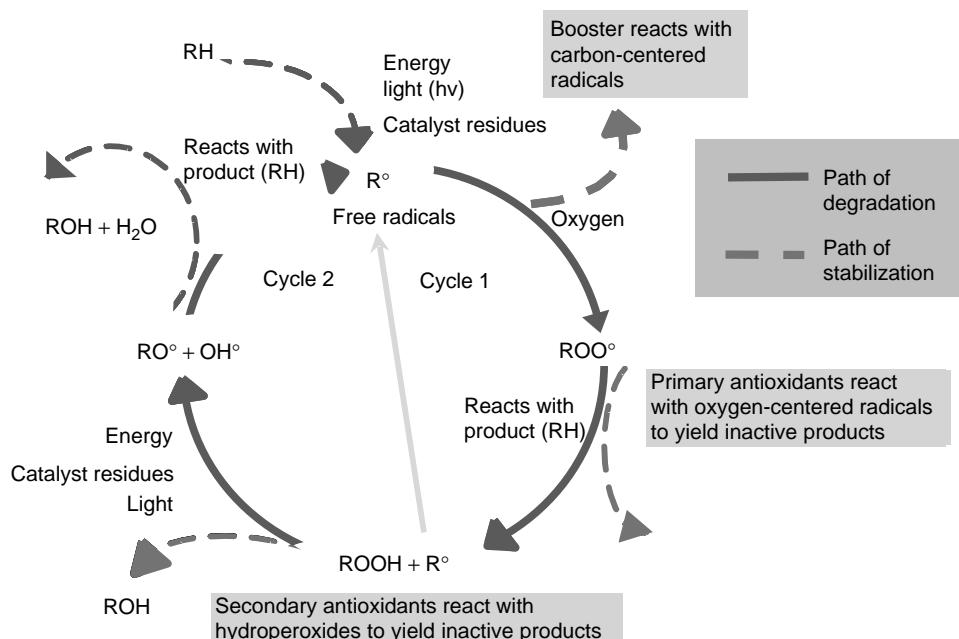


FIGURE 26.4 Schematic mechanism of oxidative degradation and the influence of antioxidants.

environmentally acceptable fluids. For such fluids, ashless phosphites and thioesters are much better suited. As a consequence of the different additive mode of action, a combination of primary and secondary antioxidants is very favorable and show synergistic effects.

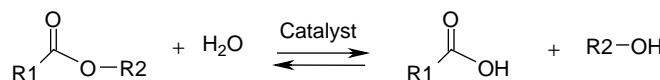
As an alternative to the aforementioned antioxidants, the use of metal dithiocarbamates is described in literature [61]. These additives show very good performance in different tests, by far exceeding the more commonly used zinc dialkyl-dithiophosphates [62]. Unfortunately, the ashless dithiocarbamates, using an ammonium salt or using a methylene bridge, do not show this performance boosting effect. On the contrary, the use of metal-containing dithiocarbamates—such as bismuth and zinc—cannot be utilized to formulate an environmentally acceptable fluid.

26.4.2 METAL DEACTIVATORS

In various applications, the lubricant can be in contact with parts made of yellow metals—typically copper—or with dissolved metal contaminants. As copper compounds catalytically decompose peroxides generating radicals, these metal species are very efficient pro-oxidants and need to be deactivated. Dissolved copper ions are deactivated with chelating agents, whereas the metal parts are protected and deactivated with film-forming metal-passivating agents. The advantage of film-forming agents is the fact that they prevent the progressive oxidation of the metal surface, which would release copper ions to the fluid. Complexing agents, on the contrary, could even promote the transfer of copper ions from the metal surface into the fluid. A typical example of a chelating agent would be disalicylidene-propylene-diamine, in which film-forming agents are very often derivatives of benzotriazol [63]. Both groups of metal deactivators are used only in very low treat rates—below 0.1%—and are active in all suitable base fluids used for the formulation of biolubricants. A critical property of some metal deactivators is the low solubility; especially when PAO is used as a base fluid, this property must be carefully checked.

26.4.3 CORROSION INHIBITORS

Another important class of additives used to protect metal surfaces is corrosion inhibitors; in this chapter, the term *corrosion inhibitor* is used synonymously with *antirust additives* and describes additives that are used to protect ferrous metals against the attack of moisture, oxygen, and other aggressive lubricant ingredients. Corrosion inhibitors possess as a general molecule design a long alkyl chain to improve the solubility in lubricants and a polar group to provide the surface activity. Corrosion inhibitors are absorbed physically or chemically on the metal surface and form a dense protective layer. Examples of corrosion inhibitors include metal sulfates, amines, carboxylic acid derivates, and amine neutralized alkyl phosphoric acid partial esters. Because of their surface activity, corrosion inhibitors tend to compete with polar base fluids for the metal surface; therefore, it can be quite complex to improve the corrosion stability of an ester or a polyalkyle glycol (PAG). Another potential problem associated with corrosion inhibitors is the fact that acids, bases, and metals can catalyze the hydrolysis of esters.



To prevent the hydrolysis of ester-based fluids, the treat rate of the corrosion inhibitors should be as low as possible, and in addition, preferably neutral additives such as the neutralized acids should be applied. It has been described that the response of corrosion inhibitors in different esters can show significant variation [64]. For example, to stabilize a rapeseed oil, twice the amount of a corrosion inhibitor was necessary, than was required for a TMP oleate. In addition, it has been found that at higher treat rates, the use of corrosion inhibitors can have a detrimental effect on the corrosion protection. This shows the importance of a careful balance of the additive treat rate.

For PAGs and PAOs, the corrosion protection is much easier as the hydrolytic stability is not an issue here. For the nonpolar PAO, additives lowering the surface tension can be used synergistically with film-forming additives.

26.4.4 EXTREME-PRESSURE AND ANTIWEAR ADDITIVES

Extreme-pressure and antiwear (EP/AW) additives are needed in lubricants to protect metal surfaces against mechanical damage in case the lubricant film is ruptured under critical conditions. These additives not only absorb onto the metal surface, but also react further in the case of a thermal fragmentation or tribofragmentation reaction, building a chemical reaction layer on the metal. The formed layers make the tribological contact softer, preventing a direct metal-to-metal contact of moving metal parts. AW additives are used for applications with medium loads. One model to explain the mode of action of these additives is to assume that polymer condensation and polymerization reactions are initiated, which provide a protecting layer on the metal. This layer is sheared off and renewed constantly during the operation [65]. Under very high loads, the performance of AW additives becomes insufficient and designated EP additives are needed. These additives undergo real reactions with the metal surface to form tribolayers consisting of iron phosphite or iron sulfides or iron chlorides. Here, the metal is a part of the protective tribolayer.

As EP/AW additives take part in real chemical reactions, they require certain activation energy to display the intended performance. The activation energy is provided partly due to the operation temperature, but more largely due to the local temperature spikes and mechanical forces in the friction zone. It is hence important to know these conditions for the selection of the correct EP/AW additives. For low-temperature applications, more active additives might be necessary, whereas for higher temperatures, it has to be ensured that the additives at least partially stay in grade in the bulk fluid.

ZDTPs are the most common EP/AW additives, but they are not suitable for environmentally friendly fluids due to the content of a heavy metal: Zink. For biolubricants, ashless additives such as triarylphosphates or trialkylphosphates, neutralized alkyl phosphoric acids, and ashless dialkyl-dithiophosphates are used. All these additives are very reactive in nonpolar PAOs, as they can easily be absorbed on the metal surface. In polar esters and PAGs, however, the situation is more complex, as these base fluids interact strongly with metal surfaces and consequently provide an already good protection against friction and wear, at least under mild conditions. For more demanding applications, in which the protective reaction layer provided from additives is required, the high surface activity of the base fluids is detrimental, as the additives are hindered to approach the metal surface in the first stage. Hence, higher treat rates of additives need to be applied, and preferentially more polar additives have to be used. A further problem is the fact that even ashless sulfur- and phosphorus-containing compounds do not necessarily have excellent ecotoxicological profiles. Of course, this statement cannot be generalized; however, so far, only a very limited number of additives are available that would be officially approved for the use in stringent environmentally friendly lubricants such as European Eco-label fluids.

If the application is very demanding and high loads need to be managed, the sometimes still-used chlorinated products should definitely be avoided for toxicological reasons. Sulfur carriers, on the contrary, could be used for biolubricants. For example, sulfurized esters, which can have a good toxicological profile as well as a high degree of biodegradability, have been tested and found to show good performance [64].

26.4.5 POUR POINT DEPRESSANTS AND VISCOSITY INDEX IMPROVERS

Pour point depressants (PPDs) and viscosity index improvers (VIIs) are added to improve the rheology of a lubricant.

At reduced temperatures, paraffinic compounds in lubricants can form wax crystals that agglomerate and crystallize, solidifying the lubricant. To prevent this crystallization, a pour point

depressant is added. PPDs are specially designed polymers, which have a bifunctional molecular structure. Some parts of the molecules are similar to paraffin wax crystals, enabling cocrystallization with the waxes, whereas other parts of the polymer have a structure very dissimilar to the wax crystals, preventing any further agglomeration and growth of the wax matrices. The effect is a better flow behavior and a depression of the pour point. As PAGs, PAO, and most synthetic esters already have good low-temperature behavior, the addition of a PPD is not very common. Natural esters, however, can crystallize relatively easily—even in some cases at ambient temperatures—and therefore the demand for a PPD can be high. The amount of PPD used varies according to the ester type, concentration of the polymer in the fluid, the type of polymer, and the degree of pour point correction desired.

VIIIs are added to minimize the extreme viscosity variation of a given fluid with change in temperature, especially important for applications working in different temperature regimes. VIIIs have a chemical structure similar to PPD, but the polymers used have a much higher molecular weight. As base fluids for biolubricants have in general already a quite high viscosity index, a further improvement of this property is not very common and only necessary for special applications.

26.4.6 ANTIHYDROLYSIS AGENTS

Antihydrolysis agent is a special class of additives, which is used only for ester-based fluids. As described earlier, the ester bond can be easily cleaved reacting with water, forming acids and alcohol. As this reaction is catalyzed by acids, the reaction has to be seen as autocatalytic, because each molecule of acid formed during the hydrolysis can itself catalyze a new hydrolysis reaction. To stabilize an ester, special carbodiimides can be added, which work as acid scavengers and hence are able to remove the catalyst [66]. The disadvantage of such acid scavengers is that they also readily react with acids intentionally added as a corrosion inhibitor or an EP/AW additive; hence, the potential for an antagonistic effect is high.

26.4.7 ANTIFOAM AGENTS, DEMULSIFIERS, AND EMULSIFIERS

To improve the surface properties of biolubricants, antifoam agents, demulsifiers, and emulsifiers can be added. In typical industrial applications, the amount of additive is extremely low (10–100 ppm) and hence will not be discussed in detail here.

26.5 SUMMARY

Currently, biolubricants are still regarded as niche products. However, in certain applications such as hydraulic fluids, the use of biolubricants is steadily growing. Government incentives and voluntary labeling schemes are aiming to create market drivers, public promotion, and compensation for potential economical disadvantages. Absolutely mandatory is, of course, suitable technical performance of the biolubricants, as well as the lowest possible harm to the environment. To achieve this, various base oils can be used. To ensure performance requirements are met, additives are needed, which are tailored for the base fluid used and well suited for the intended application. These additives need to be carefully formulated, making use of synergistic effects and avoiding any antagonism. So far, it is not yet globally accepted, but with a growing regional importance, biolubricants are required to be ecologically friendly, with criteria such as renewability of feedstocks, low aquatic toxicity, and a high rate of biodegradability becoming demanded more often. These environmental factors are not limited to the base oil, but are also valid in a certain degree for the additives; hence, in future, the demand for environmentally acceptable, high-performing additives will be growing steadily.

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Part 8

Methods and Resources

27 Testing Methods for Additive/Lubricant Performance

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This chapter contains a selection of many of the most commonly used test methods and specifications selected from the United States, Europe, and Japanese lubricant testing methods. These include methods, standards, and specifications from the American Society for Testing and Materials (ASTM), Federal Test Method (FTM), Military (Spec) (MIL), Conseil Européen de Coordination pour les Développements des Essais de Performance des Lubrifiants et des Combustibles pour Moteurs (CEC), Deutsches Institute für Normung (DIN), Japan Petroleum Institute (JPI), as well as Federal Supply Class 9150 commodities. Some cross-references are also given.

ASTM publishes an *Annual Book of ASTM Standards. Petroleum Products, Lubricants, and Fossil Fuels*, Volumes 5.01–5.04, in which a complete list of ASTM methods pertaining to lubricants may be found.

27.1 SUMMARY OF STANDARD TEST METHODS AND SPECIFICATIONS

27.1.1 AMERICAN SOCIETY FOR TESTING AND MATERIALS

D 56	Standard test method for flash point by tag closed tester
D 86	Standard test method for distillation of petroleum products
D 88	Standard test method for viscosity Saybolt seconds universal
D 91	Standard test method for precipitation number of lubricating oils
D 92	Standard test method for flash and fire points by Cleveland open cup
D 93	Standard test method for flash point by Pensky–Martens closed tester
D 94	Standard test method for saponification number of petroleum products
D 95	Standard test method for water in petroleum products and bituminous materials by distillation
D 97	Standard test method for pour point of petroleum products

(continued)

- D 130 Standard test method for the detection of copper corrosion from petroleum products by the copper strip tarnish test
- D 150-98 (2004) Standard test methods for AC loss characteristics and permittivity (dielectric constant) of solid electrical insulation
- D 156 Standard test method for Saybolt color of petroleum products (Saybolt chromometer method)
- D 189 Standard test method for Conradson carbon residue of petroleum products
- D 217 Standard test method for cone penetration of lubricating grease
- D 257-99 Standard test methods for DC resistance or conductance of insulating materials
- D 287 Standard test method for API gravity of crude petroleum and petroleum products (hydrometer method)
- D 445 Standard test method for kinematic viscosity of transparent and opaque liquids (and the calculation of dynamic viscosity)
- D 482 Standard test method for ash from petroleum products
- D 524 Standard test method for Ramsbottom carbon residue of petroleum products
- D 525-05 Standard test method for oxidation stability of gasoline (induction period method)
- D 566 Standard test method for dropping point of lubricating grease
- D 567 Standard test method for calculating viscosity index
- D 611 Standard test method for (1993)el aniline point and mixed aniline point of petroleum products and hydrocarbon solvents
- D 664 Standard test method for acid number of petroleum products by potentiometric titration
- D 665 Standard test method for rust-preventing characteristics of inhibited mineral oil in the presence of water
- D 874 Standard test method for sulfated ash from lubricating oils and additives
- D 877-02e1 Standard test method for dielectric breakdown voltage of insulating liquids using disk electrodes
- D 892 Standard test method for foaming characteristics of lubricating oils
- D 893 Standard test method for insolubles in used lubricating oils
- D 942 Standard test method for oxidation stability of lubricating grease by the oxygen bomb method
- D 943 Standard test method for oxidation characteristics of inhibited mineral oils
- D 972 Standard test method for evaporation loss of lubricating greases and oils
- D 974 Standard test method for acid and base number by color-indicator titration
- D 1091 Standard test methods for phosphorus in lubricating oils and additives
- D 1092 Standard test method for measuring apparent viscosity of lubricating greases
- D 1093 Standard test method for acidity of hydrocarbon liquids and their distillation residues
- D 1159 Standard test method for bromine numbers of petroleum distillates and commercial aliphatic olefins by electrometric titration
- D 1160 Standard test method for distillation of petroleum products at reduced pressure
- D 1209 Standard test method for color of clear liquids (platinum cobalt scale) (APHA color)
- D 1238 Standard test method for flow rates of thermoplastics by extrusion plastimeter (melt index) (or ISO 1133–1991)
- D 1264 Standard test method for determining the water washout characteristics of lubricating greases
- D 1217 Standard test method for density and relative density (specific gravity) of liquids by Bingham pycnometer
- D 1268 Standard test method for leakage tendencies of automotive wheel bearing greases
- D 1296 Standard test method for odor of volatile solvents and diluents
- D 1298 Standard test method for (1990)el density, relative density (specific gravity), or API gravity of crude petroleum and liquid petroleum products by hydrometer method
- D 1331 Standard test method for surface and interfacial tension of solutions of surface-active agents
- D 1358 Standard test method for (1995)el spectrophotometric diene value of dehydrated castor oil and its derivatives
- D 1401 Standard test method for water separability of petroleum oils and synthetic fluids
- D 1403 Standard test methods for cone penetration of lubricating grease using one-quarter and one-half scale cone equipment
- D 1478 Standard test methods for low-temperature torque of ball bearing grease
- D 1480 Standard test method for density and relative density (specific gravity) of viscous material by Bingham pycnometer

D 1481	Standard test method for density and relative density (specific gravity) of viscous material by Lipkin bicapillary pycnometer
D 1500	Standard test method for color of petroleum products (ASTM color scale)
D 1646	Standard test method for rubber viscosity, stress relaxation, and prevulcanization characteristics (mooney viscometer)
D 1662	Standard test method for active sulfur in cutting oils
D 1742	Standard test method for oil separation from lubricating grease during storage
D 1743	Standard test method for corrosion preventive properties of lubricating greases
D 1744	Standard test method for determination of water in liquid petroleum products by Karl Fischer reagent
D 1747	Standard test method for refractive index of viscous materials
D 1748	Standard test method for rust protection by metal preservatives in the humidity cabinet
D 1831	Standard test method for roll stability of lubricating grease
D 1947	Standard test method for load-carrying capacity of petroleum oil and synthetic fluid gear lubricants
D 2007	Standard test method for characteristic groups in rubber extender and processing oils and other Petroleum-derived oils by the clay-gel absorption chromatographic method
D 2070	Standard test method for thermal stability of hydraulic oils
D 2155	Discontinued from 1981, replaced by E 659
D 2161	Standard practice for conversion of kinematic viscosity to Saybolt universal viscosity or to Saybolt Furol viscosity
D 2265	Standard test method for dropping point of lubricating grease over wide temperature range
D 2266	Standard test method for wear preventive characteristics of lubricating grease (four-ball method)
D 2270	Standard test method for standard practice for calculating viscosity index from kinematic viscosity at 40 and 100°C
D 2272	Standard test method for oxidation stability of steam turbine oils by rotating bomb
D 2273	Standard test method for trace sediment in lubricating oils
D 2500	Standard test method for cloud point of petroleum oils
D 2502	Standard test method for estimation of molecular weight relative molecular mass of petroleum oils from viscosity calculation
D 2509	Standard test method for measurement of load-carrying capacity of lubricating grease (Timken method)
D 2512-95 (2002)	Standard test method for compatibility of materials with liquid oxygen (impact sensitivity threshold and pass-fail techniques)
D 2549-02	Standard test method for separation of representative aromatics and nonaromatics fractions of high-boiling oils by elution chromatography
D 2595	Standard test method for evaporation loss of lubricating greases over wide temperature range
D 2596	Standard test method for measurement of extreme-pressure properties of lubricating grease (four-ball method)
D 2602	Replaced by D 5293, standard test method for apparent viscosity of engine oils at low temperature using the cold-cranking simulator
D 2603-01	Test method for sonic shear stability of polymer-containing oils
D 2619-95 (2002)e1	Standard test method for hydrolytic stability of hydraulic fluids (beverage bottle method)
D 2620	Discontinued from 1993, replaced by D 5293
D 2622	Standard test method for sulfur in petroleum products by x-ray spectrometry
D 2625	Standard test method for determining endurance life and load-carrying capacity of dry solid film lubricants (Falex method)
D 2670	Standard test method for measuring wear properties of fluid lubricants (Falex method)
D 2710	Standard test method for bromine index of petroleum hydrocarbons by electrometric titration
D 2711	Standard test method for demulsibility characteristics of lubricating oils
D 2714	Standard test method for calibration and operation of the Falex block-on-ring friction and wear testing machine
D 2766	Standard test method for specific heat of liquids and solids
D 2782	Standard test method for measurement of extreme-pressure properties of lubricating fluids (Timken method)

(continued)

D 2783	Standard test method for measurement of extreme-pressure properties of lubricating fluids (four-ball method) (load wear index)
D 2786-91 (2001)e1	Standard test method for hydrocarbon types analysis of gas–oil saturates fractions by high ionizing voltage mass spectrometry
D 2878	Standard test method for estimating apparent vapor pressure and molecular weights of lubricating oils
D 2879	Standard test method for vapor pressure–temperature relationship and initial decomposition temperature of liquids by isoteniscope
D 2887	Standard test method for boiling range distribution of petroleum fractions by gas chromatography
D 2893	Standard test method for oxidation characteristics of extreme-pressure lubricating oils
D 2896	Standard test method for base number of petroleum products by potentiometric perchloric acid titration
D 2982	Standard test method for detecting glycol-base antifreeze in used lubricating oil
D 2983	Standard test method for low-temperature viscosity of automotive fluid lubricants measured by Brookfield viscometer
D 3120	Standard test method for trace quantities of sulfur in light liquid petroleum hydrocarbons by oxidative microcoulometry
D 3228	Standard test method for total nitrogen in lubricating oils and fuel oils by modified Kjeldahl method
D 3232	Standard test method for measurement of consistency of lubricating greases at high temperatures
D 3233	Standard test method for measurement of extreme pressure of fluid lubricants (Falex method)
D 3238	Standard test method for carbon distribution and structural group analysis of petroleum oils by the ndM method
D 3244	Standard test method for standard practice for utilization of test data to determine conformance with specifications
D 3336	Standard test method for life of lubricating greases in ball bearings at elevated temperatures
D 3427-03	Standard test method for air release properties of petroleum oils
D 3525	Standard test method for gasoline diluent in used gasoline engine oils by gas chromatography
D 3527	Standard test method for life performance of automotive wheel bearing grease
D 3704	Standard test method for wear preventative properties of lubricating grease using the (Falex) block on ring test machine in oscillating motion
D 3705	Standard test method for misting properties of lubricating fluids
D 3711	Standard test method for deposition tendencies of liquids in thin films
D 3829	Standard test method for predicting the borderline pumping temperature of engine oil
D 3850-94 (2000)	Standard test method for rapid thermal degradation of solid electrical insulating materials by thermogravimetric method (TGA)
D 3945	Standard test method for shear stability of polymer-containing fluids using diesel injector nozzle (deactivated 1998, replaced by D6278)
D 4047	Standard test method for phosphorus in lubricating oils and additives by quinoline phosphomolybdate method
D 4048	Standard test method for detection of copper corrosion from lubricating greases
D 4049	Standard test method for determining the resistance of lubricating grease of water spray
D 4057	Standard test method for standard practice for manual sampling of petroleum and petroleum products
D 4172	Standard test method for wear preventive characteristics of lubricating fluid (four-ball method)
D 4294	Standard test method for sulfur in petroleum products by energy-dispersive x-ray fluorescence spectroscopy
D 4310	Standard test method for determination of the sludging and corrosion tendencies of the inhibited mineral oils
D 4485	Standard test method for standard specification performance of automotive engine oils
D 4624	Standard test method for measuring apparent viscosity by capillary viscometer at high temperature and high shear rates
D 4627	Standard test method for iron chip corrosion for water-diluteable metalworking fluids
D 4628	Standard test method for analysis of barium, calcium, magnesium, and zinc in unused lubricating oils by atomic absorption spectrometry
D 4629	Standard test method for trace nitrogen in liquid petroleum hydrocarbons by syringe/inlet oxidative combustion and chemiluminescence detection

D 4636	Standard test method for corrosion and oxidative stability of hydraulic oils, aircraft turbine engine lubricants, and other highly refined oils
D 4683	Standard test method for measuring viscosity at high shear rate and high temperature by tapered bearing simulator
D 4684	Standard test method for determination of yield stress and apparent viscosity of engine oils at low temperature (MRV TP-1 cycle)
D 4693	Standard test method for low-temperature torque of grease-lubricated wheel bearings
D 4739	Standard test method for base number determination by potentiometric titration
D 4741	Standard test method for measuring viscosity at high temperature and high shear rate by tapered plug viscometer
D 4742	Standard test method for oxidation stability of gasoline automotive engine oils by thin-film oxygen uptake (TFOUT)
D 4781-03	Standard test method for mechanically tapped packing density of fine catalyst particles and catalyst carrier particles
D 4857	Standard test method for determination of coefficient of friction of lubricants using the four-ball wear test machine
D 4871-88	Standard guide for universal oxidation/thermal stability test apparatus
D 4898	Standard test method for insoluble contamination of hydraulic fluids by gravimetric analysis
D 4927	Standard test method for elemental analysis of lubricant and additive components, barium, calcium, phosphorus, sulfur, and zinc, by wavelength-dispersive x-ray fluorescence spectroscopy
D 4950	Standard classification and specification for automotive service greases
D 4951	Standard test method for determination of additive elements in lubricating oils by inductively coupled plasma atomic emission spectrometry
D 5119	Standard test method for evaluation of automotive engine oils in CRC I-38 spark ignition engine
D 5133	Standard test method for low temperature, low shear rate, viscosity/temperature dependence of lubricating oils using a temperature-scanning technique (scanning Brookfield test with gelation index calculation)
D 5182	Standard test method for evaluating the scuffing load capacity of oils (FZG visual method)
D 5183	Standard test method for evaluating coefficient of friction of lubricants using the four-ball wear test machine
D 5185	Standard test method for determination of additive elements, wear metals, and contaminants in used lubricating oils and determination of selected elements in base oils by inductively coupled plasma atomic emission spectrometry (ICP-AES)
D 5293	Standard test method for apparent viscosity of engine oils between -5 and -30°C using the cold-cranking simulator
D 5302	Standard test method for evaluation of automotive engine oils in the Sequence VE spark ignition engine
D 5306-92 (2002)e1	Standard test method for linear flame propagation rate of lubricating oils and hydraulic fluids
D 5480	Standard test method for engine oil volatility by gas chromatography
D 5483	Standard test method for oxidation induction time of lubricating greases by pressure differential scanning calorimetry
D 5533	Standard test method for evaluation of automotive engine oils in the Sequence IIIE spark ignition engine
D 5570	Standard test method for evaluating the thermal stability of manual transmission lubricants in a cycle durability test
D 5620	Standard test method for evaluating thin-film lubricants in a drain and dry mode using Falex pin and Vee block test machine
D 5621	Standard test method for sonic shear stability of hydraulic fluids
D 5704	Standard test method for evaluation of thermal and oxidative stability of lubricating oils used for manual transmissions and final drive axles
D 5706	Standard test method for determining extreme-pressure properties of lubricating greases using a high-frequency, linear-oscillating (SRV) test machine

(continued)

D 5707	Standard test method for measuring friction and wear properties of lubricating grease using a high-frequency, linear-oscillating (SRV) test machine
D 5800	Standard test method for evaporation loss of lubricating oils by the NOACK method
D 5862	Standard test method for evaluation of engine oils in two-stroke cycle turbo-supercharged 6V92TA diesel engine
D 5864	Standard test method for determining the aerobic aquatic biodegradation of lubricants or their components
D 5949	Standard test method for pour point of petroleum products
D 5968-04	Standard test method for evaluation of corrosiveness of diesel engine oil at 121°C
D 5969	Standard test method for corrosion preventive properties of lubricating greases in the presence of dilute synthetic sea water environments
D 6006	Standard guide for assessing biodegradability of hydraulic fluids
D 6022	Standard test method for calculation of permanent shear stability index
D 6046	Standard classification of hydraulic fluids for environmental impact
D 6079 04e1	Standard test method for evaluating lubricity of diesel fuels by the high-frequency reciprocating rig (HFRR)
D 6080 97(2002)	Standard practice for defining the viscosity characteristics of hydraulic fluids
D 6081	Standard practice for aquatic toxicity testing of lubricants: sample preparation and results interpretation
D 6082	Standard test method for high temperature foaming characteristics of lubricating oils
D 6121	Standard test method for evaluation of load carrying capacity of lubricants under conditions of low speed and high torque used for final hypoid drive axles
D 6138	Standard test method for determination of corrosion preventive properties of lubricating greases under dynamic wet conditions (Emcor test)
D 6158	Standard specification for mineral oil hydraulic oils
D 6186	Standard test method for oxidation induction time of lubricating oils by pressure differential scanning calorimetry (PDSC)
D 6203	Standard test method for thermal stability of way lubricants
D 6278	Standard test method for shear stability of polymer-containing fluids using a European diesel injector apparatus (see also D 3945)
D 6278	Standard test method for shear stability of polymer-containing fluids using a European diesel injector apparatus
D 6417	Standard test method for estimation of oil volatility by capillary gas chromatography
D 6425	Standard test method for measuring friction and wear properties of extreme-pressure (EP) lubricating oils using SRV test machine
D 6557	Standard test method for evaluation of rust preventative characteristics of automotive engine oils
D 6594-04a	Standard test method for evaluation of corrosiveness of diesel engine oil at 135°C
D 6595	Standard test method for determination of wear metals and contaminants in used lubricating oils or used hydraulic fluids by rotating disk electrode atomic emission spectrometry
E 537-02	Standard test method for the thermal stability of chemicals by differential scanning calorimetry
E 659	Standard test method for (1994)e1 autoignition temperature of liquid chemicals
E 1064	Standard test method for water in organic liquids by coulometric Karl Fischer titration
G72-82(1996)e1	Standard test method for autogenous ignition temperature of liquids and solids in a high-pressure oxygen-enriched environment
G133/95	Standard test method for linearly reciprocating ball-on-flat sliding wear
STP 315H	Multicylinder test sequence for evaluating automotive engine oils
STP 509A	Single-cylinder engine test for evaluating the performance of crankcase lubricants

27.1.2 CEC TEST METHODS

L-01-A-79 79	Test for diesel engine crankcase oils using the Petter AVI single-cylinder laboratory diesel engine
L-02-A-78 78	Oil oxidation and bearing corrosion test using the Petter W1 single-cylinder gasoline engine
L-07-A-85 85	Load-carrying capacity test for transmission lubricants using the FZG test rig

L-11-T-72	The coefficient of friction of automatic transmission fluids using the DKA friction machine
L-12-A-76 76	Evaluation of piston cleanliness in the MWM KD 12 E test engine (method B more severe)
L-14-A-93 93	Evaluation of the shear stability of lubricating oils containing polymers using the Bosch diesel fuel injector pump rig
L-18-A-80 80	Procedure for measurement of low temperature apparent viscosity by means of the Brookfield viscometer (liquid bath method)
L-19-T-77 77	Evaluation of the lubricity of two-stroke engine oils (using the Motobecane engine AV7L 50 cm ³)
L-20-A-79 79	Evaluation of two-stroke engine lubricants with respect to engine deposit formation oils (using the Motobecane engine AV7L 50 cm ³)
L-21-T-77 77	The evaluation of two-stroke engine lubricants: Sequence I—Piston antiseizure Sequence II—General performance Sequence III—Preignition (using a Piaggio Vespa 180 SS engine)
L-24-A-78 78	Engine cleanliness under severe conditions using the Petter AVB supercharge diesel engine
L-25-A-78 78	Engine oil viscosity stability test (using a Peugeot 204 engine)
L-28-T-79 79	The evaluation of outboard engine lubricant performance (using Johnson and Evinrude marine outboard engines)
L-29-T-81 81	Ford Kent test procedure for evaluating the influence of the lubricating oil on piston ring sticking and deposit formation (using a Ford Kent engine)
L-30-T-81 81	Cam and tappet pitting test procedure (using MIRA cam and tappet test machine)
L-31-T-81 81	Predicting the borderline pumping temperature of engine oils using the Brookfield viscometer
L-33-A-93 93	Biodegradability of two-stroke cycle outboard engine oils in water
L-33-A-94 94	Biodegradability of two-stroke cycle outboard engine oils in water
L-34-T-82 82	Preignition tendencies of engine lubricants (using a Fiat 132C engine)
L-35-T-84 84	Motor oil evaluation in a turbocharged passenger car diesel engine (using a VW ATL 1.6 L).
L-36-96	The evaluation of oil-elastomer compatibility (laboratory test)
L-36-A-90	The measurement of lubricant dynamic viscosity under conditions of high shear (using a Ravensfield viscometer)
L-36-A-97	HTHS
L-37-T-85	Shear stability test for polymer-containing oils (using the FZG test rig)
L-38-A-94	Valve train scuffing (using a PSA TU3 engine) wear test
L-39-T-87	Oil/elastomer compatibility test
L-40-A-93	Lubricating oil evaporative losses (using NOACK evaporative tester)
L-41-T-88	Evaluation of sludge-inhibition qualities of motor oils in a gasoline engine (using a Mercedes-Benz M102E engine)
L-42-A-92	Evaluation of bore polish, piston cleanliness, liner wear, and sludge in a DI turbo-charged diesel engine (using Mercedes-Benz OM364A engine)
L-46-T-93	VW intercooled turbo-diesel ring stitching and piston cleanliness test
L-51-T-95	OM 602A neon test
L-51-T-98	The evaluation of engine crankcase lubricants with respect to low-temperature lubricant thickening and wear under severe operating conditions (MB-OM602A engine) 'A' status granted basis cam-wear only
L-53-T-95	M111 black sludge test
L-54-T-96	Fuel economy effects of engine lubricants (MB M111 E20)
L-55-T-95	TU3 MH high-temperature deposits, ring sticking, and oil thickening test
L-56-T-95	XUD11 ATE medium-temperature dispensarity test
L-56-T-98	Oil dispersion test at medium temperature for automobile diesel engines (XUD11BTE engine)

27.1.3 GENERAL MOTORS

27.1.4 SOCIETY OF AUTOMOTIVE ENGINEERS

J183	Engine oil performance and engine service classification (other than <i>energy-conserving</i>)
J300	Engine oil viscosity classification standard
J357	Physical and chemical properties of engine oils
J1423	Classification of energy-conserving engine oil for passenger cars, vans, and light-duty trucks

27.1.5 MISCELLANEOUS TEST METHODS

CEM	Electric motor test (grease)
DIN 51350	Part 2 weld load
DIN 51350	Part 3 wear scar
DIN 51352-1	Testing of lubricants; determination of aging characteristics of lubricating oils; increase in Conradson carbon residue after aging by passing air through the lubricating oil
DIN 51381	Air release properties per temperature
DIN 51554-1	Testing of mineral oils; test of susceptibility to aging according to Baader; purpose, sampling, aging
DIN 51587	Testing of lubricants; determination of the aging behavior of steam turbine oils and hydraulic oils containing additives
DIN 51802 (IP-220)	Emcor rust test
DIN 51851	ASTM-D 5100 NOACK volatility
DIN 53169	pH at 20°C
Emcor rust test (grease)	
FE-8	Test (grease)
FTM-350	Evaporation loss
FTM 352	Wick ignition
FTM-791B	Cone bleed
FTM-791C (Method 3470.1)	Homogeneity and miscibility
FTM-3009	Contamination, particulate (oils)
FTM 3010	Contamination, gravimetric and ash residue by filtration
FTM 3011	Contamination, particulate by HIAC counter
FTM 3012	Contamination, particulate of oils by filtration
FTM 3403	Compatibility of turbine oils
FTM-3411	Thermal stability and corrosivity
FTM 3432	Compatibility of FKM elastomer
FTM 3433	Navy S silicone rubber, swelling and tensile strength
FTM 3456	Channel point of lubricating oils
FTM 3480	Volatility
FTM 3603	Swelling of rubber NBR-L
FTM 3604	Swelling of rubber NBR-H
FTM 4001.2 2	Salt spray corrosion (see ASTM B 117)
FTM 5306	Corrosiveness of cutting fluid
FTM 5307	Oxidation and corrosion stability
FTM 5308	Oxidation and corrosion stability
FTM-5309	Corrosion, copper, 24 h
FTM-5322	Corrosiveness (bimetallic couple)
GE electric motor test (grease)	
JPI-55-55-99	Hot tube test
MIL-G-22050	Gasket and packing material, rubber, for use with polar fluids, steam, and air at moderately high temperatures
MIL-G-81322	Grease, aircraft wide temperature range
MIL-H-22072C(AS)	Hydraulic fluid catapult

MIL-H-27601B	Hydraulic fluid, petroleum base, high temperature, flight vehicle MIL-H-46170, water sensitivity
MIL-H-46170B	Hydraulic fluid, rust inhibited, fire resistant, synthetic hydrocarbon base
MIL-H-53119	Corrosion rate evaluation procedure (CREP) for CTFE hydraulic fluids MIL-H-83282 high-temperature stability (sealed ampule)
MIL-H-83282	Linear flame propagation rate
MIL-H-83282C	Hydraulic fluid, fire resistant, synthetic hydrocarbon base, aircraft MIL-H-83306 hydraulic fluid, fire resistant, phosphate ester base, aircraft
MIL-H-87257	High-temperature stability (purged with nitrogen)
MIL-P-25732	Cold-resistant acrylonitrile-butadiene rubber
MIL-PRF-2104	Lubricating oil, internal combustion engine, combat/tactical service MIL-PRF-2105 lubricating oil, gear multipurpose
MIL-PRF-10924	Grease, automotive, and artillery
MIL-PRF-46170	Hydraulic fluid, rust inhibited, fire resistant, synthetic hydrocarbon base
MIL-PRF-63460	Lubricant, cleaner and preservative for weapons and weapons systems (metric)
MIL-PRF-81322	Grease, aircraft, general purpose, wide temperature range
MIL-PRF-83282	Hydraulic fluid, fire resistant, synthetic hydrocarbon base, metric, NATO code number H-537
MIL-PRF-87252	Coolant fluid, hydrolytically stable, dielectric
MIL-R-83248	Rubber, fluorocarbon elastomer, high-performance fluid, and compression set resistant
MIL-STD-1246	Cleanliness levels SKF R2F test (simulates paper mill applications)
USS	Low-temperature mobility test (grease)

27.1.6 FEDERAL SUPPLY CLASS 9150 PRODUCT COMMODITIES

Document Summarized Title and Description	QPL	Custodian	NATO Code
MIL-PRF-23699F	Synthetic aircraft turbine engine oil	Yes	Navy/AS O-156/O-154
MIL-PRF-23827C	Aircraft and instrument grease	Yes	G-354
MIL-PRF-81322F	Aircraft wide temperature range grease	Yes	G-395
MIL-PRF-81329D	Solid film lubricant	No (FAT)	S-1737
MIL-PRF-83282D	Synthetic fire-resistant hydraulic fluid	Yes	H-537
MIL-PRF-85336B	All weather lubricant for weapons	Yes	
MIL-L-19701B	Semifluid lubricant for weapons	Yes	
MIL-G-21164D	Molybdenum disulfide grease	Yes	G-353
MIL-L-23398D	Solid film lubricant, air-cure	Yes	S-748
MIL-G-23549C	General-purpose grease	Yes	
MIL-G-25013E	Aircraft bearing grease	Yes	G-372
MIL-G-25537C	Aircraft helicopter bearing grease	Yes	G-366
MIL-H-81019D	Hydraulic fluid for ultra low temperatures	Yes	
MIL-S-81087C ^a	Silicone fluid antiwear grease	Yes	H-536
MIL-G-81827A	Aircraft high loading and antiwear grease	Yes	
MIL-L-81846	Instrument ball bearing lubricating oil	No	
MIL-G-81937A	Ultra clean instrument grease	Yes	
DOD-L-85645A ^a	Dry thin-film lubricant	No	
DOD-G-85733	High-temperature catapult grease	Yes	
DOD-L-85734	Synthetic helicopter transmission lubricant	Yes	
VV-D-1078B	Silicone fluid damping fluid	No	S-1714-1732
SAE J1899	Aircraft piston engine oil, ashless dispersant	Yes	O-123/O-128
SAE J1966	Aircraft piston engine oil, nondispersant	Yes	O-113/O-117
SAE AMS-G-4343	Pneumatic systems grease	No	G-392
SAE AMS-G-6032	Plug valve grease	Yes	G-363
MIL-H-22072C	Hydraulic fluid for catapults	Yes	Navy/AS ^b H-579
A-A-59290	Arresting gear hydraulic fluid	No	Navy/AS ^b

(continued)

Document Summarized Title and Description	QPL	Custodian	NATO Code
MIL-PRF-9000H Diesel engine oil	Yes	Navy/SH	O-278
MIL-PRF-17331H Steam turbine lubricating oil	Yes		O-250
MIL-PRF-17672D Hydraulic fluid	Yes		H-573
MIL-PRF-24139A Multipurpose grease	Yes		
DOD-PRF-24574 Lubricating fluid for oxidizing mixtures	Yes		
MIL-L-15719A High-temperature electrical bearing grease	Yes		
MIL-T-17128C Transducer fluid	No		
MIL-G-18458B Exposed gear and rope grease	Yes		
MIL-H-19457D Fire-resistant hydraulic fluid (FAT)	No		H-580
MIL-L-24131B Graphite and alcohol lubricant	Yes		
MIL-L-24478C Molybdenum disulfide and alcohol lubricant	No		
DOD-G-24508A Multipurpose grease	Yes		
DOD-G-24650 Food processing equipment grease	No		
DOD-G-24651 Food processing equipment lubricating oil	No		
VV-L-825C Lubricating oil for refrigerant compressors	No		O-282/O-290
A-A-50433 Sea water-resistant grease	No		
A-A-50634 Lubricating oil for compressors using HFC-134A	No		
A-A-59004A Antigalling compound	No		
MIL-PRF-6081D Jet engine lubricating oil	Yes	Air Force/11	O-132/O-133
MIL-PRF-6085D Aircraft instrument lubricating oil	Yes		O-147
MIL-PRF-6086E Aircraft gear petroleum lubricating oil	Yes		O-153/O-155
MIL-PRF-7808L Aircraft turbine synthetic engine oil	Yes		O-148/O-163
MIL-PRF-7870C Low-temperature lubricating oil	Yes		O-142
MIL-PRF-8188D Corrosion preventive engine oil (FSC 6850)	Yes		C-638
MIL-PRF-27601C Hydraulic fluid	Yes		
MIL-PRF-27617F Aircraft and instrument grease	Yes		G-397-399/-1350
MIL-PRF-32014 Aircraft and missile high-speed grease	No		
MIL-PRF-83261B Aircraft extreme-pressure grease	No		
MIL-PRF-83363C Helicopter transmission grease	No		G-396
MIL-PRF-87100A Aircraft turbine synthetic engine oil	Yes		
MIL-PRF-87252C Dielectric coolant fluid (FSC 9160)	Yes		S-1748
MIL-PRF-87257A Synthetic fire-resistant hydraulic fluid	Yes		H-538
MIL-H-5606G ^a Petroleum hydraulic fluid for aircraft/ordnance	Yes		H-515
DOD-L-25681D Silicone fluid with molybdenum	No (disulfide)	Air Force/68	S-1735
MIL-L-87177A Synthetic corrosion preventive lubricant	No (FAT)	Air Force/70	
MIL-PRF-2104G Combat/tactical diesel	Yes (engine oil)	Army/AT	O-236/-237/-1236
MIL-PRF-2105E Multipurpose gear oil	Yes		O-186/-226/-228
MIL-PRF-3150D Preservative oil	Yes		O-192
MIL-PRF-6083F Operational and preservative hydraulic fluid	Yes		C-635
MIL-PRF-10924G Automotive/artillery grease	Yes		G-403
MIL-PRF-12070E Fog oil	No		F-62
MIL-PRF-21260E Preservative and break-in engine oil	Yes		C-64 O/C-642
MIL-PRF-32033 Preservative and water-displacing oil	Yes		0-190
MIL-PRF-46002C Vapor corrosion inhibitor (VCI)	No (FAT) preservative oil		
MIL-PRF-46010F Solid-film lubricant	Yes		S-1738
MIL-PRF-46147C Solid-film lubricant	Yes		
MIL-PRF-46167C Arctic engine oil	Yes		O-183

Document Summarized Title and Description	QPL	Custodian	NATO Code
MIL-PRF-46170C Synthetic fire-resistant hydraulic fluid	Yes		H-544
MIL-PRF-46176B Silicon brake fluid	Yes		H-547
MIL-PRF-53074A Steam cylinder lubricating oil	No		O-258
MIL-PRF-53131A Precision bearing synthetic lubricating oil	Yes		
VV-G-632B General-purpose industrial grease	No		
VV-G-671F Graphite grease	No		G-412
A-A-52039B Automotive engine oil API service SH	No		
A-A-52036A Commercial heavy-duty diesel engine oil	No		
A-A-59354 Hydraulic fluid for machines	No		
SAE J1703 Conventional brake fluid	No		H-542
MIL-PRF-63460D Cleaner-lubricant-preservative for weapons	Yes	Army/AR	S-758
MIL-L-11734C Synthetic lubricant for mechanical fuse	No		
Systems Low-temperature weapons lubricant	Yes		O-157
MIL-L-14107C			
MIL-L-45983 Heat-cured solid film lubricant	No		
MIL-L-46000C Semifluid weapons lubricant	Yes		O-158
MIL-G-46003A Rifle grease	Yes		
MIL-L-46150 Semifluid high-loading weapons lubricant	Yes		
MIL-PRF-3572B Colloidal graphite in oil	No		DSCR/GS
MIL-DTL-17111C Power transmission fluid	No		(FAT) H-575
MIL-PRF-26087C Reciprocating compressor lubricating oil	No		
MIL-L-3918A ^a Instrument lubricating oil for jewel bearings	No		
MIL-L-46014 ^a Spindle lubricating oil	No		
MIL-L-83767B ^a Vacuum pump lubricating oil	No		
VV-C-846B Emulsifiable oil-type cutting fluids	No		
A-A-50493A Penetrating oil	No		
A-A-59113 Machine tools/slideways lubricating oil	No		
A-A-59137 Breech block lubricating oil (naval ordnance)	No		
A-A-59173 Silicone grease	No		
A-A-59197 Fatty oil for metalworking lubricants	No		
SAE AS1241C Fire-resistant phosphate ester hydraulic fluid	No		

^a These specifications had been designated as "Inactive for New Design" and no longer used except for replacement purpose.
Their QPLs will be maintained until the products are no longer required.

^b See Navy/AS2 under Abbreviations section.

27.1.7 SPECIFICATIONS HAVING CROSS-REFERENCE AMONG JIS, ASTM, AND OTHERS

ASTM or Others	JIS	Title and Contents
F 312	B 9930	Hydraulic fluid—determination of particulate contamination by the particle count method
F 313	B 9931	Fluid contamination—determination of contaminants by the gravimetric method
D 117	C 2101	Testing method of electrical insulating oils
D 923		Sampling
D 4559		Evaporation
D 1218/21807		Refractive index and specific dispersion
D 974		Total acid number
D 1275		Corrosive sulfur
D 1533		Water content
D 2112/2440		Oxidation stability

(continued)

ASTM or Others	JIS	Title and Contents
D 877/1816		Dielectric strength
D 924		Dielectric loss tangent and relative dielectric constant
D 1169		Volume resistivity
	K 2249	Crude petroleum and petroleum products—determination of the density and petroleum measurement tables based on a reference temperature (15°C)
D 1298/E100		I-shaped float method
D 4052/5002		Oscillating method
ISO 3833		Wardon pycnometer method
D 941		I-shaped pycnometer method
D 70		Hubbard pycnometer method
D 1250		Density, mass, and volume conversion table
D 140/4057/4177	K 2251	Crude petroleum and petroleum products—sampling
D 1093	K 2252	Testing method for reaction of petroleum products
	K 2254	Petroleum products—determination of distillation characteristics
D 86, E133		Test method for distillation of petroleum products at atmospheric pressure
D 1160		Test method for distillation of petroleum products at reduced pressure
D 2287		Test method for boiling range distillation of petroleum products by gas chromatography
	K 2255	Petroleum products—gasoline—determination of lead content
D 3341		Iodine monochloride method
D 3237		Atomic absorption spectroscopy method
D 661	K 2256	Testing methods for aniline point and mixed aniline point of petroleum products
D 323	K 2258	Testing method for vapor pressure of crude oil and petroleum products (Reid method)
D 381	K 2261	Petroleum products—motor gasoline and aviation fuels—determination of existent gum—jet evaporation method
	K 2265	Crude oil and petroleum products—determination of flash point
D 56		Tag closed test
D 3828/3278		Small-scale closed test
D 93		Pensky—Martens closed cup test
D 92		Cleveland open cup test
	K 2269	Testing methods for pour point and cloud point of crude oil and petroleum products
D 97		Pour point
D 2500		Cloud point
	K 2270	Crude petroleum and petroleum products—determination of carbon residue
D 189		Conradson method
D 4530		Micro method
	K 2272	Testing methods for ash and sulfated ash of crude oil and petroleum products
D 482		Ash
D 874		Sulfated ash
	K 2275	Crude oil and petroleum products—determination of water content
D 95/4006		Distillation method
D 4377/1744		Karl-Fischer volumetric method
		Karl-Fischer coulometric method
DIN 9114		Hydride reaction method
	K 2276	Petroleum products—testing methods for aviation fuels
D 873		Oxidation stability (potential residue)
D 2386		Freezing point
D 1094		Water tolerance
D 235/4952		Doctor test
D 3227		Determination of mercaptan sulfur (potentiometric method)
D 1740		Luminometer number test
D 1840		Determination of naphthalene (ultraviolet spectroscopy)
FS 1151.2		Explosive vapor test

ASTM or Others	JIS	Title and Contents
D 3242		Total acid number
D 3948		Water separation index (micro separometer)
D 2550		Water separation index (water separometer)
D 3241		Thermal stability (JFTOT)
D 2276/5452		Particulate contaminant
IP 227		Copper corrosion
D 2624		Electric conductivity
D 3343		Hydrogen content
	K 2279	Crude petroleum and petroleum products—determination and estimation of heat of combustion
D 4529/4868		Net heat of combustion
D 4868		Gloss heat of combustion
K 2280		Petroleum products—fuels—determination of octane number, cetane number, and calculation of cetane index
D 2699		Research octane number
D 2700		Motor octane number
D 909		Supercharge octane number
D 613		Cetane number
D 4737		Calculation method for cetane index using four variable equation
D 1368		Small amount of lead in <i>n</i> -heptane and iso-octane (dithizone method)
D 2268		Purity of <i>n</i> -heptane and iso-octane (capillary gas chromatography)
K 2283		Crude petroleum and petroleum products—determination of kinematic viscosity and calculation of viscosity index from kinematic viscosity
D 445/446		Kinematic viscosity
D 2270		Viscosity index
D 341		Estimated relation between kinematic viscosity and temperature
D 525	K 2287	Testing methods for oxidation stability of gasoline (induction period method)
IP 309	K 2288	Gas oil—determination of cold filter plugging point
	K 2301	Fuel gas and natural gas—methods for chemical analysis and testing
D 1145		Sampling of gas sample
D 1945/1946		Chemical analysis (gas chromatography)
ISO 6326-1		Analysis of total sulfur
ISO 6326-1		Analysis of hydrogen sulfide
ISO 6327		Analysis of water (dew point method)
D 900/1826		Heat of combustion (Junkers gas calorimeter)
D 3588		Heat of combustion (calculation method)
D 1070		Specific gravity (picnometer method)
D 3588		Specific gravity (calculation method)
D 4057	K 2420	Method of sampling for aromatic hydrocarbon and tar products
	K 2501	Petroleum products and lubricants—determination of neutralization number
D 974		Color indicator titration (TAN, strong acid number, strong base number)
D 664		Potentiometric titration (TAN, strong acid number)
D 4739		Potentiometric titration (TBN, strong base number)
D 2896		Potentiometer titration (TBN, perchloric acid method)
	K 2503	Testing method of lubricating oil for aircraft
D 91/2273		Precipitation number
D 94		Saponification number
FS 3006.3		Contamination
FS 204.1		Diluted pour point
ISO 6617		Oxidation stability
FS 5308.7		Corrosiveness and oxidation stability
D 665	K 2510	Testing method for rust-preventing characteristics of lubricating oil

(continued)

ASTM or Others	JIS	Title and Contents
D 130	K 2513	Petroleum products—corrosiveness to copper—copper strip test
	K 2514	Lubricating oils—determination of oxidation stability
ISOT		Oxidation stability of lubricants for internal combustion engine
D 943		Turbine oil oxidation stability test (TOST)
D 2272		Rotating pressure vessel oxidation test (RBOT)
D 3397		Total acid number (semimicro method)
IP 280		Turbine oil oxidation stability (oil-soluble catalyst method)
D 892	K 2518	Petroleum products—lubricating oils—determination of foaming characteristics
K 2619		Lubricating oils—testing methods for load-carrying capacity
D 2619		Soda four-ball (four-ball test modified by Dr. Soda)
D 2782		Timken
K 2520		Petroleum products—lubricating oils—determination of demulsibility characteristics
D 1401		Demulsibility test
IP 19		Steam emulsion number
K 2536		Liquid petroleum products—testing method of components
D 1319/2001/2427		Fluorescent indicator adsorption analysis (FIA)
D 2267/4420/5580		Determination of aromatics by gas chromatography
D 1322	K 2537	Petroleum product—aviation turbine fuels and kerosene—determination of smoke point
K 2540		Testing method for thermal stability of lubricating oils
K 2541		Crude oil and petroleum products—determination of sulfur content
D 2785/ISO 4260		Oxy-hydrogen combustion method
D 3120		Microcoulometric titration
D 1551		Quartz tube test
D 4294/ISO 8754		Energy dispersive x-ray fluorescence spectroscopy
D 129		General bomb method
D 1266		Lamp method
D 2622		Wavelength dispersive x-ray fluorescence spectroscopy
K 2580		Petroleum products—determination of color
D 156		Saybolt
D 1500		ASTM
K 2601		Testing methods for crude petroleum
D 3828		Flash point
D 96/4007/1796		Water and sediment
IP 77		Salt content (titration)
D 3230		Salt content (coulometric)
D 2892		Distillation at atmospheric pressure
D 1159/2710	K 2605	Petroleum distillates and commercial aliphaticolefins—determination of bromine number—electrometric method
K 2609		Crude petroleum and petroleum products—determination of nitrogen content
D 3228		Macro-Kjeldahl method
D 3431		Microcoulometric titration
D 4629/5762		Chemiluminescence method

Note: ISOT = Indiana Stirring Oxidation Test.

27.2 ABBREVIATIONS USED

QPL	Qualified Products Listing
FAT	No QPL exists, but a First Article Test (FAT) is required or may be optional
Navy/AS	Naval Air Systems Command (NAVAIR), Patuxent River, MD
Navy/AS2	Naval Air Systems Command (NAVAIR), Lakehurst, NJ
Navy/SH	Naval Sea Systems Command (NAVSEA), Arlington, VA

Navy/YD	Naval Facilities Engineering Command (NAVFAC), Alexandria, VA
Air Force/11	Air Force Aeronautical Systems Center (ASC), Wright-Patterson AFB, OH
Air Force/68	Air Force San Antonio Air Logistics Center (SAALC), Kelly AFB, TX
Air Force/70	Hill Air Force Base Logistics Center, UT
Army/AT	Army Tank-Automotive and Armaments Command, Tank-Automotive Research Development and Engineering Center (TARDEC), Warren, MI
Army/AR	Army Tank-Automotive and Armaments Command, Armaments Research Development and Engineering Center (ARDEC), Picatinny, NJ
DSCR/GS	Defense Logistics Agency's Defense Supply Center Richmond (DSCR), Richmond, VA

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28 Lubricant Industry–Related Terms and Acronyms

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The plethora of acronyms related to the field of lubrication continues to grow. These acronyms and abbreviations come from a variety of diverse industries and disciplines, including original equipment manufacturers, component suppliers, lubricant additive and fluid suppliers and producers, and professional societies directly and peripherally involved in the lubricant industry. Each class of lubricants, synthetic and conventional, has its set of abbreviations reserved to describe differences in structure or performance characteristics. Terms and acronyms for lubricant additives are numerous and generally reflect the chemical structure or the type of additive. In some cases, the acronym reflects the function of the additive. Acronyms created at different times by different industries have resulted in identical abbreviations that refer to different things.

This chapter lists many of the important terms generally used in the lubricant industry. A complete list would require far more space than can be devoted in this book.

28.1 TERMS AND ACRONYMS

21 CFR	The section of the Code of Federal Regulations that deals with lubricants and incidental contact
178.3570	
2T/2-cycle	A term applied to lubricants for two-cycle engines (i.e., motorcycles, outboard marine motors, and weed whackers)
3P2E	Three-ring polyphenyl ether
4P3E	Four-ring polyphenyl ether
4T	A term applied to lubricants for four-cycle engines
5P4E	Five-ring polyphenyl ether
6P5E	Six-ring polyphenyl ether
AAM	Alliance of Automobile Manufacturers
AAMA	American Automobile Manufacturers Association
AAR	American Association of Railroads
AB	Alkylbenzene
ABIL	Agriculture-based industrial lubricants
ABMA	American Bearing Manufacturers Association—a nonprofit association of American manufacturers of antifriction bearings, spherical plain bearings, or major components thereof. The purpose of ABMA is to define national and international standards for bearing products and maintain bearing industry statistics.

ABOT	Aluminum Beaker Oxidation Test for Ford Mercon ATF approval
ABSA	Alkylbenzenesulfonic acid; precursor to overbased calcium sulfonate
ACC	American Chemistry Council
ACEA	Association des Constructeurs Européens d'Automobiles (European Auto Manufacturers Association)
ACERT	Advanced Combustion Emission Reduction Technology (Caterpillar)
ACIL	American Council of Independent Laboratories—ACIL is the national trade association representing independent, commercial engineering and scientific laboratory, testing, consulting, and R&D firms.
ACS	American Chemical Society
Additive	Chemical compound or formulation of several chemical compounds added to a base oil to alter its physical, chemical, and performance properties
AEL	Allowable exposure limit
AEOT	Engine oil aeration test
AES	Average engine sludge
AEV	Average engine varnish
A/F	Air to fuel ratio
AFNOR	Association Française de normalisation
AFOA	American Fats and Oils Association
AFR	Air/fuel ratio
AFV	Alternate fuel vehicle
AGELFI	Cooperative Research Organization of AGIP, ELF, and FINA oil companies
AGMA	American Gear Manufacturers Association—an organization for the establishment and promotion of industrial gear lubricant standards
AGO	Automotive gas oil
AHEM	Association of Hydraulic Equipment Manufacturers
AIAM	Association of International Automobile Manufacturers
AIChE	American Institute of Chemical Engineers
AIT	Autoignition temperature (ASTM D 2155)—the lowest temperature at which a gas or vaporized liquid will ignite in the absence of an ignition source
AL	Atmospheric lifetime
ALTNER	Alternative Energy Programs of the European Commission
AMA	Automobile Manufacturers Association
ANFAVEA	Brazil Auto Manufacturers Association
ANIQ	Mexican equivalent to the CMA
ANSI	American National Standards Institute
Antioxidant	A chemical component added to lubricants to reduce the tendency for oxidation-related degradation of the oil
Antiwear additive	Additives that can deposit multilayer films thick enough to supplement marginal hydrodynamic films and prevent asperity contact, or preferentially wear rather than allow contact between asperities that result in wear.
AO	Antioxidant
AOCA	American Oil Change Association—provides a link between the motoring public and auto maintenance specialists
AOCS	American Oil Chemists Society—a global forum for the science and technology of fats, oils, surfactants, and related materials
APE	Association of Petroleum Engineers (United States)
API	American Petroleum Institute—society organized to further the interest of the petroleum industry

API GL-4	Designates the type of service characteristic of gears, particularly hypoid in passenger cars and other automotive-type equipment operated under high-speed, low-torque and low-speed, and high-torque conditions; largely replaced by performance standard API GL-5
API GL-5	Designates the type of service characteristic of gears, particularly hypoid, in passenger cars and other automotive-type equipment operated under high-speed, shock load; high-speed, low-torque; and low-speed, high-torque conditions
AQIRP	Auto/Oil Air Quality Improvement Research Program
ARB	Air Resources Board (California)
ASA	American Soybean Association
ASEAN	Association of South East Asian Nations
Ashless	Additive containing no metallic elements
ASLE	American Society of Lubrication Engineers (now STLE)
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
A/T	Conventional shifting automatic transmission
ATA	American Trucking Association
ATC	Additive Technical Council (European Petroleum Additive Industry Association, European CMA)
ATD	Allison Transmission Division; division of General Motors
ATF	Automatic transmission fluid
ATIEL	Association Technique de l'Industrie Européene des Lubrifiants (European Oil marketers Association)
AT-PZEV	Advanced technology partial zero-emission vehicle
Auto-Oil-Program	A joint activity between the European Union (EU), the European Oil Industry (EUROPIA), and the European motor industry (ACEA)
AW	Antiwear agent—minimizes wear by reacting with a metal surface to provide a protective layer
b-CVT	Belt CVT
BIA	Boating Industry Association—industry body organized to specify lubricants for marine application (now NMMA)
Biodegradability	The ability of a chemical compound to be broken down by living organisms
BFPA	British Fluid Power Association
bhp-hr	Brake horsepower-hour
BHRA	British Hydromechanics Research Association
BLF	British Lubricants Federation
Block grease	A very firm grease produced as a block that is applied to large open plain bearings, which operate at low speed and high temperatures
BNA	Bureau des Normes de l'Automobile (France)
BNP	Bureau de Normalisation de Pétroles
BOCLE	Ball on cylinder lubricity evaluator
BOFT	Bearing oil film thickness
BOI	Base oil interchange
BOIG	Base Oil Interchange Guidelines
BOTD	Ball on three disks
Boundary	A regime of lubrication where there is partial contact between the metal components and partial separation of the surfaces by the lubricant fluid film
BPD	Biocidal Products Directive

BPT	Borderline pumping temperature (as defined in ASTM D 3829)
Br	Bromine number (ASTM D 1158)
Brookfield viscosity	Viscosity in centipoise, as determined on the Brookfield viscometer is the torque resistance on a spindle rotating in the fluid being tested. Although Brookfield viscosities are most frequently associated with low-temperature properties of gear oils and transmission fluids, they are in fact determined for many other types of lubricant.
BRT	Ball rust test—the new bench test to replace Sequence IID engine test to measure rust and corrosion at low temperatures
BSFC	Brake-specific fuel consumption
BSI	British Standards Institution
BTC	British Technical Council of the Motor and Petroleum Industries (CEC)
BTU	British Thermal Units
C-3	Specification by Allison Division of General Motors covering transmission application
CA (API)	Service typical of diesel engines operated in mild to moderate duty with high-quality fuels and occasionally has included gasoline engines in mild service. Oils designed for this service provide protection from bearing corrosion and from ring belt deposits in some naturally aspirated diesel engines when using fuels of such quality that they impose no unusual requirements for wear and deposit protection. They were widely used in the late 1940s and 1950s but should not be used in any engine unless specifically recommended by the equipment manufacturer.
CAA	Clean Air Act
CAAA	Clean Air Act Amendment
CAFÉ	Corporate Average Fuel Economy
CARB	California Air Resources Board
Carbon residue	Percentage of coked material remaining after a sample of lubricating oil has been exposed to high temperatures under ASTM Method D 189 (Conradson) or D 524 (Ramsbottom)
Caterpillar IP	A single-cylinder engine test designed to measure piston deposit control of an engine oil
CB (API)	Service typical of diesel engines operated in mild to moderate duty, but with lower-quality fuels that necessitate more protection for wear and deposits. Occasionally has included gasoline engines in mild service. Oils designed for this service provide necessary protection from bearing corrosion and from ring belt deposits in some naturally aspirated diesel engines with higher-sulfur fuels. Oils designed for this service were introduced in 1949.
CBO	Conventional base oil
CBOT	Chicago Board of Trade
CC (API)	Service typical of certain naturally aspirated, turbocharged, or supercharged diesel engines used when highly effective control of wear and deposits is vital or using fuels of a wide quality range including high-sulfur fuels. Oils designed for this service were introduced in 1955 and provide protection from bearing corrosion and from high-temperature deposits in these diesel engines.
	Oil meeting the performance requirements measured in the following diesel and gasoline engine tests: the 1-G2 diesel engine test has been correlated with indirect injection engines used in heavy-duty operation, particularly with regard to piston and ring groove deposits. The L-38 gasoline engine test

	requirement provides a measurement of copper–lead bearing weight loss and piston varnish under high-temperature operating conditions.
CCD	Combustion chamber deposits
CCR	Conradson carbon residue
CCS	Cold-cranking simulator
CD-II (API)	Service typical of two-stroke cycle engines requiring highly efficient control over wear and deposits. Oils designed for this service also meet all performance requirements of API service category CD.
	Oil meeting the performance requirements measured in the following diesel and gasoline engine tests: The I-G2 diesel engine test has been correlated with indirect injection engines used in heavy-duty operation, particularly with regard to piston and ring groove deposits. The 6V-53T diesel engine test has been correlated with vehicles equipped with two-stroke cycle diesel engines in high-speed operation before 1985, particularly with regard to ring and liner distress. The L-38 gasoline engine test requirement provides a measurement of copper–lead bearing weight loss and piston varnish under high-temperature operating conditions.
CDP	Cresyl diphenyl phosphate
CE (API)	Service typical of many turbocharged or supercharged high-performance diesel engines, operated under both low-speed/high-load and high-speed/high-load conditions. Oils designed for this service have been available since 1984 and provide improved control of oil consumption, oil thickening, and piston assembly deposits and wear relative to the performance potential offered by oils designed for category CD service.
	Oil meeting the performance requirements of the following diesel and gasoline engine tests: the 1-G2 diesel engine test has been correlated with indirect injection engines used in heavy-duty service, particularly with regard to piston and ring groove deposits. The T-6, T-7, and NTC-400 are direct injection diesel engine tests. The T-6 has been correlated with vehicles equipped with engines used in high-speed operation before 1980, particularly with regard to deposits, oil consumption, and wear. The T-7 test has been correlated with vehicles equipped with engines used in lugging operation before 1984, particularly with regard to oil thickening. The NTC-400 diesel engine test has been correlated with vehicles equipped with engines in highway operation before 1983, particularly with regard to oil consumption, deposits, and wear. The L-38 gasoline engine test requirement provides a measurement of copper–lead bearing weight loss under high-temperature operating conditions.
CEC	California Energy Commission
	Conseil Européen de Co-ordination pour les Développements des Essais de Performance des Lubrifiants et des Combustibles pour Moteurs (Coordinating European Council of Motor and Petroleum Industries: test standardization like ASTM)
CFFIC	Conseil Européen des Federations de l'Industrie Chimique (European Chemical Industry Council)
CEN	European Standardization Council
CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CF (API)	API service category CF denotes service typical of indirect injected diesel engines and other diesel engines that use a broad range of fuel types including those using fuel with higher sulfur content (e.g., 0.5 wt%).

Effective control of piston deposits, wear, and copper-containing bearing corrosion is essential for these engines, which may be naturally aspirated, turbocharged, or supercharged. Oils designated for this service have been in existence since 1994. Oils designated for this service may also be used when API service category CD is recommended.

CF-2 (API) API service category CF-2 denotes service typical of two-stroke cycle engines requiring highly effective control over cylinder and ring-face scuffing and deposits. Oils designated for this service have been in existence since 1994 and may also be used when API Service Category CD-II is recommended. These oils do not necessarily meet the requirements of CF or CF-4 unless passing test requirements for these categories.

CF-4 (API) This category was adopted in 1990 and describes oils for use in high-speed, four-stroke diesel engines. API CF-4 oils exceed the requirements of the CE category, providing improved control of oil consumption and piston deposits. Oil meeting the performance requirements in the following diesel and gasoline engine tests: the 1K diesel engine test, which has been correlated with direct injection engines used in heavy-duty service before 1990, particularly with regard to piston and ring groove deposits in the T-6, T-7, NTC-400, and L-38 engines: see “CE (API)” for explanation.

CFC Chlorofluorocarbon

CFPP Cold filter plugging point

CFR Coordinating Fuel and Equipment Research Committee

CFV Clean fuel vehicle

CG Conventional gasoline

CG-4 (API) API service category CD-4 describes oils for use in high-speed four-stroke cycle diesel engines used in both heavy-duty on-highway (<0.05 wt% sulfur fuel) and off-highway (<0.5 wt% sulfur fuel) applications. CG-4 oils provide effective control over high-temperature piston deposits, wear corrosion, foaming, oxidation stability, and soot accumulation. These oils are especially effective in engines designed to meet 1994 exhaust emission standards and may also be used in engines requiring API Service Categories CD, CE, and CF-4. Oils designated for this service have been in existence since 1994.

CGSB Canadian General Standards Board—a consensus organization of producers, users, and general interest groups, which develops standards for test methods and products for Canada.

CH-4 (PC-7) New (proposed) classification for the generation of heavy-duty engine oils

CI Cetraне index

CIA Chemical Industries Association (part of the CEFIC)

CIDI Compression ignition direct injection (diesel)

CIMAC International Council on Combustion Engines

CLCA Comité de Liaison de la Construction de l'Automobile

CLEPA Comité de Liaison de la Construction d'Equipments et Pièces d'Automobiles

CLR Cooperative Lubricants Research

CMA Chemical Manufacturers Association—a standardizing body composed of additive manufacturers (United States)

CMAQ Congestion Mitigation and Air Quality Improvement Program

CMMO Chemically modified mineral oil

CMVO Chemically modified vegetable oil

CN Cetane number

CNG Compressed natural gas

CNHTC	China National Heavy Truck Corporation
CNPC	China National Petroleum Corporation
CO	Carbon monoxide
CO₂	Carbon dioxide
CONCAWE	Conservation of Clean Air and Water (Europe)
Corrosion inhibitor	A lubricant additive used to protect surfaces against chemical attack from contaminants in the lubricating fluid or grease. These additives generally operate by reacting chemically and forming a film on the metal surfaces.
cP	Centipoise = mPa · s (SI unit)
CPC	Chinese Petroleum Corporation
CPPI	Canadian Petroleum Products Institute
CRC	Coordinating Research Council—an American standardizing body for performance testing
CSA	Canadian Standards Association
cSt	Centistokes
CSTCC	Continuously slipping torque converter clutch
Cummins M11	A heavy-duty engine test to measure crosshead wear
CUNA	Commission Technica di Unificazione Nel l'Autoveicolo (CEC)
CVMA	Canadian Vehicle Manufacturers Association
CVS	Constant volume sampling
CVT	Continuously variable transmission
DAP	Detroit Advisory Panel (API)
DASMIN	Deutsche Akkreditierungastelle Mineralöl (German)
DBC	Dibutyl carbonate
DBPP	Dibutyl phenyl phosphate
DCT	Dual clutch transmission
DDC	Detroit Diesel Corporation
DEC	Diethyl carbonate
DEER	Diesel engine emissions reduction
Demulsibility	A measure of the ability of an oil to separate from water to that measured by the test time required for a specified oil–water emulsion to break using ASTM D 1401.
DEO	Diesel engine oil
DEOAP	Detroit Engine Oil Advisory Panel (API/EMA)
DETA	Diethylene triamine
Detergent	Oil additive that prevents deposits from forming on engine surfaces and may remove previously formed deposits
DEXRON®-II	General Motors trademark specification for ATF
DEXRON®-III	General Motors trademark specification for ATF, issued in 1993
DEXRON®-IIIIG	General Motors trademark specification for ATF, issued in 1998
DFA	Diesel fuel additive
DGMK	Deutsche Gesellschaft fur Mineralölwissenschaft und Kohlechemie
DH-I	AJASO diesel engine oil category—a category mainly for Japanese-made heavy-duty diesel engine providing wear, soot-handling properties, and thermal-oxidative stability.
DHYCA	Direction des Hydrocarbarres et Carburants (French Ministry of Industry)
	Direct injection (normally diesel)
	Driveability index
DII	Diesel injection improver
DIN	Deutsches Institut für Normung (German Standards Institute)

Dispersant	Oil additive that keeps engines clean by holding in suspension the insoluble products for oil oxidation and fuel combustion formed during engine operation
DIOC	Diisooctyl carbonate
DiPE	Dipentaerythritol
DKA	Deutscher Koordinierungs-Ausschuss—the German National Body in the Coordinating European Council
DMC	Dimethyl carbonate
DME	Dimethyl ether
DNA	Deutsche Normenausschuss
DOA	Diocetyl adipate
DOC	Diesel oxidation catalyst
DOCP	Dispersant olefin copolymer viscosity modifier or viscosity index improver
DOD	Department of Defense
DOE	Department of Energy
DOHC	Double overhead cam
DOP	Di-2-ethylhexylphthalate
DOS	Di-2-ethylhexylsebacate
DOT	Department of Transportation (United States)
DPF	Diesel particulate filter
DPMA	Dispersant polymethacrylate viscosity modifier
Dropping point	The temperature at which a grease changes from a semisolid to a fluid under the test conditions. This temperature can be considered a measure of the upper use limit for the grease.
DSC	Differential scanning calorimetry—used to measure onset oxidation temperatures of oils
DTBP	Di- <i>tert</i> -butyl phenol
DVM	Dispersant viscosity modifier
EC	European Community
	European Commission
	Environmental Council (Japan)
	Energy conserving
	Environment Canada
ECCC	Electronically controlled computer clutch
	EC-II (API)
	Energy Conserving-II—designation that an engine oil provides 2.7% fuel economy improvement versus a reference oil in the Sequence VI test
ECE	Economic Commission for Europe
ECHA	European Chemicals Agency—control point in the REACH system established in Helsinki.
ECTC	Engine Coolants Technical Committee (CEC)
EDC	Electronic diesel control
EEB	European Environmental Bureau
EEC	European Economic Community
	Electronic Emission Controls
EELQMS	European Engine Lubricant Quality Management System
EFI	Electronic fuel injection
EFTC	Engines Fuels Technical Committee (CEC)
EGR	Exhaust gas recirculation
EHD	Elastohydrodynamic (lubrication)
EHDPP	2-Ethylhexyl diphenyl phosphate

EHEDG	European Hygiene and Equipment Design Group
EIA	Energy Information Administration (U.S. DOE)
EINECS	European Inventory of Existing Chemical Substances
ELGI	European Lubricating Grease Institute
ELINCS	European List of Notified Chemical Substances
ELTC	Engine Lubricants Technical Committee (CEC)
ELV	End-of-life vehicle
EMA	Engine Manufacturers Association (United States); heavy-duty diesel
EMPA	Swiss Federal Laboratories for Materials Testing and Research
Emulsion	A mechanical mixture of two mutually insoluble fluids. Some metalworking fluids are designed to remain as a stable emulsion by incorporation of an emulsifier.
ENGVA	European Natural Gas Vehicle Association
EOFT	Engine Oil Filterability Test (GM)
EO-J/EO-K/EO-K/2	Mack Truck Company heavy-duty diesel specifications
EO-L	Mack Truck Company heavy-duty diesel specification, issued in 1993
EOLCS	Engine Oil Licensing and Certification System (API-1520)
EO-M	Mack Truck Company heavy-duty diesel specifications, issued in 1998
EP additive	Extreme-pressure additive—an additive designed to prevent metal–metal adhesion or welding when the degree of surface control is sufficiently high that the normal protective (oxide) films are removed and other surface-active species in the oil are not reactive enough to deposit a protective film. EP additives function by reacting with the metal surface to form a metal compound, for example, iron sulfide.
EPA	Environmental Protection Agency (United States)
EPACT	The Energy Policy Act of 1992 (EPAct)
EPDM	Ethylenepropylene diene–based elastomeric seal material
EPEFE	European Program on Emission, Fuels and Engine Technologies (an advisory group consisting of 14 motor companies [ACEA] and 32 oil companies [EUROPIA])
EPM	Ethylene–propylene-based elastomeric seal material
ERC	European Registration Centre
ESCS	Engine Service Classification System
ESI	Extended service, internal
ESIS	European Chemical Substances Information System
ETC	European Transient Test Cycle
ETLP	Engine Tests of Lubricants Panel (IP)
EU	European Union
EUC	Elementary Urban Cycle
EUDC	Extra Urban Driving Cycle
EULIM	European Union of Independent Lubricant Manufacturers
EUROPIA	European Petroleum Industry Association
EV	Electric vehicle
EVA	Ethyl vinyl alcohol
FATG	Fuel Additive Task Group (CMA)
FBP	Final boiling point
FCAA	Federal Clean Air Act Amendments
FCC	Fluid catalytic cracker
FCEV	Fuel cell electric vehicle
FDA	Food and Drug Administration

FE	Fuel economy
FEI	Fuel economy improvement (fuel efficiency increase)
FERC	Federal Energy Regulatory Commission (United States)
FF	Factory fill
FFV	Flexible fuel vehicle
FIE	Fuel injection equipment
FIMS	Field ionization mass spectrometry
Fire point	ASTM D 92—a laboratory test to measure the lowest temperature at which a sample will sustain burning for 5 s
FISITA	Federation Internationale des Sociétés d'Ingenierus des Techniques de l'Automobile
Flash point	ASTM D 92—a laboratory test to measure the tendency of a sample to form a flammable mixture with air, the lowest temperature at which a test flame causes the vapor of a fluid to ignite
Four-Ball Test	<p>Two test procedures based on the same principle:</p> <ol style="list-style-type: none"> 1. Four-Ball EP Test (ASTM D 2596) 2. Four-Ball Wear Test (ASTM D 2266) <p>The three lower balls are clamped together to form a cradle upon which the fourth ball rotates in a vertical axis. The balls are immersed in the lubricant under investigation. The test is used to determine the relative wear-preventing properties of lubricants operating under boundary lubrication conditions. The test is carried out at a specified speed, temperature, and load. At the end of the specified period, the average diameter of wear scar on the three balls is reported. The Four-Ball EP Test is designed to evaluate performance under much higher loads. In this test, the top ball is rotated at a specified speed (1700 ± 60 rpm), but temperature is not controlled. The loading is increased at specified intervals until the rotating ball seizes and welds to the other balls. At the end of each interval, the average scar diameter is recorded. Two values are generally reported—load wear index and weld point.</p>
FSIS	Food Safety Inspection Service
FT	Fischer-Tropsch
FTC	Federal Trade Commission (United States)
FTIR	Fourier transform infrared spectroscopy
FTM	Federal Test Method (United States)
FTP	Federal Test Procedure (EPA)
FZG	Forschungstelle für Zahnrad und Getriebbau (Research Institute for Gears and Gearboxes)
GAO	General Accounting Office (United States)
GATC	Gross additive treat cost
GC	Gas chromatography
	In the ASTM D 4950 Standard Classification and Specification for Automotive Service Greases, the letters GC designate service typical of the lubrication of wheel bearings operating in passenger cars, trucks, and other vehicles under mild to severe duty.
GDI	Gasoline direct injection
GDTC	Gross delivered treating cost
GEO	Gas engine oil—lubricant used for natural gas engines
GEPE	Group des Experts pour la Pollution et l'Energie (Group of Experts for Pollution and Energy)
GF-2	ILSAC PCMO oil classification standard, effective from August 1997

GF-3	ILSAC PCMO oil classification after GF-2, proposed in 2000
GFC	Groupement Française de Coordination (CEC)
GHS	Global Harmonization System
GI	Gelation index (as defined in ASTM D 5133)
GL-4/5	Gear service characteristics (API)
GM	General Motors
GMO	Glycerol monoleate
GO-H	Gear lubricant specified by Mack Truck Company
GRAS	Generally recognized as safe
GRPE	Groups des Rapporteurs pour la Pollution et l'Énergie
GSA	General Service Administration (United States)
GTL	Gas-to-liquid
GWP	Global warming potential
H-1	The USDA classification that applies to lubricants with incidental food contact and to ingredients used to make these lubricants. Under NSF, H-1 applies to lubricants and HX-1 applies to ingredients for H-1 lubricants.
H-2	The USDA classification that applies to lubricants in food processing plants with no food contact and to ingredients used to make these lubricants. Under NSF, H-2 applies to lubricants and HX-2 applies to ingredients for H-2 lubricants.
HACCP	Hazard and Critical Control Point implement procedures for USDA regulators requirements
HAP	Hazardous air pollutant
HC	Hydrocarbon
HCB	Hydrocracker bottoms
HCCI	Homogeneous charge combustion ignition
HCFC	Hydrochlorofluorocarbon
HD	Heavy duty
HDD	Heavy-duty diesel
HDDEO	Heavy-duty diesel engine oil
HDDO	Heavy-duty diesel oil
HDEO	Heavy-duty engine oil
HDEOCP	Heavy-Duty Engine Oil Classification Panel
HDMO	Heavy-duty motor oil
HEFCAD	High-energy, friction characteristics and durability; part of DEXRON®-II qualification program
HEUI	Hydraulically operated electronically controlled unit injectors
HFC	Hydrofluorocarbon
HFE	Hydrofluoroether
HF-O	Denison specification for heavy-duty hydraulic antiwear fluids
HFRR	High-frequency reciprocating rig
HOOT	Hot oil oxidation test
HOPOE	Highly optimized polyol ester
HPV	High production volume
HRMS	High-resolution mass spectroscopy
HSPOE	High-stability polyol ester
HTHS	High-temperature, high-shear viscosity measured at 150°C and 10 ⁶ s ⁻¹ (ASTM D 4683, CEC L-36-A-90), (ASTM D 4741), or (ASTM D 5481)
HTHSRV	High-temperature, high-shear rate viscosity
HVI	High-viscosity index

Hydrodynamic lubrication	A lubrication regime characterized by a full-fluid film between two moving surfaces. As oil is moved between the moving parts, the action causes a high pressure in the lubricant fluid, and this separates the moving parts.
HX-1	NSF classification that applies to ingredients for H-1 lubricants.
HX-2	NSF classification that applies to ingredients for H-2 lubricants.
IBP	Initial boiling point
IC	Internal combustion
IchemE	Institution of Chemical Engineers (United Kingdom)
ICOA	International Castor Oil Association
ICOMIA	International Council of Marine Industries Association
IDDPP	Isodecyl diphenyl phosphate
IDI	Indirect injection (diesel)
IEA	International Energy Agency
IENICA	Interactive Network for Industrial Crops and Applications
IFP	Institut Français du Pétrole
IGL	Investigation Group Lubricants (CEC)
ILMA	Independent Lubricant Manufacturers Association—an association of oil companies, also called as compound blenders
ILSAC	International Lubricant Standards Approval Committee
I/M	Vehicle Inspection and Maintenance Program
IMECHE	Institution of Mechanical Engineers
IOP	Institute of Physics—Tribology Group
IP	Institute of Petroleum (United Kingdom)
IPPP	Isopropylphenyl phenyl phosphate
IR	Infrared (spectroscopy)
ISO	International Standards Organization
ISOT	Indiana Stirred Oxidation Test (adopted as JIS K 2514)
ISTEA	Intermodal Surface Transportation Act
IVD	Intake value deposit
IVT	Infinitely variable transmission
JALOS	Japanese Lubricating Oil Society
JAMA	Japan Automobile Manufacturers Association
JARI	Japan Automotive Research Institute
JASIC	Japan Automobile Standards Internationalization Center
JASO	Japan Automotive Standards Organization
JAST	Japan Society of Tribologists
JATA	Japan Automobile Transport Technology Association
JCAP	Japan Clean Air Program
JD	John Deere—a farm implement manufacturer
JIC	J. I. Case—a farm implement manufacturer
JIS	Japan Industries Standard
JISC	Japan Industrial Standards Committee
JPI	Japan Petroleum Institute
JSAE	Japan Society of Automotive Engineers
KTH	Royal Institute of Technology, Sweden
KV	Kinematic viscosity
LB	In the ASTM D 4950 Standard Classification and Specification for Automotive Service Greases, the letters LB designate service typical of lubrication of chassis components and universal joints in passenger cars, trucks, and other vehicles under mild to severe duty.

LCO	Light cycle oil
LCST	Lower critical solution temperature
LDV	Light-duty vehicle
LeRC	Lewis Research Center—NASA
LEV	Low-emission vehicle
LMOA	Locomotive Maintenance Officers Association
LNG	Liquefied natural gas
LOFI	Lubricant oil flow improver
LPG	Liquefied petroleum gas
LPV	Low production volume
LRI	Lubricant Review Institute—a body associated with SAE that qualifies heavy-duty engine oil and gear lubricants for the industry and the U.S. military
LSC	Lubricant Standards Committee
LSD	Low-sulfur diesel
M11	Cummins heavy-duty engine test (CH-4) to measure crosshead wear
M111	A Mercedes-Benz gasoline engine oil fuel economy test (CEC-L-54-T-96)
Mack T-8	Engine test used by Mack Truck Company in specifying heavy-duty diesel lubricants, extended to 300 h
Mack T-9	Engine test used by Mack Truck Company in specifying heavy-duty diesel lubricants; more severe (higher-soot loading) test required for CH-4 specifications
Mannich	A name reaction that produces unique fuel and lubricant detergent/dispersants
MB	Mercedes-Benz
MB OM364A	A Mercedes-Benz heavy-duty diesel engine oil test to measure bore polish, piston cleanliness, and turbo deposits (CEC-L-52-T-97)
MB OM602A	A Mercedes-Benz diesel engine oil test to measure cam wear (CEC-L-51-T-95)
MERCON® V	Ford Motor Company trademark ATF specification
MIL	Military specification
MIL-L-210F	Latest in a series of heavy-duty diesel lubricants designated by the U.S. military for over-the-road and off-highway applications
MIL-L-2105C	U.S. military specifications for mobile equipment gear lubricant, now superseded
MIL-L-2105D	U.S. military specification for mobile equipment gear lubricants; active through 1995
MIL-PRF-2105E	U.S. military gear specification, issued on August 22, 1995
MIRA	Motor Industry Research Association (United Kingdom)
MITI	Ministry of International Trade and Industry (Japan)
MOD	Ministry of Defense
MOE	Ministry of Energy (United Kingdom)
MOFT	Minimum oil film thickness
MOL	Ministry of Labor (Japan)
MON	Motor octane number
MOT	Ministry of Transport (United Kingdom)
MOU	Memorandum of understanding
MRV	Minirotary viscometer—a measure of oil pumpability at various temperatures (ASTM D 3829 and ASTM D 4683)
MSDS	Material Safety Data Sheets
MT-1	Manual transmissions specifications, issued in 1995 (API)
MTAC	Multiple test acceptance criteria

MTBE	Methyl <i>t</i> -butyl ether
MTF	Manual transmission fluid
MVEG	Motor Vehicle Emissions Group (Europe)
MVMA	Motor Vehicle Manufacturers Association (U.S. passenger cars)
MWF	Metalworking fluid(s)
NA	Normally (or naturally) aspirated (diesel engine)
NAAQS	National Ambient Air Quality Standards (United States)
NACE	National Association of Corrosion Engineers (United States)
NAEGA	North American Export Grain Association
NAFTA	North American Free Trade Agreement
NATC	Net additive treat rate
NCM	National Comite Motorproeven (Netherlands) (CEC)
NCPA	National Cottonseed Products Association
NCWM	National Conference on Weights and Measures
NDOCP	Nondispersant olefin copolymer
NDTC	Net delivered treat rate
NDVM	Nondispersant viscosity modifier
NEB	National Energy Board (NA)
NEDO	National Environmental Board (Thailand)
NEFI	New Energy and Technology Development Organization (Japan)
NEL	New England Fuel Institute
NESCAUM	National Engineering Laboratory (United Kingdom)
NESHAP	Northeast States for Coordinated Air Use Management
NFPA	National Emission Standard for Hazardous Air Pollutants
NGEO	National Fluid Power Association
NGFA	Natural gas engine oil
NI	National Grain and Feed Association
NIOP	Nonpolarity index
NIST	National Institute of Oilseed Products
NLEV	National Institute of Standards and Technology (United States)
NLGI	National low-emission vehicle
NLP	National Lubricating Grease Institute (United States)
NMHC	No-longer polymers
NMMA	Nonmethane hydrocarbon
NMOG	National Marine Manufacturers Association (United States) (formerly Boating Industry Association [BIA])
NMR	Nonmethane organic gases (includes alcohols)
NOACK	Nuclear magnetic resonance
NOPA	NOACK volatility; DIN 51851 (ASTM D 5800)
NORA	National Oilseed Processors Association
NOX	National Oil Recyclers Association (United States)
NPA	Nitrogen oxide
NPG	National Petroleum Association (United States)
NPI	Neopentylglycol
NPRA	Nonpolarity index
NRC	National Petroleum Refiners Association (United States)
NRCC	Natural Resources Canada
NREL	National Research Council of Canada
NRL	National Renewable Energy Laboratory
	Naval Research Laboratory

NSF	National Sanitation Foundation—a nongovernmental, nonprofit corporation assumed the role formerly held by USDA. NSF creates registry numbers for approved lubricant products.
NTC-400	Cummins diesel engine test
NUTEK	Swedish National Board for Industrial and Technical Development
OCP	Olefin copolymer viscosity modifier or viscosity index improver
ODI	Oil drain interval
ODP	Ozone depleting potential
ODS	Ozone depleting substance
OEM	Original equipment manufacturer (e.g., GM and Ford)
OICA	Organization Internationale des Constructeurs d'Automobiles (was BPICA)
OMB	Office of Management and Budget (United States)
OMS	Office of Mobile Sources (U.S. EPA)
ON	Octane number
OPEC	Organization of Petroleum Exporting Countries
OPEST	Oil Protection of Emission Systems Test
ORD	Octane requirement decrease
ORI	Office of Research and Development (U.S. EPA)
ORNL	Octane requirement increase
OSHA	Oak Ridge National Laboratory
OTA	Occupational Safety and Health Administration (United States)
OTAG	Office of Technology Assessment (United States)
OTC	Ozone Transport Assessment Group
Oxidation	Ozone Transport Commission
	One of several modes of oil degradation. The process generally involves the addition of oxygen to the lubricant structure, followed by cleavage or polymerization, resulting in unfavorable oil properties and performance.
Package	Formulation of various chemical compounds
PADD	Petroleum Administration for Defense District
PAG	Polyalkene glycols, polyalkylene glycols
PAH	Polyaromatic hydrocarbons
PAHO	Pan American Health Organization
PAJ	Petroleum Association of Japan
PAO	Polyalphaolefin; base stocks of various viscosity classifications
PAPTG	Product Approval Protocol Task Group (CMA0)
PBT	Persistent, bioaccumulative and toxic
PC	Proposed classification
PCD	Passenger car diesel
PCEO	Passenger car engine oil
PCMO	Passenger car motor oil
PCTFE	Polychlorotrifluoroethylene
PDSC	Pressure differential scanning calorimetry
PDVSA	Petroleos de Venezuela
PE	Pentaerythritol
PEA	Polyether amine
PEC	Petroleum Energy Center
PFPAE	Perfluoropolyalkylether
PFPE	Perfluoropolyether
Phenolic	Antioxidant based on 2,6-di- <i>tert</i> -butyl phenol chemistry or other alkylated phenolics

PIB	Polyisobutene
PIBSA	Polyisobutetyl succinic anhydride; precursor for ashless dispersants
PIO	Polyinternalolefins
PM	Particulate matter
PM_{2.5}	Particulate matter <2.5 μm diameter
PM₁₀	Particulate matter <10 μm diameter
PMA	Polymethacrylate
PMAA	Petroleum Marketers Association of America
PMC	Pensky-Martin Closed Cup—flash point test
PNA	Polynuclear aromatic
PNGV	Partnership for a New Generation of Vehicles (United States)
POFA	Polymerized fatty acids
Poise	The CGS unit of absolute viscosity (dyne s/cm ²) as measured by the shear stress required to move one layer of fluid along another over a total thickness of 1 cm at a shear rate of 1 cm/s. Absolute viscosity values are independent of density and are directly related to the resistance to flow.
Pour point	This is a widely used low-temperature flow indicator and is 3°C above the temperature at which normally a liquid petroleum product maintains fluidity. It is a significant factor in cold-weather start-up, but must be considered along with pumpability, the ease with which an oil forms a honeycomb or crystals at low temperatures near the pour point. A conventional measure of the lower-temperature limit for low-temperature flow of a lubricating fluid.
PPD	Pour point depressant—an additive used to lower the pour point of an oil by modifying the structure of wax crystals
PPE	Polyphenyl ether
ppm	Parts per million
PSA TU3M	A Peugeot gasoline engine test to measure cam wear and scuffing (CEC-L-38-A-94)
	A Peugeot gasoline engine test to measure high-temperature ring sticking and piston varnish (CEC-L-55-T-95)
PSA XUD 11	A Peugeot diesel engine test to measure medium-temperature dispersivity (soot-induced oil thickening) (CEC L-56-T-95)
PTFE	Polytetrafluoroethylene
PTIT	Petroleum Institute of Thailand
PTT	Petroleum Authority of Thailand
PVA	Polymethacrylate viscosity index improver or viscosity modifier
PVC	Pressure viscosity coefficient
PVE	Polyvinyl ether
QPL	Qualified Products List (U.S. military)
RBOT	Rotating bomb oxidation test
RCRA	Resource Conservation Recovery Act
RFG	Reformulated gasoline
RI	Radial isoprene (star polymer) viscosity modifier or viscosity index improver
RME	Rapeseed methyl ester
R&O	Rust and oxidation—inhibited lubricant for use in circulating systems, compressors, hydraulic systems, and gear cases
ROCOT	Rotating compressor oxidation test
RON	Research octane number
ROSE	Rose Foundation—Recovery of Oil Saves the Environment
RSI	Registration Systems, Inc. (CMA monitoring agency)

Rust inhibitor	A lubricant additive for protecting ferrous (iron and steel) components from rusting caused by water contamination or other harmful materials formed by oil degradation. Some rust inhibitors operate similarly to corrosion inhibitors by reacting chemically to form an inert film on metal surfaces. Other rust inhibitors absorb water by incorporating it into a water-in-oil emulsion so that only the oil touches the metal surfaces.
RVP	Reid vapor pressure
SA (API)	Service typical of older engines operated under such mild conditions that the protection afforded by compounded oils is not required. This category should not be used in any engine unless specifically recommended by the equipment manufacturer.
SAE	Society of Automotive Engineers
SAIC	Shanghai Automotive Industry Group
SAIT	South African Institute of Tribologists
SARA	Superfund Amendments and Reauthorization Act
SB	Styrene–butadiene viscosity modifier or viscosity index improver
SB (API)	Service typical of older gasoline engines operated under such mild conditions that only minimum protection afforded by compounding is desired. Oils designed for this service have been used since 1930s and provide only antiscuff capability and resistance to oil oxidation and bearing corrosion. They should not be used in any engine unless specifically recommended by the equipment manufacturer.
SC (A[O])	Service typical of gasoline engines in 1964–1967 models of passenger cars and some trucks operating under engine manufacturers' warranties in effect during those model years. Oils designed for this service provide control of high- and low-temperature deposits, wear, rust, and corrosion in gasoline engines.
SCAQMP	South Coast (California) Air Quality Management
Scuffing	Wear caused by the localized welding and fracture of rubbing surfaces
SD (API)	Service typical of gasoline engines in 1968–1970 models of passenger cars and some trucks operating under engine manufacturers' warranties in effect during those model years. Also may apply to certain 1971 and later models as specified (or recommended) in the owners' manuals. Oils designed for this service provide more protection against high- and low-temperature engine deposits, wear, rust, and corrosion in gasoline engine than oils that are satisfactory for API engine service category SC and may be used when API engine service category SC is recommended.
SE (API)	Service typical of gasoline engines in passenger cars and some trucks beginning with 1972 and certain 1971 models operating under engine manufacturers' warranties. Oils designed for this service provide more protection against oil oxidation, high-temperature engine deposits, rust, and corrosion in gasoline engines than oils that are satisfactory for API Engine Service Categories SD or SC and may be used when either of these classifications is recommended.
Sequence IIIE, F	Engine test to simulate expressway driving to measure oxidation and wear characteristics of formulated oils at high temperature
Sequence tests	A series of (ASTM) industry-standardized tests used to determine the quality of crankcase lubricants (i.e., Sequence IID, IIIE, VE, and VIA)
Sequence UL-38	Engine test similar to L-38 except fuel used is unleaded; test measures bearing wear and deposits
Sequence VE, F	Engine test to simulate stop-and-go driving and to measure sludge, varnish, cam wear, and oil screen plugging

Sequence VIA, B	Engine test designed to measure fuel efficiency properties of an engine oil (VIA for ILSAC GF-2 and VIB for ILSAC GF-3)
SF (API)	Service typical of gasoline engines in passenger cars and some trucks beginning with the 1980 model year operating under manufacturers' recommended maintenance procedures. Oils developed for this service provide increased oxidation stability and improved antiwear performance relative to oils that meet the minimum requirements for API service category SE. The oils also provide protection against engine deposits, rust, and corrosion. Oils meeting API service classification SF may be used where API service categories SE, SD, or SC are recommended. Oils meeting the performance requirements measured in the following gasoline engine tests: the IID gasoline engine test has been correlated with vehicles used in short-trip service before 1978, particularly with regard to rusting. The IIIE gasoline engine test has been correlated with vehicles used in high-temperature service before 1988, particularly with regard to oil thickening and valve train wear. The VE gasoline engine test has been correlated with vehicles used in stop-and-go service before 1988, particularly with regard to sludge and valve train wear. The L-38 gasoline engine test requirement provides a measurement of copper-lead bearing weight loss and piston varnish under high-temperature operating conditions. The 1-H2 diesel engine test requirement provides a measurement of high-temperature deposits.
SH (API)	Service requirement for gasoline engines and dated in 1993 for use in current and earlier passenger car, van, and light-truck operation under vehicle manufacturers' recommended maintenance procedures. Oils developed for this category may be used where SG oils are recommended. SH oil provides improved control of engine deposits, oil oxidation, wear, corrosion, and rust relative to oils developed for previous categories. Engine oils that meet SH designation may use the API Base Oil Interchangeability Guidelines and API Guidelines for SAE Viscosity-Grade Engine Testing.
SHC	Synthetic hydrocarbon
SHPD	Super high-performance diesel
SHPDO	Super high-performance diesel oil
SI	Styrene-isoprene viscosity modifier or viscosity index improver spark ignition Système Internationale—units of measurement (m, kg, s, K)
SIA	Société des Ingénieurs de l'Automobile
SIAM	Society of Indian Automotive Manufacturers
SIB	Sulfurized isobutylene—a basic EP additive for gear lubricant packages
SIEF	Substance Information Exchange Forum
SIGMA	Society of Independent Gasoline Marketers of America
SIP	Styrene-isoprene copolymer
SIP(s)	State Implementation Plan(s)
SIS	Sveriges Standardiseringskommission
SJ (API)	Service requirement adopted for gasoline engines in 1996 for use in current and earlier passenger car, sport utility vehicle, van, and light truck under vehicle manufacturers' recommended maintenance procedures Oils developed for the category may be used where API SH and earlier categories are recommended. Engine oils that meet the category may use the API Base Oil Interchangeability Guidelines and the API Guidelines for SAE Viscosity-Grade Engine Testing.

SMDS	Shell Middle Distillate Synthesis
SME	Society of Manufacturing Engineers
SMM&T	Society of Motor Manufacturers and Traders Ltd. (United Kingdom)
SMR	Svenska Mekanisters Riksforening (National Organization in Sweden [CEC])
SMRP	Society for Maintenance and Reliability Professionals
SNAP	Significant New Alternatives Policy
SNCF	Societe Nationale des Chemins de fer Francais
SNPRM	Supplemental notice of proposed rule making
SNV	Schweizerische Normenvereinigung (National Organization, Switzerland) (CEC)
SOF	Soluble oil fraction
SOT	Spin orbit tribometer
SSI	Shear stability index
SSU or SUS	Saybolt Second Universal or Saybolt Universal Second—a measure of viscosity, or a fluid's resistance to flow
STLE	Society of Tribologists and Lubrication Engineers
STOU	Super tractor oil universal—a term commonly applied to a lubricant that can be used for all applications of a tractor, including hydraulic, engine, wet brakes, and gear
SULEV	Super ultralow-emission vehicle
SUV	Sport utility vehicle
SwRI	Southwest Research Institute
T-8	Engine test used by Mack Truck Company in specifying heavy-duty diesel lubricants, extended to 300 h
T-9	Engine test used by Mack Truck Company in specifying heavy-duty diesel lubricants, more severe (higher-soot loading) test required for CH-4 specifications
TAD	Technische Vereinigung fur Mineralöladditive in Deutschland EV (subgroup of the ATC)
TAN	Total acid number—a measure of a lubricant's acidity
TBEP	Tributoxyethyl phosphate
TBN	Total base number—a measure of the acid-neutralizing property of a lubricating oil
TBP	Tributyl phosphate
TBPP	<i>tert</i> -butylphenyl phenyl phosphate
TBS	Tapered bearing simulator (ASTM D 4683)
TCP	Tricresyl phosphate
t-CVT	Toroidal CVT
TCW-3	Water-cooled two-cycle engine oil specification
TEOST	Thermal engine oil stability test
TFB	Swedish Transport Research Board
TFMO	Thin-film micro-oxidation test
TFOUT	Thin-film oxygen uptake test
TGA	Thermogravimetric analysis
THCT	Turbo hydramatic cycling test; part of DEXRON® qualification program
ThOD	Theoretical oxygen demand
THOT	Turbo hydramatic oxidation test; part of DEXRON® qualification program
TiBP	Triisobutyl phosphate
TISI	Thailand Industrial Standards Institute
TLEV	Transitional low-emission vehicle
TLTC	Transmission Lubricants Technical Committee (of CEC)

Timken OK load	This is a measure of the extreme-pressure properties of a lubricant. Lubricated by the product under investigation, a standard steel roller rotates against a block. Timken OK load is the heaviest load that can be carried without scoring.
TMC	ASTM Test Monitoring Center
TMP	Trimethylolpropane
TO-2	Caterpillar specification for transmission oil, including durability and frictional property testing
TO-3	Caterpillar specification, including TO-2 plus fluoroelastomer seal compatibility
TO-4	Caterpillar specification, including TO-2 plus fluoroelastomer seal compatibility, nearest version of Caterpillar transmission, and drive train fluid requirements
TOCP	Tri-orthocresyl phosphate
TOST	Turbine oil stability test
TOTM	Trioctyl trimellitate
TOU	Tractor oil universal—an oil that goes in all parts of the tractor, except for the engine
TPP	Triphenyl phosphate
Tribology	The science and technology of interacting surfaces in relative motion and the practice related thereto
TSCA	Toxic Substances Control Act
TÜV	Technischer Überwachungs Verein
TVMD	See TAD
TXP	Trixylenyl phosphate
UCBO	Unconventional base oil
UCST	Upper critical solution temperature
UDC	Urban Driving Cycle (Europe)
UEIL	Union Européen des Indépendants en Lubrifiants (European Union of Independent Lubricant Manufacturers)
UFIP	Union Francaise des Industries Petrolières
UIC	Union des Industries Chimiques
UKPIA	United Kingdom Petroleum Industry Association
ULEV	Ultralow-emission vehicle
ULSD	Ultralow sulfur diesel
USB	United Soybean Board
USCAR	United States Council for Automotive Research
USDA	United States Department of Agriculture
USX	Formerly U.S. Steel; dominant maker of steel and specifier of industrial lubricants for the steel, and related-industries
UTAC	L'Union Technique de l'Automobile Oil—used in all lubricating places, except the crankcase on a farm tractor
UTTO	Universal Tractor Transmission Oil—used in all lubricating places, except the crankcase on a farm tractor
VCI	Verein der Chemischen Industrie
VDA	Verband der Automobilindustrie
VDI	Verein Deutscher Ingenieure
VDS, VDS2	Volvo Long Drain Lubricant Specification
VGO	Vacuum gas oil
VGRA	Viscosity-grade read across
VHVI	Very high viscosity index

VI	Viscosity index—a measure of the rate of change in viscosity with temperature (higher VI means less change) (ASTM D 2270)
VII	Viscosity index improver—additive that increases the viscosity index beyond that which can be obtained using ordinary refining methods
Viscosity	Measure of resistance of flow of a liquid; dynamic viscosity is the ratio between the applied shear and the rate of shear, expressed in poise or centipoise; kinematic viscosity is the ratio of the viscosity (dynamic viscosity) to the density of the liquid, expressed in stokes or centistokes
Viton®	A fluoroelastomeric compound from DuPont, presently used by Caterpillar and Mercedes-Benz for use in transmission application
VM	Viscosity modifier
VMI	Viscosity modifier interchange
VOC	Volatile organic compound
VOF	Volatile organic fraction
Volatility	A measure of the amount of material evaporated from a sample under a particular set of conditions, usually expressed as a percentage of the original sample
VTC	Viscosity-temperature coefficient
VVT	Variable valve train
VW 1431 TCIC	A Volkswagen indirect injection diesel engine oil test to measure ring sticking and piston cleanliness (CEC-L-46-T-93)
VW DI	A Volkswagen direct injection diesel engine oil test to measure ring sticking and piston cleanliness (CEC-L-78-T-97)
WAFI	Wax antisettling flow improver
WASA	Wax antisettling additive
WCM	Wax crystal modifier
WSPA	Western States Petroleum Association
XDP	Xylenyl diphenyl phosphate
ZDDP	Zinc dialkyldithiophosphate—a widely used antiwear and antioxidant agent for motor oils and industrial fluids; also referred to as ZDTP, ZDP, and “zinc”
ZDP/ZDTP	Zinc dithiophosphate
ZEV	Zero-emission vehicle
ZF	German transmission manufacturer, Zahnradfabrik Friedrichshafen A.G.

28.2 SOME FEDERAL SUPPLY CHAIN ABBREVIATIONS

Air Force/11	Air Force Aeronautical Systems Center (ASC), Wright-Patterson AFB, OH
Air Force/68	Air Force San Antonio Air Logistics Center (SAALC), Kelly AFB, TX
Army/AR	Army Tank-Automotive and Armaments Command, Armaments Research Development and Engineering Center (ARDEC), Picatinny, NJ
Army/AT	Army Tank-Automotive and Armaments Command, Tank-Automotive Research Development and Engineering Center (TARDEC), Warren, MI
DSCR/GS	Defense Logistics Agency's Defense Supply Center Richmond (DSCR), Richmond, VA
FAT	No QPL exists, but a first article test (FAT) is required, or may be optional
Navy/AS	Naval Air Systems Command (NAVAIR), Patuxent River, MD
Navy/AS²	Naval Air Systems Command (NAVAIR), Lakehurst, NJ
Navy/SH	Naval Sea Systems Command (NAVSEA), Arlington, VA
Navy/YD	Naval Facilities Engineering Command (NAVFAC), Alexandria, VA
QPL	Qualified Products Listing

29 Internet Resources for Additive/Lubricant Industry

Leslie R. Rudnick

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29.1 ALPHABETICAL LISTING

- 2V Industries Inc., www.2vindustries.com
49 North, www.49northlubricants.com
76 Lubricants Company, www.tosco.com
A.W. Chesterton Company, www.chesterton.com
A/R Packaging Corporation, www.arpackaging.com
Acculube, www.acculube.com
Accumetric LLC, www.accumetric.com
Accurate Lubricants & Metalworking Fluids, Inc. (dba Acculube), www.acculube.com
Acheson Colloids Company, www.achesonindustries.com
Acme Refining, Division of Mar-Mor Inc., www.acmerefining.com
Acme-Hardesty Company, www.acme-hardesty.com
Adco Petrol Katkilari San Ve. Tic. AS, www.adco.com.tr
Advanced Ceramics Corporation, www.advceramics.com
Advanced Lubrication Technology Inc. (ALT), www.altboron.com
Aerospace Lubricants Inc., www.aerospacelubricants.com
AFD Technologies, www.afdt.com
AG Fluoropolymers USA Inc., www.fluoropolymers.com
Airflow Systems Inc., www.airflowsystems.com
Airosol Company, Inc., www.airsol.com
Akzo Nobel, www.akzonobel.com
Alco-Metalube Company, www.alco-metalube.com
Alfa Laval Separation, www.alfalaval.com
Alfa Romeo, www.alfaromeo.com
Alithicon Lubricants, Division of Southeast Oil & Grease Company, Inc., www.alithicon.com

Allegheny Petroleum Products Company, www.oils.com
Allen Filters Inc., www.allenfilters.com
Allen Oil Company, www.allenoil.com
Allied Oil & Supply Inc., www.allied-oil.com
Allied Washoe, www.alliedwashoe.com
Amalie Oil Company, www.amalie.com
Amber Division of Nidera, Inc., www.nidera-us.com
Amcar Inc., www.amcarinc.com
Amerada Hess Corporation, www.hess.com
American Agip Company, Inc., www.americanagip.com
American Bearing Manufacturers Association, www.abma-dc.org
American Board of Industrial Hygiene, www.abih.org
American Carbon Society, www.americancarbon society.org
American Chemical Society (ACS), www.acs.org
American Council of Independent Laboratories (ACIL), www.acil.org
American Gear Manufacturers Association (AGMA), www.agma.org
American International Chemical, Inc., www.aicma.com
American Lubricants Inc., www.americanlubricantsbflo.com
American Lubricating Company, www.americanlubricating.com
American Machinist, www.americanmachinist.com
American National Standards Institute (ANSI), www.ansi.org
American Oil & Supply Company, www-aosco.com
American Oil Chemists Society (AOCS), www.aocs.org
American Petroleum Institute (API), www.api.org
American Refining Group Inc., www.amref.com
American Society for Horticultural Science (ASHS), www.ashs.org
American Society for Testing and Materials (ASTM), www.astm.org
American Society of Agricultural Engineering (ASAE), www.asae.org
American Society of Agronomy (ASA), www.agronomy.org
American Society of Mechanical Engineers International (ASME), www.asme.org
American Synthol Inc., www.americansynthol.com
Amoco, www.amoco.com
Amtron Corporation, www.superslipperystuff.com/organisation.htm
Amrep Inc., www.amrep.com
AMSOIL Inc., www.amsoil.com
Ana Laboratories Inc., www.analaboratories.com
Analysts Inc., www.analystinc.com
Anderol Specialty Lubricants, www.anderol.com
Andpak Inc., www.andpak.com
ANGUS Chemical Company, www.dowchemical.com
Anti Wear 1, www.dynamicdevelopment.com
API Links, www.api.org/links
Apollo America Corporation, www.apolloamerica.com
Aral International, www.aral.com
Arch Chemicals, Inc., www.archbiocides.com
ARCO, www.arco.com
Argonne National Laboratory, www.et.anl.gov
Arizona Chemical, www.arizonachemical.com
Asbury Carbons, Inc.—Dixon Lubricants, www.asbury.com
Asbury Graphite Mills Inc., www.asbury.com
Asheville Oil Company, Inc., www.ashevilleoil.com

Ashia Denka, www.adk.co.jp/en/chemical/index.html
Ashland Chemical, www.ashchem.com
Ashland Distribution Company, www.ashland.com
Asian Oil Company, www.asianoilcompany.com
Associated Petroleum Products, www.associatedpetroleum.com
Associates of Cape Cod Inc., www.acciusa.com
Atlantis International Inc., www.atlantis-usa.com
Atlas Oil Company, www.atlasoil.com
Audi, www.audi.com
Ausimont, www.ausiusa.com
Automotive Aftermarket Industry Association (AAIA), www.aftermarket.org
Automotive News, www.autonews.com
Automotive Oil Change Association (AOCA), www.aoca.org
Automotive Parts and Accessories Association (APAA), www.apaa.org
AutoWeb, www.autoweb.com
AutoWeek Online, www.autoweek.com
Avatar Corporation, www.avatarcorp.com
Badger Lubrication Technologies Inc., www.badgerlubrication.com
Baker Petrolite, www.bakerhughes.com/bakerpetrolite/
BALLISTOL USA, www.ballistol.com
Bardahl Manufacturing Corporation, www.bardahl.com
Baron USA Inc., www.baronusa.com
BASF Corp., www.bASF.com
Battenfeld Grease and Oil Corporation of New York, www.battenfeld-grease.com
Bayer Corp., www.bayer.com
Behnke Lubricants Inc./JAX, www.jax.com
Behnke Lubricants/JAX, www.jaxusa.com
Bell Additives Inc., www.belladditives.com
Bel-Ray Company Inc., www.belray.com
Benz Oil Inc., www.benz.com
Berenfield Containers, www.berenfield.com
Bericap NA, www.bericap.com
Bestolife Corporation, www.bestolife.com
BF Goodrich, www.bfgoodrich.com
BG Products Inc., www.bgprod.com
Bharat Petroleum, www.bharatpetroleum.com
Big East Lubricants Inc., www.bigeastlubricants.com
Bijur Lubricating Corporation, www.bijur.com
Bio-Rad Laboratories, www.bio-rad.com
BioTech International Inc., www.info@biotechintl.com
Bismuth Institute, www.bismuth.be
Blackstone Laboratories, www.blackstone-labs.com
Blaser Swisslube, www.blaser.com
BMW (International), www.bmw.com/bmwe
BMW (United States), www.bmwusa.com
BMW Motorcycles, www.bmw-motorrad.com
Boehme Filatex Inc., www.boehmefilatex.com
BP Amoco Chemicals, www.bpamocochemicals.com
BP Lubricants, www.bplubricants.com
BP, www.bppetrochemicals.com
Brenntag Northeast, Inc., www.brenntag.com

Brenntag, www.brenntag.com
Briner Oil Company, www.brineroil.com
British Lubricants Federation Ltd., www.blf.org.uk
British Petroleum (BP), www.bp.com
Britsch Inc., www.britschoil.com
Brno University of Technology, Faculty of Mechanical Engineering, Elastohydrodynamic Lubrication Research Group, www.fme.vutbr.cz/en
Brugarolas SA, www.brugarolas.com/html/eng/actividades_industriales.php
Buckley Oil Company, www.buckleyoil.com
Buckman Laboratories Inc., www.buckman.com
Buick (GM), www.buick.com
Burlington Chemical, www.burco.com
BVA Oils, www.bvaoils.com
Cabot Corporation (fumed metal oxides), www.cabot-corp.com/cabosil
Cadillac (GM), www.cadillac.com
California Air Resources Board, www.arb.ca.gov
Callahan Chemical Company, www.calchem.com
Caltex Petroleum Corporation, www.caltex.com
Calumet Lubricants Company, www.calumetlub.com
Calvary Industries Inc., www.calvaryindustries.com
CAM2 Oil Products Company, www.cam2.com
Cambridge, chemfinder.cambridgesoft.com
Cambridge University, Department of Materials Science and Metallurgy, Tribology, www.msm.cam.ac.uk/tribo/tribol.htm
Cambridge University, Department of Engineering, Tribology, www.mech.eng.cam.ac.uk/Tribology/
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Cannon Instrument Company, www.cannon-ins.com
Capital Enterprises (Power-Up Lubricants), www.nnl690.com
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Cargill—Industrial Oil & Lubricants, www.techoils.cargill.com
Car-Stuff, www.car-stuff.com
Cary Company, www.thecarycompany.com
Castle Products Inc., www.castle-comply.com
Castrol Heavy Duty Lubricants, Inc., www.castrolhdl.com
Castrol Industrial North America, Inc., www.castrolindustrialna.com
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CAT Products Inc., www.run-rite.com
Caterpillar, www.cat.com
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Center for Innovation Inc., www.centerforinnovation.com
Center for Tribology, Inc. (CETR), www.cetr.com
Centurion Lubricants, www.centurionlubes.com
CEPSA (Spain), www.cepsa.es
Champion Brands LLC, www.championbrands.com
Chart Automotive Group Inc., www.chartauto.com
Chattem Chemicals, Inc., www.chattemchemicals.com
Chem Connect, www.chemconnect.com
Chem-EcoI Ltd., www.chem-ecol.com
Chemetall Foote Corporation, www.chemetall.com

Chemical Abstracts Service, www.cas.org
Chemical Resources, www.chemcenter.org
Chemical Week Magazine, www.chemweek.com
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Chemplube International Inc., www.chemlube.com
Chemsearch Lubricants, www.chemsearch.com
Chemtool Inc./Metalcote, www.chemtool.com
Chevrolet (GM), www.chevrolet.com
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Chevron Texaco, www.chevrontexaco.com
Chevron, www.chevron.com
Christenson Oil, www.christensonoil.com
Chrysler (Mercedes Benz), www.chrysler.com
Ciba Specialty Chemicals Corporation, www.cibasc.com
CITGO Petroleum Corporation, www.citgo.com
Citroen (France), www.citroen.com
Citroen (United Kingdom), www.citroen.co.uk/fleet
Clariant Corporation, www.clariant.com
Clark Refining and Marketing, www.clarkusa.com
CLC Lubricants Company, www.clclubricants.com
Climax Molybdenum Company, www.climaxmolybdenum.com
Coastal Hydraulic Engineering Ltd, www.coastalhydraulics.com/OilsLubricants.htm
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College of Petroleum and Energy Studies, www.colpet.ac.uk
Colorado Petroleum Products Company, www.colopetro.com
Colorado School of Mines Advanced Coating and Surface Engineering Laboratory (ACSEL),
www.mines.edu/research/acsel/acsel.html
Commercial Lubricants Inc., www.comlube.com
Commercial Ullman Lubricants Company, www.culc.com
Commonwealth Oil Corporation, www.commonwealthoil.com
Como Industrial Equipment Inc., www.comoindustrial.com
Como Lube & Supplies Inc., www.comolube.com
Computational Systems, Inc., www.compsys.com/index.html
Concord Consulting Group Inc., www.concordcg.com
Condat Corporation, www.condatcorp.com
Conklin Company, Inc., www.conklin.com
Conoco, www.conoco.com
Containment Solutions Inc., www.containsolutions.com
Coolants Plus Inc., www.coolantsplus.com
Co-ordinating European Council (CEC), www.cectests.org
Coordinating Research Council (CRC), www.crcao.com
Cortec Corporation, www.cortecvci.com

Cosby Oil Company, www.cosbyoil.com
Cosmo Oil, www.cosmo-oil.co.jp
Country Energy, www.countryenergy.com
CPI Engineering Services, www.cpieng.com
CRC Industries, Inc., www.crcindustries.com
Creanova, Inc., www.creanovainc.com
Crescent Manufacturing, www.crescentmfg.net
Croda Inc., www.croda.com
Crompton Corporation, www.cromptoncorp.com
Crop Science Society of America (CSSA), www.crops.org
Cross Oil Refining and Marketing Inc., www.crossoil.com
Crowley Chemical Company Inc., www.crowleychemical.com
Crystal Inc-PMC, www.pmc-group.com
CSI, www.compsys.com
Cummins Engine Company, www.cummins.com
Custom Metalcraft Inc., www.custom-metalcraft.com
Cyclo Industries LLC, www.cyclo.com
D & D Oil Company, Inc., www.amref.com
D.A. Stuart Company, www.d-a-stuart.com
D.B. Becker Company, Inc., www.dbbecker.com
D.W. Davies & Company, Inc., www.dwdavies.com
D-A Lubricant Company, www.dalube.com
Daimler Chrysler, www.daimlerchrysler.com
Danish Technological Institute (DTI) Tribology Centre, www.dti.dk
Darmex Corporation, www.darmex.com
Darsey Oil Company Inc., www.darseyoil.com
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Dayco Inc., www.dayco.com
DeForest Enterprises Inc., www.deforest.net
Delkol, www.delkol.co.il
Delphi Automotive Systems, www.delphiauto.com
Dennis Petroleum Company, Inc., www.dennispetroleum.com
Department of Defense (DOD), www.defenselink.mil
Des-Case Corporation, www.des-case.com
Detroit Diesel, www.detroitdiesel.com
Deutsches Institute Fur Normung e. V. (DIN), www.din.de
Dexsil Corporation, www.dexsil.com
Dialog, www.dialog.com
Diamond Head petroleum Inc., www.diamondheadpetroleum.com
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Division of Machine Elements Home Page Niigata University, Japan, tmtribo1.eng.niigata-u.ac.jp/index_e.html
Dixon Lubricants & Special Products Group, Division of Asbury Carbons, www.dixonlube.com
Dodge, www.dodge.com
Don Weese Inc., www.schaefferoil.com
Dover Chemical, www.doverchem.com

Dow Chemical Company, www.dow.com
Dow Corning Corporation, www.dowcorning.com
Dumas Oil Company, www.esn.net/dumasoil
DuPont-Dow Elastomers, www.dupont-dow.com
DuPont Krytox Lubricants, www.lubricants.dupont.com
DuPont, www.dupont.com/intermediates
Duro Manufacturing Inc., www.duromanufacturing.com
Dutton-Lainson Company, www.dutton-lainson.com
Dylon Industries Inc., www.dylon.com
E. I. DuPont de Nemours and Company, www.dupont.com/intermediates
Eagle, www.eaglecars.com
Eastech Chemical Inc., www.eastechchemical.com
Eastern Oil Company, www.easternoil.com
Easy Vac Inc., www.easyvac.com
Ecotech Div., Blaster Chemical Companies, www.pbblaster.com
Edjean Technical Services Inc., www.edjetech.com
EidgenSSische Technische Hochschule (ETH), Zurich Laboratory for Surface Science and
Technology (LSST), www.surface.mat.ethz.ch
EKO, www.eko.gr
Elco Corporation, The, www.elcocorp.com
El Paso Corporation, www.elpaso.com
Elementis Specialties-Rheox, www.elemetis-specialties.com
Elf Lubricants North America Inc., www.keystonelubricants.com
Eljay Oil Company, Inc., www.eljayoil.com
EMERA Fuels Company, Inc., www.emerafuels.com
Emerson Oil Company, Inc., www.emersonoil.com
Energy Connection, The, www.energyconnect.com
Engel Metallurgical Ltd., www.engelmet.com
Engen Petroleum Ltd., www.engen.co.za
Engineered Composites Inc., www.engineeredcomposites.net
ENI, www.eni.it
Environmental and Power Technologies Ltd., www.cleanoil.com
Environmental Lubricants Manufacturing, Inc. (ELM), www.elmusa.com
Environmental Protection Agency (EPA), www.epa.gov
Equilon Enterprises LLC-Lubricants, www.equilonmotivaequiva.com
Equilon Enterprises LLC-Lubricants, www.shellus.com
Equilon Enterprises LLC-Lubricants, www.texaco.com
Ergon Inc., www.ergon.com
Esco Products Inc., www.escopro.com
Esslingen, Technische Akademie, www.tae.de
Ethyl Corporation, www.ethyl.com
Ethyl Petroleum Additives, www.ethyl.com
ETNA Products Inc., www.etna.com
Etna-Bechem Lubricants Ltd., www.etna.com
European Automobile Manufacturers Association (ACEA), www.acea.be
European Oil Companies Organization of E. H. and S. (CONCAWE), www.concawe.be
European Patent Office, www.epo.co.at/epo/
EV1, www.gmev.com
Evergreen Oil, www.evergreenoil.com
Exxon, www.exxon.com
ExxonMobil Chemical Company, www.exxonmobilchemical.com

ExxonMobil Corp., www.exxonmobil.com
ExxonMobil Industrial Lubricants, www.mobilindustrial.com
ExxonMobil Lubricants & Petroleum Specialties Company, www.exxonmobil.com
F. Bacon Industriel Inc., www.f-bacon.com
F.L.A.G. (Fuel, Lubricant, Additives, Grease) Recruiting, www.flagsearch.com
Fachhochschule Hamburg, Germany, www.haw-hamburg.de/fh/forum/f12/indexf.html/
tribologie/etribology.html
Falex Corporation, www.falex.com
Falex Tribology NV, www.falexint.com
Fanning Corporation, The, www.fanncorp.com
Far West Oil Company Inc., www.farwestoil.com
Farmland Industries Inc., www.farmland.com
Federal World, www.fedworld.gov
Ferrari, www.ferrari.com
Ferro/Keil Chemical, www.ferro.com
FEV Engine Technology, Inc., www.fev.com
Fiat, www.fiat.com
Finia Oil and Chemical Company, www.totalpetrochemicalsusa.com
Findett Corporation, www.findett.com
Finish Line Technologies Inc., www.finishlineusa.com
FINKE Mineralolwerk, www.finke-mineraloel.de
Finnish Oil and Gas Federation, www.oil.fi
Flamingo Oil Company, www.pinkbird.com
Flo Components Ltd., www.flocomponents.com
Flowtronex International, www.flowtronex.com
Fluid Life Corporation, www.fluidlife.com
Fluid Systems Partners US Inc., www.fsp-us.com
Fluid Technologies Inc., www.Fluidtechnologies.com
Fluidtec International, www.fluidtec.com
Fluitec International, www.fluitec.com
FMC Blending & Transfer, www.fmcblanding-transfer.com
FMC Lithium, www.fmclithium.com
FMC, www.fmc.com
Ford Motor Company, www.ford.com
Fortum (Finland), www.fortum.com
Forward Corporation, www.forwardcorp.com
Freightliner, www.freightliner.com
Frontier Performance Lubricants Inc., www.frontierlubricants.com
Fuchs Lubricants Company, www.fuchs.com
Fuchs, www.fuchs-oil.de
Fuel and Marine Marketing (FAMM), www.fammlc.com
Fuels and Lubes Asia Publications, Inc., www.flasia.inf
Fuki America Corporation, www.fukiamerica.com
Functional Products, www.functionalproducts.com
G-C Lubricants Company, www.gclube.com
G & G Oil Co. of Indiana Inc., www.ggoil.com
G. R. O'Shea Company, www.groshea.com
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Royal Purple, Inc., www.royalpurple.com
Russell-Stanley Corporation, www.russell-stanley.com
RWE-DEA (Germany), www.rwe-dea.de
RyDol Products, www.rydol.com
Saab, www.saab.com
Saab Cars USA, www.saabusacom
Safety Information Resources on the Internet, www.siri.org/links1.html
Safety-Kleen Corporation, www.safety-kleen.com
Safety-Kleen Oil Recovery, www.ac-rerefined.com
Saitama University, Japan Home Page of Machine Element Laboratory, www.mech.saitama-u.ac.jp/youso/home.html
San Joaquin Refining Company, www.sjr.com
Sandia National Laboratories Tribology, www.sandia.gov/materials/sciences/
Sandstrom Products Company, www.sandstromproducts.com
Sandy Brae Laboratories Inc., www.sandy/brae.com
Santic Oil Company, www.santiemidwest.com

Santotrac Traction Lubricants, www.santotrac.com
Santovac Fluids Inc., www.santovac.com
Sasol (South Africa), www.sasol.com
SATEC Inc., www.satec.com
Saturn (GM), www.saturncars.com
Savant Group of Companies, www.savantgroup.com
Savant Inc., www.savantgroup.com
Saxton Industries Inc., www.schaefferoil.com
Scania, www.scania.se
Schaeffer Manufacturing, www.schaefferoil.com
Schaeffer Oil and Grease, www.schaefferoil.com
Schaeffer Specialized Lubricants, www.schaefferoil.com
Scully Signal Company, www.scully.com
Sea-Land Chemical Company, www.sealandchem.com
Selco Synthetic Lubricants, www.synthetic-lubes.com
Senior Flexonics, www.flexonics-hose.com
Sentry Solutions Ltd., www.sentrysolutions.com
Sexton & Peake Inc., www.sexton.qpg.com
SFR Corporation, www.sfrcorp.com
SGS Control Services Inc., www.sgsgroup.com
Shamrock Technologies, Inc., www.shamrocktechnologies.com
Share Corp., www.sharecorp.com
Shell, www.shellus.com
Shell (United States), www.shellus.com
Shell Chemicals, www.shellchemical.com
Shell Global Solutions, www.shellglobalsolutions.com
Shell International, www.shell.com/royal-en
Shell Lubricants (United States), www.shell-lubricants.com
Shell Oil Products US, www.shelloilproductsus.com
Shepherd Chemical Company, www.shepchem.com
Shrieve Chemical Company, www.shrieve.com
Silvas Oil Company, Inc., www.silvasoil.com
Silverson Machines Inc., www.silverson.com
Simons Petroleum Inc., www.simonspetroleum.com
Sinclair Oil Corporation, www.sinclairoil.com
Sinopec (China Petrochemical Corporation), www.sinopec.com.cn
SK Corporation (Houston Office), www.skcorp.com
SKF Quality Technology Centre, www.qtc.skf.com
Sleeveco Inc., www.sleeveco.com
Slick 50 Corporation, www.slick50.com
Snyder Industries, www.snydernet.com
Sobit International, Inc., www.sobitinc.com
Society of Automotive Engineers (SAE), www.sae.org
Society of Environmental Toxicology and Chemistry (SETAC), www.setac.org
Society of Manufacturing Engineers (SME), www.sme.org
Society of Tribologists and Lubrication Engineers (STLE), www.stle.org
Soltex, www.soltexinc.com
Sourdough Fuel, www.petrostar.com
Southern Illinois University, Carbondale Center for Advanced Friction Studies, www.frictioncenter.com
Southwest Grease Products, www.stant.com/brochure.cfm?brochure=155&location_id=119

Southwest Research Institute (SwRI) Engine Technology Section, www.swri.org/default.htm
Southwest Research Institute, www.swri.org
Southwest Spectro-Chem Labs, www.swsclabs.com
Southwestern Graphite, www.asbury.com
Southwestern Petroleum Corporation (SWEPCO), www.swepco.com
Southwestern Petroleum Corporation, www.swepcousa.com
SP Morell & Company, www.spmorell.com
Spacekraft Packaging, www.spacekraft.com
Spartan Chemical Company Inc. Industrial Products Group Division, www.spartanchemical.com
Spartan Oil Company, www.spartanonline.com
Specialty Silicone Products Inc., www.sspinc.com
Spectro Oils of America, www.goldenspectro.com
Spectro Oils of America, www.spectro-oils.com
SpectroInc. Industrial Tribology Systems, www.spectroinc.com
Spectronics Corporation, www.spectroline.com
Spectrum Corp., www.spectrumcorporation.com
Spencer Oil Company, www.spenceroil.com
Spex CertiPrep Inc., www.spexcsp.com
SQM North America Corporation, www.sqmna.com
St. Lawrence Chemicals, www.stlawrencechem.com
Star Brite, www.starbrite.com
State University of New York, Binghamton Mechanical Engineering Laboratory, www.me.binghamton.edu
Statoil (Norway), www.statoil.com
Steel Shipping Containers Institute, www.steelcontainers.com
Steelco Industrial Lubricants, Inc., www.steelcolubricants.com
Steelco Northwest Distributors, www.steelcolubricants.com
STP Products Inc., www.stp.com
Stratco Inc., www.stratco.com
Suburban Oil Company, Inc., www.suburbanoil.com
Summit Industrial Products Inc., www.klsummit.com
Summit Technical Solutions, www.lubemanagement.com
Sunnyside Corporation, www.sunnysidecorp.com
Sunoco Inc., www.sunocoinc.com
Sunohio, Division of ENSR, www.sunohio.com
Superior Graphite Company, www.superiorgraphite.com
Superior Lubricants Company, Inc., www.superiorlubricants.com
Superior Lubrication Products, www.s-l-p.com
Surtec International Inc., www.surtecinternational.com
Swiss Federal Laboratories for Materials Testing and Research (EMPA) Centre for Surface Technology and Tribology, www.empa.ch
Syncro Chemical Corporation, www.super-lube.com
SynLube Inc., www.synlube.com
Synthetic Lubricants Inc., www.synlube-mi.com
Syntroleum Corporation, www.syntroleum.com
T.S. MolY-Lubricants Inc., www.tsmoly.com
T.W. Brown Oil Company, Inc., www.brownoil.com/soypower.html
Taber Industries, www.taberindustries.com
TAI Lubricants, www.lubekits.com
Tannas Company, www.savantgroup.com

Tannis Company, www.savantgroup.com/tannas.sht
Technical Chemical Company (TCC), www.technicalchemical.com
Technical University of Delft, Netherlands Laboratory for Tribology, www.tudelft.nl
Technical University, Munich, Germany, www.fzg.mw.tu-muenchen.de
Tek-5 Inc., www.tek-5.com
Terresolve Technologies, www.terresolve.com
Texaco Inc., www.texaco.com
Texas Refinery Corporation, www.texasrefinery.com
Texas Tech University, Tribology, www.ttu.edu
Textile Chemical Company, Inc., www.textilechem.com
The Maintenance Council, www.trucking.org
Thermal-Lube Inc., www.thermal-lube.com
Thermo Elemental, www.thermoelemental.com
Thomas Petroleum, www.thomaspetro.com
Thornley Company, www.thornleycompany.com
Thoughtventions Unlimited Home Page, www.tvu.com/%7Ethought/
Tiodize Company, Inc., www.tiodize.com
Titan Laboratories, www.titanlab.com
TMC, www.truckline.com
Tokyo Institute of Technology, Japan Nakahara Lab. Home Page, www.mep.titech.ac.jp/data/labs_staffE.html
Tomah Products, Inc., www.tomah3.com
Tom-Pac Inc., www.tom-pac.com
Top Oil Products Company Ltd., www.topoil.com
Torco International Corporation, www.torcoracingoils.com
Tosco, www.tosco.com
Total, www.total.com
Total, www.totalfinaelf.com/ho/fr/index.htm
Totalfina Oleo Chemicals, www.totalfina.com
Tower Oil & Technology Company, www.toweroil.com
Toyo Grease Manufacturing (M) SND BHD, www.toyointernational.com
Toyota (Japan), www.toyota.co.jp
Toyota (United States), www.toyota.com
TransMontaigne, www.transmontaigne.com
Transmountain Oil Company, www.transmountainoil.com
Tribologist.com, www.wearcheck.com/sites.html
Tribology Group, www.msm.cam.ac.uk/tribo/tribol.htm
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Tribology/Tech-Lube, www.tribology.com
Tribos Technologies, www.tribostech.com
Trico Manufacturing Corporation, www.tricomfg.com
Trilla Steel Drum Corporation, www.trilla.com
Troy Corporation, www.troycorp.com
Tsinghua University, China, State Key Laboratory of Tribology, www.pim.tsinghua.edu.cn
TTI's Home Page, www.tti-us.com
Turmo Lubrication Inc., www.lubecon.com

TXS Lubricants Inc., www.txsinc.com
U.S. Data Exchange, www.usde.com
U.S. Department of Energy (DOE), www.energy.gov
U.S. Department of Transportation (DOT), www.dot.gov
U.S. Energy Information Administration, www.eia.doe.gov
U.S. Oil Company, Inc., www.usoil.com
U.S. Patent Office, www.uspto.gov
UEC Fuels and Lubrication Laboratories, www.uec-usx.com
Ultimate Lubes, www.ultimatelubes.com
Ultra Additives, Inc., www.ultraadditives.com
Ultrachem Inc., www.ultracheminc.com
Unilube Systems Ltd., www.unilube.com
Unimark Oil Company, www.gardcorp.com
Union Carbide Corporation, www.unioncarbide.com
Uniqema, www.uniqema.com
Uniroyal Chemical Company Inc., www.uniroyalchemical.com
UniSource Energy Inc., www.unisource-energy.com
Unist, Inc., www.unist.com
Unit Pack Company, Inc., www.unitpack.com
United Color Manufacturing Inc., www.unitedcolor.com
United Lubricants, www.unitedlubricants.com
United Oil Company, Inc., www.duralene.com
United Soybean Board, www.unitedsoybean.org
Universal Lubricants Inc., www.universallubes.com
University of Applied Sciences, Hamburg, Germany, www.haw-hamburg.de
University of California, Berkeley Bogey's Tribology Group, cml.berkeley.edu/tribo.html
University of California, San Diego Center for Magnetic Recording Research, orpheus.ucsd.edu/cmrr/
University of Illinois, Urbana-Champaign Tribology Laboratory, www.mie.uiuc.edu
University of Kaiserslautern, Germany Sektion Tribologie, www.uni-kl.de/en/
University of Leeds, M.Sc. (Eng.) Course in Surface Engineering and Tribology, leva.leeds.ac.uk/tribology/msc/tribmsc.html
University of Leeds, United Kingdom, Research in Tribology, leva.leeds.ac.uk/tribology/research.html
University of Ljubljana, Faculty of Mechanical Engineering, Center for Tribology and Technical Diagnostics, www.ctd.uni-lj.si/eng/ctdeng.htm
University of Maine Laboratory for Surface Science and Technology (LASST), www.ume.maine.edu/LASST/
University of Newcastle upon Tyne, United Kingdom, Ceramics Tribology Research Group, www.ncl.ac.uk/materials/materials/resgrps/certrib.html
University of Northern Iowa, www.uni.edu/abil
University of Notre Dame Tribology/Manufacturing Laboratory, www.nd.edu/<ame
University of Pittsburg, School of Engineering, Mechanical Engineering Department, www.engrng.pitt.edu
University of Sheffield, United Kingdom, Tribology Research Group, www.shef.ac.uk/mecheng/tribology/
University of Southern Florida, Tribology, www.eng.usf.edu
University of Texas at Austin, Petroleum & Geosystems Engineering, Reading Room, [www.pe.utexas.edu/Dept/Reading/petroleum.html](http://pe.utexas.edu/Dept/Reading/petroleum.html)
University of Tokyo, Japan, Mechanical Engineering Department, www.mech.t.u-tokyo.ac.jp/english/index.html

University of Twente, Netherlands Tribology Group, www.wb.utwente.nl/en/index.html
University of Western Australia Department of Mechanical and Material Engineering,
www.mech.uwa.edu.au/tribology/
University of Western Ontario, Canada Tribology Research Centre, www.engga.uwo.ca/research/tribology/Default.htm
University of Windsor, Canada, Tribology Research Group, venus.uwindsor.ca/research/wtrg/index.html
Unocal Corporation, www.unocal.com
Uppsala University, Sweden Tribology Group, www.angstrom.uu.se/materials/index.htm
U.S. Department of Agriculture (USDA), www.usda.gov
U.S. Department of Energy (DOE), www.energy.gov
U.S. Department of Defense (DOD), www.dod.gov
USX Engineers & Consultants, www.uec.com/labs/ctns
USX Engineers and Consultants: Laboratory Services, www.uec.com/labs/
Vacudyne Inc., www.vacudyne.com
Valero Marketing & Supply, www.valero.com
Valvoline Canada, www.valvoline.com
Valvoline, www.valvoline.com
Van Horn, Metz & Company, Inc., www.vanhornmetz.com
Vauxhall, www.vauxhall.co.uk
Vesco Oil Corporation, www.vesco-oil.com
Victoria Group Inc., The, www.victoriagroup.com
Viking Pump Inc., A Unit of IDEX Corporation, www.vikingpump.com
Vikjay Industries Inc., www.vikjay.com
Virtual Oil Inc., www.virtualoilinc.com
Viswa Lab Corporation, www.viswalab.com
Vogel Lubrication System of America, www.vogel-lube.com
Volkswagen (Germany), www.vw-online.de
Volkswagen (United States), www.vw.com
Volvo (Sweden), www.volvo.se
Volvo Cars of North America, www.volvocars.com
Volvo Group, www.volvo.com
Vortex International LLC, www.vortexfilter.com
VP Racing Fuels Inc., www.vpracingfuels.com
Vulcan Oil & Chemical Products Inc., www.vulcanoil.com
Vulsay Industries Ltd., www.vulsay.com
Wallace, www.wallace.com
Wallover Oil Company, www.walloveroil.com
Walthall Oil Company, www.walthall-oil.com
Warren Distribution, www.wd-wpp.com
Waugh Controls Corporation, www.waughcontrols.com
WD-40 Company, www.wd40.com
Web-Valu Intl., www.webvalu.com
Wedeven Associates, Inc., members.aol.com/wedeven/
West Central Soy, www.soypower.net
West Penn Oil Company, Inc., www.westpenn.com
Western Michigan University Tribology Laboratory, www.mae.wmich.edu/labs/Tribology/Tribology.html
Western Michigan University, Department of Mechanical and Aeronautical Engineering,
www.mae.wmich.edu
Western States Oil, www.lubeoil.com

Western States Petroleum Association, www.wspa.org
Whitaker Oil Company, Inc., www.whitakeroil.com
Whitmore Manufacturing Company, www.whitmores.com
Wilks Enterprise Inc., www.wilksir.com
Winfield Brooks Company, Inc., www.tapfree.com
Winzer Corp., www.winzerusa.com
Witco (Crompton Corporation), www.witco.com
Wolf Lake Terminals Inc., www.wolfakeinc.com
Worcester Polytechnic Institute, Department of Mechanical Engineering, www.me.wpi.edu/research/labs.html
Worldwide PetroMoly, Inc., www.petromoly.com
WSI Chemical Inc., www.wsi-chem-sys.com
WWW Tribology Information Service, www.shef.ac.uk/~mpe/tribology/
WWW Virtual Library: Mechanical Engineering, www.vlme.com/
Wynn Oil Company, www.wynnsusa.com
X-1R Corporation, The, www.x1r.com
Yahoo Lubricants, dir.yahoo.com/business_and_economy/shopping_and_services/automotive/supplies/lubricants/
Yahoo Tribology, ca.yahoo.com/Science/Engineering/Mechanical_Engineering/Tribology/
Yocum Oil Company, Inc., www.yocumoil.com
YPF (Argentina), www.ypf.com.ar
Yuma Industries Inc., www.yumaind.com
Zimmark Inc., www.zimmark.com
Zinc Corporation of America, www.zinccorp.com

29.2 INTERNET LISTINGS BY CATEGORY

29.2.1 LUBRICANT FLUIDS

2V Industries Inc., www.2vindustries.com
49 North, www.49northlubricants.com
76 Lubricants Company, www.tosco.com
A/R Packaging Corporation, www.arpackaging.com
Acculube, www.acculube.com
Accurate Lubricants & Metalworking Fluids Inc. (dba Acculube), www.acculube.com
Acheson Colloids Company, www.achesonindustries.com
Acme Refining, Division of Mar-Mor Inc., www.acmerefining.com
Acme-Hardesty Company, www.acme-hardesty.com
Advanced Ceramics Corporation, www.advceramics.com
Advanced Lubrication Specialties Inc., www.advancedlubes.com
Aerospace Lubricants Inc., www.aerospacelubricants.com
African Lubricants Industry, www.mbendi.co.za/aflu.htm
AG Fluropolymers USA Inc., www.fluropolymers.com
Airosol Company Inc., www.airsol.com
Akzo Nobel, www.akzonobel.com
Alco-Metalube Company, www.alco-metalube.com
Alithicon Lubricants, Division of Southeast Oil & Grease Company, Inc., www.alithicon.com
Allegheny Petroleum Products Company, www.oils.com
Allen Oil Company, www.allenoil.com
Allied Oil & Supply Inc., www.allied-oil.com
Allied Washoe, www.alliedwashoe.com

Alpha Grease & Oil Inc., www.alphagrease.thomasregister.com/olc/alphagrease/
ALT Inc., www.altboron.com
Amalie Oil Company, www.amalie.com
Amber Division of Nidera, Inc., www.nidera-us.com
Amcar Inc., www.amcarinc.com
Amerada Hess Corporation, www.hess.com
American Agip Company, Inc., www.americanagip.com
American Eagle Technologies Inc., www.frictionrelief.com
American Lubricants Inc., www.americanlubricantsbflo.com
American Lubricating Company, www.alcooil.com
American Oil & Supply Company, www.aosco.com
American Petroleum Products, www.americanpetroleum.com
American Refining Group Inc., www.amref.com
American Synthol Inc., www.americansynthol.com
Amtron Corporation, www.superslipperystuff.com/organisation.htm
Amrep Inc., www.amrep.com
AMSOIL Inc., www.amsoil.com
Anderol Specialty Lubricants, www.anderol.com
Anti Wear 1, www.dynamicdevelopment.com
Apollo America Corporation, www.apolloamerica.com
Aral International, www.aral.com
Arch Chemicals, Inc., www.archbiocides.com
ARCO, www.arco.com
Arizona Chemical, www.arizonachemical.com
Asbury Carbons, Inc.—Dixon Lubricants, www.asbury.com
Asbury Graphite Mills Inc., www.asbury.com
Asheville Oil Company Inc., www.ashevilleoil.com
Ashland Chemical, www.ashchem.com
Ashland Distribution Company, www.ashland.com
Aspen Chemical Company, www.aspenchemical.com
Associated Petroleum products, www.associatedpetroleum.com
Atlantis International Inc., www.atlantis-usa.com
Atlas Oil Company, www.atlasoil.com
ATOFINA Canada Inc., www.atofinacanada.com
Ausimont, www.ausiusa.com
Avatar Corporation, www.avatarcorp.com
Badger Lubrication Technologies Inc., www.badgerlubrication.com
BALLISTOL USA, www.ballistol.com
Battenfeld Grease and Oil Corporation of New York, www.battenfeld-grease.com
Behnke Lubricants/JAX, www.jaxusa.com
Behnke Lubricants Inc./JAX, www.jax.com
Bell Additives Inc., www.belladditives.com
Bel-Ray Company Inc., www.belray.com
Benz Oil Inc., www.benz.com
Berry Hinckley Industries, www.berry-hinckley.com
Bestolife Corporation, www.bestolife.com
BG Products Inc., www.bgprod.com
Big East Lubricants Inc., www.bigeastlubricants.com
Blaser Swisslube, www.blaser.com
Bodie-Hoover Petroleum Corporation, www.bodie-hoover.com
Boehme Filatex Inc., www.boehmefilatex.com

BoMac Lubricant Technologies Inc., www.bomaclubetech.com
Boncosky Oil Company, www.boncosky.com
Boswell Oil Company, www.boswelloil.com
BP Amoco Chemicals, www.bpamocochemicals.com
BP Lubricants, www.bplubricants.com
BP, www.bptechchoice.com
BP, www.bppetrochemicals.com
Brascorp North America Ltd., www.brascorp.on.ca
Brenntag Northeast, Inc., www.brenntag.com
Brenntag, www.brenntag.com
Briner Oil Company, www.brineroil.com
British Petroleum (BP), www.bp.com
Britsch Inc., www.britschoil.com
Brugarolas SA, www.brugarolas.com/english.htm
Buckley Oil Company, www.buckleyoil.com
BVA Oils, www.bvaoils.com
Callahan Chemical Company, www.calchem.com
Caltex Petroleum Corporation, www.caltex.com
Calumet Lubricants Company, www.calumetlub.com
Calvary Industries Inc., www.calvaryindustries.com
CAM2 Oil Products Company, www.cam2.com
Canner Associates, Inc., www.canner.com
Capital Enterprises (Power-Up Lubricants), www.nnl690.com
Cargill-Industrial Oil & Lubricants, www.techoils.cargill.com
Cary Company, www.thecarycompany.com
CasChem, Inc., www.cambrex.com
Castle Products Inc., www.castle-comply.com
Castrol Heavy Duty Lubricants, Inc., www.castrolhdl.com
Castrol Industrial North America Inc., www.castrolindustrialna.com
Castrol International, www.castrol.com
Castrol North America, www.castrolusa.com
CAT Products Inc., www.run-rite.com
Centurion Lubricants, www.centurionlubes.com
Champion Brands LLC, www.championbrands.com
Charles Manufacturing Company, www.tsmoly.com
Chart Automotive Group Inc., www.chartauto.com
Chem-EcoI Ltd., www.chem-ecol.com
Chemlube International Inc., www.chemlube.com
Chempet Corporation, www.rockvalleyoil.com/chempet.htm
Chemsearch Lubricants, www.chemsearch.com
Chemtool Inc./Metalcote, www.chemtool.com
Chevron Chemical Company, www.chevron.com
Chevron Oronite, www.chevron.com
Chevron Phillips Chemical Company LP, www.cpchem.com
Chevron Phillips Chemical Company, www.chevron.com
Chevron Products Company, Lubricants & Specialties Products, www.chevron.com/lubricants
Chevron Products Company, www.chevron.com
Christenson Oil, www.christensonoil.com
Ciba Specialty Chemicals Corporation, www.cibasc.com
Clariant Corporation, www.clariant.com
Clark Refining and Marketing, www.clarkusa.com

Clarkson & Ford Company, www.clarkson-ford.com
CLC Lubricants Company, www.clclubricants.com
Climax Molybdenum Company, www.climaxmolybdenum.com
Coastal Unilube Inc., www.coastalunilube.com
Cognis, www.cognislubechem.com
Cognis, www.cognis-us.com
Cognis, www.cognis.com
Cognis, www.na.cognis.com
Colorado Petroleum Products Company, www.colopetro.com
Commercial Lubricants Inc., www.comlube.com
Commercial Oil Company Inc., www.commercialoilcompany.com
Commercial Ullman Lubricants Company, www.culc.com
Commonwealth Oil Corporation, www.commonwealthoil.com
Como Lube & Supplies Inc., www.comolube.com
Condat Corporation, www.condatcorp.com
Conklin Company Inc., www.conklin.com
Coolants Plus Inc., www.coolantsplus.com
Cortec Corporation, www.cortecvci.com
Cosby Oil Company, www.cosbyoil.com
Country Energy, www.countryenergy.com
CPI Engineering Services, www.cpieng.com
CRC Industries, Inc., www.crcindustries.com
Crescent Manufacturing, www.crescentmfg.net
Crompton Corporation, www.cromptoncorp.com
Crown Chemical Corporation, www.brenntag.com
Cyclo Industries LLC, www.cyclo.com
D & D Oil Company, Inc., www.amref.com
D. A. Stuart Company, www.d-a-stuart.com
D. W. Davies & Company, Inc., www.dwdavies.com
D-A Lubricant Company, www.dalube.com
Darmex Corporation, www.darmex.com
Darsey Oil Company Inc., www.darseyoil.com
David Weber Oil Company, www.weberoil.com
Davison Oil Company, Inc., www.davisonoil.com
Dayco Inc., www.dayco.com
D.B. Becker Co. Inc., www.dbbecker.com
Degen Oil and Chemical Company, www.eclipse.net/<degen
Delkol, www.delkol.co.il
Dennis Petroleum Company, Inc., www.dennispetroleum.com
Diamond Head Petroleum Inc., www.diamondheadpetroleum.com
Diamond Shamrock Refining Company LP, www.udscorp.com
Digilube Systems Inc., www.digilube.com
Dion & Sons Inc., www.dionandsons.com
Dixon Lubricants & Special Products Group, Division of Asbury Carbons, www.dixonlube.com
Don Weese Inc., www.schaefferoil.com
Dow Chemical Company, www.dow.com
Dow Corning Corp., www.dowcorning.com
Dryden Oil Company, Inc., www.castrol.com
Dryson Oil Company, www.synergynracing.com
DSI Fluids, www.dsifluids.com
Dumas Oil Company, www.esn.net/dumasoil

DuPont Krytox Lubricants, www.lubricants.dupont.com
DuPont, www.dupont.com/intermediates
E.I. DuPont de Nemours and Company, www.dupont.com/intermediates
Eastech Chemical Inc., www.eastechchemical.com
Eastern Oil Company, www.easternoil.com
Ecotech Div., Blaster Chemical Companies, www.pbblaster.com
EKO, www.eko.gr
El Paso Corporation, www.elpaso.com
Elf Lubricants North America Inc., www.keystonelubricants.com
Eljay Oil Company, Inc., www.eljayoil.com
EMERA Fuels Company Inc., www.emerafuels.com
Emerson Oil Company, Inc., www.emersonoil.com
Engen Petroleum Ltd., www.engen.co.za
Enichem Americas, Inc., www.eni.it/english/mondo/americhe/usa.html
Environmental Lubricants Manufacturing, Inc. (ELM), www.elmusa.com
Equilon Enterprises LLC, www.equilon.com
Equilon Enterprises LLC-Lubricants, www.equilonmotivaequiva.com
Equilon Enterprises LLC-Lubricants, www.shellus.com
Equilon Enterprises LLC-Lubricants, www.texaco.com
Esco Products Inc., www.escopro.com
ETNA Products Inc., www.etna.com
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Lubrizol Corporation, The, www.lubrizol.com
Lubrizol Metalworking Additive Company, www.lubrizol.com
Mantek Lubricants, www.mantek.com
Marcus Oil and Chemical, www.marcusoil.com
Master Chemical Corporation, www.masterchemical.com
Mays Chemical Company, www.mayschem.com
McIntyre Group Ltd., www.mcintyreregroup.com
Mega Power Inc., www.megapowerinc.com
Metal Mates Inc., www.metalmates.net
Metalworking Lubricants Company, www.metalworkinglubricants.com
Milatec Corporation, www.militec.com
Nagase America Corporation, www.nagase.com
Naptec Corporation, www.satec.com
Northern Technologies International Corporation, www.ntic.com
Oil Center Research Inc., www.oilcenter.com
OKS Speciality Lubricants, www.oks-india.com
Omega Specialties, www.omegachemicalsinc.com
OMG Americas Inc., www.omg.com
OMGI, www.omg.com
Oronite, www.oronite.com
PATCO Additives Division-American Ingredients Company, www.patco-additives.com
Pflaumer Brothers Inc., www.pflaumer.com
Pilot Chemical Company, www.pilotchemical.com
PMC Specialties Inc., www.pmcsg.com
Polartech Ltd., www.polartech.co.uk
Precision Fluids Inc., www.precisionfluids.com
Purac America, Inc., www.purac.com
R.T. Vanderbilt Company Inc., www.rtvanderbilt.com
R.H. Foster Energy LLC, www.rhfoster.com
Reade Advanced Materials, www.reade.com
Rhein Chemie Corporation, www.bayer.com
Rhein Chemie Rheinau GmbH., www.rheinchemie.com
Rheox Inc., www.rheox.com
Rhodia, www.rhodia.com
Rhone-Poulenc Surfactants & Specialties, www.rpsurfactants.com

RiceChem, A Division of Stilling Enterprises Inc., www.ricechem.com
Rohm & Haas Company, www.rohmhaas.com
RohMax Additives GmbH, www.rohmax.com
Ross Chem Inc., www.rosschem.com
Santotrac Traction Lubricants, www.santotrac.com
Santovac Fluids Inc., www.santovac.com
Sea-Land Chemical Company, www.sealandchem.com
Shamrock Technologies, Inc., www.shamrocktechnologies.com
Shell Chemicals, www.shellchemical.com
Shepherd Chemical Company, www.shepchem.com
Soltex, www.soltexinc.com
SP Morell & Company, www.spmorell.com
Spartan Chemical Company Inc. Industrial Products Group Division, www.spartanchemical.com
SQM North America Corporation, www.sqmna.com
St. Lawrence Chemicals, www.stlawrencechem.com
Stochem, Inc., www.stochem.com
Thornley Company, www.thornleycompany.com
Tiodize Company, Inc., www.tiodize.com
Tomah Products, Inc., www.tomah3.com
Troy Corporation, www.troycorp.com
Ultra Additives Inc., www.ultraadditives.com
Uniqema, www.uniqema.com
Uniroyal Chemical Company Inc., www.uniroyalchemical.com
United Color Manufacturing Inc., www.unitedcolor.com
United Lubricants, www.unitedlubricants.com
Valhalla Chemical, www.valhallachem.com
Van Horn, Metz & Company, Inc., www.vanhornmetz.com
Virtual Oil Inc., www.virtualoilinc.com
Wynn Oil Company, www.wynnsusa.com
Zinc Corporation of America, www.zinccorp.com

29.2.3 OIL COMPANIES

Adco Petrol Katkilari San Ve. Tic. AS, www.adco.com.tr
Amoco, www.amoco.com
Aral International, www.aral.com
Asian Oil Company, www.nilagems.com/asianoil/
Bharat Petroleum, www.bharatpetroleum.com
BP, www.bp.com
CEPSA (Spain), www.cepsa.es
Chevron Texaco, www.chevrontexaco.com
Chevron, www.chevron.com
CITGO Petroleum Corporation, www.citgo.com
Coastal Corporation, www.elpaso.com
Conoco, www.conoco.com
Cosmo Oil, www.cosmo-oil.co.jp
Cross Oil Refining and Marketing Inc., www.crossoil.com
Ecopetrol (Columbian Petroleum Company), www.ecopetrol.com.co
ENI, www.eni.it
Ergon Inc., www.ergon.com

ExxonMobil Corp., www.exxonmobil.com
Fortum (Finland), www.fortum.com
Gasco Energy, www.gascoenergy.com
Hindustan Petroleum Corporation, Ltd., www.hindpetro.com
Idemitsu, www.idemitsu.co.jp
Indian Oil Corporation, www.indianoilcorp.com
Interline Resources Corporation, www.interlineresources.com
Japan Energy Corporation, www.j-energy.co.jp/eng/index.html
Japan Energy, www.j-energy.co.jp
Kuwait National Petroleum Company, www.knpc.com.kw
LukOil (Russian Oil Company), www.lukoil.com
Marathon Ashland Petroleum LLC, www.mapllc.com
Marathon Oil Company, www.marathon.com
Mobil, www.mobil.com
MOL Hungarian Oil & Gas, www.mol.hu
Murphy Oil Corporation, www.murphyoilcorp.com
PDVSA (Venezuela), www.pdvsa.com
PEMEX (Mexico), www.pemex.com
Pertamina (Indonesia), www.pertamina.com
Petrobras (Brazil), www.petrobras.com.br
Petrogal (Portugal), www.petrogal.pt
Petroleum Authority of Thailand, www.nectec.or.th/users/htk/SciAm/12PTT.html
Petroperu (Peru), www.petroperu.com
Phillips Petroleum Company/Phillips 66, www.phillips66.com/phi11ips66.asp
RWE-DEA (Germany), www.rwe-dea.de
San Joaquin Refining Company, www.sjr.com
Sasol (South Africa), www.sasol.com
Shell (United States), www.shellus.com
Shell International, www.shell.com/royal-en
Shell Oil Products US, www.shelloilproductsus.com
Sinclair Oil Corp., www.sinclairoil.com
Sinopec (China Petrochemical Corporation), www.sinopec.com.cn
Statoil (Norway), www.statoil.com
Sunoco Inc., www.sunocoinc.com
Texaco Inc., www.texaco.com
Tosco, www.tosco.com
Total, www.total.com
Total, www.totalfinaelf.com/ho/fr/index.htm
YPF (Argentina), www.ypf.com.ar

29.2.4 UNIVERSITY SITES

Brno University of Technology, Faculty of Mechanical Engineering, Elastohydrodynamic Lubrication Research Group, fyzika.fme.vutbr.cz/ehd/
Cambridge University, Department of Materials Science and Metallurgy, Tribology, [www.msma.cam.ac.uk/tribo/tribol.htm](http://msm.cam.ac.uk/tribo/tribol.htm)
College of Petroleum and Energy Studies CPS Home Page, www.colpet.ac.uk/index.html
College of Petroleum and Energy Studies, www.colpet.ac.uk
Colorado School of Mines Advanced Coating and Surface Engineering Laboratory (ACSEL), www.mines.edu/research/acsel/acsel.html
Danish Technological Institute (DTI) Tribology Centre, www.tribology.dti.dk

Departments of Mechanical Engineering Luleå Technical University, Sweden, www.luth.se/depts/mt/me/

Division of Machine Elements Home Page Niigata University, Japan, tmtribo1.eng.niigata-u.ac.jp/index_e.html

Ecole Polytechnique Federale de Lausanne, Switzerland, igahpse.epfl.ch

Eidgenössische Technische Hochschule (ETH), Zurich Laboratory for Surface Science and Technology (LSST), www.surface.mat.ethz.ch

Esslingen, Technische Akademie, www.tae.de

Fachhochschule Hamburg, Germany, www.haw-hamburg.de/fh/forum/f12/indexf.html?tribologie/etribology.html

Georgia Tech Tribology, www.me.gatech.edu/research/tribology.html

Imperial College, London ME Tribology Section, www.me.ic.ac.uk/tribology/

Indian Institute of Science, Bangalore, India, Department of Mechanical Engineering, www.mecheng.iisc.ernet.in

Institut National des Sciences Appliquées de Lyon, France, Laboratoire de Mécanique des Contacts, www.insa-lyon.fr/Laboratoires/LMC/index.html

Iowa State University, Tribology Laboratory, www.eng.iastate.edu/coe/me/research/labs/tribology_lab.html

Israel Institute of Technology (Technion), meeng.technion.ac.il/Labs/energy.htm#tribology

Kanazawa University, Japan, Tribology Laboratory, web.kanazawa-u.ac.jp/<tribolabo5e.html

Kyushu University, Japan, Lubrication Engineering Home Page, www.mech.kyushu-u.ac.jp/index.html

Luleå University of Technology, Department of Mechanical Engineering, www.luth.se/depts/mt/me/

Northwestern University, Tribology Lab, cset.mech.northwestern.edu/member.htm

Ohio State University, Center for Surface Engineering and Tribology, Gear Dynamics and Gear Noise Research Laboratory, gearlab.eng.ohio-state.edu

Pennsylvania State University, The, www.me.psu.edu/research/tribology.html

Purdue University, Materials Processing and Tribology Research Group, www.ecn.purdue.edu/<farrist/lab.html

Purdue University, Mechanical Engineering Tribology Web Site, widget.ecn.purdue.edu/<metrib/

Royal Institute of Technology (KTH), Sweden Machine Elements Home Page, www.damek.kth.se/mme

Saitama University, Japan Home Page of Machine Element Laboratory, www.mech.saitama-u.ac.jp/youso/home.html

Sandia National Laboratories Tribology, www.sandia.gov/materials/sciences/

Shamban Tribology Laboratory Kanazawa University, Japan, web.kanazawa-u.ac.jp/<tribolabo5e.html

Southern Illinois University, Carbondale Center for Advanced Friction Studies, www.frictioncenter.com

State University of New York, Binghamton Mechanical Engineering Laboratory, www.me.binghamton.edu/me_labs.html

Swiss Federal Laboratories for Materials Testing and Research (EMPA) Centre for Surface Technology and Tribology, www.empa.ch

Swiss Tribology Online, Nanomechanics and Tribology, dmxwww.epfl.ch/WWWTRIBO/home.html

Technical University of Delft, Netherlands Laboratory for Tribology, www.ocp.tudelft.nl/tribo/

Technical University, Munich, Germany, www.fzg.mw.tu-muenchen.de

Technische Universität Ilmenau, Faculty of Mathematics and Natural Sciences, www.physik.tu-ilmenau.de/index_e.html

Texas Tech University, Tribology, www.osci.ttu.edu/ME_Dept/Research/tribology.html

The Pennsylvania State University, www.me.psu.edu/research/tribology.html

Tokyo Institute of Technology, Japan Nakahara Lab. Home Page, www.mep.titech.ac.jp/~Nakahara/home.html

Trinity College, Dublin Tribology and Surface Engineering, www.mme.tcd.ie/Groups/Tribology/

Tsinghua University, China, State Key Laboratory of Tribology, www.pim.tsinghua.edu.cn/index_cn.html

University of Akron Tribology Laboratory, www.ecgf.uakron.edu/<mech

University of Applied Sciences, Hamburg, Germany Dept of Mech. Eng Tribology, www.fh-hamburg.de/fh/fb/m/tribologie/e_index.html

University of Applied Sciences, Hamburg, Germany, www.haw-hamburg.de/fh/fb/m/tribologie/e_index.html

University of California, Berkeley Bogey's Tribology Group, cml.berkeley.edu/tribo.html

University of California, San Diego, Center for Magnetic Recording Research, orpheus.ucsd.edu/cmrr/

University of Florida, Mechanical Engineering Department, Tribology Laboratory, grove.ufl.edu/<wg sawyer/

University of Illinois, Urbana-Champaign Tribology Laboratory, www.mie.uiuc.edu

University of Kaiserslautern, Germany Sektion Tribologie, www.uni-kl.de/en/

University of Leeds, M.Sc. (Eng.) Course in Surface Engineering and Tribology, leva.leeds.ac.uk/tribology/msc/tribmsc.html

University of Leeds, United Kingdom, Research in Tribology, leva.leeds.ac.uk/tribology/research.html

University of Ljubljana, Faculty of Mechanical Engineering, Center for Tribology and Technical Diagnostics, www.ctd.uni-lj.si/eng/ctdeng.htm

University of Maine Laboratory for Surface Science and Technology (LASST), www.ume.maine.edu/LASST/

University of Maine, NanoTribometer System, www.ume.maine.edu/LASST

University of Newcastle upon Tyne, United Kingdom, Ceramics Tribology Research Group, www.ncl.ac.uk/materials/materials/resgrps/certrib.html

University of Northern Iowa, www.uni.edu/abil

University of Notre Dame Tribology/Manufacturing Laboratory, www.nd.edu/<ame

University of Pittsburg, School of Engineering, Mechanical Engineering Department, www.engrng.pitt.edu/<mewww

University of Sheffield, United Kingdom, Tribology Research Group, www.shef.ac.uk/mecheng/tribology/

University of Southern Florida, Tribology, www.eng.usf.edu/<hess/

University of Texas at Austin, Petroleum & Geosystems Engineering, Reading Room, www.pe.utexas.edu/Dept/Reading/petroleum.html

University of Tokyo, Japan, Mechanical Engineering Department, www.mech.t.u-tokyo.ac.jp/english/index.html

University of Twente, Netherlands Tribology Group, www.wb.utwente.nl/vakgroep/tribeng.htm

University of Western Australia Department of Mechanical and Material Engineering, www.mech.uwa.edu.au/tribology/

University of Western Ontario, Canada Tribology Research Centre, www.engga.uwo.ca/research/tribology/Default.htm

University of Windsor, Canada Tribology and Wear Research Group, zeus.uwindsor.ca/research/wtrg/index.html

University of Windsor, Canada, Tribology Research Group, venus.uwindsor.ca/research/wtrg/index.html

Uppsala University, Sweden Tribology Group, www.angstrom.uu.se/materials/index.htm

Western Michigan University Tribology Laboratory, www.mae.wmich.edu/labs/Tribology/Tribology.html

Western Michigan University, Department of Mechanical and Aeronautical Engineering, www.mae.wmich.edu

Worcester Polytechnic Institute, Department of Mechanical Engineering, www.me.wpi.edu/Research/labs.html

29.2.5 GOVERNMENT SITES/INDUSTRY SITES

American Bearing Manufacturers Association, www.abma-dc.org

American Board of Industrial Hygiene, www.abih.org

American Carbon Society, www.americancarbonsoociety.org

American Chemical Society (ACS), www.acs.org

American Council of Independent Laboratories (ACIL), www.acil.org

American Gear Manufacturers Association (AGMA), www.agma.org

American National Standards Institute (ANSI), www.ansi.org

American Oil Chemists Society (AOCS), www.aocs.org

American Petroleum Institute (API), www.api.org

American Society of Agricultural Engineering (ASAE), www.asae.org

American Society of Agronomy (ASA), www.agronomy.org

American Society for Horticultural Science (ASHS), www.ashs.org

American Society for Testing and Materials (ASTM), www.astm.org

American Society of Mechanical Engineers International (ASME), www.asme.org

Argonne National Laboratory, www.et.anl.gov

Automotive Aftermarket Industry Association (AAIA), www.aftermarket.org

Automotive Oil Change Association (AOCA), www.aoca.org

Automotive Parts and Accessories Association (APAA), www.apaa.org

Automotive Service Industry Association (ASIA), www.aftmkt.com

British Lubricants Federation Ltd., www.blf.org.uk

California Air Resources Board, www.arb.ca.gov

Center for Tribology, Inc. (CETR), www.cetr.com

Co-ordinating European Council (CEC), www.cectests.org

Coordinating Research Council (CRC), www.crao.com

Crop Science Society of America (CSSA), www.crops.org

Department of Defense (DOD), www.dodssp.daps.mil/dodssp.htm

Deutsches Institut Fur Normung e. V. (DIN), www.din.de

Environmental Protection Agency (EPA), www.fedworld.gov

European Automobile Manufacturers Association (ACEA), www.acea.be

European Oil Companies Organization of E. H. and S. (CONCAWE), www.concawe.be

Federal World, www.fedworld.gov

Independent Lubricant Manufacturers Association (ILMA), www.ilma.org

Industrial Maintenance & Plant Operation (IMPO), www.mcb.co.uk/cgi-bin/mcb_serve/table1.txt&ilt&stanleaf.htm

Institute of Materials Inc. (IOM), www.savantgroup.com

Institute of Mechanical Engineers (ImechE), www.imeche.org.uk
Institute of Petroleum (IP), <http://212.78.70.142>
Institute of Physics (IOP), Tribology Group, www.iop.org
Internal Energy Agency (IEA), www.iea.org
International Organization for Standardization (ISO), www.iso.ch
Japan Association of Petroleum Technology (JAPT), www.japt.org
Japan Automobile Manufacturers Association (JAMA), www.japanauto.com
Japanese Society of Tribologists (JAST) (in Japanese), www.jast.or.jp
Los Alamos National Laboratory, www.lanl.gov/worldview/
NASA Lewis Research Center (LeRC) Tribology & Surface Science Branch, www.lerc.nasa.gov/Other_Groups/SurfSci
National Centre of Tribology, United Kingdom, www.aeat.com/nct/
National Fluid Power Association (NFPA), www.nfpa.com
National Institute for Occupational Safety and Health, www.cdc.gov/homepage.html
National Institute of Standards and Technology, webbook.nist.gov/chemistry
National Lubricating Grease Institute (NLGI), www.nlgi.org
National Metal Finishing Resource Center, www.nmfc.org
National Oil Recyclers Association (NORA), www.recycle.net/Associations/rs000141.html
National Petrochemical & Refiners Association (NPRA), www.npradc.org
National Petroleum Refiners Association (NPRA), www.npra.org
National Research Council of Canada Lubrication Tribology Services, 132.246.196.24/en/fsp/service/lubrication_trib.htm
Naval Research Lab Tribology Section—NRL Code 6176, stm2.nrl.navy.mil/<wahl/6176.htm
Oak Ridge National Laboratory (ORNL) Tribology Test Systems, www.ms.ornl.gov/htmlhome
Occupational Safety and Health Administration (OSHA), www.osha.gov
Petroleum Authority of Thailand, www.nectec.or.th/users/htk/SciAm/12PTT.html
Petroleum Marketers Association of America (PMAA), www.pmaa.org
Society of Automotive Engineers (SAE), www.sae.org
Society of Environmental Toxicology and Chemistry (SETAC), www.setac.org
Society of Manufacturing Engineers (SME), www.sme.org
Society of Tribologists and Lubrication Engineers (STLE), www.stle.org
Southwest Research Institute (SwRI) Engine Technology Section, www.swri.org/4org/d03/engres/engtech/
Southwestern Petroleum Corporation (SWEPCO), www.swepco.com
U.S. Department of Agriculture (USDA), www.usda.gov
U.S. Department of Defense (DOD), www.dod.gov
U.S. Department of Energy (DOE), www.energy.gov
U.S. Department of Transportation (DOT), www.dot.gov
U.S. Energy Information Administration, www.eia.doe.gov
U.S. Patent Office, www.uspto.gov
U.S. Data Exchange, www.usde.com
Western States Petroleum Association, www.wspa.org

29.2.6 TESTING LABS/EQUIPMENT/PACKAGING

A.W. Chesterton Company, www.chesterton.com
A/R Packaging Corporation, www.arpackaging.com
Accumetric LLC, www.accumetric.com
Airflow Systems Inc., www.airflowsystems.com

Alfa Laval Separation, www.alfalaval.com
Allen Filters Inc., www.allenfilters.com
Ana Laboratories Inc., www.analaboratories.com
Analysts Inc., www.analystinc.com
Anatech Ltd., www.anatechltd.com
Andpak Inc., www.andpak.com
Applied Energy Company, www.appliedenergyco.com
Aspen Technology, www.aspentechn.com
Associates of Cape Cod Inc., www.acciusa.com
Atico-Internormen-Filter, www.atico-internormen.com
Baron USA Inc., www.baronusa.com
Berenfield Containers, www.berenfield.com
Bericap NA, www.bericap.com
BF Goodrich, www.bfgoodrich.com
Bianco Enterprises Inc., www.bianco.net
Bijur Lubricating Corporation, www.bijur.com
Biosan Laboratories, Inc., www.biosan.com
Bio-Rad Laboratories, www.bio-rad.com
BioTech International Inc., www.info@biotechintl.com
Blackstone Laboratories, www.blackstone-labs.com
Cannon Instrument Company, www.cannon-ins.com
Certified Laboratories, www.certifiedlaboratories.com
Chemicolloid Laboratories Inc., www.colloidmill.com
Como Industrial Equipment Inc., www.comoindustrial.com
Computational Systems, Inc., www.compsys.com/index.html
Containment Solutions Inc., www.containsolutions.com
CSI, www.compsys.com
Custom Metalcraft Inc., www.custom-metalcraft.com
Delphi Automotive Systems, www.delphiauto.com
Des-Case Corporation, www.des-case.com
Dexsil Corporation, www.dexsil.com
Diagnetics, www.entek.com
Digilube Systems Inc., www.digilube.com
Dingo Maintenance Systems, www.dingos.com
DSP Technology Inc., www.dspt.com
Duro Manufacturing Inc., www.duromanufacturing.com
Dutton-Lainson Company, www.dutton-lainson.com
Dylon Industries Inc., www.dylon.com
Easy Vac Inc., www.easyvac.com
Edjean Technical Services Inc., www.edjetech.com
Engel Metallurgical Ltd., www.engelmet.com
Engineered Composites Inc., www.engineeredcomposites.net
Environmental and Power Technologies Ltd., www.cleanoil.com
Evans Industries Inc., www.evansind.com
Falex Corporation, www.falex.com
Falex Tribology NV, www.falexint.com
FEV Engine Technology, Inc., www.fev-et.com
Flo Components Ltd., www.flocomponents.com
Flowtronex International, www.flowtronex.com
Fluid Life Corporation, www.fluidlife.com
Fluid Systems Partners US Inc., www.fsp-us.com

Fluid Technologies Inc., www.fluidtechnologies.com
Fluids Analysis Lab, www.butler-machinery.com/oil.html
Fluidtec International, www.fluidtec.com
Fluitec International, www.fluitec.com/
FMC Blending & Transfer, www.fmcblanding-transfer.com
Framatome ANP, www.framatech.com
Fuel Quality Services Inc., www.fqsgroup.com
G.R. O'Shea Company, www.groshea.com
G.T. Autochemilube Ltd., www.gta-oil.co.uk
Galactic, www.galactic.com
Gamse Lithographing Company, www.gamse.com
Gas Tops Ltd., www.gastops.com
Generation Systems Inc., www.generationsystems.com
Georgia-Pacific Resins, Inc.—Actrachem Division, www.gapac.com
Gerhardt Inc., www.gerhardtshs.com
Globetech Services Inc., www.globetech-services.com
Graco Inc., www.graco.com
Gulfgate Equipment, Inc., www.gulfgateequipment.com
Hedwin Corporation, www.hedwin.com
Hercules, Inc., Aqualon Division, www.herc.com
Herguth Laboratories Inc., www.herguth.com
Hi-Port Inc., www.hiport.com
Hi-Tech Industries, Inc., www.hi-techind.com
Hoover Materials Handling Group Inc., www.hooveribcs.com
Horix Manufacturing Company, www.sgi.net/horix
Hydraulic Repair & Design, Inc., www.h-r-d.com
Hysitron Incorporated: Nanomechanics, www.hysitron.com
Indiana Bottle Company, www.indianabottle.com
Industrial Packing Inc., www.industrialpacking.com
Insight Services, www.testoil.com
Instruments for Surface Science, www.omicron-instruments.com/index.html
Interline Resources Corporation, www.interlineresources.com
International Group Inc., The (IGI), www.igiwax.com
Intertek Testing Services-Caleb Brett, www.itscb.com
Invicta a.s., www.testoil.com
J & S Chemical Corporation, www.jschemical.com
J.R. Schneider Company, Inc., www.jrschneider.com
JAX-Behnke Lubricants Inc., www.jax.com
Johnson Packings & Industrial Products Inc., www.johnsonpackings.com
K.C. Engineering, Ltd., www.kceng.com
K.I.S.S. Packaging Systems, www.kisspkg.com
Kafko International Ltd., www.kafkointl.com
Kennedy Group, The, www.kennedygrp.com
Kittiwake Developments Limited, www.kittiwake.com
Kleenoil Filtration Inc., www.kleenoilfiltrationinc.com
Kleentek—United Air Specialists Inc., www.uasinc.com
Koehler Instrument Company, www.koehlerinstrument.com
Kruess USA, www.krussusa.com
Laub/Hunt Packaging Systems, www.laubhunt.com
Lawler Manufacturing Corporation, www.lawler-mfg.com
Leding Lubricants Inc., www.automatic-lubrication.com

Legacy Manufacturing, www.legacymfg.com
Liftomatic Inc., www.liftomatic.com
Lilyblad Petroleum, Inc., www.lilyblad.com
Linpac Materials Handling, www.linpacmh.com
Liqua-Tek/Moraine Packaging, www.globaldialog.com/<mpi
Liquid Controls Inc., A Unit of IDEX Corporation, www.lcmeter.com
Lormar Reclamation Service, www.lormar.com
LubeCon Systems Inc., www.lubecon.com
Lubricant Technologies, www.lubricanttechnologies.com
Lubrication Engineers of Canada, www.lubeng.com
Lubrication Systems, www.lsc.com
Lubrication Technologies Inc., www.lube-tech.com
Lubriport Labs, www.ultralabs.com/lubriport
Lubriquip Inc., www.lubriquip.com
Lubrizol Corporation, The, www.lubrizol.com
Lubromation Inc., www.lubromation.com
Lub-Tek Petroleum Products Corporation, www.lubtek.com
Machines Production Web Site, www.machpro.fr
Manor Technology, www.manortec.co.uk
Metalcote/Chemtool Inc., www.metalcote.com
Metorex Inc., www.metorex.fi
Mettler Toledo, www.mt.com
Michel Murphy Enterprises Inc., www.michelmurphy.com
Micro Photonics Inc., www.microphotonics.com
Mid-Michigan Testing Inc., www.tribologytesting.com
Monlan Group, www.monlangroup.com
Motor Fuels/Combustibles Testing, www.empa.ch/englisch/fachber/abt133/index.htm
Mozel Inc., www.mozel.com
Nalco Chemical Company, www.nalco.com
Naptec Corporation, www.satec.com
National Tribology Services, www.natrib.com
NCH, www.nc.com
Newcomb Oil Company, www.newcomboil.com
Nordstrom Valves Inc., www.nordstromaudco.com
Oden Corporation, www.oden.thomasregister.com
Oden Corporation, www.odencorp.com
Oil Analysis (Noria), www.oilanalysis.com
OMICRON Vakuumphysik GmbH, www.omicron-instruments.com/index.html
OMS Laboratories, Inc., members.aol.com/labOMS/index.html
Owens-Illinois Inc., www.o-i.com
Oxford Instruments Inc., www.oxinst.com
Paper Systems Inc., www.paper-systems.com
PARC Technical Services Inc., www.parctech.com
Patterson Industries Ltd. (Canada), www.pattersonindustries.com
PCS Instruments, www.pcs-instruments.com
PdMA Corporation, www.pdma.com
PED Inc., www.ped.vianet.ca
Perkin Elmer Automotive Research, www.perkinelmer.com/ar
Perkins Products Inc., www.perkinsproducts.com
Perma USA, www.permausa.com
Petrolab Corporation, www.petrolab.com

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