

LUBRICANTS

DEFINITION

The substance which is introduced in between two moving/ sliding surfaces in order to reduce wear and tear or frictional resistance between them is known as lubricant.

The process of reducing frictional resistance between two moving/ sliding metal surfaces, by introduction of lubricants in between them is called lubrication.

FUNCTIONS OF LUBRICANT

1. Reduce wear and tear
2. Reduce loss of energy in the form of heat (coolant)
3. Reduce expansion of metal by local frictional heat
4. Avoid seizure
5. Increases life of machinery
6. Act as seal

Mechanism of lubrication

When two metal surfaces are in contact /sliding with each other however smooth they are, there develops a friction. Based on the different type frictions developed on the metal surfaces the mechanism of lubrication is of two types

1. Fluid film lubrication or thick film lubrication or hydrodynamic lubrication

- The two metal surfaces are separated by thick film (fluid) of lubricant (at least 1000°A or thick) so that there is no direct contact between two metal surfaces
- Applied in the cases where the coefficient of friction is very low i.e, 0.001-0.03
- It occurs in the case of a shaft running at a fair speed in well lubricated bearing or where the rolling friction takes place
- The thick film introduced in the metal surfaces reduce wear, any resistance to movement of moving/sliding parts is only due to the internal resistance between the particles of the lubricant moving over each other.
- Thus the lubricant chosen should have the minimum viscosity under working conditions and they should remain in place and separate the surfaces

Mechanism applied in delicate instruments like watches, clocks, guns and sewing machines etc.

Hydrocarbon oils blended with selected long chain polymers with antioxidants like amino-phenols.

2. Thin film or boundary lubrication

- The two metal surfaces are separated by thin layer of lubricant which is adsorbed by physical or chemical forces or both on both the metallic surfaces.
- These adsorbed layers avoid direct metal to metal contact
- The coefficient of friction should be 0.05-0.15
- Applied when

1. A shaft starts moving from rest or
 2. The speed is very slow or
 3. The load is very high
 4. Viscosity of oil is very low
- Vegetable oils & animal oils and their soaps, graphite, molybdenum disulphide or active groups or atoms which can form chemical linkages with metals or other surfaces
 - These substances either physically adsorb on the metal surface or react chemically at the metal surface, forming a thin film of metal soap, which act as lubricant.

Extreme pressure lubrication

- Where thin film lubricant fails to stick and may decompose or vaporize due to high local temperatures are attained under very high pressure and speed.
- To meet these extreme pressure conditions, special additives are added to mineral oils
- These are called extreme pressure additives
- These additives are organic compounds having active radicals or groups such as chlorine (as chlorinated esters), sulphur (as sulphurized oils) or phosphorous (as in tricresyl phosphate)
- These compounds react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphides or phosphides.
- These metallic compounds possess high melting points (e.g., iron chloride and iron sulphide melts at respectively at 650°C and 1100°C)

CLASSIFICATION OF LUBRICANTS

On the basis of their physical state lubricants can be broadly classified as

1. Liquid lubricants: Vegetable oils e.g., olive oil, palm oil, castor oil, etc
Animal oils e.g., Whale oil, Lard oil, Tallow oil etc
Mineral oils e.g., petroleum fractions
Blended oils e.g., Mineral oils with various additives
Synthetic oils e.g., silicones, etc
2. Semi solid lubricants or greases; Greases and Vaseline's etc
3. Solid lubricants: Soap stone, talc, graphite, Teflon etc

Blended oils:- give desired lubricating properties required for a particular machinery

Blended oils: To impart specific property to the lubricant the following additives should be added

1. **oiliness carriers:** increased by addition of an oiliness carrier like vegetable oils and fatty acids
2. **extreme pressure additives:** fatty ester, acids or organic materials which contain sulphur, chlorine or phosphorous compounds
3. **Pour point depressive additives:** prevents the separation of wax from the oil e.g., phenol and chlorinated wax with naphthalene

4. **Viscosity index improvers:** High molecular weight compounds like hexanol
5. **Thickeners:** increase viscosity of a film polystyrene, polyester
6. **Antioxidants or inhibitors:** retard oxidation of oil e.g., aromatic phenols, and amino compounds
7. **Corrosion preventers:** compounds of phosphorous and antimony
8. **Antifoaming agents:** Glycols and glycerol

PROPERTIES OF LUBRICANTS

1. Viscosity and Viscosity Index

- Viscosity is the one of the most important property of lubricating oil
- Viscosity is the measure of the internal resistance to motion of a fluid and is mainly due to the forces of cohesion between the fluid molecules
- Viscosity of oil is Low- the fluid lubricant film cannot be maintained between the moving surfaces as result of which wearing will takes place.
- Viscosity of oil is high-excessive friction due to the shearing of oil itself would result
- It is expressed in poise or cent poise
- Viscosity of oil changes with temperature and shows inverse relation.
- The rate at which the viscosity of oil changes with temperature is measured by **viscosity-index**
- **High viscosity-index** slightly affected on raising a temperature
Low viscosity-index viscosity of oil falls rapidly as the temperature is raised

Determination of Viscosity – index

- Viscosity-index is measured by

$$V.I = \frac{VL - VX}{VL - VH} \times 100$$

VL = Viscosity at $100^{\circ}F$ of Gulf oil standard which has same viscosity at $210^{\circ}F$ as that of oil under test

VX = Viscosity of the oil under test

VH = Viscosity at $100^{\circ}F$ of Pennsylvanian oil standard which has same viscosity at $210^{\circ}F$ as that of oil under test

Viscosity is measured by using redwood viscometer I (For thin lubricating oils)and II (for highly viscous oils)

Flash point and fire point:

- The flash point is the lowest temperature, at which a lubricant oil gives enough vapours that ignite for a moment, when a tiny flame is brought near it.
- The fire point is the lowest temperature at which the lubricant oil burns continuously at least five seconds, when a tiny flame is brought near it.
- The flash and fire points are useful in determining a lubricants volatility and fire resistance.

- The flash point can be used to determine the transportation and storage temperature requirements for lubricants.
- Lubricant producers can also use the flash point to detect potential product contamination.
- A lubricant exhibiting a flash point significantly lower than normal will be suspected of contamination with a volatile product.
- Products with a flash point less than 38 C (100F) will usually require special precautions for safe handling. The fire point for a lubricant is usually 8 to 10 percent above the flash point.
- The flash point and fire point should not be confused with the auto-ignition temperature of a lubricant, which is the temperature at which a lubricant will ignite spontaneously without an external ignition source.
- The flash and fire point can be measured by using Pensky Marten's apparatus

Cloud and Pour Point

- When an oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance is called cloud point.
- The temperature at which the oil ceases to flow or pour is called its pour point
- Cloud and pour point indicates the suitability of the lubricant in cold conditions.
- Machine works at low temperature should possess low pour point.
- Presence of waxes present in lubricant raises the pour point.
- The cloud and pour point can be measured by pour point apparatus.

Aniline Point

- Lowest temperature at which equal volumes of fresh aniline and oil are completely miscible.
- Aniline point gives an indication of possible deterioration of oil in contact with rubber sealings packings etc.
- Field experience and laboratory tests have indicated that oils with a high aromatic content were more detrimental to rubber products than those with a low aromatic content.
- The relative aromatic content of oil is indicated by its aniline point.
- Oils having a high aromatic content have a low aniline point, and oils with a low aromatic content have a high aniline point.
- Therefore the oils with high aniline points are the most desirable for use in drilling fluid in order to minimize damage to rubber equipment on the rig.

Procedure

- Clean and dry the apparatus. Measure 4 ml of aniline and 4 ml of the oil to be tested into the test tube.
- Place stopper into the test tube and insert thermometer, making sure the bulb does not touch the sides or bottom of the tube.
- Heat the tube slowly while stirring the mixture (stir by moving the thermometer up and down) until complete miscibility (the mixture becomes clear) occurs.

- Remove from heat source and continue stirring until aniline-oil mixture becomes cloudy. Read thermometer temperature at cloud point and report aniline point.

NOTE: If the aniline and oil are miscible at room temperature, the sample will have to be cooled below this temperature to obtain the aniline point. The aniline point of an oil should be 150°F or higher in order to minimize damage to rubber parts in a mud circulating system.

GREEN CHEMISTRY

Definition:

Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances

Green chemistry is based on twelve principles developed by Paul Anastas and John Warner. They are

- 1. Prevention**
It is better to prevent waste than to treat or clean up waste after it has been created.
- 2. Atom Economy**
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3. Less Hazardous Chemical Syntheses**
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4. Designing Safer Chemicals**
Chemical products should be designed to affect their desired function while minimizing their toxicity.
- 5. Safer Solvents and Auxiliaries**
The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- 6. Design for Energy Efficiency**
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- 7. Use of Renewable Feedstocks**
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- 8. Reduce Derivatives**
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- 9. Catalysis**
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 10. Design for Degradation**
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Alternative solvents used in Green Synthesis

Solvents are used in chemical processes to aid in mass and heat transfer, cleaning or to facilitate separations and purifications. Solvents are often volatile organic compounds (VOCs) highly toxic and flammable like CCl_4 , CHCl_3 or CH_2Cl_2 and can cause a number of adverse health effects including eye irritation, headaches and allergic skin reactions or suspected carcinogens (benzene). Alternative solvents suitable for green chemistry are those that have low toxicity, are easy to recycle, are inert and do not contaminate the product.

The safer green solvents used in recent are ionic liquids, super critical CO_2 or H_2O , water and also solvent free systems.

Ionic Liquids

Ionic liquids are mixtures of anions and cations which are liquids at room temperature or molten salts (with melting point around 100°C), which can be used as alternative solvents in organic synthesis. Although the ionic liquids do not comply full with green chemistry principles, they are very promising as alternatives to organic solvents due to their nonvolatile nature. They can serve optimal replacement for volatile solvents. The first ionic liquid discovered was $[\text{EtNH}_3][\text{NO}_3]$

Ex. The use of chloroaluminate compounds for electrophilic alkylation, acylation and polymerization

Super critical CO_2 fluid

It is a fluid state of carbon dioxide. Carbon dioxide is a gas at STP or solid (dry ice) when frozen. If the temperature and pressure increased from STP above critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid i.e., more specifically behave as a supercritical fluid (31.1°C / 72.9 atm). This is a versatile solvent as alternative solvent due to its low toxicity, low viscosity and non inflammability. Its high stability at relatively low temperature process allows most of the compounds to be extracted with little damage.

Because CO_2 is obtained as a by-product of other industrial process, it is inexpensive and being a gas it is easily evaporated leaving no residue.

Similarly **Supercritical water** is a clean and cheap green solvent as though many organic compound insoluble in water they are soluble in water at its supercritical state at 374°C and 218 atm

Ex. used to extract caffeine from coffee, in dry cleaning, in determination of total recoverable hydrocarbons from soil and sediments etc

Aqueous solvent systems

Water is non toxic and non inflammable, renewable and inexpensive solvent, the minimum solubility of many hydrocarbon reactants in water has been a limitation in its utility. However in recent years water is using as alternative solvent.

ex. some Diels Alder reaction dimerisation of 1,3 -cyclopentadiene were found to be accelerated in water.

