COMBUSTION CHAMBER DEPOSITS

As Related to Carbon-Forming Properties of Motor Oils

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THE past few years have seen a renewed interest in the subject of combustion chamber deposits (4, 6, 8, 9, 11, 20), undoubtedly because of the higher octane requirements of the newer engine designs and the increasing cost of octane numbers. Most of the recent studies have dealt with the property of octane requirement increase (ORI) as related to the lead content of fuels or detergent content of oils. Between 1925 and 1939 a number of papers appeared in the literature dealing with the effect of motor oil composition on combustion chamber deposits, but since 1939 this subject has been relatively neglected.

PRIOR STUDIES

As early as 1925 Orleup (19) pointed out that most of the carbonaceous combustion chamber deposit was formed from lubricating oil. In 1931 Bahlke (1) reported a relationship between oil volatility and carbon-forming properties. This was called the "carbonization index," and it related the 90% point of an oil distillation at 1-mm. pressure to the tendency of oils to form combustion chamber carbon. In 1935 Merrill, Moore, and Bray (18) re-emphasized that motor oil is a major contributor to carbonaceous combustion chamber deposits, and pointed out that the use of distillate oils and solvent extraction, particularly in the presence of propane, decreased the carbon-forming properties of oils. This study also demonstrated the increased volatility and low carbon-forming properties of aromatic or coastal oils as compared with Pennsylvania oils.

In early work on motor oils the Conradson or similar carbon tests had been used as a criterion of carbon-forming properties (5). However, in a review article in 1937, Gruse and Livingstone(13,14) concluded that the carbon residue method of predicting coke deposits from oil had ceased to be more than roughly indicative because of the new solvent-refining methods used in oil manufacture. They also raised an objection to the only other method of predicting the amount of coke formed by an oil, the "carbonization index" method—the difficulty in duplicating distillations at 1-mm. pressure. Their over-all conclusion was that both the carbon residue method and the vacuum distillation method were capable of giving precise indication of carbon-forming tendencies only when applied to a given class of oils.

Everett and Keller (10), in 1939, made several attempts at developing a bench-scale laboratory test for evaluating the deposit-forming tendencies of oils. They reached the conclusion that the only way to get carbon deposits which would simulate those obtained in practice was by means of the cylinder of an internal combustion engine. They also concluded that the Conradson carbon residue had no reasonable correlation with the deposits found in service.

Thus, a review of the prior work shows the best laboratory evaluation procedure is the vacuum distillation technique. This method is not applicable to materials having low decomposition temperatures, nor is it suitable for studying the effect of additives on the "carbon" property of oils.

The effect of additives on the carbon-forming properties of motor oil has received little attention. Widmaier and Nenninger (22), using the Conradson carbon test, showed that formic acid, ethylene glycol, and dichlorohydrin reduced the coking tendencies of lubricating oils. This work is of limited interest because the test procedure used has little relationship to the combustion chamber deposit property of oils.

A recent engine study of Carr (4) evaluated the effect of motor oil additives at different detergency levels on octane requirement increase, power loss, and spark plug performance. Because the major interest in this study was evaluation of the metallic constituents of the oil additives, the test procedure employed high combustion chamber temperatures (21). These severe test conditions probably did not form carbonaceous deposits and therefore minimized any base oil effects. This study did show that unleaded paraffinic fuels or propane fuel gave much lower octane requirement increase and deposit weights than leaded cracked fuels. The authors concluded that fuel characteristics had a greater effect than motor oil on octane requirement increase.

On the other hand, Gibson (11) reported a distinct difference between a "naphthenic" and a "paraffinic" oil in one car under unspecified operating conditions, and Merrill et al. reported the same for a twelve-car test fleet in "routine operation."

PRESENT WORK

These results suggest that an engine study of the effect of motor oil on octane requirement increase and deposits should be conducted under low combustion chamber temperature conditions (moderate speed and light load) and in the absence of lead and cracked fuels. It is believed that the highest octane requirements are reached under such mild duty operation. Therefore, a laboratory engine test procedure was selected to fit this situation and was used to determine octane requirement increase for a considerable number of oils and fuels with and without additives.

Parallel with this work was the development of a laboratory carbonizing test designated "air evaporation test." This technique allowed the study of additives and synthetic oils under conditions more approaching the engine than the "carbonization index."

Using these tools, the authors attempted to relate engine octane requirement increase and deposits to the following oil compositional variables:

Oil volatility or distillation range
Method of refining
Crude source, viscosity index level, or, as commonly stated, "naphthenic vs. paraffinic"
High viscosity blending components—bright stocks vs. viscosity index improvers
Synthetic oils
Exploratory oil additives designed to minimize deposits

ENGINE TEST PROCEDURE

It was desired to select an engine test procedure that would accentuate the contribution of motor oil to combustion chamber deposits and yet have as much significance in terms of road operation as possible. The four requirements which it was designed to meet were:

1. To operate under cycling conditions in order to avoid abnormal deposit accumulation.
2. To use mild conditions typical of city stop-and-go driving, so that carbonaceous deposits would be accentuated.

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3. To run the test long enough to attain equilibrium, so that the results would be as reproducible as possible.

4. To start each test with approximately the same initial octane requirement, as this factor is known to affect octane requirement increase and engine temperatures and pressures (17).

The engine used in the tests was a standard model, 1948 Chevrolet. It was new, or rebuilt according to the manufacturer's specifications. The auxiliary equipment, such as exhaust system, pan and jacket cooling, carburetion, etc., was the same as that used in the CRC-L-4-545 test (7). A modified L-4 break-in schedule was used. The combustion chamber and head assembly was rebuilt after each test. A complete engine overhaul was done after every four tests, or more often if necessary. The test engines were considered to have normal oil consumption, the rule being that consumption should be less than 1 quart per 1000 miles. The test was discontinued and the engine rebuilt if oil was consumed at a higher rate, if the beam load fell below 100 pounds at full throttle, or if the final compression pressures were less than 110 pounds per square inch.

The test conditions which were adopted are shown in Table I. Initial octane requirement used was 72 ± 2. Octane requirement measurements were made at 15-hour intervals and the tests were run to 100 hours, or approximately 4000 miles. This period was extended if necessary to obtain octane requirement equilibrium. The test was reproducible both as to deposit weights and octane requirement increase, as shown by check experiments. At the conclusion of the test, a final octane requirement measurement was made and piston top and valve deposits were removed and weighed.

TABLE I. CHEVROLET COMBUSTION CHAMBER DEPOSIT TEST CONDITIONS

(Time, 100 hours)

	Idle	Cruise
Time, minutes	1	5
Speed, r.p.m.	500	2000
Load, brake horse power	0	0
Air-fuel ratio	11.2	13.5–14.5
Water outlet, ° F.	...	165
Water inlet, ° F.	...	155
Oil sump, ° F.	...	195
Spark, degrees	11	...

OCTANE DEMAND MEASUREMENT

Speed, r.p.m.	1000
Load	Full throttle
Jacket, ° F.	160
Spark advance, degrees	11 before top center

LABORATORY AIR EVAPORATION TEST

The factors involved in the formation of carbonaceous residues from motor oil in engine combustion chambers are (1, 14, 18, 19):

1. Volatilization
2. Oxidation
3. Thermal decomposition
4. Iron catalysis (new factor)

In devising a test it was attempted to include all these factors.

APPARATUS. The apparatus was a horizontally mounted electric furnace, 32 inches long, with a steel core 4.5 inches in inside diameter. The ends of the furnace were closed with Transite disks, one of which was removable to allow the introduction of a sample tray. The removable disk contained holes for an air inlet tube and a thermocouple. The thermocouple was centrally located in the furnace and was connected to a Micromax controller recorder.

A double-deck Transite tray, which held the oil sample dishes, 2 inches in diameter, fitted into the furnace. Six dishes could be positioned in the center part of the furnace.

Additional furnace end windings and a small fan mounted in the closed end of the furnace were used to reduce temperature gradients. The temperature gradient in the sample area of the furnace, when operating at 625° F., was ± 5° F.

TEST PROCEDURE. Approximately 2 grams of oil were weighed into the containers. The samples were placed in the

furnace at the operating temperature and maintained under selected time and temperature conditions. Three cubic feet per hour of laboratory compressed air were passed through the furnace to furnish oxidizing conditions. At the end of the test period the sample dishes were removed from the furnace, cooled, and weighed. The weight of the residue was determined and the physical characteristics, such as appearance and adherence, were noted.

The low-carbon steel dishes were prepared for use by burning off carbonaceous deposits from the preceding test by placing in a muffle furnace at 1000° F., and scale was then removed from the dishes by polishing with steel wool.

TABLE II. EFFECT OF IRON CATALYST AND TEMPERATURE ON OIL RESIDUE WEIGHT

(Time, 3 hours. Oils, 95 V.I. solvent-refined Mid-Continent, heart-cut)

	Wt. % Residue		
	Steel dish,	Glass dish	
Oil 100° F. Vis. (SUS)	625° F.	625° F.	650° F.
157	8.5	1.5	1.2
516	19.2	8.4	2.8
452ᵃ	21.6	11.1	5.8
1590	57.2	31.6	20.4

ᵃ Blend of 40% (157 at 100° F. vis.) + 60% (880 at 100° F. vis.).

TEST DEVELOPMENT STUDIES: The first variable investigated was temperature. Several oils were tested in glass dishes at 550°, 650°, and 750° F. The coking temperature was about 650° F.; at 750° F. very low results were obtained, while at 550° F. the residues were semiliquid and did not resemble carbonaceous deposits. A narrower temperature range, 625° to 650° F., was studied with a series of solvent-refined oils of varying distillation range (Table II). These data illustrate several significant points:

The heavier oils gave increasing amounts of residue, in agreement with the engine experience described above.

Much less residue remained at 650° F. than at 625° F. This illustrates that small temperature variations can affect the competing phenomena of oil oxidation and evaporation.

Steel dishes gave much higher residues than did the glass containers. As iron is encountered by oil in almost all engine combustion chambers, this catalytic factor was considered to be very important, and steel dishes were adopted.

Aluminum, in other tests, was found to be noncatalytic, giving results similar to those obtained in glass dishes. The test, therefore, gives results on aluminum vs. steel pistons similar to those reported by Merrill, Moore, and Bray (18) in engines.

Another important question in residue formation is the relative contribution of oxidation and thermal decomposition. This point is illustrated in Table III, which reports several oils in steel dishes at 625° F. for 3 hours in an air atmosphere and a nitrogen atmosphere. The inert atmosphere resulted in a decreased residue weight for all mineral oils, and it was particularly noticeable with the coastal oil. As engine combustion chambers are subject to oxidizing conditions, it was thought that air should be present in any test intended to measure the combustion chamber deposit-forming properties of a motor oil.

TABLE III. EFFECT OF OXIDIZING ATMOSPHERE ON OIL RESIDUE WEIGHT

(Time, 3 hours. Temp., 625° F. Steel dish)

			Wt. % Residue	
Oil Type	V.I.	100° F. vis. (SUS)	Nitrogen	Air
Coastal A	34	525	0.8	9.5
Solvent refined Mid-Continent	98	452	9.9	21.6
Conventionally refined Mid-Continent	65	225	1.7	7.9
Paraffin wax (127° F. m.p.)		...	1.3	3.4
Synthetic polyether	141	312	1.4	0.7

On the basis of these and other studies, the test conditions adopted for the air evaporation test were: 3 hours, 625° F., steel container, 2-gram oil sample, 3 liters of air per hour. A photograph of the apparatus is shown in Figure 1. Figure 2 shows the appearance of typical deposits formed from a synthetic, a coastal, and a solvent-refined Mid-Continent oil.

To illustrate the reproducibility of the air evaporation test under the standard conditions, oil 5 (Table IV) was submitted to a series of eighteen tests. The average residue value obtained was 22.2 ± 1.3%, indicating an average deviation of 5.8%.

EFFECT OF OIL COMPOSITION

EFFECT ON EQUILIBRIUM OCTANE REQUIREMENT INCREASE AND DEPOSIT WEIGHT. In the first engine study, unleaded straight-run fuel was used in order to eliminate any lead or fuel effect on octane requirement increase and deposits, so that the lubricant contribution would be clearly evident. Table IV shows the results obtained on a variety of oils under these conditions.

A synthetic polyether oil (No. 1) gave a zero octane requirement increase and a very low deposit weight. The coastal, conventionally refined, and blend of solvent-refined oils gave equivalent engine results. The results illustrate that under the conditions involved, minor variations in mineral oil lubricant composition were not reflected in changes in octane requirement increase or deposit weight. Major compositional variations, such as the addition of residual bright stock or a detergent additive, gave significantly different deposit and octane requirement increase results. However, they were well below reported field results in which leaded fuels had commonly been used. The possibility always exists that longer operation of the engines would give higher values, although the increase in requirement had leveled off for a minimum of 12 hours before the end of the experiment.

An unusual result was noted in test 7, in which chromium and manganese naphthenates were blended (2) with oil 5. The test showed a normal deposit weight, but only 1 octane requirement increase, which might be attributable to the catalytic influence of the oil additives. A similar catalytic effect has been reported for boron and silicon compounds when used as fuel additives (16).

EFFECT ON OCTANE REQUIREMENT INCREASE AND DEPOSIT WEIGHT. In order to reduce possible fuel effect, but to introduce the lead effect, several engine tests were done in which oil composition was varied using straight-run fuel containing 0.5 ml. of tetraethyllead (see Table V). As with no tetraethyllead, two of
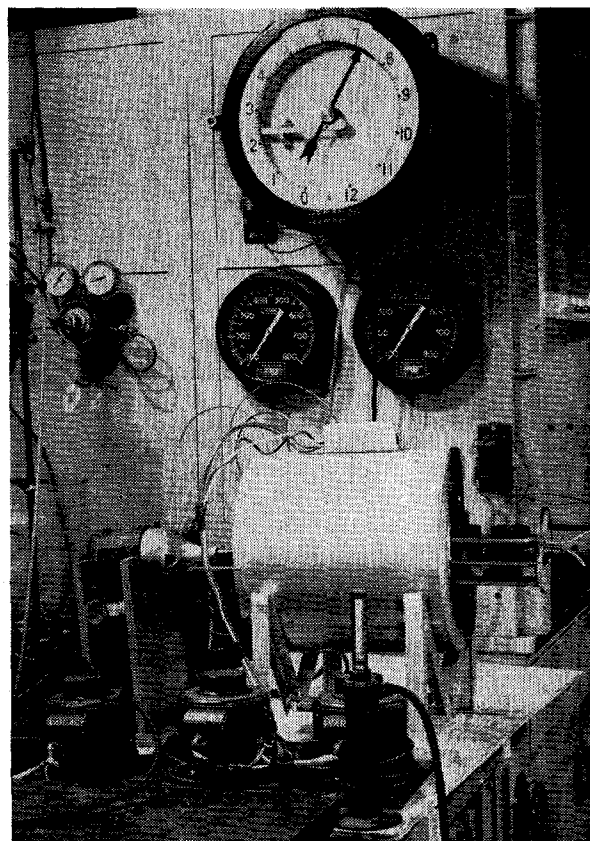

Figure 1. Air Evaporation Test Apparatus

the oils in this study, the coastal oil (test 9) and a blend of solvent-refined neutral and overhead bright stock (test 10) gave similar octane requirement increase values (14 and 12) and deposit weights, although these were substantially higher than in the absence of tetraethyllead. The solvent-refined neutral (test 11), used in the afore-mentioned blend, gave a lower octane requirement increase value of 9 and a much lower deposit weight.

The solvent-refined neutral was also blended with sufficient amounts of Paratone, Acryloid, and a polybutene oil to obtain about the same viscosity as the oil used in test 10, which contained an overhead bright stock. These three oils (tests 12, 13, and 14) all showed octane requirement increase values of 8, and two of them, the Paratone and Acryloid blends, gave only half as much deposit weight as was obtained with the base oil (test 11).

A comparison of the oils containing polymers with the bright stock blend (test 10) is of interest. Compared with the neutral oil, the bright stock caused an increase in octane requirement increase and deposit weight, whereas the polymers did not affect octane requirement increase and caused a reduction in deposit weight. The polymers, probably because of their relative ease of thermal decomposition, not only did not contribute to deposit formation, but appeared to cause deposit removal. The polymer concentrations used here were much higher than are normally used for viscosity index improvement.

A comparison which may be made between the data shown in Tables IV and V is the effect of the addition of 0.5 ml.

TABLE IV. OIL COMPOSITION vs. ENGINE DEPOSIT WEIGHT AND OCTANE REQUIREMENT INCREASE

(Unleaded straight-run fuel)

No.	Oil Type	V.I.	100° F. Vis.	Engler 90% Pt., ° F.	Equilibrium ORI	Piston Top Deposit Wt., G.	Weight % Residue, Air Evaporation Test
1	Synthetic polyether	141	312	821[a]	0	0.5	2.1
2	Coastal A	34	525	900	6	3.3	9.5
3	Conventionally refined Mid-C.	65	313	888	7	3.6	13.4
4	Heart-cut S.R. Mid-C.	95	157	870	3	3.8	8.5
5	Blend of S.R. Mid-C. 40% 4 + 60% (85 at 210° F. vis.)	98	452	1003	5	3.3	21.6
6	Blend of S.R. Mid-C. 68% 4 + 32% (250 at 210° F. vis.)	98	459	1063[a]	7	4.7	24.8
7	5 + 0.25% chromium naphthenate + 0.25% manganese naphth.	98	452	1003	1	3.6	39.0
8	5 + 2% metal + P₂S₅ additive	98	452	1003	8	5.1	...

[a] Decomposition temperature.
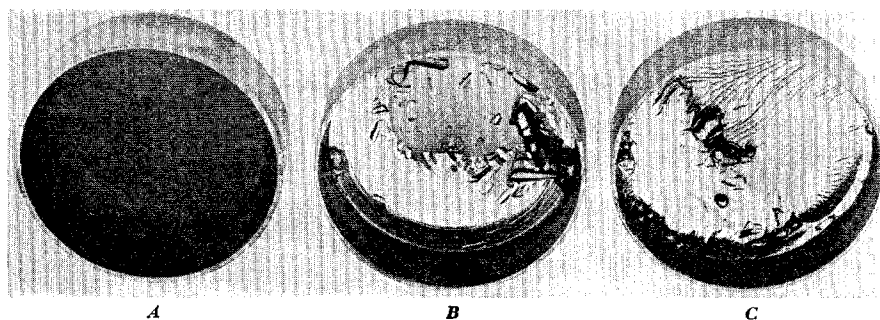
Figure 2. Typical Results of Air Evaporation Test
A. Synthetic   B. Coastal   C. Mid-Continent

special interest. In the recent litera-ture (*6, 11*) it has been customary to ascribe poor engine deposit properties to "paraffinic" oils and improved perform-ance to "naphthenic" oils. The good result shown for paraffin wax suggests that paraffinic materials are not inher-ently objectionable. A more accurate nomenclature would classify oils as naphthenic (poor deposit properties) and aromatic (good deposit properties). On this basis there are volatility differ-ences which can explain the observed results.

per gallon of tetraethyllead in the tests on the coastal oil, the solvent-refined neutral, and the solvent-refined blend (tests 1, 4, and 5 with 9, 11, and 10). The effect of the tetraethyllead in straight-run fuel was to increase the octane requirement increase by 6 to 8 numbers.

EFFECT ON OCTANE REQUIREMENT INCREASE AND DEPOSIT WEIGHT. To include both the lead effect and commercial fuel effect, a series of tests was done using L-4 (CRC-L-4-545 test) fuel, which was a blend of 20% straight-run and 80% cracked con-taining 3 ml. of tetraethyllead per gallon (see Table VI). In this series of tests four oils gave much higher deposit weights than at 0.5 ml. of tetraethyllead, but about the same octane requirement increase (high). These oils were: white oil, a coastal oil, a blend of solvent-refined neutral and overhead bright stock, and the latter containing chromium and manganese naphthenates. The oil con-taining the naphthenates is the same composition, which showed an octane re-quirement increase value of 1 with un-leaded straight-run fuel. With the leaded fuel the octane requirement in-crease increased to 16—perhaps because of the inactivation of a catalytic effect by lead compounds.

The other three oils which were tested might be considered as synthetic oils. These gave low octane requirement in-crease values. The oils were a synthetic polyether oil (test 19) giving an octane requirement increase of 3 and a low de-posit weight, a synthetic polybutene oil (No. 20) with an octane requirement increase of 4 and a very low deposit weight, and a 132° F. melting point paraffin wax (No. 21) with an octane requirement increase of 3 and an inter-mediate deposit weight. These three oils all have a high volatility or low decomposition temperature, which may explain the low deposit weight and octane requirement increase. These re-sults were obtained even though a high lead content and a gasoline containing a high proportion of cracked materials were used.

These studies show that lead residues are collected in the combustion chamber by oil residues under these mild engine conditions. The amount of lead residue collected apparently is dependent on the deposit-forming properties of the oil.

The low octane requirement increase obtained with paraffin wax has some

AIR EVAPORATION TESTS ON ENGINE-TESTED OILS

In Table VII are shown the physical properties of the oils used in the engine studies described above. No relation was found between the Conradson carbon values and the engine results. The air evaporation test showed some qualitative relationships with the engine data.

For example, the two synthetic oils and the paraffin wax (Table VI), which gave low engine octane requirement increase and de-posits, showed very low air evaporation residues. The white oil and coastal oil had intermediate residue values, and the solvent-refined blend gave a high result. These residue values rated the oils in the same order as the Engler 90% point, or the highest (decomposition) temperature recorded in an attempt at distilla-tion. Thus, the air evaporation test predicted the engine proper-

TABLE V.   OIL COMPOSITION *vs.* ENGINE DEPOSIT WEIGHT AND OCTANE REQUIREMENT INCREASE

(Straight-run fuel, 0.5 ml. TEL)

No.	Oil Type	V.I.	100° F. Vis.	Engler 90% Pt., ° F.	Equilib-rium ORI	Piston Top Deposit Wt., G.	Weight % Residue, Air Evaporation Test
9	Coastal A	34	525	900	14	12.4	9.5
10	Blend of solv.-ref. Mid-C. 40% 4 + 60% (85 at 210° F. vis.)	98	452	1003	12	14.8	21.6
11	Heart-cut solv.-ref. Mid-C. (test 4)	95	157	870	9	8.7	8.5
12	11 + 16% Paratone	127	557		8	4.5	9.7
13	11 + 11% Acryloid[a]	141	478		8	4.6	7.4
14	11 + 31% Polybutene[b]	105	500		8	8.5	12.8

[a] Blend of 50 parts 150 + 125 parts 710.
[b] Indopol H-35.

TABLE VI.   OIL COMPOSITION *vs.* ENGINE DEPOSIT WEIGHT AND OCTANE REQUIREMENT INCREASE

(L-4 fuel[a])

No.	Oil Type	V.I.	100° F. Vis.	Engler 90% Pt., ° F.	Equilib-rium ORI	Piston Top Deposit Wt., G.	Weight % Residue, Air Evaporation Test
15	Heavy white oil	83	368	918	13	23.0	9.9
16	Coastal B	28	616	939	13	..	11
17	Blend of solv.-ref. Mid-C. 68% 4 + 60% (85 at 210° F. vis.)	98	452	1003	11[b]	29.7[b]	21.6
18	5 + 0.25% chromium naphthenate + 0.25% manganese naphthenate	98	452	1003	16	21.5	39
19	Synthetic polyether	141	312	821[c]	3	7.5	2.1
20	Polybutene[d]	105	516	792[c]	4	4.4	3.5
21	132° F. m.p. pffn. wax	..	...	806	3	12.5	3.4

[a] 20% straight-run + 80% cracked.   TEL content 3 ml. per gallon.
[b] Premium commercial fuel.   TEL content 1.1 ml. per gallon.
[c] Decomposition temperatures.
[d] Indopol L-50, mol. wt. 660.

TABLE VII. PROPERTIES OF OILS USED IN INITIAL ENGINE STUDIES

Eng. Test No.	Oil	V.I.	Vis. (SUS) 100° F.	Vis. (SUS) 210° F.	% Residue, Air Evap. Test	% Conradson Carbon	API Grav.	IBP	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	FBP	% Recovered
														Engler Distillation[a]							
2, 9	Coastal A	34	525	55.5	9.5	0.039	22.5	643	727	734	799	814	825	835	848	859	878	900		933	97.5
3	Conventionally refined Mid-C.	65	313	50.0	13.4		24.9	659	736	766	809	845	851	859	864	873	884	888		919	98.3
1, 13	Synthetic polyether	141	312	62.7	2.1	0.012	11.0	570		813	833	839	838	821	Decomposition						
4, 11	Heart-cut solv.-ref. Mid-C.	95	157	43.7	8.5	0.002	32.2	688	751	753	770	780	783	804	832	839	860	870	898	910	97.6
5, 10, 17	Blend of solv.-ref. Mid-C. 40% 4 + 60% (85 at 210° F. vis.)	98	452	60.8	21.6	0.03	30.5	693	714	777	806	824	892	939	960	974	989	1003	1016	1035	98.4
6	Blend of solv.-ref. Mid-C. 68% 4 + 32% (250 at 210° F. vis.)	98	459	61.5	24.8	0.185	29.3	709	751	763	784	804	830	863	993	1058	1063[b]				
15	Heavy white oil	83	368	54.3	9.9	0.005	29.3	687	783	794	825	830	856	868	879	891	905	918		944	98.0
16	Coastal B	28	616	58.0	11.0	0.054	23.0	601	622	733	785	802	810	836	849	870	900	939		954	96.0
20	Polybutene	105	516	66.5	3.5	0.018		438		537	564	614	665	694	797	797	792	Decomposition			99.0
21	Paraffin wax microcrystalline wax			37.1	3.4 / 30.8			671 / 643	712	714	750	752	760	766	775	785	794	806		843	
A	Heart-cut solv.-ref. Mid-C.	95	516		19.2			840		873	880	890	903	916	930	942	950	958		1000	
B	Heart-cut solv.-ref. Mid-C.	95	1590		57.2			1020		1050	1060	Decomposition									

[a] ASTM method D 1160-51T.
[b] Highest recorded temperature at 75% distilled point.

ties of the low deposit-forming oils, but the engine did not differentiate between an intermediate and high air evaporation residue.

The air evaporation test showed a wide difference in residue weight for the solvent-refined neutral and its blend containing overhead bright stock (Table V) in agreement with the engine deposit data. The addition of polymers to the solvent-refined neutral did not increase the air evaporation residue weight or engine deposits. So in this comparison the air evaporation test gave the same relative differentiation as the engine on the effect of the addition of a bright stock and polymers to a solvent-refined neutral.

EVALUATION OF OIL BLENDS

In the preceding sections it was shown, in an exploratory manner, that special combinations of lubricants and fuels could be selected which would minimize octane requirement increase and deposits. An important question was the performance which would be obtained with typical petroleum-derived oil blends when used in combination with a leaded commercial fuel. To answer this question, the eight oil blends whose physical properties are shown in Table VIII were prepared and subjected to the Chevrolet CCD test and the air evaporation test. The oil blends were made up to an SAE 20 viscosity grade, with all of the oils having the same 210° viscosity of 45 Saybolt seconds. The oils included a heart-cut solvent-refined neutral and a neutral blended with the following:

1. Overhead, solvent-refined bright stock
2. Residual, solvent-refined bright stock
3. Residual, Pennsylvania bright stock
4. VI improver A
5. VI improver B

Also tested were a low viscosity index coastal neutral and a blend of a coastal neutral and coastal bright stock. One per cent of a commercial zinc dithiophosphate lubricating oil additive was added to each blend.

The three bright stock blends were tested in duplicate engine tests, while the other five oils were submitted to single tests. The results (Table IX) from the duplicate tests illustrate the repeatability of the engine procedure on octane requirement increase and deposit weights. A commercial regular fuel having a lead content of 1.5 ml. per gallon was used. In the engine tests the piston top, inlet valve, and exhaust valve deposits were weighed separately and their carbon contents were determined.

The test results are shown in Table IX. On the basis of deposit weights, the fuels fell into two groups, one of which gave two or three times as much deposit weight as the other. In spite of these large differences in deposit weights, no significant differences in octane requirement increase were observed. The similarity in octane requirement increase results might be attributed to the commercial fuel (4, 11, 12).

Even though octane requirement increase differences were not observed, it would appear desirable to minimize combustion chamber deposits as much as possible by using the optimum techniques of motor oil blending. The data show that the residual solvent-refined bright stock and the residual Pennsylvania bright stock gave the highest deposit weights and total grams of engine carbon. The overhead, solvent-refined bright stock gave nearly as much total engine deposit, but a slightly smaller amount of carbonaceous deposit. The solvent-refined neutral oil gave only about one half as much deposit as the bright stock blends. The addition of viscosity index improver A to the neutral oil blend gave results similar to the neutral oil, but the use of viscosity index improver B caused a decrease in deposit weight similar to that shown in Table VI. It is noteworthy that such a low concentration (1.15%) of viscosity index improver could affect deposit weight. The coastal neutral and the coastal bright stock blends gave low deposit weight results which were even below those obtained with the high viscosity index neutral. Thus, the
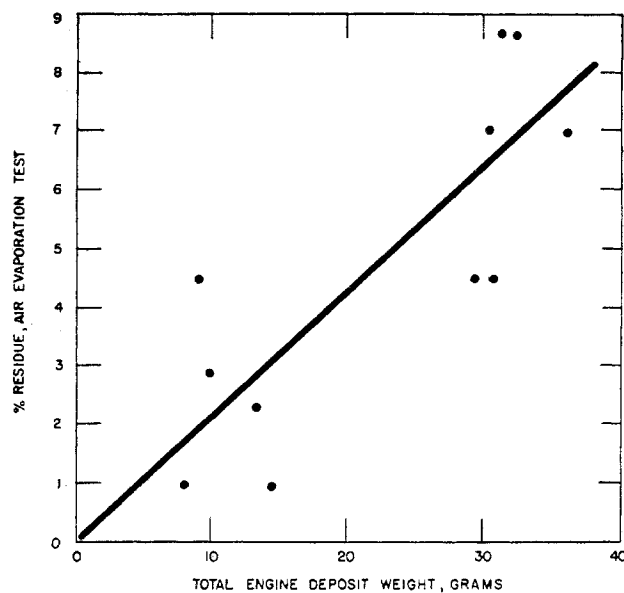
Figure 3. Total Engine Deposit Weight *vs*. Per Cent of Air Evaporation Test

Data from Table IX

coastal bright stock did not contribute to deposit formation as did the high viscosity index bright stock.

The carbon contents of the deposits showed little variation between the oils, again suggesting that the oil residues capture the lead residues. The inlet valve deposits showed a much higher carbon content than the piston top deposits, undoubtedly because this is a cooler region of the combustion chamber. The ratio of deposit weights between the low deposit-forming oils and the high deposit-forming oils was similar for both inlet valve and piston tops.

An interesting and unexpected result was the variation in exhaust valve deposit weights. The oils containing high viscosity index bright stocks showed two to three times as much exhaust valve deposit as the other oils. The result was unex-
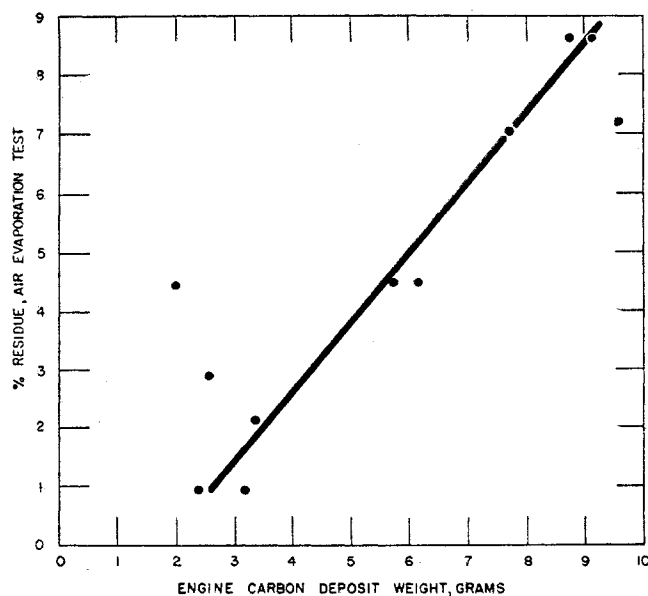

Figure 4. Engine Carbon Deposit Weight *vs*. Per Cent Residue of Air Evaporation Test

Data from Table IX

TABLE VIII. COMPOSITION AND PROPERTIES OF OILS[a] AND BLENDING STOCKS USED IN ENGINE DEPOSIT STUDY

Eng. Test No.	Name	Oil Composition	Vis. (SUS) 100° F.	Vis. (SUS) 210° F.	V.I.	Wt. % Residue, Air Evap. Test	Conradson C	IBP	Engler Distillation[b] 2%	5%	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP
22	Overhead brt. stk. blend	86.5% A + 13.5% overhd. solv.-ref. brt. stk. (92 V.I., 154 vis. at 210° F.)	179	45	97	7.0	0.01	708	723	742	754	769	780	791	806	818	830	865	921	969	1012
23	Residual brt. stk. blend	92.5% A + 7.5% resid. solv.-ref. brt. stk. (94 V.L., 238 vis. at 210° F.)	182	45	94	8.6	0.07	692	732	742	757	768	777	790	798	809	823	851	896	1042	1142
24	Penn brt. stock blend	91.5% A + 8.5% resid. Penn. brt. stk. (99 V.I., 154 vis. at 210° F.)	178	45	98	4.6	0.12	699	727	743	756	763	783	788	803	811	829	850	889	1008	1100
25	Heart-cut high V.I. neutral	Heart-cut solv.-ref. Mid-C.	180	45	96	1.0	0.27	670	..	712	725	733	743	756	770	783	800	820	840	858	..
26	Improver blend	98.25% A + 1.75% V.I. improver A	169	45	109	2.2	0.20	620	..	714	722	734	741	753	761	770	783	790	811	860	..
27	Improver blend	97.7% A + 1.15% V.I. improver B	163	45	115	1.0	0.20	611	..	718	722	730	738	743	751	762	778	790	813	829	..
28	Coastal neutral	51.9% Coastal neut. (8 VI-47 vis. at 210° F.) + 48.1% Coastal neut. (-2 V.I., 43 vis. at 210° F.)	262	45	2	2.9	0.22	588	..	649	655	670	683	696	710	728	745	769	801	823	..
29	Coastal brt. stk. blend	87.5% Coastal neut. (-2VI, 43 vis. at 210° F.) + 12.5% coastal brt. stk. (-38 V.I., 83 vis. at 210° F.)	262	45	5	4.5	0.29	640	..	668	679	690	701	712	729	741	760	780	822	853	
	Oil A	Heart-cut solv.-ref. neut.	145	42.7	95																

[a] All oils contained 1% zinc hexyl dithiophosphate additive.
[b] ASTM Method D 1160-51T.

TABLE IX.   ENGINE OCTANE REQUIREMENT INCREASE, DEPOSIT WEIGHT, AND DEPOSIT ANALYSIS DATA

(Fuel, commercial regular, 1.5 ml. TEL per gallon)

Eng. Test No.	Blend	Corr. Equil. ORI[a]	Total Combus. Zone Deposit, G.	Total Eng. Carbon, G.	Piston Top Deposits			Inlet Valve Deposits			Exhaust Valve Deposit	
					Weight, g.	Carbon, %	Carbon, g.	Weight, g.	Carbon, %	Carbon, g.	Deposit, g.	% Carbon
22	Overhead brt. stk.	9	29.8	6.3	20.7	15.3	3.2	9.1	33.7	3.1	2.2	
		9	30.1	5.6	21.5	11.8	2.5	9.4	33.0	3.1	2.2	
23	Residual brt. stk.	9	35.5	9.8	23.7	24.4	5.8	11.9	33.4	4.0	2.0	2.5
		11	30.4	7.5	20.1	18.4	3.7	10.3	36.6	3.8		
24	Penn brt. stk.	14	32.4	8.6	22.2	22.8	5.0	10.3	35.1	3.6	1.2	
		11	31.5	9.1	18.8	21.9	4.1	12.8	39.1	5.0	1.7	
25	Heart-cut high V.I. neutral	10	14.5	3.1	9.2	20.8	1.9	5.3	22.9	1.2	0.8	
26	V.I. improver A blend	9	13.1	3.2	6.7	19.7	1.3	6.4	30.0	1.9	0.9	
27	V.I. improver B blend	8	8.8	2.2	5.1	20.5	1.0	3.7	33.7	1.2	0.9	
28	Coastal neutral	8	10.0	2.7	5.2	22.3	1.1	4.8	32.9	1.6	0.7	1.5
29	Coastal brt. stk.	9	9.6	2.0	6.4	18.5	1.2	3.2	24.8	0.8	0.9	

[a] Corrected ORI (equilibrium) = measured ORI + 2 (29.4 − barometric pressure in inches of Hg (+ 0.25) humidity, grains/lb. of dry air − 80).

pected because this zone of the combustion chamber operates at a rather high temperature and the deposits were not carbonaceous in nature, as indicated by the low carbon analyses of 1.5 to 2.5%. These results suggest that oil composition, aside from additive content, may play a part in the amount and type of exhaust valve deposit and valve durability.

CORRELATION OF TEST RESULTS

Good correlation was found between the air evaporation test residue and engine deposit weights. As shown in Figure 3, the air evaporation test roughly predicted the total engine deposit weight, although the engine did not differentiate to the same degree as the test. The total engine carbon deposit weight (Figure 4, based on piston top and inlet valve deposits) is more closely reflected in the air evaporation test. The only oil which deviated from the correlation line was the coastal bright stock blend, which formed more residue in the air evaporation test than in the engine.

Oil volatility, as originally suggested by Bahlke (1), also predicted the amount of engine deposit. As shown in Figure 5, the Engler 95% point showed correlation with the total engine deposit weights, although again the engine was not so sensitive as
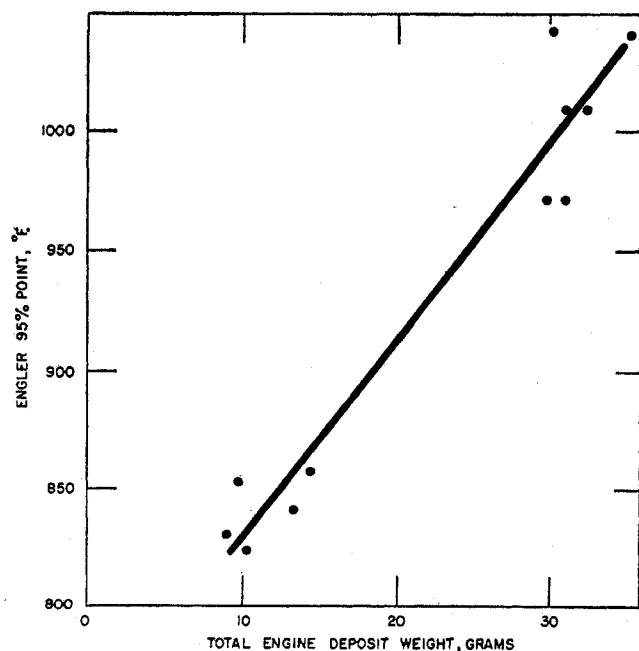
the test. A clearer picture of oil volatility differences is shown in Figure 6. These data illustrate the tail-end volatility difference between the residual and overhead bright stock blends and the fact that the coastal bright stock blend, even though it contained a high viscosity blending agent, was more volatile than the high viscosity index neutral oil.

EFFECT OF PHOSPHORUS COMPOUNDS

Another approach to the problem of minimizing the contribution of motor oils to combustion chamber deposits is the use of additives. Such additives probably should function as antioxidants at combustion chamber temperatures. By delaying oxidation, a larger percentage of the oil would have an opportunity to vaporize and leave the combustion chamber.

To evaluate this concept, a series of phosphorus compounds was tested in the air evaporation test. Two of the more promising additives were then submitted to Chevrolet CCD tests with leaded and unleaded fuels. The oil used in this study was a blend of solvent-refined neutral and overhead bright stock (see Table VIII, engine tests 5, 10, and 20).

As shown in Table X, P_4S_3 and P_4Se_3 (3, 15) effected a reduction in air evaporation residue weight by 40%. These two additives, when engine tested in the same oil, using unleaded straight-run fuel, reduced piston top deposit weights by 45 and 30%, and gave significant decreases in octane requirement increase (Table X).

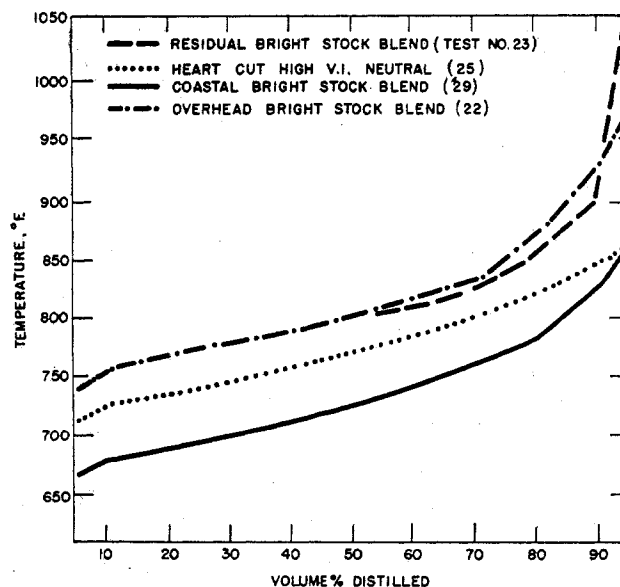Figure 5.   Engine Deposit Weight vs. Engler 95% Point

Figure 6.   Engler Distillation Curves of Four Oils

TABLE X. EFFECT OF PHOSPHORUS ADDITIVES ON ENGINE OCTANE REQUIREMENT INCREASE AND DEPOSIT WEIGHT

(Oil blend[a] of 95 V.I. heart-cut solvent-refined Mid-Continent oils)

Concn., %	Additive	Fuel	TEL Content	Equilibrium ORI	Piston Top Deposit Wt. G.,	% Reduction in Engine Deposit Wt. Due to Addtv.	Air Evap., Test, Wt. %
	None	Straight-run	0	5	3.3		22.3
	None	L-4	3	11	29.7		
0.25	Phosphorus sesquisulfide	Straight-run	0	1	1.8	45.3	13.5
0.25	Phosphorus sesquisulfide	L-4	3	10	33.8		
0.25	Phosphorus sesquiselenide	Straight-run	0	2	2.3	30.3	12.6
0.25	Phosphorus sesquiselenide	L-4	3	12	31.1		

[a] 40% (43.7 at 210° F. vis) + 60% (85 at 210° F. vis.).

at 625° F. The antioxidants were shown to decrease engine deposits and octane requirement increase in the absence of the fuel and lead factors.

The reduction in engine deposit weight was comparable to that obtained in air evaporation test residue.

These same additives were also engine tested using a leaded fuel containing cracked components (L-4 fuel). In the presence of the lead and fuel factors the effectiveness of the additives was not evident.

Several significant deductions may be made from these results.

Lubricating oil oxidation may be retarded in the temperature region of 625° F.

Such antioxidant action decreases residue formation, probably by increasing the time for oil volatilization before carbonization.

The air evaporation test can be used to study such effects.

This antioxidant activity can be observed in terms of reduced engine combustion chamber deposits and octane requirement increase, in the absence of fuel and lead effects.

SUMMARY

A bench-scale test, called the air evaporation test for measuring the combustion chamber deposit-forming tendencies of motor oil, and a laboratory engine procedure called the Chevrolet CCD test were developed. Utilizing these tools, it was demonstrated that lubricant composition is an important variable in the formation of carbonaceous combustion chamber deposits.

The tendencies of an oil to form deposits may be predicted by oil volatility or air evaporation test residue. Several high volatility or thermally decomposed oils gave low engine deposit values and low octane requirement increase when used with leaded commercial fuels.

Two coastal oils, a light neutral and its blends with two viscosity improvers, gave substantially lower engine deposit weights than comparable blends containing relatively nonvolatile bright stocks. Octane requirement increase differences were not observed between these petroleum-derived oils.

The air evaporation test was used to demonstrate that oil antioxidants may be effective in minimizing residue formation

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