

Aug. 26, 1958

L. E. MOODY ET AL

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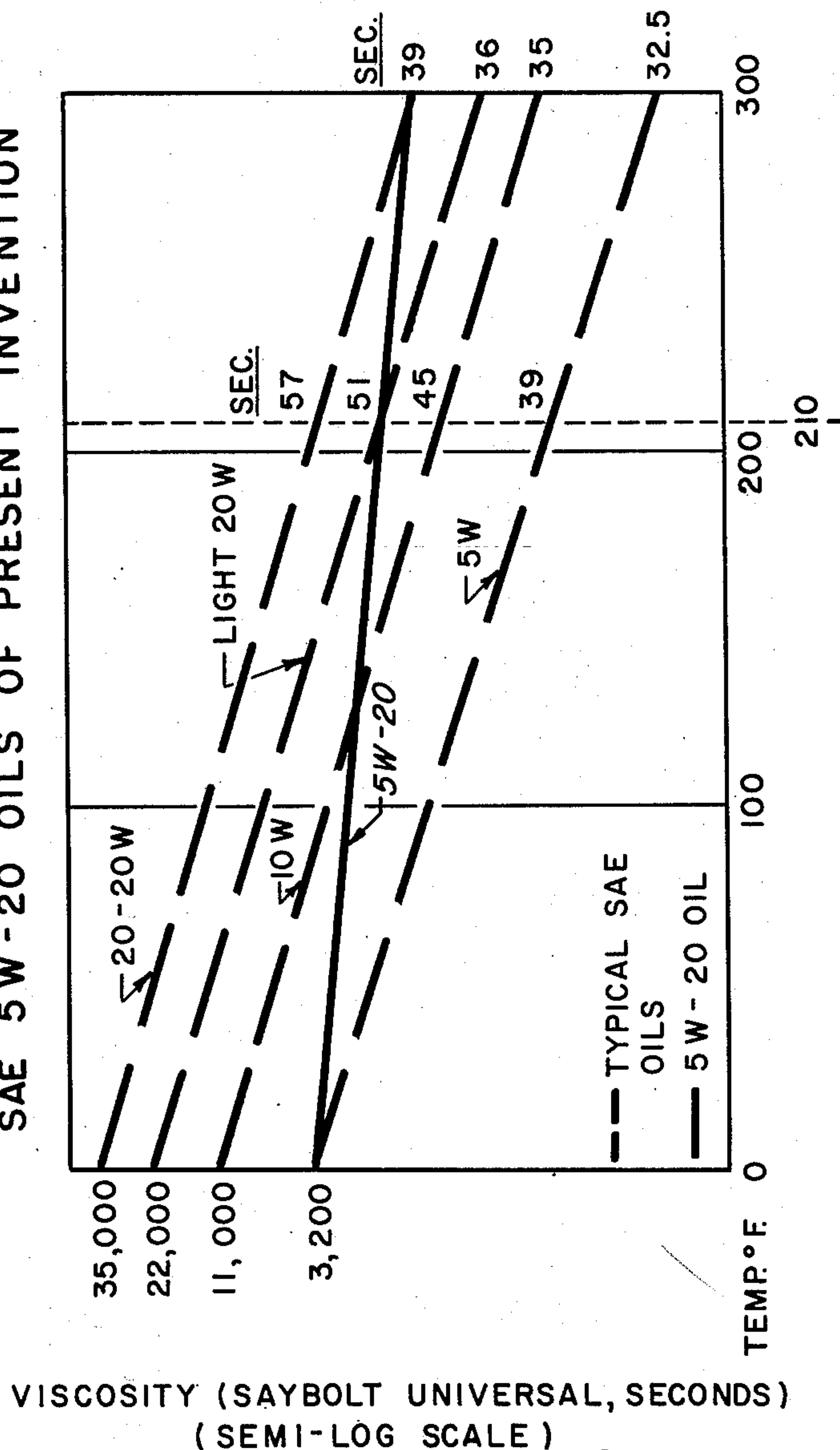
MINERAL-BASE LUBRICATING OILS AND METHODS FOR USING SAME

Filed Aug. 19, 1953

2 Sheets-Sheet 1

FIGURE 1

VISCOSITY - TEMPERATURE CHARACTERISTICS  
OF TYPICAL COMMERCIAL OILS AND THE  
SAE 5W-20 OILS OF PRESENT INVENTION



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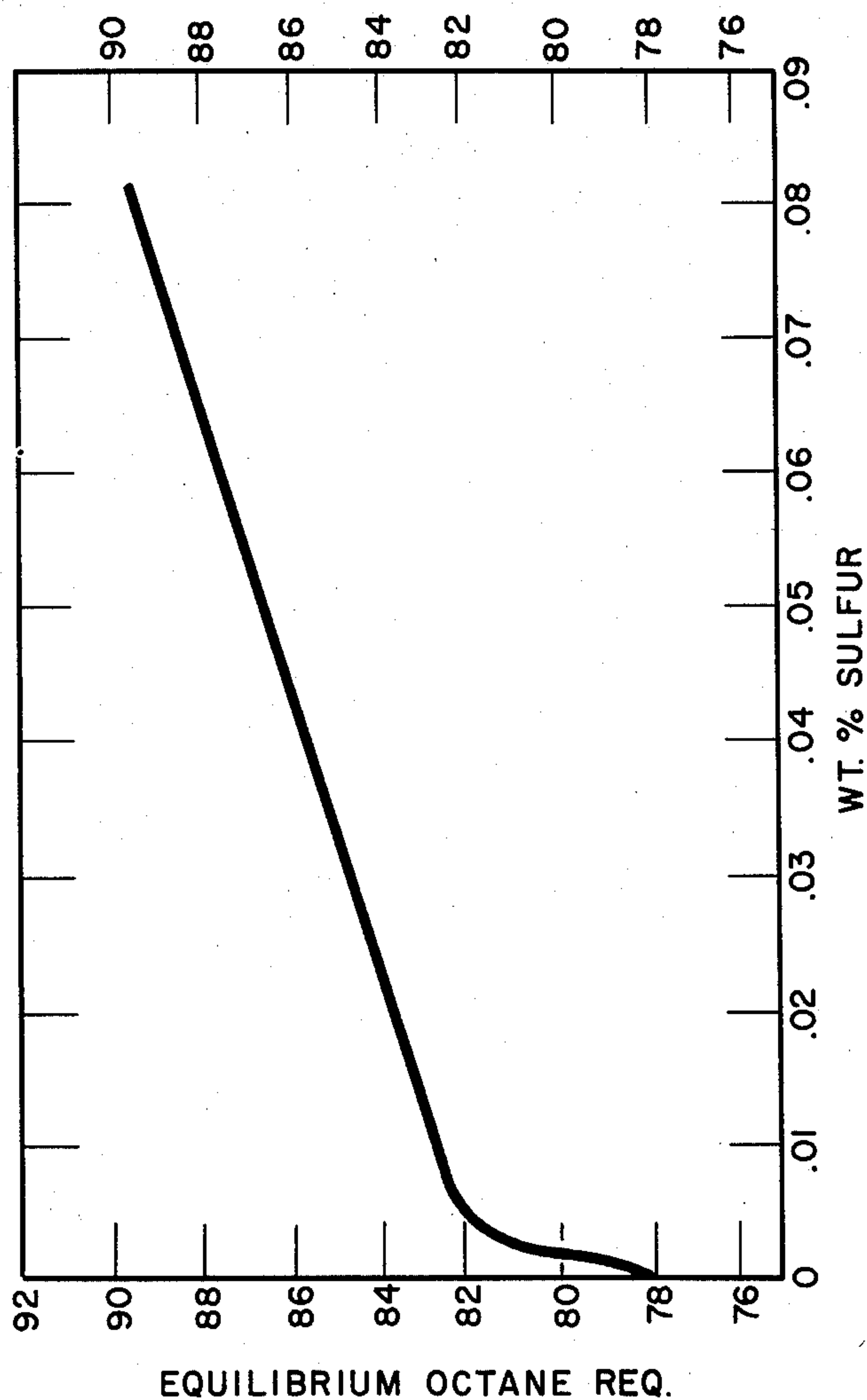
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2 Sheets-Sheet 2

FIGURE 2

EFFECT OF SULFUR CONTENT ON THE  
PERFORMANCE OF TEL-CONTAINING GASOLINES



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## MINERAL-BASE LUBRICATING OILS AND METHODS FOR USING SAME

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3 Claims. (Cl. 252—32.7)

The present invention relates to improved lubricating oils for use in internal gasoline combustion engines of the reciprocating type. More particularly, the invention is concerned with improved automotive motor oils which are mineral-base lubricating oil compositions having, in comparison with prior art formulations, reduced tendency to contribute to an increase in the requirement of octane number of gasoline for knock-free operation of high compression ratio internal combustion engines. The invention is also concerned with methods for operating automotive engines having compression ratios above about 7.0:1 with these improved lubricating oils in combination with essentially hydrocarbon gasoline fuels, which are essentially hydrocarbon mixtures, under conditions that result in a decrease of the formation of combustion chamber deposits of the type which contributes to "octane requirement increase." This invention is particularly concerned with motor oils containing mineral oil base stocks and addition agents improving the characteristics of the composition, in which neither the base stock nor at least one of the addition agents contributes substantially to "octane requirement increase" during the operation of high compression ratio engines.

For several decades considerable attention has been given to the importance of maintaining engine cleanliness in the operation of internal combustion engines such as those used in automobiles and similar vehicles. One aspect of this problem was concerned with the formation of carbon deposits in the combustion chamber of the engine. It was found that these carbon deposits reduced the volume of the combustion chamber thereby increasing the compression ratio and also led to the formation of localized "hot-spots" in the chamber that caused the air-fuel charge to ignite prior to the proper time for spark ignition. These effects resulted in "knock" in the engine.

During the nineteen-thirties it was recognized that, in order to overcome that knock, it was necessary to increase the octane number of a gasoline in comparison with that of the fuel required for knock-free operation in a clean combustion zone. In studies carried out on automobiles having relatively low compression ratios, such as those below about 6.5:1, it was also found that the con-

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ventional oils which were used at that time to lubricate the engines, contained components that formed carbon in the combustion zone. In characterizing various mineral oil lubricating oil components as to their tendency toward carbon deposition affecting octane requirement increase, the following conclusions were reached: The more highly aromatic portions of mineral oils generally were conducive to carbon formation. The high boiling components of paraffinic-base lubricants, such as residual stocks called bright stocks, also contributed to such carbon formation. For example, in one study a Pennsylvania base lubricating oil containing residual components was found to increase the octane requirement of new cars in 1935 at a rate of about one octane number per 400 miles operation until the octane requirement had increased by about 7 to 14 units.

It was found that selective extraction of mineral oils with solvents such as furfural and phenol produced lubricating oils that either did not contribute or contributed relatively little to this type of octane requirement increase. Removing certain types of high boiling components from the bright stocks also improved the finished lubricant. Deasphalting, acid-treating, solvent extraction and other refining processes were used for treating the bright stocks or residuals to decrease their contribution to octane requirement increase. Merrill et al. have given an interesting discussion of this problem (Refiner, 14, 313 (1935)).

It has been conventional practice for approximately the past twenty years to employ solvent-refined mineral oil base stocks in premium grade motor lubricants. However, heavy components such as bright stock have been considered to be necessary ingredients of such oils in order to improve oiliness characteristics and other properties. Therefore, conventional lubricants have contained minor amounts of bright stocks prepared by deasphalting, dewaxing, acid-treating or solvent extraction of crude oil residues. Such formulations were reasonably satisfactory as regards knock using the fuels available in relatively low compression ratio engines, and the engines generally did not require overhauling or cleaning until about 25,000 to 35,000 miles of operation. Good engine performance was frequently obtained for even longer periods.

Another aspect of the engine cleanliness problem has been directed to preventing or retarding bearing corrosion, piston ring sticking, cylinder wear, sludge deposition and varnish formation on various parts of the engine. Noteworthy advances have been made during the past fifteen years in the development of detergent, viscosity improving, antioxidant, and corrosion inhibiting additives for lubricating oils that reduce these and other difficulties thereby increasing engine life and improving engine performance.

A new aspect of the general problem of engine cleanliness has appeared during recent years with the development and widespread use of automobiles and other ve-



hicles having relatively high compression ratio engines, when using modern additive-containing mineral oil lubricants. Users of such vehicles frequently found, after relatively short operating periods, that the engines knocked and lost power even though premium additive-containing lubricating oils were used and even though fuels having high octane ratings meeting the automobile manufacturer's recommendations were employed. Considerable speculation arose as to what factors contributed to these difficulties and to possible solutions for overcoming them. It was generally believed that engine deposits contributed in some manner to these difficulties.

In order to determine the cause of the problem, road tests have now been carried out under carefully controlled conditions on new cars having high compression ratio engines (above about 7:1). It was found that the cars which eventually knocked and lost power contained films of dark deposits having the characteristics of resins in the combustion chamber proper, these deposits forming chiefly on the piston top, on valve tops, and on the underside of the cylinder head. Under these conditions the octane requirement to prevent knocking increased by as much as 10-15 units during the first 3,000 to 5,000 miles of service. Power losses as high as 10%, as indicated by decreased ability to accelerate, were observed. On the other hand, cars containing no such deposits in the combustion chamber proper did not knock or lose power when using the same fuel. It was therefore established that deposits in the combustion chamber proper and not other types of deposits, such as those on the piston rings and the like, are critical as regards octane requirement increase.

That combustion chamber deposits of this type are responsible for such substantial effects seems anomalous. They are not strictly speaking of the carbon type. Furthermore, careful measurements of the deposit volumes showed that the decrease in combustion chamber volume due to them (and thus the increase in compression ratio) could account for only about 10 to 15% of the octane requirement increase observed. It was then found that temperature effects (heat capacity and heat transfer) account for the remainder of the deposit harm. The insulating nature of these resin-like deposits was found to retain heat in the combustion chamber. Thus, the deposits decrease cooling through the combustion chamber walls. This results in heating up the incoming charge and raises the overall combustion temperature, which in turn makes the engine more prone to knock. These effects are due to the poor heat conductivity of the deposits.

Chemical analyses showed that the combustion chamber deposits generally contained in the organic portion, carbon, hydrogen and oxygen in the atomic ratio of about 5:5:2, respectively, with small amounts of sulfur and nitrogen (0.5 to 4% by weight). Lead compounds (as oxides, chlorides, sulfates, etc.) were also present in amounts as high as 50 to 80% of the total deposits when the gasoline contained tetraethyl lead (TEL) and halide scavengers for the TEL.

Full-scale road tests with various combinations of lubricants and fuels established that both the fuel and the lubricant could contribute to the difficulty. Further tests also revealed that under otherwise constant conditions, mild driving conditions, such as urban and suburban driving, aggravated the build-up of deposits. High speed driving and its attendant higher gas velocity and temperature in the engines appears to dislodge the deposits, and the problem is less acute under these conditions.

This problem has serious economic implications. The fuel anti-knock quality has been increased to meet the demands of new engines, but, in addition, the octane number must also be increased by the incremental amount demanded by the same engines after use. There are several adverse effects. The car owner must use a gasoline that is relatively more resistant to knock and more expen-

sive, than is required for a clean engine. Otherwise he is confronted with objectionable knocking and power loss.

Gasoline manufacturers must increase markedly the anti-knock quality of fuels now being supplied to satisfy the existing car population. Each inherently unnecessary increase in anti-knock quality places an undue burden on production facilities, requires relatively more expensive refining procedures and increases fuel costs to the consumer. The incremental requirement in octane number also limits the extent to which car manufacturers can increase compression ratios to provide more efficient engines which will take advantage of improved anti-knock quality fuels. Thus compression ratios could be increased substantially above present levels if octane requirement increase could be reduced. It is obvious that a large incentive exists for improving the efficiency of operation of present-day and future vehicles and for minimizing the deleterious effects of octane requirement increase.

It is therefore a principal object of the present invention to teach the use of motor lubricants that have reduced tendency to cause octane requirement increase in high compression ratio engines or to cause the formation of poor heat conductivity deposits in the combustion chamber. It is a further object to teach methods of operating such engines with gasolines having specific and critical properties whereby advantage may be taken of the improved lubricating oils.

A further object of this invention is directed to improved mineral oil-base lubricating oils containing one or more characteristic improving addition agents in which the base stock and at least one of the addition agents do not substantially contribute to octane requirement increase when used to lubricate high compression ratio engines.

These and other objects of the present invention will be amplified in the following description taken in conjunction with the examples and claims.

In accordance with the present invention, it has been found that an important criterion of the tendency of the lubricating oil composition, contacting the parts of a combustion chamber subject to friction, to form deposits contributing to octane requirement increase is its "resinification index." The term "resinification index" as used in this specification and claims refers to the relative freedom of a fuel or lubricant from tendency to form tenaciously adhering resin-like deposits when subjected to combustion in a container under a hot, smokeless, flame, e. g., a hydrogen flame, as will be explained in more detail below.

Full-scale road tests with new cars have established that the extent to which the lubricating oil forms such resin-like deposits under a hydrogen flame is substantially a direct function of the extent to which it contributes to the formation of harmful combustion chamber deposits. It has further been shown that this property is not a function of the amount of ash-forming materials present in the lubricating oils and is not a function of the carbon-forming tendency of the oil components as measured by conventional tests such as the well-known "Conradson carbon test," the "Ramsbottom coke test," etc. This property to form adherent resins in the combustion zone, while not fully explainable at this time, appears to be closely associated with the tendency of a given component to form high molecular weight cross-linked resins at hot flame conditions of the type prevailing in combustion zones. This cross linking phenomenon appears to derive from the property of the component itself as well as from catalytic effects caused by addition agents in the oil and fuel. These resins not only resist combustion but also appear to have a binding effect in retaining carbon and inorganic substances in the deposits.

With reference to the present invention, it has particularly been found that a superior motor oil composition suitable for use in present day high compression ratio engines consists of a mineral oil base stock that has a low resinification index in combination with at least one



addition agent that, when dissolved in the base stock, has also a low resinification index. An oil formulated by this procedure not only reaps the advantages of having improved characteristics imparted by the addition agent, but also has unexpectedly improved properties with regard to decreased contribution to octane requirement increase in engine use.

A more specific aspect of this invention contemplates a composition in which a substantially non-contributing mineral oil base stock has dissolved therein a multi-additive system in which at least two of the addition improving agents do not themselves contribute to octane requirement increase. Under these conditions it is possible to tolerate the presence of octane requirement increase contributing agents in small amounts and yet obtain the advantages of this composition.

A preferred composition in accordance with this invention contains a substantially non-contributing mineral oil base stock and at least three different non-mineral oil addition agents, each of which improves a different characteristic of the composition without at the same time contributing substantially to octane requirement increase. More preferably, all of the components of the finished composition are non-contributing to octane requirement increase.

Examples of mineral oil base stocks are refined mineral oil distillates that are free of mineral oil bright stock residuums. It has been found that bright stocks, even of the highly refined variety, have high resinification indexes. They contribute substantially to the formation of harmful deposits even when present in small concentrations. Although it is known that bright stocks can deposit carbon, as mentioned above, they have been used heretofore in concentrations ranging from as low as about 5% up to as high as 98% in premium grade mineral oil compositions. It is therefore surprising to find that they are harmful even at low concentrations. More particularly, refined mineral oil distillates or so-called neutrals that are substantially free of constituents that boil above about 600° F. at a pressure of 10 mm. (Hg) absolute, are preferred. The higher boiling mineral oil constituents contribute to the formation of harmful deposits. For example, base stocks boiling within the range of about 275° to 600° F. at this pressure are quite useful. Those boiling below about 575° F. at this pressure have excellent low resinification indexes, substantially independent of the origin and chemical constitution of the crude oil. The initial boiling point is not critical as regards deposit-forming characteristics, but it should be high enough to avoid excessive oil consumption by vaporization when used in the motor.

The discovery that such relatively low boiling base stocks can be used per se as the only mineral oil component of a finished oil composition for high-powered internal combustion engines is unexpected. Prior art formulations using neutral oil components contained bright stock residuals and other heavy mineral oil components, added to improve oiliness, to increase viscosity and to lower oil consumption, and even the neutral oils in these formulations only remotely approached the low boiling range of the neutral oils of the present invention. The present base stocks, however, when formulated with suitable synthetic or non-petroleum additives, are not only not contributing to the formation of poor heat conductivity deposits, but also give superior all-weather motor lubricants having excellent viscosity and viscosity index characteristics, low pour-point, good stability, and low oil consumption when used in high compression ratio engines.

Addition agents employed in combination with the above base stocks include high molecular weight synthetic hydrocarbon viscosity index improvers, such as polyolefins, particularly polyisobutylenes, sulfur- and phosphorus-containing hydrocarbons, especially those that have been treated to reduce acidity, such as neutralized

phospho-sulfurized polyolefins, metal dithiophosphates, phosphosulfurized terpenes, and the like. At least one of these non-contributing additives will be used in the present invention. It is preferred that no more than two, and preferably no more than one, of a different type of additive that contributes substantially to octane requirement increase, be used in combination with the non-contributing additive. Specifically preferred compositions include a combination of at least two of the above different types of addition agents that are non-contributing with no more than one contributing agent.

It has also been found that substantial improvements in the operation of automotive engines and the like having high compression ratios, such as above about 7:1, and preferably above 7.5 to 1, can be achieved by employing the lubricating oils of this invention in combination with a gasoline fuel having decreased tendency to contribute to octane requirement increase of the type discussed above, i. e., a fuel having a low resinification index. In general, conventional commercial high octane gasolines containing mixtures of straight run petroleum distillates, cracked naphtha stocks, polymers, tetraethyl lead and the like have high resinification indexes and contribute substantially to the formation of combustion chamber deposits having low heat conductivity. In some cases the fuel can almost entirely mask the benefits obtained by using the oil of the present invention.

For example, when using a fuel having a relatively high resinification index in combination with an improved oil, octane requirement increase can be reduced by about two or three units in contrast to performance with the same fuel and a relatively high resinification index lubricating oil. Although this improvement is substantial, unexpectedly better engine performance is obtained by using fuels having low resinification index characteristics in combination with the improved oils. For example, a leaded fuel containing low and critical amounts of sulfur when used in combination with the lubricating oil of this invention, will give improved engine operation. Leaded fuels containing certain high boiling scavenging agents also give superior results. Certain high octane fuels containing no tetraethyl lead are also superior to conventional fuels in this respect. Since aromatic hydrocarbon compounds, particularly those boiling above about 300° F., are harmful for the purpose of this invention, it also contemplates operations with gasolines containing relatively low concentrations of such aromatics. The most superior results have been obtained with fuels having very low resinification indexes.

Various methods for preparing and formulating lubricating oil compositions of the present invention and of employing them as lubricants in high compression ratio engines are presented in the following examples. It is to be understood that these examples are given as illustrations of the present invention and are not to be construed as limiting the scope thereof in any way.

In the drawings, to be described in detail in connection with the examples:

Figure 1 is a plot of the viscosity-temperature characteristics of typical commercial oils and of the SAE 5W-20-type oils of the present invention.

Figure 2 is a plot of the effect of sulfur content of leaded gasolines on equilibrium octane requirement.

## TESTING PROCEDURES

### Test 1.—Automotive road test

Automobile road tests were carried out to evaluate the performance of various crankcase lubricating oils and gasolines by the following procedure:

The cars used were new 1951 Oldsmobile 88 sedans (compression ratio—7.5:1). The initial octane requirements of the engines were determined, both before and after spark settings were adjusted to the manufacturer's



recommendation, using the Co-ordinating Research Council's Standard Uniontown procedure. The cars were charged with the gasolines and lubricating oils to be tested and were road tested in caravans, usually consisting of seven cars, over a predetermined course for up to about 7000 miles. 50% of the accumulated miles were city stop-and-go-type driving, and 50% were in intercity, moderate speed-type driving with top speeds of no more than 45 miles per hour. Octane requirement, acceleration time and spark settings were determined every 800 miles. Crankcase oil was changed about every 2000 miles. Complete records were kept for each car, including preignition, acceleration time, oil consumption, fuel consumption, air fuel ratio, etc. At the end of the test, octane requirement was determined, the engine was dismantled, and the combustion chambers were photographed and inspected.

Octane requirement was determined by the Standard Uniontown procedure, CRC Designation E-1-943, as described in the C. R. C. Handbook, p. 90 et seq., 1946 edition. Octane requirement increase (ORI) is the difference in the final and initial octane requirement of the engine. Equilibrium octane requirement (EOR) is the octane requirement of the engine after several thousand miles (usually 5000 miles) of use at which octane requirement reaches a substantially constant level. ORI and EOR are based on road octane numbers using primary reference fuels.

#### Test 2.—Combustion test for resinification index

This test is described in detail in copending application Serial No. 352,373, filed in the name of Alexander H. Popkin on May 1, 1953, now U. S. 2,761,766. In this test a known weight of a sample of material to be tested such as a lubricating oil, a gasoline or other material is placed in an open vessel having smooth non-absorptive inner surfaces, such as a glass beaker, porcelain crucible, etc. A hot, smokeless, clean flame, preferably a hydrogen flame, although other clean flames such as methane, etc. may be used, is directed into the opening of the vessel. The burner tip, for introducing the gas and air or oxygen (if needed), is directed toward the interior of the vessel. The sample is burned until only a dry residue remains. The flame is discontinued and the vessel is allowed to cool. The total weight of the resinous residue is then determined. When testing oils, the interior of the vessel is wiped carefully, before weighing, with a soft cloth or other soft material to remove carbonaceous deposits but to leave the tenaciously adhering resin-like deposits. The total deposits are weighed when burning fuels. The weight of deposits for a given weight of charge gives the resinification index. Specific testing conditions used for oils, additive-containing oils, additives, and gasolines are shown below:

Conditions	Oils and additives	Gasoline
Sample charge, g. ....	5.000	200.0
Pyrex beaker size, cc. ....	250	400
H <sub>2</sub> :Air ratio, in cubic feet/min. ....	0.16:0.12	0.59:0
Burning time, minutes. ....	5-10	25-35

#### Test 3.—Lauson engine test

Lauson single cylinder engines were also used to evaluate fuel and lubricating oil effects on octane requirement increase. These engines had a 6.5:1 compression ratio head and were operated with an induction motor at 1840 R. P. M. and at 0.5 b. kw. (brake-kilowatt) load. Each test was usually run for a period of 120-200 hours with the particular lubricant or fuel being tested using a spark advance of 12° BTDC. The ratings were conducted with

secondary reference fuels using an oscilloscope which gave visual ratings of knock intensity via a sensitive pickup attached to one of the studs of the engine. This procedure was found to be more accurate than the audio-type ratings usually used in the Standard Uniontown procedure, because knocking in the Lauson engine is difficult to hear. Operations at the low power level of 0.5 b. kw. gave good ORI and EOR correlations with full scale road tests of the type described in Test 1.

The above-described testing procedures were used in the evaluations to be discussed in the examples.

### DESCRIPTION OF LUBRICATING OIL BASE STOCKS, ADDITIVES, AND FUELS

The following discussion gives information on the source, composition, inspections, and the like of the various materials that were evaluated as described in the examples.

#### A. Oil base stocks

**Base stock A.**—A distillate having a Saybolt Universal viscosity at 210° F. of about 43 seconds was obtained by conventional distillation of paraffin-base Mid-Continent crudes. This distillate was then extracted with phenol solvent under usual conditions to obtain about a 60% yield of raffinate. The raffinate was dewaxed using a conventional methyl ethyl ketone-benzene solvent to obtain approximately 67% yield of dewaxed product having a 5° F. pour point. The dewaxed product was then distilled to obtain a bottoms fraction designated as base stock A.

**Base stock B.**—This product was obtained by dewaxing the above solvent raffinate to about a 74% yield of dewaxed product having a pour point of about 15° F. This dewaxed product was then distilled to obtain an overhead fraction designated as base stock B.

**Base stock C.**—This base stock was a light solvent neutral overhead fraction obtained by the distillation of the same charge stock used in making base stock A.

**Base stock D.**—This base stock was a light solvent neutral overhead fraction obtained by distilling the same charge stock used in making base stock A to obtain a fraction intermediate base stocks B and C.

**Base stock E.**—This base stock was a light solvent neutral overhead fraction obtained by distilling the same charge stock used in making base stock A.

**Base stock F.**—This was a bright stock residuum obtained by conventional deasphalting, dewaxing, acid-treating and phenol extraction of a residuum obtained from the distillation of a Panhandle, Mid-Continent crude.

**Base stock G.**—This base stock was a blend containing 92% by volume of base stock B and 8% by volume of base stock F.

**Base stock H.**—This base stock was obtained by the sulfuric acid treatment of a lube oil distillate obtained from a Texas Coastal crude.

**Base stock J.**—This base stock was also obtained by the sulfuric acid treatment of a lube oil distillate obtained from a Texas Coastal crude.

**Base stock K.**—A cycle stock was made by catalytic cracking a Mid-Continent type gas oil using a silica-alumina catalyst. This cycle oil boiled in approximately the same range as the original gas oil feed stock. The cycle stock was then selectively extracted with phenol solvent to a 50% raffinate yield. The raffinate was solvent dewaxed to a +25° F. pour point, the dewaxed oil yield being 80% based on the solvent raffinate. The dewaxed oil was then distilled to obtain a 0-27% light neutral overhead fraction designated as base stock K.

**Base stock L.**—This base stock was a polybutene having a Staudinger average molecular weight of about 400. The polybutene was prepared by the conventional polymerization of isobutylene using a Friedel-Crafts catalyst.

Typical inspections on the various oil base stocks are shown in Table I, below:



TABLE I.—TYPICAL INSPECTIONS OF OIL BASE STOCKS

Base stock.....	A	B	C	D	E	F	G	H	J	K	L
Inspections:											
Gravity, ° API.....	29.4	31.9	36.9	35.0	34.4	26.5	31.1	28.6	23.4	34.0	36.5
Flash point, ° F.....	475	405	345	360	365	555	410	340	390	355	235
Viscosity, S. U. S. at—											
100° F.....	371	150	66	74	83.3	220	192	100	513	81	239
210° F.....	57.3	43.8	36.0	37.0	38.1	145	46.7	38.4	57.2	37.6	51.3
Viscosity index.....	102	112	107	107	107	100	109	48	54	104	120
Pour point, ° F.....	+15	+15	0	—5	+15	+15	+15	—35	—5	+20	—50
Crude source.....	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(2)	(2)	(1)	(3)
Distillation range, ° F. (10 mm. Hg pressure absolute Engler distn.):											
Initial boiling point.....	420	370	325	320	320	390	376	315	360	(6)	(6)
Final boiling point.....	(4)	660	508	555	561	-----	-----	544	645	-----	-----
Temperature at, percent distilled:											
2.....	483	392	348	343	356	524	403	338	418	-----	-----
5.....	506	412	366	363	373	577	424	357	440	-----	-----
10.....	518	425	380	380	396	614	444	372	466	-----	-----
20.....	535	446	398	401	418	635	473	386	488	-----	-----
30.....	548	470	411	418	438	654	491	401	508	-----	-----
40.....	562	490	422	431	452	661	508	414	521	-----	-----
50.....	574	511	432	444	461	667	521	429	534	-----	-----
60.....	587	533	440	455	474	676	540	443	548	-----	-----
70.....	601	550	450	466	488	(4)	558	458	562	-----	-----
80.....	615	584	460	483	502	-----	597	477	584	-----	-----
90.....	643	614	479	501	520	-----	650	502	611	-----	-----
95.....	661	647	494	526	538	-----	-----	525	633	-----	-----
Sulfur, weight percent.....	0.31	(6)	0.05	(6)	0.24	0.47	0.34	0.07	0.21	0.04	Nil
Conradson carbon, weight percent.....	<0.1	<0.1	<0.1	<0.1	<0.1	0.7	0.1	<0.1	0.1	<0.1	<0.1

<sup>1</sup> Mid-Continent. <sup>2</sup> Coastal. <sup>3</sup> Synthetic. <sup>4</sup> Started cracking.  
<sup>5</sup> Not determined—distilled below 600° F. at 10 mm. Hg pressure. <sup>6</sup> Not determined.

B. Additives

Additive 1.—This additive was a polybutene concentrate viscosity index improver consisting of about 24% by weight of polyisobutylene having a Staudinger average molecular weight of about 15,000 and 76% by weight of a mineral oil base stock consisting of 85% base stock B and 15% base stock C.

Additive 2.—This was another polybutylene concentrate consisting of 22% by weight of polyisobutylene having a Staudinger average molecular weight of about 15,000 and 78% by weight of base stock A.

Additive 3.—This was a commercially available detergent additive containing a high proportion of alkaline earth metals (approximately 1.5 wt. percent barium and 2.0 wt. percent calcium).

Additive 4.—This was a commercially available polymethacrylate ester-type viscosity index improver consisting of about 37% by weight of a polymerized C<sub>8</sub>–C<sub>10</sub> alcohol ester of methacrylic acid (of about 12,000 molecular weight) and 63% by weight of mineral lubricating oil.

Additive 5.—This was a commercially available antioxidant consisting of about 55 weight percent of zinc dialkyl dithiophosphate in mineral lubricating oil.

Additive 6.—This was a commercially available antioxidant consisting of about 50% of a P<sub>2</sub>S<sub>5</sub>-treated alpha-pinene in a mineral lubricating oil. The oil concentrate analyzed about 13% sulfur and 4.6% phosphorus.

Additive 7.—This was an ashless detergent additive prepared by treating a polyisobutene having an average Staudinger molecular weight of about 1100 with about 10 weight percent P<sub>2</sub>S<sub>5</sub> at a temperature of about 330°–420° F. for 11 hours. The filtered acidic product, having sulfur and phosphorus contents of about 2.4 and 4.4% by weight, respectively, was used in a mineral oil concentrate containing 60 weight percent active ingredient.

Additive 8.—This additive was prepared by neutralizing the above acidic reaction product, additive 7, with an aqueous solution of guanidine carbonate at a temperature of about 240–290° F., the resulting product ultimately heated to 400° F., total heating time being 6 hours. The finished additive was a 50% concentration of the active ingredient in mineral lubricating oil. The sulfur content of the active ingredient was about 1.7 weight percent.

Additive 9A.—This was a commercial detergent additive containing the potassium salt of P<sub>2</sub>S<sub>5</sub>-treated polybutene and having a potassium content of 2.6% and a phosphorus content of 1.8%.

Additive 9B.—This was a commercial detergent additive containing the barium salt of P<sub>2</sub>S<sub>5</sub>-treated polybutene, having a barium content of 4.1% and a phosphorus content of 1.6%.

Additive 10.—This was an experimental polymethacrylate-type ester useful as an ashless detergent additive. It consisted of about 40% by weight of a polymerized long chain aliphatic ester of methacrylic acid in mineral lubricating oil. The active ingredient appeared to have an empirical formula of about C<sub>127</sub>H<sub>248</sub>O<sub>13.2</sub>N.

Additive 11.—This was a pour depressant containing as the active ingredient a copolymer of the fumaric acid ester of coconut alcohols and of vinyl acetate in an 80/20 weight ratio. It was a 20% by weight concentrate in a lubricating oil.

C. Fuels

Fuel 1.—This fuel was a synthetically prepared isooctane.

Fuel 2.—This was a paraffinic fuel consisting of a blend of isopentane, alkylate and virgin mineral oil naphtha.

Fuel 3.—This was a motor gasoline comprising a blend of isopentane, catalytic, and virgin naphthas.

Fuel 4.—This was a commercial grade unleaded fuel.

Fuel 5.—This was a blend of a hydroformed naphtha and a light catalytically cracked naphtha.

Fuel 6.—This fuel consisted essentially of diisobutylene.

Typical inspections on the above unleaded fuels are shown in Table II. These fuels, both with and without about 2 cc. TEL (plus halide-type lead scavenging agent) were used in the various tests described below.

TABLE II.—TYPICAL INSPECTIONS OF GASOLINE FUELS (NO TEL)

Fuel number.....	1	2	3	4	5	6
Gravity, ° API.....	71.3	71.8	63.5	60.2	53.0	64.3
R. V. P., p. s. i.....	1.8	9.3	8.2	10.4	3.7	1.3
Research octane No.....	99.1	79.0	85.6	90.0	91.5	(1)
Motor octane No.....	98.8	77.3	76.6	79.9	79.8	85.8
Sulfur, weight percent.....	0.0008	0.024	0.056	0.034	0.028	0.024
Olefins, weight percent.....	0	3.8	40.7	36.3	39	100
Aromatics, weight percent.....	0	4.2	9.3	18.2	22	0
Engler distillation: <sup>2</sup>						
I. B. P., ° F.....	205	95	100	93	136	205
50% off, ° F.....	210	214	208	228	363	216
F. B. P., ° F.....	264	372	376	414	434	235

<sup>1</sup> Equivalent to iso-octane plus 0.3 cc. TEL.  
<sup>2</sup> Atmospheric pressure.



### EXAMPLE I.—COMBUSTION CHARACTERISTICS OF LUBRICANTS AND ADDITIVES

A series of Lauson engine and road tests were carried out using various oil base stocks, oil blends, and additives as the motor lubricants when running the motors with fuel 1 (isooctane). This minimized any contribution by the fuel to octane requirement increase since tests had shown that iso-octane does not lead to the formation of harmful combustion chamber deposits. Equilibrium octane requirements were determined from these tests. Hydrogen combustion tests were also carried out on various materials. Lauson engine EOR data were converted by a standardized correlation to field test EOR levels in order to obtain direct comparisons. The comparative results are shown in Table III, below:

TABLE III

Oil base stock, oil blend, or additive tested <sup>1</sup>	Equilibrium octane requirement	Resinification index, mg. resin/5 g. oil (combustion test)
Base stock L (polybutene).....	79	2
Base stock C.....	(1)	4
Base stock C+10% additive 1.....	78	1
15,000 M. W. polybutene per se <sup>2</sup> .....	(1)	0
Additive 2.....	(1)	0.5
Base stock D+11% additive 2.....	78	(1)
Base stock K+10.5% additive 1.....	78	(1)
0-98% overhead cut of base stock B <sup>3</sup> .....	84	7
Base stock B.....	86	18
Base stock J.....	83	13
Base stock C+5% additive 3+0.2% additive 6+10.5% additive 2.....	83	17
Base stock H+5% additive 3+0.2% additive 6+10.5% additive 2.....	83	17
Base stock G.....	90	38

<sup>1</sup> Not determined.

<sup>2</sup> Active ingredient of additives 1 and 2.

<sup>3</sup> Obtained by distilling base stock B.

The deposits formed in the combustion tests, after wiping off the loose carbonaceous deposits, were generally light colored resinous materials insoluble in organic solvents. The deposits in the combustion chambers of the cars and Lauson engines were resinous-base deposits (as shown by their insolubility in solvents) containing carbon or other dark substances imbedded therein. In some cases flaky, dark deposits covered the resin-base. However, although the two types of deposits did not have exactly the same appearance, an excellent correlation was obtained between the amount of resinous deposits as determined by the hydrogen combustion test and the EOR in actual engine tests.

Lube oil base stocks and additives having low resinification indexes do not contribute to ORI. Lubricating oil base stocks having resinification indexes below about 10 mg./5 g., preferably below 5 mg./5 g., give outstanding results. Additives having low resinification indexes, such as below 10 mg./5 g., are greatly preferred. A useful method for testing the contribution of a particular additive is to carry out a combustion test on a blend of the additive at a desired concentration in a non ORI-contributing oil base stock. This will give information on the tendency of the additive to contribute to ORI, regardless of the type of base stock eventually employed for the additive.

Finished additive-containing lubricating oil compositions preferably have a resinification index below about 20 mg./5 g., although those having an index level below 10, more especially below 5 mg./5 g., will give superior engine performance.

### EXAMPLE II.—COMBUSTION CHARACTERISTICS OF FUELS

A series of engine tests were also carried out on various types of gasolines using a lubricating oil having a resinification index of about 4 mg./5 g. Resinification

indexes were also obtained on the fuels by the combustion test. In the case of fuels, resinification index is reported on total deposits formed in the combustion test. Data are shown in Table IV, below:

TABLE IV.—CORRELATION OF FUEL DEPOSITS IN HYDROGEN COMBUSTION TEST WITH AUTOMOBILE FIELD TESTS

Fuel <sup>1</sup>	Equilibrium octane requirement	Resinification index, mg. deposit in hyd. comb. test/200 g. fuel
1.....	77	13
2.....	78	13
3.....	80	38
4.....	82	64
5.....	88	88

<sup>1</sup> Fuels contained no tetraethyl lead.

The correlation between equilibrium octane requirement and resinification index is quite good. Generally at a resinification index below about 40 mg./200 g., particularly below 20 mg./200 g., octane requirement increase could be maintained below about 3 units. When similar tests were carried out on the same fuels containing tetraethyl lead, resinification indexes were much higher, particularly if the fuel contained appreciable sulfur.

### EXAMPLE III.—EFFECT OF BRIGHT STOCK ON OCTANE REQUIREMENT INCREASE

Road tests were carried out using oil base stock B and base stock G (a blend of base stock B and base stock F) as lubricating oils using iso-octane as fuel. Equilibrium octane requirements for each oil (average rating of two cars) are shown below:

Base stock	Amount of bright stock in oil, vol. percent	Equilibrium octane requirement
B.....	0	84
G.....	8	90

The highly refined bright stock contributed about one unit increase in octane requirement for each one percent added to the oil.

### EXAMPLE IV.—EFFECT OF BOILING RANGE OF MINERAL OIL BASE STOCK ON OCTANE REQUIREMENT INCREASE

Road tests (test 1) were carried out using iso-octane as fuel and several of the base stocks of Table I as oils. Base stocks B and J per se were used. Base stocks C, D, K, and H each were blended to contain either additive 1 or additive 2 in order to increase their viscosity and viscosity index. Octane requirement increases are shown below in Table V:

TABLE V

Base oil.....	B	C	D	K	J	H
Additive in oil, percent:						
1 (polybutene conc.).....	0	11	0	10.5	0	7
2 (polybutene conc.).....	0	0	11	0	0	0
Type of base stock.....	(1)	(1)	(1)	(1)	(2)	(2)
Boiling range of base oil (10 mm. Hg absolute):						
I. B. P., ° F.....	370	325	320	(3)	360	315
F. B. P., ° F.....	660	508	555	(3)	645	544
Octane requirement increase <sup>4</sup> .....	5.5	0	0	0	5.5	0

<sup>1</sup> Mid-Continent.

<sup>2</sup> Coastal.

<sup>3</sup> Not determined, boils below 600° F. at 10 mm. Hg.

<sup>4</sup> Averages of tests made with same oil on at least two cars.

The mineral oil base stocks boiling below about 600° F. at 10 mm. Hg pressure gave no octane requirement



increase, regardless of whether they were Mid-Continent or Coastal types. Those boiling above about 600° F. at 10 mm. (about 500° F. at 1 mm. Hg pressure) contributed substantially to octane requirement increase.

#### EXAMPLE V.—EFFECT OF VARIOUS ADDITIVES ON OCTANE REQUIREMENT INCREASE

Field tests and Lauson engine tests were carried out on blends of various additives in non-ORI contributing base stock C using substantially non-contributing fuels in the operation of the engines. The EOR of this base stock and of ORI contributing base stock B are shown for comparative purposes.

A comparison of the effect of various viscosity index improvers is shown below in Table VI:

TABLE VI

Amount of V. I. improver in base stock C, weight percent	Approximate octane requirement increase	
	Lauson	Car field tests
None (base stock C per se).....	11	11
11% additive 2 (polybutene).....	0	0
8% additive 4 (polymethacrylate ester-type).....	10	29
None (base stock B).....	9	29

<sup>1</sup> Estimated from resinification index of 4 mg./5 g.

<sup>2</sup> Estimated from Lauson-field test correlation.

The polybutene-type viscosity index improver, as shown previously, was non-contributing to ORI in both the Lauson and full-scale tests. The polymethacrylate ester additive contributed slightly over one unit octane requirement increase for each percent present. It is interesting to note that the use of the ORI contributing additive in base stock C is about equivalent to the performance of ORI-contributing base stock B. The combination of a low ORI contributing oil base stock with at least one low ORI contributing additive gives greatly superior results.

A comparison of the effect of various detergent-type additives is shown below in Table VII. These additives were blended in non-ORI contributing oil base stocks C, D or E, and tested in Lauson engines. Substantially non-ORI contributing fuels were used in these tests.

TABLE VII

Amount of detergent additive in mineral oil lubricant <sup>1</sup>	Lauson octane requirement increase
None.....	0
5.0% additive 7 (P <sub>2</sub> S <sub>5</sub> -trt. polybutene).....	9
2.5% additive 8 (guanidine salt of additive 7).....	0
5.0% additive 8 (guanidine salt of additive 7).....	0
2.5% additive 9A (K salt of P <sub>2</sub> S <sub>5</sub> -trt. polybutene).....	0
5.0% additive 9A (K salt of P <sub>2</sub> S <sub>5</sub> -trt. polybutene).....	1
5.0% additive 9B.....	0
5.0% additive 10 (polymethacrylate ester-type).....	7
5.0% additive 3.....	7
14.0% additive 3.....	14

<sup>1</sup> All blends adjusted to SAE 5W-20 grade by addition of 7-11% additive 2.

Both the unneutralized phospho-sulfurized polybutene and the polymethacrylate ester type detergent additives contributed to octane requirement increase. The phosphosulfurized polybutenes that were at least partially neutralized with either ashless or ash-forming basic reagents gave excellent performance. Commercial additive 3 contributed substantially to ORI.

Full-scale field tests were also carried out on oil compositions in which either a non ORI-contributing base stock (either base stock C or E) or an ORI-contributing base stock (base stocks C or E containing about 5% base

stock F (bright stock)) were blended with various additives. The cars were operated with ORI contributing fuel 3 containing about 2 cc. TEL/gallon. The results of these tests are shown in the table below:

Oil composition <sup>1</sup>	Average equilibrium octane requirement	
	With about 5% bright stock	With no bright stock
Base stock C+about 10% additive 2.....	92	89
Base stock E+about 5% additive 10.....	92	91

<sup>1</sup> All compositions contained about 5% additive 3.

The use of a non-contributing base stock gave a noticeable decrease in EOR in comparison with the contributing base stock regardless of the additive system used, even though an ORI-contributing fuel was used. When the non-contributing additive (additive 2) was used in the multi-additive system in combination with the contributing additive 3, no effective decrease in EOR was obtained in comparison with the combination of contributing additives 3 and 10 when an ORI contributing base stock was used. A decrease of about two EOR units was obtained, however, when additive 2 replaced additive 10 in the non-contributing base stock.

In general, when using a multi-additive system in a substantially non-contributing oil base stock, at least one, and preferably more than one of the additives should be substantially non-ORI contributing. This applies particularly to the additives, such as viscosity index improvers and detergency improvers, that are present in substantial amounts.

#### EXAMPLE VI.—EFFECT OF VARIOUS FINISHED LUBRICATING OIL FORMULATIONS ON OCTANE REQUIREMENT INCREASE

A number of mineral base lubricating oils containing various types and concentrations of additives were tested in full-scale car tests (test 1) and Lauson engines (test 3). The formulations follow:

##### Formula 1

Component:	Amount, weight percent
Base stock D (74 S. U. S. at 100° F.).....	85.3
Additive 3.....	5.0
Additive 6.....	0.2
Additive 1.....	7.0
Additive 4.....	2.5

Formulations with solvent neutrals of this type have the following typical inspections:

Flash point, ° F.....	385
Pour point, ° F.....	-35
Stable pour point, ° F.....	<-20
S. U. S. viscosity at 0° F.....	3200
S. U. S. viscosity at 100° F.....	165
S. U. S. viscosity at 210° F.....	50.4
S. U. S. viscosity at 300° F.....	38.2
Viscosity index.....	155

The excellent viscosity-temperature characteristics of this type of blend are shown in the plot of Figure 1 in comparison with typical light commercial oils varying in S. A. E. grades from 5W to 20-20W. This plot shows temperature versus S. U. S. viscosity (semi-log scale). Formula 1 is seen to possess the excellent low temperature flow characteristics of conventional light 5W oils and the desirable high viscosity characteristics at high temperatures of conventional S. A. E. 20 oils. Thus it is essentially a 5W-20 SAE-grade oil.



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Formula 2

This was also an SAE 5W-20 oil.

Component:	Amount, weight percent
Base stock D (74 S. U. S. at 100° F.)	85.55
Additive 3	4.20
Additive 5	0.55
Additive 6	0.20
Additive 1	7.00
Additive 4	2.50

Formula 3

This was also an SAE 5W-20 grade oil.

Component:	Amount, weight percent
Base stock C (66 S. U. S. at 100° F.)	84.3
Additive 3	5.0
Additive 6	0.2
Additive 2	10.5

Formula 4

This was also an SAE 5W-20 grade oil.

Component:	Amount, weight percent
Base stock D (74 S. U. S. at 100° F.)	84.8
Additive 1	10.0
Additive 8	5.0
Additive 6	0.2

Road tests and Lauson tests were carried out on some of the above formulations using various types of fuels.

The following road tests were carried out using fuel 3 containing 2 cc. tetraethyl lead/gallon. A commercially available Pennsylvania-base motor oil (about 60 S. U. S. at 210° F.) was also run. Results are shown in Table VIII, below:

TABLE VIII

Lubricant	Number of cars tested	Average equilibrium octane requirement
Commercial Pennsylvania-base oil	2	95
Base stock G	4	92
Formula 3	6	89

The oil of the present invention (Formula 3) was clearly superior to the others. The higher boiling mineral oil components in the commercial oil and base stock G contributed from 3 to 6 units more octane requirement than the light mineral oil. It is to be noted that all of these tests were carried out with a high ORI-contributing fuel.

The results shown in Table IX, below, were obtained with fuels that did not contribute substantially to octane requirement increase.

TABLE IX

Lubricant	Equilibrium octane requirement	
	Lauson	Field tests
Base stock G	73	90
Formula 1	63.5	(1)
Formula 2	63.5	(1)
Formula 3	63	84
Formula 4	56	(1)

<sup>1</sup> Not run.

All of the formulations, (1) to (4), free from bright stock, were superior to base stock G. The Formula 4 SAE 5W-20 oil containing the guanidine neutralized detergent additive (additive 8) gave especially good performance superior to the others containing ORI-contributing detergent additive 3. It is seen that in a multi-additive system, significant improvements are obtained

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by using two rather than only one non-ORI contributing additive in combination with the non-ORI contributing oil base. This is particularly significant when the additives, as is the case here, are used in relatively large amounts.

EXAMPLE VII.—EFFECT OF FUEL COMPOSITION ON OCTANE REQUIREMENT INCREASE

Road tests and Lauson engine tests were carried out by the procedure of tests 1 and 3 on various gasolines having relatively low aromatic contents, both unleaded and containing TEL fluid (2 cc. TEL per gallon). The gasolines contained varying amounts of sulfur. A motor oil non-contributing to octane requirement increase was used in these tests. In the following Table X, all data are reported on the basis of road test results.

TABLE X

Fuel	Weight percent sulfur in fuel	Equilibrium octane requirement	
		Clear fuel	Leaded fuel
High sulfur fuel <sup>1</sup>	0.065	80	88
Fuel 3 (commercial)	0.056	80	87
Fuel 6 (diisobutylene)	0.024	77	84
Fuel 2 (paraffinic)	0.024	77	83
Fuel 1 (iso-octane)	0.0008	78	77

<sup>1</sup> Similar to fuel 3 but containing more sulfur.

No substantial octane requirement increase was obtained in the clear gasolines regardless of sulfur level. With leaded fuels, as shown in the plot of Figure 2 of sulfur content vs. equilibrium octane requirement, large decreases in octane requirement take place at sulfur levels below about 0.025% especially below about 0.01% by weight of sulfur. However, it was found that combustion chamber deposits formed with low sulfur content, leaded gasolines. This finding leads to the conclusion that in the absence of sulfur, TEL fluid leaves deposits that have anti-knock properties which offset the proknock effect due to their thermal insulating properties and volume. When sulfur is present, lead sulfate and possibly other lead salts having no anti-knock properties are formed. This causes octane requirement increase.

Similar test were carried out on low-sulfur fuels containing aromatic and non-aromatic hydrocarbons of various types, with and without TEL. In general, paraffins, olefins and naphthenes were found not to contribute to the formation of harmful combustion chamber deposits, even though TEL is present. Low-boiling aromatic hydrocarbons, such as benzene and toluene are relatively harmless components from the standpoint of ORI. The higher aromatics are less desirable, the extent of contribution to increased octane requirement increasing as boiling point and molecular weight increases. For example, 40% by weight of mixed xylenes in a non-contributing fuel will increase octane requirement by 6-8 units. 40% of a hydroformate fraction (55% aromatics, 95% boiling above about 300° F.) in the same fuel contributed an octane requirement increase of about 10 units.

Therefore, the amount of aromatics boiling above 300° F. should be maintained at low levels in the preferred fuel mixtures. Lower boiling aromatics, particularly those boiling between about 250° to 300° F. should not be present in amounts above about 20%, based on the total fuel.

EXAMPLE VIII.—EFFECT OF OPERATING AUTOMOBILES WITH CONTRIBUTING AND NON-CONTRIBUTING FUELS AND LUBRICANTS

The following data (Table XI) illustrate the effect of operating with a combination of contributing and non-contributing lubricating oils and fuels.



TABLE XI

Lubricating oil	Fuel No.	Approximate octane requirement increase
Base stock G.....	3 <sup>1</sup> .....	14
Do.....	1 (iso-octane).....	12
Formula 3.....	3 <sup>1</sup> .....	11
Do.....	1 (iso-octane).....	6

<sup>1</sup> Contained 2 cc. TEL/gallon.

The combination of the typical commercial, high ORI contributing oil base stock G, containing bright stock, with a non-contributing fuel gave a decrease in octane requirement of 2 units over the combination of both contributing oil and fuel. The combination of a low ORI-contributing oil of this invention (Formula 3) with a contributing fuel gave a decrease of 3 units. It would therefore be expected that the combination of a non-ORI contributing fuel and the low-ORI contributing lubricant would give at most a reduction of only about 5 units. Actually an unexpected improvement of 8 units was obtained. Even greater improvements can be obtained by using a non-ORI contributing oil with a non-ORI contributing fuel.

The following Table XII presents the levels of equilibrium octane requirement obtainable with various combinations of mineral base lubricants and fuels of varying degrees of contribution. EOR data are reported at field test levels regardless of whether the tests were run in Lauson engines or full scale engines.

TABLE XII

Lubricating oil		Fuel		Equilibrium octane requirement
Type	Tendency to contribute to ORI	Type	Tendency to contribute to ORI	
Typical commercial oil.....	High.....	3 <sup>1</sup> .....	High.....	95
Base stock G.....	do.....	3 <sup>1</sup> .....	do.....	92
Formula 1.....	Medium.....	3 <sup>1</sup> .....	do.....	89
Do.....	do.....	Iso-octane.....	Low.....	84
Formula 4.....	Low.....	do. <sup>2</sup> .....	Medium.....	84
Do.....	do.....	do. <sup>3</sup> .....	Low.....	80
Do.....	do.....	do.....	do.....	79
Modified Formula 4 <sup>4</sup> .....	do.....	do. <sup>3</sup> .....	do.....	79

<sup>1</sup> Contained about 0.056% sulfur and 2 cc. TEL/gal.

<sup>2</sup> Iso-octane contained 2 cc. TEL/gallon and 0.014 wt. percent added sulfur.

<sup>3</sup> Iso-octane contained 2 cc. TEL/gallon and about 0.0008% sulfur.

<sup>4</sup> Formula 4 containing 5 wt. percent additive 9B instead of 5% additive 8.

A definite improvement was obtained using an oil having a medium tendency to contribute to ORI when using a high ORI fuel. Better results were obtained with either low or medium ORI oils of this invention when used in combination with medium ORI fuels. The best results, as shown previously, were obtained with low ORI fuels and lubricants. It is interesting to note that a low-sulfur, leaded fuel (iso-octane plus TEL), when used in combination with a low ORI contributing oil gave very little ORI increase.

Oils (1) and (4) not only gave superior performance as low-ORI contributing oils but also had excellent engine oil consumption characteristics for such low viscosity oils. Oil consumptions much less than one quart per 500 miles were consistently obtained in the field tests.

EXAMPLE IX

Lauson engine tests were carried out with a motor oil having a resinification index of about 4 mg./5 g. In one case the fuel consisted of fuel 3 (containing 0.056 wt. percent sulfur), 2 cc. TEL/gallon, and 1.5 stoichiometric equivalents (to make lead halide) of an ethylene chloride-ethylene bromide scavenging agent mixture. An EOR of

about 69 was obtained. In another case, with the same fuel containing 2 cc. TEL/gallon and 1.5 stoichiometric equivalents of mixed mono-bromoxylenes, and EOR of about 60 was obtained. It is seen that the use of the high-boiling scavenging agent, bromoxylene, in the high-sulfur, leaded fuel, in combination with a low ORI oil, gave much superior engine performance in comparison with the same fuel containing low-boiling scavenging agents.

EXAMPLE X

A bright-stock free, SAE 5W-20 oil was formulated consisting essentially of 87.5 volume percent oil base stock C, 10.5 vol. percent additive 1, 0.2 vol. percent additive 6, 1.3 vol. percent of a mixed calcium-barium salt of tert-octyl phenol sulfide and 0.5 vol. percent alkaline calcium petroleum sulfonate (about 950 average molecular weight). This oil composition had a resinification index of below 20 mg./5 grams oil and a viscosity index above 150. Two cars were tested with this oil by the procedure of test 1 using fuel 3 containing 2 cc. TEL/gallon. An average oil consumption level of about 700 miles per quart oil and an average EOR of about 87 was obtained in these tests. The combination additive, metal alkyl phenol sulfide-metal petroleum sulfonate, imparted excellent detergency characteristics to the oil. Metal alkyl phenol sulfides, especially the alkaline earth metal salts, either alone or in combination with oil soluble, alkaline earth metal petroleum sulfonates, are useful detergent additives in the oils of the present invention. Additives of this type are taught in such U. S. Patents as 2,362,289; 2,362,291; 2,379,241; 2,409,686; and 2,480,664.

The non-contributing mineral lubricating oil base stocks used in the practice of the present invention may be obtained from Mid-Continent, Coastal, Middle East, Pennsylvania, and the like crudes, but Mid-Continent distillates having good viscosity characteristics are preferred. These are preferably distillates that have been refined by conventional procedures to remove the bulk of the relatively more aromatic, carbon-forming constituents (such as measured by the Conradson test), and that have also been treated to remove those constituents that form resins when subjected to combustion under a smokeless flame as heretofore described, to give a final product having a resinification index below about 10 mg./5 g. The conventional refining procedures useful for removing the more aromatic portions, sulfur and other harmful constituents include treatment with mineral acids, such as sulfuric acid; treatment with alkalis; solvent refining with various solvents such as phenol, furfural, sulfur dioxide, and the like; treatment with aluminum halides; extraction with silica gel; clay treatment; hydrogenation; desulfurization such as hydrofining; propane precipitation; solvent dewaxing; catalytic cracking; etc.

The resin forming constituents remaining in these refined distillates are probably higher molecular weight paraffinic-naphthenic or paraffinic-aromatic compounds although their exact constitution is not understood at this time. Therefore it is generally desirable to use a combination of refining methods to effect substantially complete removal of them. Thus a lubricating oil distillate obtained from a suitable crude may be distilled to obtain a fraction of approximately the desired boiling range, acid-treated or solvent extracted (and dewaxed if necessary to remove high pour point constituents) and then redistilled to remove resinifying heavy ends.

Another suitable source of mineral oil base stocks is in refined catalytically cracked cycle stocks. Such cycle stocks are the more refractory hydrocarbons that resist cracking to lower boiling constituents when residual hydrocarbons, gas oils or other relatively high boiling hydrocarbons are cracked in the presence of metal oxide catalysts or the like. The cycle oil that has been recycled through the cracking zone several times is withdrawn, refined for the removal of the relatively more aromatic constituents, dewaxed if desired, and distilled to recover



a fraction of the proper boiling range and viscosity. Such refined fractions are stable, low sulfur content materials that make excellent base stocks per se or may be blended with other mineral oil distillates to form suitable base stocks. White oils, i. e., mineral oils refined with fuming sulfuric acid for the complete removal of aromatic-type constituents, may also be used as blending agents for the base stocks.

The preferred mineral oil base stocks of the present invention are those from which mineral oil components boiling much above about 600° F. (in a simple distillation at a pressure of 10 mm. Hg, which corresponds to about 890° F. at a pressure of 760 mm. Hg) have been removed. A suitable boiling range is within the range of about 275° to 575° F., or preferably within about 300° to 575° F., at 10 mm. Hg pressure absolute, with less than about 5 to 10% of components boiling about 550° F. The lower end of the boiling range will depend to a large extent on oil consumption characteristics of the lubricant, and generally components boiling much below about 275° to 300° F. at 10 mm. Hg absolute are too high in volatility for use in most high compression ratio internal combustion engines. The distillation test is ASTM Method D1160-52-T.

The above lower boiling oils are particularly useful in formulating SAE 5W-20 oils. In the event higher viscosity oils, such as SAE 10W-30 grade oils, are desired to reduce oil consumption in the engine, blends of the low-boiling stocks and higher boiling stocks may be made that meet both resinification index and viscosity requirements. Thus a blend of 60% light solvent neutral having a resinification index of about 3 and of 40% of a solvent refined distillate having an S. U. S. viscosity at 100° F. of about 150 and a resinification index of about 20 will have a resinification index below about 10 mg./5 g. and meet certain high viscosity requirements. It will be realized that this invention contemplates base stock blends made from various components providing the base stock is low in ORI contribution. It is also preferred that the base stocks have viscosity indexes above 100 in order to make premium grade lubricants. For this reason oils that have only been refined by acid treatment are less preferred than the extracted Mid-Continent Middle East and other such high V. I. oils. Base stocks having pour points below about +15° F. are also preferred.

An example of a suitable SAE 10W-30 oil is one in which the base stock is a 50-50 mixture of oil base stocks B and D (described above) containing 20% of 5 different additives for V. I., detergency, corrosion inhibition, antioxidant and pour point improvement, and in which one of the additives, constituting a major portion of the additive system, has a resinification index below 5 mg./5 grams. The total lubricating oil will have a resinification index below 20 mg./5 grams, S. U. S. viscosities at 0° F., 100° F., 210° F., and 300° F., respectively, of 10,000; 356; 69.3; and 44.5 and a V. I. of 140.

In order to meet viscosity specifications required of suitable oil base stocks, it is preferred that these stocks have a viscosity in the range of 50 to 160 S. U. S. at 100° F. and of about 33 to 50 S. U. S. at 210° F. If the base stock is to have a viscosity of much above 40 S. U. S. at 210° F., relatively narrow cut distillates, such as those boiling in the range of about 400° to 550° F., 450° to 600° F., 500° to 575° F., and the like (at 10 mm. Hg absolute) may also be used to reduce the concentration of higher boiling, ORI-contributing components. Mineral oil base stocks having less than about 5 to 10% of components boiling below 390° F. at 10 mm. Hg are preferred from the standpoint of oil consumption.

Other suitable base stock constituents and blending agents which may be used in combination with mineral oils of the type described include low resinification index hydrogenated oils, synthetic oils resembling petroleum oils (polymerized olefins, synthesis products from the

reaction of oxides of carbon with hydrogen or from hydrogenated coals, shale oil derivatives, etc.), synthetic polyester and polyether-type lubricants and the like. Synthetic oils include esters made from a monohydric alcohol and a monobasic organic acid or diesters made from alcohols dibasic acids. Specific examples include di-2-ethyl hexyl sebacate and di-C<sub>8</sub> "Oxo" alcohol sebacate. Alcohols include the C<sub>7</sub>, C<sub>9</sub>, C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub> and C<sub>13</sub> alcohols made by the Oxo process from olefins. Suitable dibasic acids include adipic, azelaic and sebacic acid. Complex esters made from a monohydric alcohol, a dihydric alcohol (glycol) and a dibasic acid may also be used. Polyalkylene oxide-type synthetic oils with suitable terminal alcohol groups, complex formals, mercaptals and their esters, and the like are also useful.

Oil base stocks containing synthetic lubricating oils preferably consist of a major portion of a suitable mineral oil base stock of the type described with only minor amounts of low resinification-index synthetic-types of blending agents having lubricating oil characteristics. Generally less than 10 to 20% by weight of synthetic or non-petroleum oil blending agents of the type described, based on the total base stock, will be used.

The additive components useful in the practice of the present invention to formulate finished lubricants must be selected with great care not only from the standpoint of the specific characteristic of the oil to be improved but also with regard to the extent to which the additive itself will contribute to octane requirement increase at the concentration level needed to improve a specific characteristic. It is preferred that the multi-additive system have a resinification index below 20 mg./5 grams, preferably below 10 mg./5 grams. Useful systems include those in which at least two different additives constituting a major portion of the additive system have a combined resinification index below 5 mg./5 grams. Especially useful mixtures of additives, preferably three or more different types, will have resinification indexes below about 5 mg./5 grams. The following paragraphs will give due consideration to suitable additives with particular emphasis being placed on the types that have low resinification indexes when blended with various oils.

One of the most important additive materials used with the base stock of the present invention is a viscosity index improver. The finished lubricating oil should have a high viscosity index. To achieve this it is usually essential to add a non-mineral oil constituent that will improve these characteristics without at the same time contributing substantially to the ORI of the engine using the oil. A preferred viscosity index improver as well as thickening agent is a high molecular weight hydrocarbon such as an olefin, including the polymerized C<sub>3</sub> to C<sub>5</sub> olefins. For example polymerized butenes and preferably polymerized isobutylene having a molecular weight in the range of about 5,000 to 50,000, preferably about 10,000 to 25,000, are quite useful. These polymerized olefins are readily prepared by procedures well known to the art. These additives are especially suitable for increasing the viscosity of light neutral oils and other light distillates. For example, oils having S. U. S. viscosities below about 40 at 210° F. may be increased to higher viscosity oils such as those having viscosities above about 45 S. U. S. at 210° F., by the use of these V. I. thickening agents. In order to increase viscosity and to improve viscosity index of the finished lubricant by as much as 10 to 70 units, it is generally desired to employ in the range of about 0.5 to 30.0 weight percent, preferably 1 to 15%, of the polyolefin based on the finished lubricating oil. Other viscosity index improvers include the polymethacrylate esters, fumarate-vinyl acetate copolymers, polyalkylstyrenes, and the like. Since the polymerized esters generally contribute to octane requirement increase, they are less preferred than the polymerized olefins as viscosity index improvers. As a general rule, ORI-contributing types may be used in amounts below about 3%,



preferably below 1.0% by weight. Finished lubricants containing a mixture of polyolefins and polyesters may be formulated to avoid substantial increases in octane requirement. Thus from 3 to 10% of polybutene and 0.5 to 3% of a polyester may be used. However, it is much preferred to employ only the olefins as viscosity index improvers.

Another important additive to be employed in the finished lubricating oil of the present invention consists of at least one detergency improving additive. These agents will help maintain oil insoluble oxidation products and the like suspended in the oil and will in general improve engine cleanliness.

A wide variety of detergency improvers may be employed. One class of additives for this use consists of the phosphorus and sulfur-containing hydrocarbons prepared by treatment of an essentially hydrocarbon material with a sulfide of phosphorus or a combination of the elements phosphorus and sulfur. These reaction products are well known to the art.

As a general rule, the desired hydrocarbon, such as a paraffin, an olefin, a naphthene, an aromatic, a terpene, hydrocarbon resins, high molecular weight polymerized olefins, mineral oils such as lubricating oil distillates, and the like are treated with a sulfide of phosphorus using a ratio of about one mole of phosphorus sulfide for 1 to 10, preferably 2 to 5, mols of hydrocarbon at a temperature in the range of about 275° to 550° F. The resulting reaction product may be used as such, but it is preferred to refine it further by treatment with a suitable agent such as by reaction with a basic reacting material or by reaction with an esterification agent. Suitable basic reacting materials include the alkaline metal and alkaline earth metal oxides, carbonates, hydroxides, hydrides and the like, specifically, potassium, sodium, barium, and calcium compounds. Basic inorganic compounds of heavier metals may be used, such as those of molybdenum, tin, zinc, chromium, manganese, nickel and the like.

Suitable ashless treating agents include nitrogen bases such as ammonia, and organic nitrogen bases such as amines and amine derivatives, guanidines and their derivatives, morpholine, pyridine, quinoline and like substances. Guanidine and its derivatives are particularly useful, the symmetrical tri-substituted compounds such as trialkyl, triphenyl and trinaphthenyl guanidines and the like being useful. Other useful compounds include the biguanides, dicyandiamides, dicyandiamidines, hydrazines, ureas, thioureas, semicarbazides, thiosemicarbazides maleate and fumarate esters, aminoalcohols, acrylonitrile, alcohols, vinyl esters, phenols, olefins such as diisobutylene, dipentene and the like. Such treating agents are disclosed in the art such as U. S. Patents U. S. 2,613,205; 2,640,030; and 2,640,053.

Treatment of the product with these and other agents may be carried out at any suitable temperature, such as from about room temperature up to 400° F. or so using sufficient treating agent at least to partially neutralize, esterify, or combine with the titratable acidity of the phosphosulfurized material. Completely neutralized materials are usually preferred.

The essentially hydrocarbon material to be treated with the combination of phosphorus and sulfur is preferably one that itself has a low resinification index. Thus paraffins, olefins, naphthenes, neutral oils and the like give better results than aromatics, bright stocks, etc. The hydrocarbon to be treated preferably has a resinification index below about 10 mg./5 grams.

In a preferred embodiment, the phosphorus and sulfur containing product is obtained by treating a high molecular weight olefin such as a polyisobutene having a molecular weight in the range of about 300 to 30,000 with the sulfur and phosphorus containing agent, followed by treatment of the acidic product with one of the agents outlined above. Those obtained by treatment with alkali and alkaline earth hydroxides or guanidine or one

of its substituted derivatives and the basic reacting salts thereof, such as guanidine carbonate, are specifically useful. These reaction products not only give superior detergency characteristics but do not contribute to the formation of harmful combustion chamber deposits.

The treating procedure may be varied in several different ways. For example, the acidic phosphosulfurized hydrocarbon may be hydrolyzed by treatment with steam followed by treatment with the treating agent. The partially or completely neutralized products may be hydrolyzed by steam treatment, or the neutralization and hydrolysis may be carried out simultaneously. Hydrolysis in general reduces sulfur content, particularly helping to remove unstable sulfur, and improves the resinification index characteristics of the additive.

Other detergents that may be used in the practice of the present invention include metal soaps, metal organic sulfonates such as hydrocarbon sulfonates including metal salts of petroleum sulfonic acids, metal phenates, metal alkylates, metal alkyl phenol sulfides such as barium tert-octyl phenol sulfide, phosphates, dithiophosphates and thiophosphites, metal xanthates and thioxanthates, mixtures of these and other agents, coneutralized mixed metal additives such as coneutralized petroleum sulfonates and phenolic compounds, such as alkyl phenol sulfides, etc.

Since detergent additives are usually employed in rather large amounts, from as low as about 0.5 up to 10.0 or 15.0% by weight, based on the total oil, specific attention must be given to the extent to which the particular detergent additive will contribute to resin-type combustion chamber deposits. Many commercial detergent additives are harmful in this respect, and oils containing only non-contributing types are greatly preferred. Mixtures of both contributing and non-contributing types are also useful, in which case a blend consisting of a major portion of a non-contributing additive with only minor amounts of a contributing additive may be used. A mixture of non-contributing types is a combination of the alkali or alkaline earth metal salt of a phosphorus sulfide-treated polybutene, such as a barium or potassium salt, and a guanidine neutralized phosphorus sulfide-treated polybutene.

In order to minimize oxidation characteristics of the oils of the present invention, it is generally desired to add a small amount of a suitable anti-oxidant or bearing corrosion inhibitor additive. Some of the detergent additives listed above have anti-oxidant characteristics, but in other cases they may adversely affect this property of the lubricant. Here again the type of additive employed is preferably one that does not substantially contribute to octane requirement increase.

Particularly useful additives in this respect are lower olefinic hydrocarbons, particularly terpene hydrocarbons, that have been treated with a sulfide of phosphorus or with a combination of sulfur and phosphorus by the procedure described above. A specifically preferred additive is prepared by treating alpha pinene with phosphorus pentasulfide. This product may be used in amounts in the range of about 0.05 to 2.0% by weight in the finished composition without harmful effects. Other anti-oxidants include metal and non-metal salts of dihydrocarbon dithiophosphates, such as zinc dialkyl dithiophosphate, and amine dialkyl dithiophosphates, phenols, such as alkyl phenols, bis-alkyl phenols and the like, phenol sulfides such as a tert-alkyl phenol sulfides, metal dithiocarbamates, phenothiazine and its alkylated derivatives, sulfohalogenated olefins that have been dehalogenated by known means, such as diisobutylene treated with a sulfur chloride followed by dehalogenation, sulfurized dipentenes, etc. Various combinations of these and other well-known anti-oxidants and corrosion inhibitors may be used.

The amount of anti-oxidant employed in the finished lubricant will depend to a large extent on the type of base stock and the types of other improving agents added



thereto. As a general rule, in the range of about 0.01 to 5.0% by weight, based on the total composition, will suffice to minimize the deleterious effects of oxidation. In the event the particular anti-oxidant contributes substantially to octane requirement increase, it is preferred that it be used in small amounts in combination with a non-contributing anti-oxidant.

A pour depressant additive is preferably employed in small amounts in order to meet pour point specifications. This additive should be one that not only reduces the pour point substantially when used in small concentrations but should also be relatively stable in this regard when the oil is subjected to alternate cycles of heating and cooling; i. e., have a good pour point stability. Such pour point depressants include the chlorinated wax naphthalene condensation products, various polymers and copolymers of unsaturated esters and the like. These additives are generally used in rather small amounts, in the range of about 0.01 to 2.0 weight percent based on the total composition. Such small amounts will not generally contribute to the octane requirement increase difficulty discussed above.

Other agents than those that have been mentioned may also be present in the composition, such as dyes, oiliness agents, anti-rust agents, plasticizers and defoamers, extreme pressure agents and the like. Suitable anti-rust agents, for example, include the partial esters of polyhydroxy compounds such as the oleate of sorbitan, polyglycerols, etc.; "Lorol" mercapto-acetic acid; ditiricin-oleates; alkyl phosphoric acids; acid phosphates, etc. Although the above additives have been described in connection with specific characteristic improving properties, it will be recognized that some of them have multi-functional properties and will improve two or more characteristics at the same or different concentration levels. The above constitutes only a partial list of the many additive improving agents useful in the practice of the present invention.

The finished oils of the present invention will be compounded to include at least one substantially non-ORI contributing additive, although two, and preferably three or more different types of additives are generally desirable to formulate compositions meeting all of the requirements of modern high compression ratio engines. Based on the total composition, the additives will usually constitute a minor amount, and generally will be present in amounts below about 25% by weight, preferably about 3 to 20% by weight. The base stock of the present invention will make up the remaining portion of the lubricating oil. The finished oil will preferably have a resinification index below about 20 mg./5 grams, especially below 15 mg./5 grams.

The gasolines to be used in the high compression ratio automotive engines and the like lubricated by the oils of the present invention may be any suitable high octane, essentially hydrocarbon gasoline such as one having an ASTM Research octane number in the range of about 75 to 100. In a preferred aspect of the present invention, however, the gasoline will have a reduced resinification index in comparison with conventional commercial fuels. It is particularly preferred that the gasoline be one that will contribute no more than about 5 octane requirement units, preferably below one unit, increase when used in combination with the preferred lubricating oils of the present invention.

Conventional components may be used in formulating such gasolines. These components include straight run distillates from various types of crudes, alkylates prepared by the alkylation of olefins with isoparaffins; high octane polymers prepared by the catalytic polymerization of lower molecular weight olefins; hydroformates prepared by hydroforming naphthenic-type hydrocarbon distillates to form high octane aromatic components; reformed gasoline fractions prepared from straight run gasolines using conventional platinum catalysts, metal oxide catalysts and the like; catalytic cracked naphthas prepared by cracking

gas oils, residuals, etc., in the presence of metal oxide catalysts such as silica-alumina, silica-magnesia, and the like; and various other types of components that are conventionally employed in gasolines. Such gasolines are usually formulated by mixing two or more of the above general types of components in order to form gasolines meeting octane requirement, vapor pressure, stability, and other specifications.

It has generally been found of the various hydrocarbon compounds present in gasolines that paraffins, naphthenes and olefins will not contribute substantially to ORI. Aromatic components, particularly those having a boiling point higher than toluene contribute substantially to octane requirement increase. Those boiling above about 300° F. are especially undesirable for this purpose. Therefore it is preferred that the gasoline contain no more than 20% by weight, of aromatic hydrocarbons boiling above about 300° F., and more especially less than 20% by weight of aromatics boiling above about 250° F.

Lead tetraethyl is used in most commercial gasolines in concentrations ranging from about 0.1 to 3.0 cc./gallon in order to increase octane number. Lead scavenging agents such as ethylene dibromide and ethylene dichloride may be present in such compositions.

It has been found in the past that the presence of substantial amounts of sulfur in the gasoline is deleterious to the effectiveness of tetraethyl lead for increasing the octane number of gasoline. It has therefore been preferred that leaded fuels contain below about 0.20% by weight, preferably about 0.1% by weight, of sulfur. It has now been found that unexpected advantage in decreased ORI can be achieved by lowering the sulfur content of gasoline critically below the level at which the sulfur has any effect on the actual octane number of the gasoline containing TEL. For minimizing ORI it is important to decrease the sulfur content of leaded gasoline below about 0.02%, and preferably below about 0.005% by weight. This may be achieved by treating the various components that go into the gasoline, in order to reduce the sulfur content to relatively non-contributing amounts.

Treating procedures for sulfur reduction include prompt caustic washing of the sulfur-containing material in the absence of oxygen soon after a catalytic cracking operation; hydrofining of cracked naphthas in which the naphtha is treated with a catalyst in the presence of hydrogen; treating naphtha with formaldehyde at elevated temperatures, with or without sulfuric acid; and treatment of sulfur-containing naphthas with finely divided sodium in the presence of secondary or tertiary alcohols, ethers or ketones; and the like. The extent to which any or all of the components treated will of necessity depend on the amount of sulfur contained in each of them and the amount of the particular component going into the gasoline blend. It is preferred to employ a fuel that contains relatively small amounts of sulfur as heretofore described, and non-contributing amounts of aromatics when the fuel is leaded with tetraethyl lead.

Excellent results can be obtained with the lubricating oil of the present invention when it is operated in an engine in combination with a clear gasoline, i. e., one that contains no tetraethyl lead. In this event the amount of sulfur present in the fuel is not extremely critical.

In order to minimize the contribution of a conventional leaded gasoline containing a normal complement of sulfur, say above 0.1% by weight, a lead scavenging agent that is relatively high boiling may be added to the fuel. Although it is conventional to use such materials as ethylene dibromides and the like as scavenging agents, these materials are not so effective for complete removal of lead as the higher boiling scavenging agents including halogenated aliphatic hydrocarbons such as hexachlorobutadiene, and halogenated alkyl aromatics such as bromo xylenes, including mixed dibromoxylenes; dibromo toluenes; 3,4-dichlorocumene; 1,2-dibromobenzene; 1,2,4-trichlorobenzene; 2,4-dichlorotoluene, their mixtures and



the like. "Higher boiling" means those agents having substantially the volatility characteristics of tetraethyl lead; preferably they have vapor pressures at 120° F. of about 0.5 to 5.0 mm. Hg. In excess of about 0.5, preferably above about 1.0 stoichiometrical equivalents of these agents, based on the TEL, may be added to the fuel. Such higher boiling scavenging agents are taught in U. S. patents including 2,496,983; 2,574,321; 2,479,900; etc.

The gasoline fuel may also contain other addition agents such as antioxidants, gum inhibitors, solvent oils, rust inhibitors, metal deactivators, etc.

This invention has particular application to the operation of automotive engines and the like that have compression ratios above about 7:1, and is particularly applicable to those having higher compression ratios, for example 7.5 to 1 and as high as 12 to 1 and higher. Such engines are extremely susceptible to octane requirement increase as mentioned heretofore, especially when they are run under rather mild conditions such as stop and go city traffic, suburban driving at relatively low speeds, and the like. Under these conditions the combustion chamber is particularly susceptible to deposit formation from resinous forming constituents in the lubricant and/or fuel. However the invention is not restricted to automotive engines but will apply generally to the operation of any relatively high compression engine of this type, such as those in small motor boats, aircraft and the like where automotive-type engines are subject to a substantial amount of mild operation.

What is claimed is:

1. A lubricating oil composition having a resinification index less than 20 mg./5 gr., comprising at least 75 weight percent of a petroleum oil having an initial boiling point above 300° F. and a final boiling point below 600° F., both at 10 mm. Hg abs., a viscosity in the range of 50 to 160 S. U. S. at 100° F. and in the range of 33 to 50 S. U. S. at 210° F., a pour point below 15° F. and a resinification index less than 10 mg./5 gr., and up to 25 weight per-

cent of additives improving the properties of said composition, said additives including in the range of 1 to 15 weight percent of a viscosity index improver selected from the group consisting of polyolefins having a molecular weight in the range of 5,000 to 50,000 and polymethacrylate esters; in the range of 1 to 15 weight percent of a detergent consisting of a phosphosulfurized hydrocarbon having a molecular weight in the range of 300 to 30,000 neutralized with a metal containing reagent; and in the range of 0.01 to 5 weight percent of a zinc dialkyl dithiophosphate as an antioxidant.

2. The lubricating oil composition of claim 1 wherein said viscosity index improver is a polyisobutylene having a molecular weight in the range of 10,000 to 25,000.

3. The lubricating oil composition of claim 1 wherein said detergent inhibitor is a barium salt of a phosphosulfurized polyisobutylene.

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