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LOW SULFUR, MINERAL BASE LUBRICATING OILS AND METHODS FOR USING SAME

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The present invention relates to improved lubricating oils for use in internal combustion gasoline engines of the recriprocating 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, very low sulfur contents thereby reducing their tendency to contribute to an increase in the requirement of octane number of gasoline for a knock free operation of high compression ratio internal engines. The invention is especially concerned with lubricating oil compositions containing low-sulfur mineral oil base stocks and non-sulfur containing addition agents adapted to improve one or more characteristics of the composition. The invention is also concerned with methods for operating automotive engines having compression ratios of above about 7.0:1 with these improved lubricating oils in combination with essentially hydrocarbon mixtures, under conditions that result in a decrease of the formation of combustion chamber deposits of the type which contribute to "octane requirement increase."

During recent years, the development and wide spread use of automobiles and other vehicles having relatively high compression ratio engines has focused attention to a problem of engine cleanliness that has serious economic implications. It has been consistently found by users of vehicles containing such engines, particularly, when they are run under mild driving conditions such as urban and suburban driving, that the engines knocked and lost power after relatively short operating periods. This difficulty occured even though detergent additive-containing lubricating oils and gasolines having high octane ratings meeting the automobile manufacturers recommendations were employed. Studies have shown that these difficulties occured when the combustion chambers of the high compression ratio engines contained films of resin-like deposits forming chiefly on the piston top, on valves, and on the under side of the cylinder head. The octane requirement to prevent knocking frequently increases by as much as 10 to 15 units during the first 3,000 to 5,000 miles of service and power losses as high as 10% are frequently observed.

A study of these deposits 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 further found that the resin-like deposits were insulating in nature and decreased cooling through the combustion chamber walls. This results in heating up the incoming fuel charge and raises the overall combustion temperature, which in turn makes the engine more prone to knock. Thus the poor heat conductivity of the deposits accounts for the remaining octane requirement increase observed.

Chemical analyses have shown that the deposits in the organic portion generally contained 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, such as the oxides, chlorides, sulfates, etc., are also present in amounts as high as 50 to 80% of the total deposits, when the gasoline contains tetraethyl lead (TEL) and halide scavengers for the TEL.

It has been found further that both the gasoline and the lubricant can be substantial contributors to the formation of combustion chamber deposits of the type that cause octane requirement increase (ORI). The mechanism of a particular component in forming such deposits is not known with certainty, but at least a substantial proportion of the resins appears to be closely associated with a tendency of a given component to form high molecular weight cross-linked resins at the hot flame conditions 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. This resin not only resisted combustion but also appears to have a binding effect in retaining carbon and inorganic substances in the deposits. Not only certain types of mineral oil components, but also additions agents improving the characteristics of the oil and certain components of the gasoline can contribute to formation of such harmful deposits.

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 gasolines contain below about 0.20% by weight, preferably about 0.10% by weight, of said sulfur. More recent studies have shown that unexpected advantages in decrease ORI can be achieved by lowering the sulfur content of gasoline below the level at which the sulfur has any effect on the actual octane number of the gasoline containing tetraethyl lead. For minimizing ORI, it has been found important to decrease the sulfur content of leaded gasoline below about 0.02% and preferably below about 0.005% by weight. With such low-sulfur leaded fuels it has been found that combustion chamber deposits are formed, indeed; but these deposits are not of the type that contribute to ORI, and on the contrary they have catalytic anti-knock properties that seem to offset completely the physical pro-knocking effect of their thermal insulating properties and volume. If substantial sulfur is present in the fuel, however, lead sulfate and possibly other lead salts having pro-knock properties are formed in the combustion chamber leading to octane requirement increase. It is evident that a sulfur-lead interaction of some type takes place in the combustion zone under combustion conditions that leads to the formation of harmful deposits.

It has been conventional practice to formulate motor oil compositions, particularly of the mineral oil base variety, that contain substantial amounts of sulfur, this sulfur being present not only in the mineral oil base stock, but also in the addition agents used to improve such characteristics as detergency, oxidation resistance, and the like of the finished composition. No particular attention has been given to reducing the sulfur content of such oils because the amount of such oil introduced into the combustion chamber was relatively small in comparison with the fuel, and therefore its effect in contributing to harmful sulfur deposits was negligible. It has been found however that this situation no longer obtains when using low sulfur fuels or fuels that, with the use of proper lead scavenging agents and the like, will not contribute to sulfur-containing deposits that have pro-knocking effects. Indeed, it has been found that the lubricating oil can contribute a substantial amount of potentially harmful sulfur during an engine operation with improved fuels. It is therefore a principal object

of the present invention to provide a lubricating oil composition of exceptionally low sulfur content that will not in itself contribute to the formation of harmful sulfur deposits. It is a further object to teach a means for using this improved lubricating oil for lubricating the parts of a combustion chamber subject to friction in combination with an improved gasoline wherein neither the fuel nor lubricant will contribute substantially to harmful sulfur-containing deposits.

In accordance with the present invention, a lubricating oil composition is provided that comprises a lubricating oil base stock having a low sulfur content with at least one non-sulfur containing addition agent adapted to improve at least one characteristic of the finished composition. In a preferred embodiment of this invention, the total lubricating oil composition will have a sulfur content below about 0.1% by weight, preferably below 0.05% by weight. The lubricating oil base stock will comprise a major proportion of a low-sulfur mineral oil having lubricating characteristics, but more preferably the base stock consists completely of such a mineral oil. The non-sulfur containing additives dissolved in the finished composition will consist of one or more of those that improve such characteristics as viscosity index, detergency, resistance to oxidation or to the causing of bearing corrosion, pour point depressing, rust inhibition or other properties. A preferred composition will contain at least two different types of additives conveying at least two characteristics. The best results are obtained with mineral oil-base compositions containing a minor portion of a multi-additive system containing at least three different types of these or other additives that will form a finished oil having superior viscosity index, low pour point, more engine cleanliness and the like characteristics.

The lubricating oil components of the present invention are also preferably those types that do not contribute to ORI in the combustion chambers of the high compression ratio engines. These components preferably have relatively low resinification indexes e. g., low tendency to form resin-like deposits during a combustion under a hot, smokeless flame such as a hydrogen flame. Mineral lubricating oil base stocks particularly adapted for this purpose are those that are substantially free of hydrocarbon components boiling above about 600° F. at a pressure of 10 mm. Hg, such as bright stocks, residuums or heavier distillate components. A particularly suitable fraction is one that boils within the range of about 275° to 600° F. at this pressure and more preferably within the range of about 300° to 575° F. at this pressure.

A specifically preferred composition of the present invention is formulated with a major portion of a catalytic cycle oil, resulting from the catalytic cracking of gas oils and the like, which has been selectively treated for the removal of relatively more aromatic components and sulfur and which has been, if desired, dewaxed and/or clay treated. These refined catalytic fuel stocks have extremely low sulfur contents, such as below about 0.05% by weight, and possess excellent stability and high viscosity index characteristics. If the proper boiling range is selected, they do not themselves contribute to the formation of resinous-like combustion chamber deposits. Treating methods other than catalytic cracking for producing mineral oils of low sulfur content are, however, contemplated in the present invention, although catalytic cracking is a particularly preferred method.

The non-sulfur additive system employed as a minor component of the oils of the present invention will be discussed in detail below. Preferably, these additives comprise about 3 to 30% and preferably about 5 to 25% of the total oil composition.

The advantage to be obtained in the practice of the present invention in the operation of automotive engines is demonstrated in Table I, which shows a comparison of the amount of sulfur contributed by fuels and lubricants in operations with conventional fuels and lubricants, with low sulfur fuels and conventional lubricants, and with low sulfur fuels and the lubricants of the present invention.

TABLE I

Sulfur contributed by lubricants vs. fuel in an average automobile

[Consumptions assumed: 1 quart of oil per 1,000 miles, 13.0 miles per gallon of gasoline or 1.8# of oil and 469# of gasoline/1,000 miles.]

	Lbs. of Sulfur Burned Per 1,000 Miles	Percent of Sulfur Burned Contributed by Lube
Case A		
Present day Fuels[1] and Lubes:		
Fuel at 0.1% Sulfur	0.469	
Oil at 0.5% Sulfur	0.009	
Total	0.478	1.9
Case B		
Improved Fuel but Current Lube:		
Fuel at 0.005% Sulfur	0.024	
Oil at 0.5% Sulfur	0.009	
Total	0.033	27.0
Case C		
Improved Fuel and Improved Lube:		
Fuel at 0.005% Sulfur	0.0240	
Oil at 0.05% Sulfur	0.0009	
Total	0.0249	3.8

[1] Fuels containing about 2 cc. TEL/gal. and conventional scavenging agent.

In Case A, it is seen that the conventional high sulfur lubricant will contribute only about 1/50 of the total sulfur entering the combustion chamber of the average automobile. In Case B, however, the lubricant will contribute almost 1/3 of the total sulfur when using a low sulfur fuel. By using a combination of a low sulfur fuel (about 0.005% S) and the low sulfur lubricant of the present invention, the proportional contribution by the lubricant can be reduced to about 1/25 or to levels equally as low as those now conventional with high-sulfur lubricants and high-sulfur fuels.

Therefore, this invention also contemplates the improved results to be obtained in operating automotive engines with the low-sulfur lubricants of the present invention in combination with low-sulfur, leaded fuels. The invention also contemplates operations with the oils of the present invention in combination with high-sulfur leaded fuels containing high boiling lead scavenging agents, such as various aromatic halides and the like to be defined more fully herein, whereby the harmful sulfur-like deposits are not formed in substantial amounts in the combustion chamber.

Various methods for preparing and formulating lubricating oil compositions of the present invention and of employing them as lubricants in automotive engines and the like 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.

Example I.—Preparation of mineral lubricating oil base stocks

Mineral oil base stocks were prepared by catalytically cracking gas oils and recovering a cycle oil boiling above the heating oil range in accordance with a procedure disclosed and claimed in U. S. Serial No. 187,709 filed September 30, 1950 in the name of Forrest H. Blanding. This patent issued on November 24, 1953, as Patent No. 2,660,552. In one series of operations, gas oil distillates from various types of crudes including Mid-Continent

crudes was subjected to fluid catalytic cracking, employing a silica-alumina type catalyst under conventional cracking conditions. The refractory cycle oil produced in this catalytic cracking operation, the cycle oil consisting of hydrocarbon components resistant to further degradation under the conditions employed, was segregated and selectively extracted with phenol solvent using approximately at 204 volume per cent treatment, based on the feed stock, and an extraction temperature of about 140° to 157° F. A 50% solvent raffinate yield was obtained. The solvent raffinate was then dewaxed to obtain a yield of 80 volume percent of dewaxed oil, based on the stripped raffinate, the dewaxed raffinate having a pour point of about +25° F. The dewaxed raffinate was then distilled to obtain an initial to 27% overhead fraction.

For comparative purposes, a lubricating oil distillate obtained from the same type of Mid-Continent crude was solvent extracted with phenol and dewaxed under conventional conditions to obtain a distillate fraction having approximately the same gravity, boiling range and viscosity characteristics as the 0 to 27% extracted and dewaxed cycle oil. The refined distillate is designated as a solvent neutral. Both the 0 to 27% fraction and the solvent neutral boiled below 600° F. in an ASTM Engler-type distillation at 10 mm. pressure Hg.

Various physical inspections and analysis were obtained on the various feeds and extracts. Comparative data are shown in Table II below.

TABLE II

Premium lubes made from various crudes

Base Stock Inspections	A	B	C	D	E
	Cycle Stock			Virgin Distillate Dewaxed Raff.	Cycle Stock Phenol Extract
	Waxy Feed	Dewaxed Raffinate	0 to 27% of Dewaxed Raff.		
Gravity, °API	14.8	32.4	34.3	34.8	−0.2
Visc. @ 100° F., SSU	(1)	152	81	74.7	(1)
Visc. @ 210° F., SSU	45.4	43.8	37.6	37.0	(1)
Viscosity Index	(1)	110	104	101	(1)
Pour, °F	90	+25	+20	+5	(1)
Flash, °F., open-cup	365	(1)	355	340	(1)
Color, Tag Robinson	¼	½	10½	20½	(1)
Neutralization No., mgs. KOH/gm	.01	(1)	.03	.01	(1)
Conradson Carbon, Wt. Percent	3.3	.04	.01	.01	(1)
Sulfur, Wt., Percent	0.87	.04	.035	0.3	1.67
Sligh-test, mgs. Sludge/10 g. Oil (24 Hrs.)	619	1.0	1.2	10–15	(1)
Aromatics, Wt., Percent	48	6	(1)	(1)	87

[1] Not determined.

Base Stock A, the feed to the solvent extraction unit, had a sulfur content of 0.87%. Solvent extraction produced Base Stocks B and C having extremely low sulfur contents of about 0.04%. Note that the sulfur content of the phenol extract was 1.67% (column E) showing that the predominant portion of the sulfur compounds is concentrated in the material removed by solvent extraction. In contrast, the typical commercial dewaxed raffinate, Solvent Neutral oil (column D), had a sulfur content approximately 10 times that of the refined cycle oils. This Solvent Neutral is made from virgin lubricant distillates rather than cracked cycle stock. It is also noted that the oxidation stability of the refined cycle oils, as measured by the conventional Sligh test, was exceptionally better than that of the virgin Solvent Neutral. The viscosity indexes of the refined cycle oils were also quite high.

Another operation was carried out in which a gas oil obtained from a mixture of Middle East crude was catalytically cracked and cycle stock recovered therefrom was phenol extracted to obtain a 34 volume percent raffinate which was then dewaxed and clay contacted under conventional conditions to obtain a finished lubricating oil cycle stock representing 25 volume percent of the original cycle oil.

For comparative purposes, a lubricating oil distillate from a Middle East crude was solvent extracted and dewaxed. Inspections and tests on the various base stocks are shown in Table III below:

TABLE III

Lubes made from Middle East-type crude

Base Stock Inspections	F	G	H	J
	Cycle Stock		Dewaxed Raffinate from Virgin Distillate	Cycle Stock Extract
	Waxy Feed	Dewaxed Decolorized Raffinate		
Gravity, °API	10.7	37.2	32.8	0
Visc. @ 100° F., SSU	161	88.8	150.9	(1)
Visc. @ 210° F., SSU	42.2	39.2	43.9	(1)
Viscosity Index	52	135	114	(1)
Pour, ° F	+80	+25	+15	(1)
Flash, ° F	365	390	415	(1)
Color, Tag-Robinson	¼	20½	20¾	(1)
Color after prolonged heating, Tag-Robinson	(1)	20½	18¾	(1)
Neutralization No., mgs. KOH/gm	.01	0.0	.03	(1)
Conradson Carbon, Wt. percent	1.85	0.0	.05	(1)
Sulfur, Wt. percent	3.52	0.01	0.27	5.3
Sligh, mgs. Sludge/10 gms. (24 Hrs.)	(1)	1.4	26	(1)
Aromatics, Wt. percent	64	4	13	83

[1] Not determined.

It is noted that Base Stock G, the extracted and dewaxed cycle oil, had an exceptionally high viscosity index of 135, an exceptionally low sulfur content of .01% and excellent stability as measured by the Sligh test.

Example 2.—Engine performance characteristics of cycle oil-base lubricating oil compositions

A blend containing approximately 90 weight percent of Base Stock C and 10 weight percent of a viscosity index improving additive was prepared. The V. I. improver consisted of about 25% by weight of polyisobutylene having a Staudinger average molecular weight of about 15,000 and 75% by weight of a mineral oil base stock.

This blend was tested in a Lauson single cylinder engine having a 6.5:1 compression ratio head. The engine was loaded with an induction motor at 1840 R. P. M. and 10.5 brake kilowatt load for a period in the range of about 120 to 200 hours using a spark advance of 12° BTDC. These operating conditions have been found to correlate with full scale field tests of automobiles having 7.5:1 compression ratio engines with respect to octane requirement increase. In these tests the engine was operated with a hydrocarbon fuel that itself did not contribute to ORI.

The results of these tests are shown in Table IV below:

TABLE IV

Octane requirement increase in Lauson engine

Lubricant	Octane Requirement	
	Initial	Equilibrium
Refined Cycle Stock +10% Polybutene	60	61

It is seen that the blend of refined cycle stock and polybutene additive, which blend contained less than 0.05

weight percent sulfur, did not contribute to any appreciable extent to ORI.

The mineral oil base stocks used in the practice of the present invention may be obtained from various types of crudes such as those of paraffinic, naphthenic or mixed base components. Mid-Continent type crudes are useful as well as those of the Middle Eastern type, Texas Coastals and the like. The lubricating oil components of these crudes should be refined in order to reduce sulfur contents to the low levels required to obtain the benefits of the present invention. Such refining procedures include catalytic cracking, hydrofining, treatment with finely divided sodium in the presence of alcohols, ethers, ketones and the like, formaldehyde treatment, treatment with mineral acids, and the like. As a general rule conventional treating procedures such as acid treatment and the like will not be effective for obtaining extremely low sulfur levels, and a combination of treating procedures will usually be required to obtain the desired results. Such combinations of treating procedures may include catalytic cracking to obtain highly stable cycle stocks of the type discussed above, following which the relatively more aromatic components are removed by selective adsorption or extraction with silica gel or various solvents such as phenol cresylic acids, liquid SO_2 furfural or the like. Catalytically hydrogenated lubricating oil distillates may likewise be subjected to additional refining steps to reduce sulfur content further and to improve other characteristics of the oils. The mineral oil base stocks may also be subjected to such treating procedures as dewaxing, clay treating and the like. These stocks preferably contain below about 10% by weight of aromatic rings and have a ratio of aromatic rings to naphthenic rings of below about 0.3.

It is also preferred that the base stock be distilled to exclude relatively high boiling mineral oil components, particularly those boiling above about 600° F. at a pressure of 10 mm. Hg; more preferably the base stock will boil below about 575° F. at this pressure in the simple distillation test of the so-called "vacuum Engler" type.

Although bright stock, or residuum components may be employed in the practice of the present invention provided their sulfur content is sufficiently low, it is preferred to exclude such residual components particularly if the base stock is to be substantially non-contributing to ORI. It is generally desired that a low sulfur mineral oil base stock be the major portion of the lubricating oil base stock, and preferably constitute all of the base stock. However minor amounts of other lubricating oil base stocks and blending agents include hydrogenated oils, synthetic oils such as polymerized olefins, synthesis products from the reaction of oxides of carbon with hydrogen, hydrogenated coals, shale oil derivatives, synthetic polyester and polyether type lubricating oils, and the like.

The base stock preferably has a viscosity index above about 100 and has a Saybolt Universal (SUS) viscosity at 100° F. in the range of about 50 to 160, and at 210° F. to about 33 to 50. As mentioned heretofore, the base stock should have a sulfur content below about 0.10 weight percent, preferably below 0.05 weight percent sulfur.

The non-sulfur containing additives useful in the practice of the present invention may be selected from a variety of materials that have characteristic improving properties without contributing to sulfur increase.

It is generally desired to add a viscosity index improver. High molecular weight hydrocarbon V. I. improvers such as the polymerized lower olefins (i. e., polymerized C_3–C_5 olefins) are quite effective. For example, polymerized butenes, such as 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.

Other V. I. improvers include the polymethacrylate esters, fumarate-vinyl acetate copolymers, polyalkyl styrenes, and the like. The viscosity index improver may be used in amounts in the range of about 0.5 to 30% by weight, preferably about 1 to 10% by weight, based on the finished lubricating oil. In producing a finished lubricant having a low ORI, it is preferred that the V. I. improver be of the non-contributing type. The high molecular weight olefins such as the polyisobutylenes are particularly advantageous in this respect. However, mixtures of various types of V. I. improvers may be used.

Detergency improving additives may be selected from a large group of materials, particularly the metal containing materials that are useful in this respect. Certain types of ashless synthetic detergent additives however are also useful. Such detergent additives include metal salts and soaps such as metal naphtenates, including zinc soaps of petroleum naphthenic acids, particularly soaps obtained from naphthenic acids having molecular weights of about 150 to 400, metal phenates such as the alkali metal, alkaline earth metal and heavy metal phenates. Such compounds include calcium decyl phenate, barium tert.-octyl phenol, metal bis phenols and the like.

Specific alkyl phenols from which such detergents can be made include the xylenols, thymol, decyl phenols and other long-chain alkyl substituted phenols, wax phenols, petroleum phenols recovered from distillate petroleum oils, and particularly tertiary aliphatic substituted phenols such as tert.-amyl phenol, tert.-octyl phenol and the like may be used. Bis phenols such as 2,2-bis-(2-hydroxy-3-tert.-butyl-5-methylphenol) - propane, 2,2-methylene bis (4-methyl-6-tert.-butyl phenol) and the like may likewise be employed. Various amino phenols and their substituted derivatives such as alkyl para amino phenols and the like may also be used. It is also to be understood that these phenols may be used as such for improving oxidation characteristics.

Other suitable detergent additives include metal phosphates and metal phosphites, high molecular weight polymethacrylate-type esters which may be used as ashless detergents and the like. The detergent additives may be present in amounts from as low as about 0.5% up to about 10% by weight or even higher, based on the total composition, although an amount in the range of about 2 to 8% are generally effective. It is generally preferred that the detergent inhibitor, as in the case of the V. I. improver, contribute very little to ORI.

The phenols and phenolic type compounds mentioned above may also be used per se as antioxidants. Other types of nonsulfur containing materials may however be employed as anti-oxidants and bearing corrosion inhibitors. As a general rule in the range of about 0.1 to 5% by weight, based on the total lubricating composition, of these compounds will be sufficient to improve these characteristics of the lubricating oil.

A small amount of a pour depressant additive may also be incorporated in the finished composition in order to obtain improved pour-point stability and decreased pour point. Such pour depressants include condensation products of chlorinated waxy naphthalene or phenol, various polymers and co-polymers of unsaturated esters and the like. For example, a co-polymer of the fumaric acid esters of coconut oils and of vinyl acetate in a 10/20 weight ratio is an extremely effective pour depressant when used in relatively small concentrations. In the range of about 0.01 to 5% by weight of such materials will usually be adequate.

Other additives that may be used in the lubricating oil composition include anti-rust agents such as the partial esters of polyhydroxy compounds including the oleate of sorbitan polyglycol, acid phosphates, and the like; dyes, oiliness agents, assisting agents such as the higher alcohols including octyl alcohol, lauryl alcohol, and stearyl alcohol, extreme pressure agents, etc.

As mentioned heretofore, the finished lubricating oil composition may contain one or more of the above types

of non-sulfur additives, depending on the extent to which a particular characteristic is to be improved and on the number of characteristics to be improved. It will be realized that some of the above addition agents are multifunctional in that a given additive may improve more than one characteristic.

As an example of a finished premium grade lubricating oil having excellent detergency, viscosity index, pour and anti-oxidant characteristics, the following composition is given:

Component	Amount, Volume Percent
Base Stock C (Example 1)	85
Polyisobutene V. I. Improver (Example 2)	8
Chlorinated Wax-Naphthelene Pour Depressant	2
Barium Cetyl Phenate Detergent	4.5
1,6-Ditertiary Butyl-4-Methyl Phenol (Antioxidant)	0.5

This blend has a sulfur content below about 0.04%.

The gasolines used in high compression engines and the like with the oils of the present invention may be any suitable high octane, essentially hydrocarbon gasoline such as those having ASTM research octane numbers in the range of about 75 to 100. Hydrocarbon components that may be used in formulating such gasolines include straight run distillates from various types of crudes, alkylates, high octane polymers of low molecular weight olefins, hydroformates, reformed gasoline fractions sch as platformed gasolines, catalytically cracked naphthas and the like. Such gasolines are usually formulated by mixing 2 or more of the above general types of components to form fuels meeting octane requirement, vapor pressure, stability, and other specifications.

In order to form finished gasolines containing below about 0.02% by weight, preferably below 0.005% by weight, of sulfur, some or all of the various components that go into the gasoline will usually have to be treated for sulfur reduction. Such treating procedures include prompt caustic washing of the sulfur-containing material in the absence of oxygen soon after a catalytic cracking operation, hydrofining of cracked naphthas, treatment of naphthas with finely divided sodium in the presence of oxygen-containing organic compounds such as alcohols or ethers, and the like.

The amount of tetra-ethyl lead used in such gasolines will generally range from about 0.5 to 3 ccs. per gallon. The TEL fluid will also contain a lead scavenging agent such as ethylene chloride, ethylene bromide and the like. These amounts of TEL will be sufficient to increase octane numbers to high levels under ordinary conditions.

The advantages of the present invention may also be obtained by operating an engine with the improved oil using a sulfur-containing fuel, such as one having above 0.1 weight percent sulfur, containing a lead scavenging agent that is relatively high boiling and stable. The higher boiling agents are more suitable than the conventional ethylene halides, for example, for effecting complete removal of the lead from the combustion chamber or for forming deposits that do not have a pro-knock effect. The higher boiling scavenging agents are those having substantially the volatility characteristics of tetraethyl lead. These materials include halogenated aliphatic hydrocarbons such as hexa chloro-butadiene, 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. Preferably these compounds 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. These higher boiling scavenging agents are taught in U. S. patents such as 2,496,983; 2,574,321; 2,479,900; etc.

It will be obvious that the gasoline fuels used in the practice of the present invention may also contain other addition agents such as anti-oxidants, gum inhibitors; solvent oils, rust inhibitors; metal deactivators and the like.

What is claimed is:

1. In the operation of an internal combustion engine of the reciprocating type having a compression ratio above about 7:1 in which an essentially hydrocarbon tetraethyl lead-containing fuel composition is introduced into the combustion chamber thereof under combustion conditions, the improvement for reducing the formation in said combustion chamber of sulphur-containing deposits of the type that increase the fuel octane requirement of the engine, which comprises lubricating the parts of said combustion chamber subject to friction with a lubricating oil having a decreased tendency to contribute towards octane requirement increase in said engine, said lubricating oil consisting essentially of a major portion of a mineral oil base stock which is a solvent extracted and dewaxed catalytic cycle oil distillate boiling within the range of about 300° to 600° F. at an absolute pressure of about 10 mm. Hg and a minor portion of at least one non-sulfur addition agent sufficient in amount to improve at least one characteristic of said composition, said lubricating oil having a total sulfur content not substantially above about 0.1 weight percent.

2. The method defined by claim 1 wherein said fuel contains less than about 0.02 weight percent sulfur.

3. The method defined by claim 1 wherein said fuel contains a relatively high boiling lead scavenging agent characterized by having volatility characteristics similar to those of said tetraethyl lead.

4. The method defined by claim 1 wherein said fuel contains less than about 0.005 weight percent sulfur.

5. The method defined by claim 1 wherein said fuel contains a halogenated aromatic lead scavenging agent having a vapor pressure within the range of about 0.5 to 5 mm. Hg at 120° F.

6. The method defined by claim 1, wherein said lubricating oil has a total sulfur content below 0.05% by weight.

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