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LUBRICATING OIL COMPOSITIONS

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The present invention relates to compounded lubricating oil compositions, which are particularly suitable for use in spark ignition internal combustion engines operating with knock-inhibited fuels.

It is known that fuels and lubricants (including additives therefor) affect the operations of the engine parts. The deleterious effect which some fuel decomposition products have upon the motor lubricating oil is becoming of greater significance. Also, it has become increasingly evident that still further components normally left in a lubricating oil base are undesirable for engine lubrication, and should therefore be removed therefrom. Thus, it has been proposed that, in order to obtain good viscosity index lubricating oils, the base stock should be separated (fractionated) into certain of its component parts and only certain of said parts should be reblended to obtain a desired lubricant base.

It has now been discovered that an excellent lubricating oil base suitable for use with various types of knock inhibited fuels, such as leaded fuels and adaptable for compounding with various additives, e. g., dispersants or detergents, which may also prevent engine fouling, corrosion and wear, can be obtained by fractionating the oil such as a distillate fraction as by extraction, adsorption, acid washing, etc., and then reblending specific proportions of certain of the components which are present in the base oil stock. These blends consist essentially of a distillate mixture of (1) at least 50% and preferably between 55% and 80% of predominantly saturated paraffinic lubricating oil components, preferably being a saturate fraction consisting essentially of naphthenic hydrocarbons of one or more rings and up to about 20% isoparaffinic hydrocarbons, (2) from about 5% to about 30% of monoaromatic hydrocarbons such as alkyl benzenes and naphtheno-benzenes and (3) from about 5% to about 40% of polyaromatic hydrocarbons which contain two aromatic nuclei and a co-fused naphthenic ring, and preferably such substances as alkyl naphthalenes. Aromatic fractions (2) and (3) should contain alkyl radicals attached thereto, and preferably co-fused naphthenic rings.

The three fractions which constitute the novel lubricating oil base of this invention can be obtained from various types of lubricating oil stocks, such as lube oils from California, Texas, Oklahoma, Mid-Continent, Pennsylvania, Near East or Gulf Coast crudes. The essential fractions can be obtained by treating suitable lube distillates with solid adsorbents, such as silica gel, alumina, activated carbon and the like, and/or with one or more of the well-known selective solvents, such as phenol, furfural, sulfur dioxide, ketones, nitrobenzene and the like. The most effective method of treating (fractionating) the lubricating oils is by adsorptive separation with silica gel, e. g., by the methods described in U. S. Patents 2,674,568 or 2,643,217.

Particularly suitable base oil stocks (for treatment with solid adsorbents, such as silica or silica-alumina gels to obtain the separate defined fractions which, when blended,

produce the final lubricating oil product of this invention) include lubricating oil distillates, such as from East Texas, West Texas Ellenburger and Ventura petroleum crudes, having a boiling range at one atmosphere pressure within the temperature range of from about 400° C. to about 750° C., and preferably between about 450° C. and about 600° C.

The desorbing agents which can be used to displace the various hydrocarbon components from the solid adsorbent in the adsorptive separation process should be solvents which have complete miscibility with the charge stock at all concentrations. When distillation is to be used to remove the desorbing agent from the product, it should have a boiling point substantially different from the charge components to permit ready separation. The desorbing agent used is preferably a low molecular weight saturated non-aromatic hydrocarbon having from about 3 to about 10 carbon atoms per molecule. Suitable desorbing agents include the alkanes and cycloalkanes, such as isopentane, isobutane, hexane, heptane, cyclopentane, cyclohexane, and the like, as well as their isomers, and various mixtures thereof, such as in petroleum ether.

In the adsorption process either a batch or continuous technique can be used. In a batch process, the lubricating oil fraction to be treated is introduced into a stationary column of the solid adsorbent until the capacity of the solid adsorbent for adsorbing further portions of lubricating oil is exhausted. The desorbing agent is then passed through the solid adsorbent containing the oil adsorbed thereon to selectively desorb the various fractions in succession. After the desired saturates and aromatics have been collected, separate from the undesirable fractions, the solid adsorbent is further treated with the desorbing agent to displace the remaining components. The solid adsorbent can then be reused for treating further portions of the lubricating oil. It is preferred to subject the solid adsorbent, after the desorption operation, to steaming to remove any residual organic material. In a continuous process, the adsorbent is suitably utilized in the form of a moving bed. The adsorbent is introduced into the adsorption zone and is passed therethrough in the form of a moving bed. A stream of lubricating oil is continuously fed to the adsorption zone. The adsorbent, containing the lubricating oil substantially completely adsorbed thereon, is then introduced into a desorption zone and therein treated with a suitable desorbing agent to displace successively the various components of the oil. The desirable saturates and aromatics are collected and blended in suitable proportions, and the undesirable fractions are rejected. The treated solid adsorbent is then returned to the adsorption zone. The desorbed components are suitably separated from the desorbing agent, as by distillation. The process is generally carried out at ambient atmospheric temperature.

The following examples illustrate methods of treating base stocks to produce compositions of this invention which will be identified hereinbelow as compositions A, B, C and D.

EXAMPLE I

An East Texas lubricating oil distillate having a viscosity of about 120 SSU at 130° F. was substantially completely adsorbed on silica gel, the gel-to-oil ratio being about 8:1. The adsorbent was then treated with isopentane to desorb successive fractions of saturated and aromatic fractions. The isopentane was removed from each of the fractions by distillation. Oil fractions so produced comprised (1) about 60% of a saturate fraction (containing about 20% isoparaffins and about 80% alkyl naphthenes of 1 to 5 ring and averaging 2 rings), (2) about 20% monoaromatics, and (3) about

20% of a polyaromatic fraction consisting of alkyl naphthalenes, naphthenonaphthalenes, phenanthrenes, naphtheno-phenanthrenes and chrysenes. The compositions of the saturate and aromatic fractions was determined by mass spectrometry and the ultraviolet spectra technique as described in Friedel and Orchin text "Ultraviolet Spectra of Aromatic Compounds" (John Wiley and Sons). An oil composition (A) of this invention was prepared by blending about 77% by weight of fractions (1) about 17% by weight of fraction (2) and about 6% by weight of alkyl naphthelenes of fraction (3).

EXAMPLE II

A West Texas Ellenburger lubricating oil distillate having a viscosity of about 135 SSU at 130° F. was substantially completely adsorbed on silica gel, the gel-to-oil ratio being about 8:1. The adsorbent was then treated with isopentane to desorb successive fractions of saturated and aromatic fractions. The isopentane was removed from each of the fractions by distillation. Oil fractions so produced comprised (1) 60% of a saturate fraction containing about 15% isoparaffins and about 85% alkyl naphthenes of 1 to 4 ring and averaging 2 rings, (2) about 20% monoaromatics and (3) about 20% of a poly aromatic fraction consisting of alkyl naphthalenes, naphtheno-naphthalenes, phenanthrenes, naphtheno-phenanthrenes and chrysenes. An oil composition (B) of this invention was prepared by blending about 65% by weight of fraction (1) about 27% by weight of fraction (2) and about 8% by weight of alkyl naphthalenes of fraction (3).

The blends of the three fractions as already described are further improved with respect to stability, lacquer prevention and other properties, in accordance with a preferred aspect of the invention, by addition thereto of from about 3% to about 25% by weight of a Bright Stock fraction containing a substantial amount of alkyl naphthalenes and having a molecular weight range of from about 750 to about 1000. If desired a broader fraction can be used and which contains in addition to alkyl naphthalenes other hydrocarbons such as saturates, mono- and polyaromatic but having a molecular weight of at least 700. The term Bright Stock refers to a residue lubricating oil fraction as defined in standard texts on the subject as "Motor Oils and Engine Lubrication" by Georgi. Thus, the three-fraction blend (compositions A and B) can be greatly improved particularly where the lubricant is used in conjunction with leaded fuels containing halogenated scavengers such as chlorinated and brominated alkanes, by addition thereto of from about 3% to about 25% of a Bright Stock alkyl naphthalene fraction having a molecular weight greater than 700 and preferably in the molecular weight range of from about 750 to about 1000.

A specific example of a composition (C) of this invention containing Bright Stock was prepared by blending 80 parts by weight of Composition B with 20 parts by weight of Bright Stock having a molecular weight between 750 and 1000.

Lubricating oil compositions of this invention are particularly suitable for use with dispersant or detergent additives. Such compounds include oil-soluble salts (metal or non-metal) of organic acidic compounds or inorganic acids containing organic radicals such as alkali, alkaline earth and heavy metal salts of carboxylic acids, sulfonic acids, naphthenic acids, carbamic acids, phenolic compounds, organic acid phosphates, phosphonic acids and the thio analogues of said acidic compounds. Preferred are the oil-soluble polyvalent metal sulfonates and phenates such as the Ca, Ba, Mg, Al, Zn and Pb petroleum sulfonate, naphthenate and alkyl phenates.

The sulfonates for use in compositions of this invention include petroleum sulfonates described in U. S. Patents 2,280,419, 2,344,988, 2,361,804, 2,375,222, 2,480,638, 2,485,861, 2,509,863, 2,501,731, 2,523,582, and 2,585,520. If desired, the sulfonates can be purified by the methods described in United States Patents 2,441,258 and 2,488,721. The aromatic sulfonates which can be utilized in compositions of this invention include those described in United States Patents 2,411,583, 2,418,894, 2,442,915, 2,483,501, 2,531,325, 2,556,198 and 2,556,848. Although various metal sulfonates are contemplated in the practice of the invention, including alkali metal sulfonates, alkaline earth metal sulfonates (including magnesium) and other polyvalent metal sulfonates, particularly other divalent metal sulfonates and trivalent metal sulfonates, the sulfonates of the metals of group II of the periodic table and having an atomic number from 12 to 56 are preferred, and especially of the alkaline earth metals within that group of metals. Specific sulfonates which are particularly suitable for use in compositions of this invention include oil-soluble metal sulfonates such as Na, K, Li, Ca, Ba, Mg, Sr, Al, Zn, Sn, Cr and Co petroleum sulfonate, tetra-tertiary butyl naphthalene sulfonate, diwax benzene sulfonate, stearyl benzene sulfonate, diwax naphthalene sulfonate, diisobutylene phenol sulfonate, tertiary octyl phenol sulfonate, ditertiary amyl phenol sulfonate, alkylated dibenzothiophene sulfonate and mixtures thereof.

The phenates suitable for use in compositions of this invention include those described in United States Patents 2,197,833, 2,228,654, 2,280,419, 2,344,988, 2,361,804, 2,410,652, 2,501,991, 2,501,992 and 2,610,982. Specifically, they can be either simple phenates such as metal alkylphenates (Ca cetylphenate), polar substituted simple phenates (Ca or Zn alkylsalicylates) or polyphenates such as where a plurality of the simple phenates are condensed at positions ortho and/or para to the phenolic hydroxy group through alkylidene (methylene) radicals or other suitable divalent non-metallic radicals, such as sulfur or selenium. Although various metal phenates are contemplated in the practice of the invention including mono- and polyvalent metal phenates, such as the alkali, alkaline earth and heavy metal phenates of which preferred are the polyvalent metal phenates of the metals of group II of the periodic table and having an atomic number from 12 to 56, especially the alkaline earth metals within that group of metals. Illustrative compounds are: Na, K, Li, Ca, Ba, Sr, Mg, Zn, Al, Cd, Ni, Fe, Co cetyl phenate, dibutyl phenate, C_{14}–C_{18} salicylate, octyl thiophenate, cyclohexyl phenate, cetyl phenol sulfide, waxyl phenate, as well as the above metal salts of the condensation product of alkyl phenol with formaldehyde, acetaldehyde, or benzaldehyde, e. g., Ca, Ba, or Mg salts of octyl phenol-formaldehyde condensation product ranging in molecular weight of from 400 to 1,100.

Although the above salts are preferred oil-soluble sodium, calcium, barium zinc, lead aluminum, salts of alicyclic acid, e. g., naphthenic acid, fatty acids such as oleic, stearic, phenyl mercapto stearic, aromatic acids, e. g., dibutyl phthalic acid, dioctyl benzoic acid; nitrogen-containing acids, e. g., dibutyl dithiocarbamic acid; organic phosphorus-containing acids, e. g., di(methylcyclohexyl)dithiophosphate, butyl trichloromethanephosphonic acid and the like can be used in place of the sulfonates and/or phenates described above or used in combination therewith.

The detergent salts can be incorporated into the present base lubricating oils in an effective amount of from about 0.01% to about 10% and preferably can vary from about 0.1% to about 5% by weight or as low as 0.05% and even 0.01% by weight.

In order to show the superiority of lubricating compositions of this invention over other types of lubricating blends, the following engine tests were made.

Compositions A, B and C of this invention were tested in a Lauson engine for bearing corrosion and at the end

of the test period gave a value of about 15±10 mg., whereas Composition X (80% saturates of Ex. I+20% monoaromatics of Ex. I), Composition XX (80% saturates of Ex. II+20% monoaromatics of Ex. II), Composition Y (saturate fraction of Ex. I) and Composition YY (saturate fraction of Ex. II) resulted in bearing weight losses of from 670 to 1200 mg.

Composition C containing 0.2% sulfate ash of Ca salt of octyl phenol-formaldehyde condensation product operating in a Lauson engine with leaded fuel gave a piston lacquer rating of 7.0, whereas Compositions X, XX, Y and YY containing 0.2% sulfate ash of Ca salt of octyl phenol-formaldehyde condensation product in the same engine and same operating conditions gave lacquer rating of around 3.9. When polyaromatics of Ex. I and II were substituted for the monoaromatics in Compositions X, XX, Y and YY each containing the Ca salt as noted above, the lacquer ratings were around 4.1.

A Composition D of this invention was compared with Compositions Z and ZZ (identified below) by testing them (in the L–4 Chevrolet engine using leaded fuel) and the results were as given in Table I.

Table I

Composition	Chevrolet L–4 Test: Overall rating (100—perfect, 95 and below—fail)
Composition D:	
51% Saturate fraction of Ex. II	
22% Monoaromatic fraction of Ex. II	
6% Alkylnaphthalenes of Ex. II	
20% Bright Stock (Mol. wt. 750–1,000)	
0.3% SA [1] Ca salt of octyl phenol-formaldehyde condensation product	96
0.4% SA [1] Ca petroleum sulfonate	
0.2% Phenyl alpha-naphthylamine	
Composition Z:	
79% Saturates (Example II)	
20% Monoaromatics (Example II)	
0.3% SA [1] Ca salt of octyl phenol-formaldehyde condensation product	78
0.4% SA [1] Ca petroleum sulfonate	
0.2% Phenyl alpha-naphthylamine	
Composition ZZ:	
63% Saturates (Example II)	
16% Monoaromatics (Example II)	
20% Bright Stock (Mol. wt. 750–1,000)	
0.3% Ca salt of octyl phenol-formaldehyde condensation product	90
0.4% SA [1] Ca petroleum sulfonate	
0.2% phenyl-alpha-naphthylamine	

[1] SA=percent Wt. of sulfate ash, other percentages are by percent by wt.

Compositions of this invention can be modified by addition thereto of minor amounts (0.1–2%) of pour point depressants, viscosity index improvers, blooming agents, corrosion inhibitors, oiliness agents, solubilizers, and the like. Among such materials can be included high molecular weight polymers, e. g., "Acryloids," which are polymeric esters of methacrylic acid and coconut fatty acids, wax naphthalene condensation products, isobutylene polymers, alkyl styrene polymers; inorganic and organic nitrites such as $NaNO_2$ or $LiNO_2$ and diisopropylammonium nitrite or dicyclohexylammonium nitrite, organic sulfides, e. g., wax disulfide, bis-ethylene tolyl sulfide, amine, e. g., octadecylamine and the like. Also, phenolic antioxidants such as 2,6-ditertiary-4-methyl phenol and 2,2'-methylene bis(4-methyl-6-tertiarybutyl phenol) can be used in conjunction with the additive combination of this invention.

Compositions of this invention are particularly effective when used in combination with primary fuels such as fuels containing tetraethyl lead (TEL), iron carbonyl, ferrocene and ferrocene derivatives with or without the added presence of organic phosphates such as tricresyl phosphate, triphenylphosphate, triethylphosphites, or various combustion chamber deposit inhibitors, pre-ignition agents, spark plug anti-foulants, anti-oxidants, and the like.

We claim as our invention:

1. A mineral lubricating oil composition consisting essentially of a major amount of a mineral lubricating oil containing (1) from about 55% to about 80% of a mixture of mineral oil saturated hydrocarbons of lubricating viscosity consisting of up to 20% isoparaffins and the balance being naphthenes, (2) from about 5% to about 30% of a mixture of mineral oil monoaromatic hydrocarbons and (3) from about 5% to about 40% of a mixture of polyaromatic comprising a mixture of alkyl naphthalenes, essentially free from other types of components of mineral lubricating oil, and from about 0.01% to about 10% of a mixture of an oil-soluble metal sulfonate and an oil-soluble metal phenate.

2. A mineral lubricating oil composition consisting essentially of a major amount of a mineral lubricating oil containing (1) from about 55% to about 80% of a mixture of mineral oil saturated hydrocarbons of lubricating viscosity consisting of up to 20% isoparaffins and the balance being naphthenes, (2) from about 5% to about 30% of a mixture of mineral oil monoaromatic hydrocarbons and (3) from about 5% to about 40% of a mixture of polyaromatic comprising a mixture of alkyl naphthalenes containing co-fused naphthene rings, essentially free from other types of components of mineral lubricating oil, and from about 0.1% to about 5% of a mixture of an oil-soluble alkaline earth metal petroleum sulfonate and an oil-soluble alkaline earth metal phenate.

3. A mineral lubricating oil composition consisting essentially of a major amount of a mineral lubricating oil containing (1) from about 55% to about 80% of a mixture of mineral oil saturated hydrocarbons of lubricating viscosity consisting of up to 20% isoparaffins and the balance being naphthenes, (2) from about 5% to about 30% of alkylbenzenes and (3) from about 5% to about 40% of alkyl naphthalenes, essentially free from other types of components of mineral lubricating oil, and from about 0.1% to about 5% of a mixture of oil-soluble calcium petroleum sulfonate and oil-soluble calcium salt of octyl phenolformaldehyde condensation product.

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