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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 operation of the engine parts. The deleterious effect which some fuel decomposition products have upon the motor lubricating oil is becoming of greater significance. In work done to combat this, it has been observed that when Bright Stock (lubricating oil obtained from vacuum reduced oil residues) is added to lubricating oils for use in engines operating with knock-inhibited fuels, the engine is clean even after long periods of use. However, to effect this, rather large amounts of Bright Stock (10–30%) are required, and this in turn has been found to have a detrimental effect on octane level of the fuel required for knock-free operation. Thus, the addition of Bright Stock to a lubricating oil results in engine cleanliness but in turn causes an increase in octane requirement.

It has now been discovered that an excellent lubricating oil composition for use with various types of knock-inhibited fuels, such as leaded gasoline, and adaptable for compounding with various additives, e.g. dispersants or detergents, which may also reduce engine fouling, corrosion and wear, without causing increase in octane requirement, can be obtained by addition to a lubricating oil a minor amount of from about 0.1% to about 10% and preferably from 3% to 6% of an alkyl naphthenodiaromatic hydrocarbon. The alkyl radical or radicals may contain from 1 to 30 and preferably from 6 to 22 carbon atoms in the chain and can be attached either to the naphtheno or aromatic and preferably to the aromatic component of the molecule.

The alkyl naphtheno-diaromatic hydrocarbons, such as alkyl naphtheno-naphthalenes can be synthesized by suitable methods, such as described in U.S. Patents 2,390,363, 2,414,118 and 2,645,669. The preferred alkyl naphthenonaphthalenes are those wherein the alkyl radical contains from 1 to 30 and preferably from 6 to 22 carbon atoms. Examples of alkyl naphtheno-naphthalenes suitable for use as the essential additive in lubricating oil compositions of this invention in addition to those extractable from Bright Stock include, alkyl acenaphthenes or alkylfluorenes, e.g. tricosylacenaphthene, dodecylacenaphthene, ditricosylacenaphthene, didodecylacenaphthene, benzylacenaphthene; the corresponding fluorenes, e.g. octylfluorene, hexadecylfluorene, didodecylfluorene, benzylfluorene, cyclopentylfluorene, and other compounds of this type, such as alkylated benzfluorene and mixtures thereof.

Alkyl naphtheno-naphthalenes can be also obtained from short residue oil fractions derived from various types of oil stocks, such as California, Texas, Oklahoma, Mid-Continent, Pennsylvania, Near East or Gulf Coast crudes. The short residue fraction is topped to form a residue or bottoms fraction having a molecular weight of about 650 or higher. An intermediate cut of this high molecular weight fraction is what is means by a Bright Stock

fraction which is rich in alkyl naphtheno-naphthalenes. Bright Stock fractions generally contain from 50% to 65% saturates, 20% to 30% monoaromatics, 5% to 20% polyaromatics and from 1 to 5% sulfur compounds. The polyaromatic fraction can contain from 4% to 10% diaromatic fractions and the balance being higher polyaromatics. By any suitable means, such as fractionation, solid adsorbents or selective solvents, the diaromatics containing alkyl naphtheno-naphthalenes can be removed or concentrated in the Bright Stock fraction so that the fraction contains about 15% to 35% alkyl naphtheno-naphthalenes. This Bright Stock fraction enriched in alkyl naphtheno-naphthalenes (R) can be used as additives in lubricating oil compositions of this invention. In addition heterocyclics of similar structure may be used, such as alkyl carbazole, alkyl dibenzofuran, or ketone oxidation products, such as alkyl keto acenaphthene.

Lubricating oil compositions of this invention containing minor amounts of alkyl naphtheno-naphthalenes are particularly suitable for use with dispersant or detergent additives such as oil-soluble salts (metal or non-metal) of sulfonic acids, and phenolic compounds. The oil-soluble polyvalent metal sulfonates and phenates are preferred, such as Ca, Ba, Mg, Al, Zn and Pb petroleum sulfonates, 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, 2,285,861, 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 the 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 alkyl salicylates) 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 (e.g., 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 cetylphenate, dibutylphenate, C_{14}–C_{18} salicylate, octylthiophenate, cyclohexylphenate, cetyl phenol sulfide, waxy 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.

The detergent salts can be used effectively in amounts of from about 0.01% to about 10%, the amount preferably being from about 0.1% to about 5% by weight.

Lubricating oils for additives of this invention can be natural or synthetic hydrocarbons having lubricating properties. Thus, the base may be hydrocarbon oils of wide viscosity range, e.g., 100 SUS at 100° F. to 150 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils, such as castor oil, lard oil, and the like, and/or with synthetic lubricants, such as polymerized olefins and the like. If desired, the synthetic lubricants may be used as the sole base lubricant or admixed with fixed oils and their derivatives.

Refined mineral lubricating oils obtained from West Texas Ellenburger crudes, East Texas crudes, Oklahoma crudes, and California crudes are particularly useful as base oils for compositions of the invention. An example of a Mid-Continent neutral mineral oil suitable as a base oil has the following properties:

Gravity, ° API	29.4
Refractive index n_D^{20}	1.4855
Viscosity, SUS at 100° F.	57.2
Viscosity index	105

The outstanding properties of compositions of this invention were demonstrated when 5% of didodecylfluorene was added to this neutral mineral oil containing 1% calcium salt of octyl phenol-formaldehyde condensation product (composition A) and 5% of didodecylacenaphthene was added to another portion of the same oil (composition B) and these compositions A and B were tested in the Lauson engine operating on leaded gasoline. The piston ratings were 6.3 and 7.8, respectively, for compositions A and B as compared to 4.0 for neutral base oil alone. (A rating of zero is poor while 10 is clean.) In the $FeCl_3$ tolerance test, which is a bench test indicating the cleanlines characteristics of test compositions, compositions A and B showed a cleanliness improvement of 150% and 300%, respectively, over the base oil. The ferric chloride tolerance test is made by blending into a test composition 10 grams of a 1% solution of anhydrous ferric chloride in ether and allowing the composition to stand in a steam oven for one hour, after which the composition is allowed to cool to room temperature and the amount of precipitate formed is noted. The amount of precipitate formed is correlative to the cleanliness characteristic of the test composition in an engine. To obtain the same improvement in both the Lauson engine and $FeCl_3$ tolerance test, as given by compositions A or B, about 20% of Bright Stock had to be added to the neutral mineral oil. Compositions A and B in an automotive engine operating on leaded fuel showed no increase in octane requirement over that found with the base oil alone whereas with the 250 neutral mineral oil containing 20% Bright Stock about 50% increase in octane requirement was noted.

Compositions C and D comprising a neutral mineral lubricating oil each containing 1% calcium salt of octyl phenol-formaldehyde condensation product and 10% and 5%, respectively, of Bright Stock fraction (R) gave piston ratings of 8.6 and 7.1, respectively, as compared to 4 for the base oil alone.

Other compositions of this invention which can be used in engines operating on leaded fuels without causing increase in octane requirement and which give clean engines include mineral lubricating oils containing from 0.1% to 2% calcium salt of octyl phenol-formaldehyde condensation product plus calcium petroleum sulfonate or the latter alone, and from 3% to 6% of didodecylfluorene, hexadecylfluorene, or a Bright Stock fraction containing from 15% to 35% alkyl naphthenonaphthalenes.

The compositions may contain minor amounts (0.1–10%) of pour point depressants, viscosity index improvers, blooming agents, corrosion inhibitors, oiliness agents, solubilizers, and the like. Among such materials are high molecular weight polymers, e.g., "Acryloids," which are polymeric esters of methacrylic acid and alcohols derived from coconut fatty acids, wax naphthalene condensation products, isobutylene polymers, alkyl styrene polymers; inorganic and organic nitrites such as $NaNO_2$ and $LiNO_2$ and diisopropylammonium nitrite or dicyclohexylammonium nitrites, organic sulfides, e.g., wax disulfide, bis-ethylene tolyl sulfide; amines, e.g., octadecylamine and the like. Also, phenolic antioxidants, such as 2,6-ditertiarybutyl-4-methyl phenol and 2,2'-methylene bis(4-methyl-6-tertiarybutyl phenol) can be used.

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 together with alkyl halide scavenger, and with or without the added presence of organic phosphates, such as tricresyl phosphate, triphenyl phosphate, tri(β-chloroethyl) phosphate, or various combustion chamber deposit inhibitors, preignition agents, spark plug anti-foulants, anti-oxidants, and the like.

We claim as our invention:

1. A lubricating oil composition, beneficial for reducing the octane requirement and for keeping engines clean which operate on a knock-inhibited fuel, consisting essentially of a major amount of mineral lubricating oil containing from 0.1% to 10% of a C_{6-22} alkyl naphthenodiaromatic hydrocarbon compound selected from the group consisting of an enriched Bright Stock fraction containing about 15% to 35% of an alkyl naphthenonaphthalene, C_{16}–C_{22} alkyl acenaphthene and C_{16}–C_{22} alkyl fluorene and from 0.1% to 5% of an alkaline earth metal alkyl phenate.

2. A lubricating oil composition, beneficial for reducing the octane requirement and for keeping engines clean which operate on a knock-inhibited fuel, consisting essentially of a major amount of mineral lubricating oil containing from 0.1% to 10% of a C_{6-22} alkyl acenaphthene and from 0.1% to 5% of an alkaline earth metal alkyl phenate.

3. A lubricating oil composition, beneficial for reducing the octane requirement and for keeping engines clean which operate on a knock-inhibited fuel, consisting essentially of a major amount of mineral lubricating oil containing from about 3% to about 6% of dodecylacenaphthene and from 0.1% to about 2% of Ca salt of octyl phenol-formaldehyde condensation product.

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