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LUBRICATING OIL COMPOSITION

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8 Claims. (Cl. 252—53)

This invention relates to compounded mineral lubricating oils and more particularly deals with lubricating oils containing oil-soluble metallo-organic detergent which possess the property of softening carbon, preventing or retarding sticking of piston rings and deposition of lacquer in internal combustion engines when running these engines for long periods of time under severe conditions of loading.

It is known that in modern internal combustion engines, such as aviation gasoline engines operating at relatively high temperatures due to their high power output, or in high-speed Diesel engines due to incomplete combustion, piston rings have a tendency to become stuck in the grooves. Lacquer and/or carbon formation appear to be the principal reasons for this occurrence.

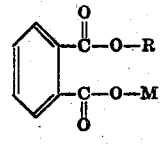
Moreover, scuffing of top lands due to the formation of hard carbon, particularly when using high viscosity-index oils, may cause serious damage to the engine.

To eliminate or reduce the lacquer deposition, ring-sticking, and hard carbon forming characteristics of oils it is necessary to compound them with additives, normally metal soaps, which seek to improve the oils in one or more of its properties.

Polyvalent metal salts have been considered in the past as the best of such metallic detergents as shown by their general acceptance by the lubricating industry. Salts of the monovalent alkali metals, however, due to their notable insolubility in petroleum, have been little used, except where resort has been had to colloidal dispersion by mechanical means, or to the use of auxiliary solvents or to other procedures for obtaining an adequate concentration of such additives.

It has now been found, however, that the alkali metal—that is, sodium, potassium, and lithium—salts of certain phthalic acid mono esters possess not only unexpected solubility in refined lubricating oil but lubricating oils containing them are also characterized by extraordinary detergency and the ability to render the remaining small carbon deposits which form in engine operation extremely soft as contrasted with the usual hard (and abundant) carbon deposit ordinarily found. The use of such a lubricant in an internal combustion engine results in a most unique decrease or elimination of stuck piston rings, absence of the usual lacquer deposition, and associated phenomena.

The compounds of the invention have the formula



in which M is sodium, potassium or lithium and R represents an aliphatic highly branched hydrocarbon radical, containing from about 10 to 20 carbon atoms and preferably about 14 to 20 carbon atoms, at least two of which carbon atoms, and preferably more, are tertiary or quaternary carbon atoms. For reason of stability R should contain not more than one, and preferably no olefinic double bonds. Suitable values of R are the alkyl radicals corresponding to the following illustrative list of branched paraffins found in petroleum:

- 10 carbon atoms: dimethyloctane, trimethylheptane, methylethylheptane, isopropylheptane, tetramethylhexane, diethylhexane
- 11 carbon atoms: dimethylnonane, trimethyloctane, tetramethylheptane, pentamethylhexane
- 12 carbon atoms: dimethyldecane, tetramethyloctane, methylpropyloctane, diethyloctane, dimethylpropylheptane, dimethylisopropylheptane, pentamethylheptane
- 13 carbon atoms: dimethylundecane, trimethyldecane
- 14 carbon atoms: dimethyldodecane, dipropyloctane, dimethyldiethyloctane, dimethylisobutyloctane
- 15 carbon atoms: trimethyldodecane, methylethyldodecane, methylpropylundecane
- 16 carbon atoms: dimethyltetradecane, diethyldodecane, tetramethyldodecane, dipropyldecane, octamethyloctane
- 17 carbon atoms: dibutylnonane
- 18 carbon atoms: diethyltetradecane, dibutyldecane
- 19 carbon atoms: trimethylisobutyldodecane, trimethylhexadecane
- 20 carbon atoms: dimethyloctadecane, tetramethylhexadecane, triethyltetradecane.

However, suitable alkyl radicals are not limited to those naturally occurring in petroleum. Such radicals may also contain halogens, for example chlorine, or other suitable substituents of high thermal stability.

Suitable amounts of the present metallo-organic detergents which an anti-ring-sticking and soft

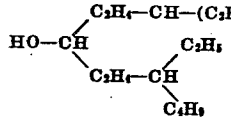
carbon forming oil should contain range from about 0.25% up to the solubility limit or 10.0% whichever is the lower and preferably from about 0.75 to 5.0% but not exceeding the solubility limit.

The lubricating oils in which these additives may be used include petroleum or mineral oils as well as various hydrogenated, polymerized and otherwise synthetic and treated oils such as voltolized oils, oils produced by polymerization of olefins and the like. Furthermore, the lubricating oil may contain varying minor amounts of animal or vegetable oils such as castor oil, lard oil, whale oil, corn oil, cottonseed oil, sperm oil, and the like.

The art has taught that metallo-organic compounds of the present type might be rendered soluble in lubricating oil by the incorporation of an ester radical. This has been found not to be the case for the case for the monovalent metal salts, however. For example, sodium monocetyl phthalate is almost completely insoluble in mineral lubricating oil, while a corresponding phthalate containing a highly branched alkyl radical instead of the cetyl radical, was quite soluble in the same oil, as shown in the example below.

Example

The sodium mono n-cetyl ester of phthalic acid was found to be soluble in a Mid-Continent lubricating oil distillate less than 0.25%, and caused gel formation in the oil. On the other hand, the barium salt of this acid and the sodium heptadecyl phthalate, prepared from a branched alcohol of the formula



were observed to be readily soluble in more than 6% in the same oil without causing gelling of the oil.

Samples of a refined commercial SAE 10 motor oil were compounded with 2% w. each of the barium n-cetyl phthalate and the above sodium heptadecyl phthalate respectively. The doped oils as well as a sample of the undoped oil were tested individually in a Fairbanks-Morse Diesel engine operating at 1200 R. P. M. with a crank case temperature of 150°±10° F. for 40 hours. The base oil alone gave a very unsatisfactory hard top land deposit. The oil containing the barium salt produced a smaller but fairly hard deposit of borderline acceptability. The oil containing the sodium salt however, produced only a very small deposit of unusually soft carbon.

This sodium heptadecyl phthalate also proved to be an excellent peptizer and anti-ringsticking compound as determined by 40 hour lubricating oil tests in a standard Lauson engine operated at a jacket temperature of 100° C.

The compounds of this invention may, if desired, be advantageously used in connection with other lubricating oil additives, for example, auxiliary detergents formed from the oil-soluble salts of various bases with other detergent forming acids. Such bases include metallic as well as organic bases. Metallic bases include those of the alkali metals, as well as Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary and quaternary amines.

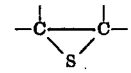
Examples of detergent forming acids are the various fatty acids of, say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax), chlorinated fatty acids, aromatic carboxylic acids including aryl fatty acids, aryl hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicyclic acids, phthalic acid mono esters, aromatic keto acids, aromatic ether acids; diphenols as di-(alkylphenol) sulfides and disulfides, methylene bisalkylphenols; sulfonic acids such as may be produced by treatment of alkyl aromatic hydrocarbons or high boiling petroleum oils with sulfuric acid, sulfuric acid mono esters; phosphoric acid mono and di esters, including the corresponding thiophosphoric acids; phosphonic and arsonic acids, etc.

Non-metallic detergents include compounds as the phosphatides (such as lecithin); certain fatty oils as rapeseed oils; voltolized fatty or mineral oils; etc.

Other detergents are the alkali earth phosphate di-esters, including the thiophosphate di-esters; the alkali earth diphenolates, specifically the calcium and barium diphenol mono and poly sulfides.

Anti-oxidants which may be present comprise several types, for example, alkyl phenols such as 2, 4, 6-trimethyl phenol, pentamethyl phenol, 2, 4-dimethyl-6-tertiary-butyl phenol, 2, 4-dimethyl 6-octyl phenol, 2, 6-ditertiary-butyl-4-methyl phenol, 2, 4, 6-tri-tertiary-butyl phenol, etc.; amino phenols as benzyl amino phenols; amines such as dibutyl phenylene diamine, diphenyl amine, phenyl-alpha-naphthyl amine, phenyl-beta-naphthyl amine, dinaphthyl amines; etc.

Antioxidant sulfur may be in the form of mercaptans, as in decyl mercaptains, dodecyl mercaptans, cetyl mercaptans, oleyl mercaptans, stearyl mercaptans, butyl or other higher alkyl thiophenes, thionaphthols, alkyl thionaphthols, etc.; or of disulfides (RSSR', as in diamyl disulfide and higher dialkyl disulfides, e. g. wax disulfides, diphenyl disulfides, dibenzyl disulfide, dinaphthyl disulfides, etc.); or of sulfur compounds formed by attaching sulfur to an olefinic double bond (as by reacting sulfur with olefins at temperatures of about 150° C. to 300° C.) which compounds are believed to contain the structure



(sulfur in epithio linkage).

Many sulfur compounds naturally occurring in petroleum oils are useful antioxidants, provided they have the necessary reactivity. These have been described in detail in the copending application, Serial No. 496,678, filed July 28, 1943, by Paul R. Van Ess, Forrest J. Watson and Gary N. Whitney.

Thiazoles such as mercaptobenzothiazole are also good antioxidants.

Among the sulfurized olefins found to be especially useful are, for example: sulfurized paraffin wax (as produced by chlorination of paraffin wax, having a molecular weight between about 225 and 425, dehydrochlorination of the chlorinated product to produce wax olefins, and sulfurization of the latter); sulfurized olefin or diolefin polymers boiling above about 400° C. such as are obtained as by-products in the refining of cracked distillates with clay or other refining agents, or in the polymerization of normally gasseous olefins to produce gasoline or the like (e. g. sulfur-

ized methyl pentadiene polymer); sulfurized esters of unsaturated fatty acids with monohydric alcohols, as methyl, ethyl, propyl, etc. oleate, or linoleate; sulfurized sperm oil, sulfurized jojoba oil; etc.

Corrosion inhibitors may also be present such as dicarboxylic acids of 16 and more carbon atoms, alkali metal and alkali earth salts of sulfonic acids and fatty acids, organic compounds containing a nitrile, nitro, or nitroso radical attached to a carbon atom which is alpha or beta to an acidic radical as in alpha cyano stearic acid, alpha hydroxy fatty acid esters, oxalic acid esters, organic amines, etc.

Likewise, other additives such as blooming agents, anti-foaming agents, viscosity regulators, etc. may also be present in the lubricating oil.

The invention claimed is:

1. A mineral lubricating oil suitable for internal combustion engines, containing dissolved a carbon softening amount of an oil-soluble alkali metal salt of a phthalic acid mono alkyl ester in which the alkyl radical contains about 10 to 20 carbon atoms and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms.

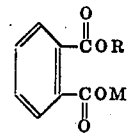
2. A mineral lubricating oil suitable for internal combustion engines, containing dissolved about 0.25% to 10% of an oil-soluble alkali metal salt of a phthalic acid mono alkyl ester in which the alkyl radical contains about 10 to 20 carbon atoms and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms.

3. A mineral lubricating oil suitable for internal combustion engines, containing dissolved a carbon softening amount of an oil-soluble sodium metal salt of a phthalic acid mono alkyl ester in which the alkyl radical contains about 10 to 20 carbon atoms and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms.

4. A mineral lubricating oil suitable for internal combustion engines, containing dissolved a carbon softening amount of an oil-soluble potassium metal salt of a phthalic acid mono alkyl ester in which the alkyl radical contains about 14 to 20 carbon atoms and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms.

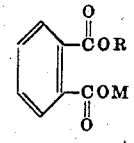
5. A mineral lubricating oil suitable for internal combustion engines, containing dissolved a carbon softening amount of an oil-soluble lithium metal salt of a phthalic acid mono alkyl ester in which the alkyl radical contains about 10 to 20 carbon atoms and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms.

6. A mineral lubricating oil containing dissolved a detergent amount of an oil-soluble compound of the formula



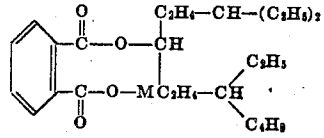
wherein R is a branched aliphatic radical having 10–20 carbon atoms and imparting oil-solubility to the compound and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms and M is an alkali metal.

7. A mineral lubricating oil containing dissolved a detergent amount of an oil-soluble compound of the formula



wherein M is an alkali metal and R is a branched aliphatic radical having no more than one olefinic double bond and containing about 14 to 20 carbon atoms which render the compound oil soluble and has at least two atoms selected from the class consisting of tertiary and quaternary carbon atoms.

8. A mineral lubricating oil containing dissolved a detergent amount of an oil soluble compound of the formula



wherein M is an alkali metal.

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