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COMPOUNDED LUBRICATING OIL

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This invention is a continuation-in-part of my copending applications Serial Nos. 286,236 and 338,238, filed July 24, 1939, and May 31, 1940, respectively, the latter application now issued as Patent No. 2,270,577 of January 20, 1942, and relates to compounded mineral lubricating oils containing certain oil-soluble detergent soaps and, in addition, a sulfurized organic compound. More particularly, it deals with lubricating oils containing small amounts of salts combining polyvalent metals with oil-soluble hydrocarbon-sulfonic acids, and, in addition, contain an amount of a sulfurized ester of a monovalent alcohol with a monocarboxylic acid.

In my copending application Serial No. 338,238 it is disclosed that salts of polyvalent metals and oil-soluble hydrocarbon-sulfonic acids are useful as anti-ringsticking agents in lubricating oils. There it is shown that these salts tend to cause corrosiveness of the lubricating oil, and that this corrosiveness can be inhibited by the addition of oxidation inhibitors.

In my earlier copending application Serial No. 286,236, I have shown that the corrosive properties of detergent soaps in lubricating oils can be reduced materially by the addition of an extreme pressure compound which contains at least one of the elements phosphorus, sulfur or chlorine, stably attached to the compound in such a way that it (this element) will not be liberated with sufficient ease under ordinary lubricating conditions of internal combustion engines to cause corrosion of the engine.

I have found that well-refined lubricating oils which contain oil-soluble hydrocarbon sulfonates of polyvalent metals and, in addition, certain sulfurized esters of monohydric alcohols with monocarboxylic acids are particularly useful for the lubrication of internal combustion engines, and more specifically of Diesel engines. Even in the absence of oxidation inhibitors, oils so compounded are remarkably stable and substantially non-corrosive in addition to having the valuable property of positively retarding or preventing piston ringsticking. If desired, oxidation inhibitors may, of course, be added further to improve the desirable properties of my compounded oils.

Metals suitable for my purpose are particularly the light-weight metals Mg, Ca, Sr, Ba and Al, and the heavier Zn. However, other polyvalent metals may be used, if desired, especially those having only one oxide, or one of several oxides which is much more stable than and is not readily convertible to the others under ordinary lubrication conditions in internal combustion engines. For example, fair anti-ringsticking oils may be produced with Cd, Sn, Co, Ni, etc.

Hydrocarbon oil sulfonic acids which may be used advantageously to produce the metal sul-

fonates of this invention are preferably of the oil-soluble type which are obtained, for example, in the treatment of relatively heavy mineral oils, preferably so-called paraffinic oils such as Pennsylvania or Mid-Continent gas oils or lubricating oils, with concentrated or preferably fuming sulfuric acid. In this kind of treatment, two types of sulfonic acids are produced—so-called green acids which are substantially oil-insoluble, and mahogany acids which are oil-soluble. It is the mahogany acids which I prefer to use for my purpose, although green acids may also yield certain oil-soluble salts which are applicable for my purpose. These acids constitute complicated mixtures of many different hydrocarbon sulfonic acids, many of which are believed to be of aromatic character, although others are probably of naphthenic and aliphatic origin. Some of them produce better anti-ringsticking salts than others. In order to isolate the most effective components, the oil-soluble acids or their salts may be subjected to a fractionation by countercurrent extraction with two mutually immiscible solvents, a hydrocarbon liquid such as toluene, benzene, xylene, naphtha, kerosene, etc., and a water-soluble organic solvent such as a lower alcohol, glycol, glycerine, the latter preferably containing some water. The active component of the mahogany acid is concentrated in the hydrocarbon solvent. This method of separation has been described by Retalliau in U. S. Patent No. 2,153,680.

If desired, lubricating oils containing the sulfonic acid salts may also be produced by heavy acid treatment with concentrated or fuming sulfuric acid of a suitable lubricating oil, separating precipitated and suspended sludge, and neutralizing dissolved sulfonic acid with lime or other oxide or hydroxide of a suitable polyvalent metal.

While in general I prefer the oil-soluble petroleum sulfonates produced from so-called paraffinic crudes, those obtained from naphthenic or asphaltic crudes may also be used.

Other oil-soluble hydrocarbon sulfonic acids suitable for my purpose may be produced by sulfonating alkyl aromatic hydrocarbons, such as alkyl benzenes, alkyl naphthalenes, alkyl anthracene, alkyl phenanthrenes, alkyl picones, alkyl chrysenes, alkyl diphenyls, etc., provided the number of carbon atoms in the alkyl chain or chains is sufficient to render the resulting sulfonic acids and their salts soluble in hydrocarbon oil. It is desirable that at least one alkyl radical be relatively long, i. e., contain at least 8 or more carbon atoms, not only because of solubility in hydrocarbon oils, but also for the reason that long, alkyl chains improve the anti-ringsticking efficiency of the salts formed with the sulfonic acids. Thus, one may produce an aromatic hydrocarbon suitable for the produc-

tion of highly efficient sulfonic acids by condensing chlorinated paraffin wax, alkyl chlorides such as octyl, decyl, cetyl, etc., chlorides, fatty alcohols, long chain olefines such as may be obtained in the cracking of wax, etc., with the aromatic hydrocarbons by means of suitable condensing agents such as Friedel-Crafts catalysts, sulfuric acid, P_2O_5 , phosphoric acid, etc.

The hydrocarbon sulfonic acids may, if desired, contain substitution radicals, such as hydroxyl, primary, secondary or tertiary amine, ether, sulfide, hydrosulfide, disulfide, halogen, etc., radicals which may be attached to the ring or to side chains or both. For example, excellent for my purpose are paraffin wax substituted naphthalene monosulfonic acids which contain a sulfonic radical attached to one ring of the naphthalene nucleus and a hydroxyl or amino radical attached to the other ring.

Salts suitable for my purpose must be free of free acid, and may be normal or basic. In general, it is preferable to employ a mixture of normal and basic salts. It is also highly desirable that sulfate esters be absent, as they are liable to liberate sulfuric acid which may cause corrosion, or precipitation of at least a portion of the metal component of the sulfonate, or both. If necessary, the sulfonic acids may be subjected to a hydrolyzing treatment before use in the compounded oil, to eliminate sulfate or other harmful esters which may be present. If desired, salts of two or more metals may be employed.

Sulfurized esters which I have found to be particularly useful may be produced by merely heating with free sulfur relatively high-boiling esters of a monohydric alcohol and a monocarboxylic acid; or else a suitable ester may be treated with sulfur monochloride, phosphorus polysulfide such as phosphorus sesquisulfide, or other compound capable of sulfurizing, i. e., of introducing sulfur in non-oxidized form into the esters. When using chlorine or phosphorus sulfides, usually the treated esters will also contain in addition to the sulfur some chlorine or phosphorus, as the case may be. The presence of these elements is beneficial for my purpose, provided they are held sufficiently strongly by the treated compound so that they do not turn corrosive during use of the oil containing them under ordinary lubricating conditions as may occur in internal combustion engines.

Sulfurization is facilitated if the ester is unsaturated. However, unsaturation is not essential.

If the ester is unsaturated, the unsaturation may be in the alcohol or acid portion of the ester or in both.

It is desirable that the ester be relatively high-boiling, and therefore should contain at least 10 carbon atoms and preferably more than 16. Any simple monohydric alcohol may be combined with any hydrocarbon monocarboxylic acid, provided the combined alcohol and acid possess the necessary minimum number of carbon atoms. Thus methyl, ethyl, propyl, vinyl, butyl, crotonyl, amyl, hexyl, cyclohexyl, heptyl, octyl, lauryl, cetyl, stearyl, etc., alcohols may be used. Of the large number of carboxylic acids, the following are particularly useful: fatty acids, preferably those of 10-20 carbon atoms, e. g., lauric, palmitic, oleic, linoleic, stearic, arachic, behenic, etc., acids, aromatic fatty acids such as phenyl acetic acid, phenyl propionic acid, phenyl stearic acid; naphthenic acids such as those naturally contained in many petroleum oils; wool fat acids; acids obtained by oxidation of paraffin wax or

other hydrocarbons; aromatic acids such as benzoic, alkyl benzoic acids, naphthoic acids, alkyl naphthoic acids, etc. If desired, the acid may contain an alcoholic OH radical as, for example, in ricinoleic acid, alpha-hydroxy phenyl acetic acid, salicylic acid, alkyl salicylic acids, hydroxy naphthoic acids, etc.

An ester which occurs naturally and meets my requirements is sperm oil.

After sulfurization the ester should contain between 1%-20% sulfur.

The amount of the sulfonate salts and the sulfurized ester may vary between fairly wide limits. Thus to retard or prevent piston ringsticking, I may use the sulfonate salt in amounts from .25%-5%, and preferably from .75%-2.5% by weight of the oil. The sulfurized ester may be used in amounts up to about 10% by weight of the oil, and preferably from about 1%-7%.

The combination of sulfonate salts and sulfurized esters is particularly active in oils of relatively high V. I., e. g., oils having V. I. of 50 and higher.

The following example further illustrates my invention:

The corrosiveness of three oils containing calcium petroleum sulfonate (produced by converting a commercial mahogany soap to the corresponding salt) was determined by a test which I call the inertia-bearing test. This test is conducted as follows: Two automobile connecting rods are mounted on a shaft which is machined to give a throw of one-half inch (radius) to the connecting rods. One rod is fitted with a copper-lead and one with cadmium-silver bearing. An inertia load of steel discs is fastened to each connecting rod. The small end of each connecting rod is connected to a hinged link. The shaft on which the bearings are mounted is driven by a synchronous electric motor. Two fly wheels are mounted on the shaft in order to reduce vibration. An open sump is steam jacketed to provide heat and an auxiliary electrical heater, with a variable resistance in series with the heater blade, provides additional heat and temperature control. A pump circulates the oil through the system. The sump is charged with one and three-fourths gallons of the oil to be tested. After the oil has been brought to 225° F., the pressure to the bearings is adjusted to 20 pounds per square inch and the machine brought up to the testing speed of 2450 R. P. M., which is maintained for 25 hours.

In the table below are given corrosion data in mg. loss of bearing obtained when testing crank case drainings of the several oils run for 100 hours in a high speed Diesel engine:

Oil composition	Bearing weight loss after 2450 R. P. M. with oil drained from Diesel engine after 100 hours	
	Copper-lead alloy mg. loss	Cadmium-silver alloy mg. loss
1 24% calcium petroleum sulfonate in mineral oil of 30 V. I.	533.7	53.4
2 24% calcium petroleum sulfonate + 3% sulfurized sperm oil containing 5.86% sulfur, in mineral oil of 55 V. I.	37.4	36.7
3 24% calcium petroleum sulfonate + 3% of a commercial sulfurized fatty acid ester containing 9.25% sulfur, in mineral oil of 30 V. I.	30.9	15.0

I claim as my invention:

1. Lubricating oil suitable for internal combustion engines containing dissolved from

.25%-5% of a sulfonate salt and from 1%-10% of a sulfurized ester having at least 10 carbon atoms combining a monohydric alcohol with a monocarboxylic acid, said sulfonate being oil-soluble, free of free acid and combining a hydrocarbon sulfonic acid with a polyvalent metal which forms an oxide that is not readily converted to other oxides under conditions of crank case lubrication.

2. The oil of claim 1 in which at least a portion of said salt is basic.

3. The oil of claim 1 wherein said polyvalent metal is selected from the group consisting of Mg, Ca, Sr, Ba, Al and Zn.

4. The oil of claim 1 which is free from sulfate esters.

5. The oil of claim 1 wherein the content of the sulfonate soap is from .75% to 2.5%.

6. Lubricating oil suitable for internal combustion engines containing dissolved from .25-5.0% of a sulfonate salt and from 1%-10% of a sulfurized ester having at least 10 carbon atoms and combining a monohydric alcohol with a monocarboxylic acid, said sulfonate being oil-soluble is free of free acid and combining a sulfonic acid of an alkyl aromatic compound containing an alkyl radical of at least 8 carbon atoms with a polyvalent metal which forms an oxide that is not readily converted to other oxides under conditions for crank case lubrication.

7. The oil of claim 6 wherein said compound is an aromatic hydrocarbon.

8. Lubricating oil suitable for internal combustion engines containing dissolved from .25%-5.0% of a sulfonate salt and from 1%-10% of a sulfurized ester having at least 10 carbon atoms and combining a monohydric alcohol with a monocarboxylic acid, said sulfonate being oil-soluble, free of free acid, and combining the petroleum sulfonic acid with a polyvalent metal which forms an oxide that is not readily converted to other oxides under conditions of crank case lubrication.

9. The oil of claim 8 wherein the petroleum sulfonic acid is an oil-soluble mahogany acid.

10. Lubricating oil suitable for internal combustion engines containing dissolved from .25%-5.0% of a sulfonate salt and from 1%-10% of an ester having at least 10 carbon atoms combining a monohydric alcohol with a carboxylic acid selected from the group consisting of fatty acids, aromatic fatty acids, naphthenic acids, wool fat acids, acids obtained by oxidation of hydrocarbons, acids having a carboxylic radical directly attached to an aromatic hydrocarbon nucleus, said sulfonate being oil-soluble, free of free acid, and combining the petroleum sulfonic acid with a polyvalent metal which forms an oxide that is not readily converted to other oxides under conditions of crank case lubrication.

11. The oil of claim 10 wherein said ester is sperm oil.

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