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COMPOUNDED OILS

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This invention relates to compounded hydrocarbon oils, more particularly, to mineral lubricating oils containing a metal salt of a phenol and a metal salt of an ester of sulfuric acid.

This application is a continuation-in-part of our copending application Serial No. 280,124, filed June 20, 1939, now U. S. Patent No. 2,322,307.

Hydrocarbon oils, such as mineral lubricating oils, when heated to temperatures of about 425° to 525° F. in the presence of an oxidizing gas such as air or partial combustion products, become partially oxidized and tend to deposit an adhesive gum or resinous material on surfaces with which they are in contact. It is an object much sought in the art of lubricating oils and in related arts to obviate this tendency of hydrocarbon oils to deteriorate at elevated temperatures in the presence of oxidizing gases. Thus the deterioration of hydrocarbon lubricants employed in internal combustion engines, especially those of the Diesel type and others in which high temperatures and pressures prevail, causes among other things, stickage of piston rings, fouling of the relatively moving parts of the engine, increased wear and improper lubrication. A major effort has been made to obviate these difficulties.

However, many oxidation inhibitors used for this purpose and effective at lower temperatures to prevent or retard deterioration of oils are ineffective or insufficiently effective at higher temperatures, such as 425° to 525° F.

Metal salts of various sorts of organic and organo-inorganic acids have been employed to obviate some of the difficulties mentioned, especially to promote engine cleanliness and to prevent or retard piston ring sticking. However, most of these salts have the defect that they cause increased corrosion of cadmium-silver or copper-lead types of bearings. Many of the salts have other defects as well.

In accordance with the present invention a combination of desirable properties is imparted to hydrocarbon oils by including therein both a metal salt of a phenol and a metal salt of an acid ester of sulfuric acid. Among the advantages of this combination are improved detergency (i. e., cleaner pistons, piston rings, piston ring slots, etc., and less piston ring sticking) and low corrosivity of the oil toward cadmium-silver, copper-lead and other similar alloy bearings.

This low corrosivity is shown by the data in the table below:

Strip corrosion test copper-lead strip 325° F.

	Milligrams loss at—		
	24	48	72
	Hours	Hours	Hours
Oil + 0.5% Ca cetyl phenate.....	11.1	13.9	17.3
+ 0.25% Ca cetyl phosphate.....			
Oil + 0.78% Ba keryl phenate.....	40.3	43.7	44.3
+ 0.25% Ca cetyl phosphate.....			
Oil + 0.99% Ba bornyl phenate.....	22.2	22.2	22.2
+ 0.25% Ca cetyl phosphate.....			
Oil + 0.6% Ba cetyl phenate.....	2.8	3.3	3.3
+ Ba dodecyl sulfate.....			

The data in the table above are taken from strip corrosion tests in which strips of copper-lead alloy are dipped in the oil under test, which is maintained at 325° F., and air is bubbled through the oil. The loss in weight of the strips measures the amount of corrosion. For further details concerning this test, reference is made to Farrington et al. U. S. Patent No. 2,308,502, page 4, right-hand column, line 70 to page 5, left-hand column, line 13. In the present example, only copper-lead strips were used and the test temperature was 325° F.; otherwise the test was carried out as described in said patent.

The oil used was a 50 V. I. blended stock. The calcium cetyl-phenate was the normal calcium salt of an alkylated phenol produced by alkylating phenol in the presence of sulfuric acid with a butylene polymer averaging C₁₈ per molecule (four butylene units), separating the alkylated phenol and forming the calcium salt. The barium keryl phenate and the barium bornyl phenate were, respectively, the normal barium salt of phenol substituted in the nucleus by a long chain alkyl group derived from kerosene, and the normal barium salt of phenol substituted in the nucleus by the bornyl radical. The barium cetyl phenate was the barium salt corresponding to calcium cetyl phenate. The calcium cetyl phosphate was the calcium salt of acid n-cetyl ester of phosphoric acid and the barium dodecyl sulfate was the barium salt of acid n-dodecyl ester of sulfuric acid.

The barium cetyl phenate and barium dodecyl

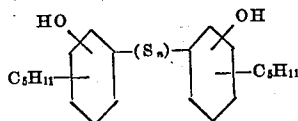
sulfate at the bottom of the above table are indicated as separate salts but it is believed that they were present in the oil as a complex salt. The oil solution was prepared as follows: 29 grams of dodecyl acid sulfate were dissolved in 150 cc. of benzene and 31 grams of basic barium cetyl phenate were dissolved in a like amount of benzene. The dodecyl acid sulfate did not dissolve completely in the benzene. The whole of the two solutions (including undissolved portions) were mixed together and the whole of the mixture was mixed with 3940 grams of the base oil. The oil was then heated to 220° F. while being stirred and was filtered through filter paper and then through Super Cel. A small proportion of the contained salts was removed from the oil by filtration but approximately 0.6% based on the oil of the mixture of salts or complex salt of barium cetyl phenate and barium dodecyl sulfate remained dissolved in the oil.

All of the salt combinations represented in the above table are capable of reducing piston ring sticking and in general are capable of improving a lubricating oil with regard to deterioration and tendency to foul the relatively moving parts of an internal combustion engine. It will be observed, however, that the phenate-sulfate combination was much less corrosive to the copper-lead bearing alloy than any of the other salt combinations. Likewise the phenate-sulfate combination of the above table, and phenate-sulfate combinations in general, not only provide an oil of low corrosivity but of generally improved performance characteristics such as reduced fouling of engines, reduced wear or reduced piston ring sticking and the like.

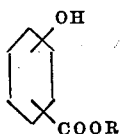
Regarding the phenates and organo sulfates that may be used in the combination of improvement agents of the present invention, it is preferred to use the polyvalent metal salts, such as aluminum, barium, calcium, zinc, magnesium, cobalt, cadmium, manganese, tin and chromium salts of phenols and of acid esters of sulfuric acid. The phenols whose salts are used are preferably oil-soluble phenols and the acid esters of sulfuric acid used are preferably those which contain a high molecular weight, oil solubilizing group, such as the cetyl and cetyl-phenyl groups. Examples of phenols and of acid esters of sulfuric acid that may be used in combination, when converted into their salts, are the following:

Phenols

Amyl phenol, diamyl phenol, cetyl phenol, diamyl diphenol sulfide, diamyl diphenol disulfide, cetyl chlorophenol and the carboalkoxy phenols, such as carbocetoxy phenol. The diamyl diphenol sulfides correspond to the formula—



($n=1$ in the case of diamyl diphenol sulfide and $n=2$ in the case of diamyl diphenol disulfide). The carboalkoxy phenols correspond to the formula—



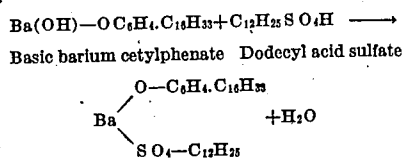
(In the case of carbocetoxy phenol, $R=C_6H_5$, A specific example is cetyl salicylate.

Acid esters of sulfuric acid

Cetyl acid sulfate, terpinyl acid sulfate, cyclohexyl acid sulfate, methyl cyclohexyl acid sulfate, cetylphenyl acid sulfate and cetylbenzyl acid sulfate.

Examples of phenate-organo sulfate pairs that may be used are as follows: Calcium cetylphenate-calcium dodecyl sulfate, aluminum amylphenate-zinc terpinyl sulfate, zinc cetyl chlorophenate-zinc methylcyclohexyl sulfate and calcium cetyl salicylate-calcium cetylphenyl sulfate.

In general the metal organo sulfates are less soluble in oil than the phenates. However, by mixing an oil-soluble phenate such as calcium or barium cetylphenate with an oil-insoluble sulfate such as barium dodecyl sulfate, greater oil solubility of the sulfate is obtained. Best results are obtained, with respect to oil solubility of the sulfate, by forming a basic phenate, such as basic barium cetylphenate, and reacting the basic phenate with an acid sulfate, such as dodecyl acid sulfate. It is believed that the following reaction occurs (using basic barium cetylphenate and dodecyl acid sulfate as examples of the reactants):



Double salt of barium cetylphenate and barium dodecyl sulfate

In any event, the product of reaction is surprisingly soluble in oil considering the low oil solubility of barium dodecyl sulfate.

In general, metal salts of lower molecular weight phenols are less soluble in oil than metal salts of higher molecular weight phenols; likewise, in general metal salts of lower molecular weight acid sulfates are less soluble in oil than are metal salts of higher molecular weight acid sulfates. Guided by these principles, one should select a pair of salts that will be oil soluble. Thus, if a phenate of low molecular weight and low oil solubility is used, it will be advisable to use with it a sulfate of high molecular weight, hence of greater oil solubility. Likewise a low molecular weight acid sulfate indicates the use of a high molecular weight phenate.

In general it is preferred to use salts of phenols containing ten or more carbon atoms in a substituent group and it is preferred to use metal salts of acid esters of sulfuric acid wherein the esterifying group contains at least 12 carbon atoms. However, where one member of the pair of salts (phenate-sulfate) is of high molecular weight and is freely oil soluble, the other member may be of relatively low molecular weight and of relatively low oil solubility. It will be understood, of course, that more than one phenate and more than one sulfate may be included in the oil, and that other salts of organic and/or organo-inorganic acids may also be included in the oil.

Oil solubility does not necessarily imply a high degree of solubility in oil, but sufficient solubility or dispersibility to effect the desired improvement and not to settle out on standing. Usually a solubility of a few tenths of a per cent is effective to produce marked improvements in lubricating oils.

One of the advantages of the present invention is that by using salt pairs the oil solubility of one

or both members of the pair is frequently enhanced.

Besides the method of preparation of the salt mixtures described above (reaction of a basic salt with an acid), the method of coprecipitation from an aqueous solution of alkali metal salts of the acids may be used. Thus to an aqueous solution of sodium cetylphenate and sodium dodecyl sulfate may be added an aqueous solution of calcium chloride or aluminum sulfate, producing, respectively, a mixed precipitate of calcium cetylphenate and calcium dodecyl sulfate or a mixed precipitate of aluminum cetylphenate and aluminum dodecyl sulfate. Such coprecipitation is preferably carried out in the presence of an organic solvent to take up the oil-soluble organic salt as it is formed. Lubricating oil will serve this purpose.

Less advantageously the salts in question may be mixed mechanically and the mechanical mixture added to the oil or they may be added separately to the oil.

The proportion of metal salts added to the hydrocarbon mixtures may vary widely, depending upon the salt selected and the conditions to be encountered. The present invention is primarily concerned with the production of liquid hydrocarbon compositions and the proportion of the metal salts should therefore preferably be insufficient to solidify the hydrocarbon mixture. In general, it has been found that from approximately 0.5% to approximately 2% of total salt content, based on the weight of the hydrocarbons, serve the purposes of the invention although as little as 0.1% or as much as 5% is not precluded. From about 0.1 to 2% by weight based on the oil of phenate and the same range of concentrations of sulfate are generally sufficient. The metal salts may be incorporated in high boiling hydrocarbons of widely different types. Hydrocarbons of petroleum origin are the most commonly available and will be most generally utilized. Pennsylvania, Mid-Continent or California petroleums are suitable sources for high boiling hydrocarbons of the type here involved. Although paraffinic oils such as commonly obtained from Pennsylvania crudes are not precluded, it has been found that acid refined naphthenic base oils are more readily susceptible to improvement as respects formation of adhesive resinous deposits on metal surfaces at elevated temperature. Synthetic hydrocarbons, for example, hydrogenated olefin polymers such as hydrogenated butene, isobutene or mixed isobutene butene polymers, may be utilized. In general, the hydrocarbon should be of a liquid consistency at ordinary atmospheric temperatures and should preferably have a boiling point above approximately 500° F. at atmospheric pressure.

The relative proportion of the respective acid radicals in the complex or mixed salts contained in the compounded lubricating oils herein disclosed will vary, depending upon the purposes to be served and conditions encountered during use. In general, the stoichiometric ratio of phenate radical to radical of acid ester of sulfuric acid (i. e., the $[ArO-]/[RSO_4-]$ ratio) will be from 10:1 to 1:10. Preferably such ratio will be from 4:1 to 1:4.

The compositions of this invention have a number of applications and will be found to have utility where it is desirable to inhibit deposition and/or formation of adhesive gums on metal surfaces which are bathed in or are in contact with high boiling hydrocarbons subjected to elevated

temperatures in the presence of an oxidizing agent such as an oxygen-containing gas. One example of such an application comprises the lubrication of Diesel engines in which the oil is spread in a thin film over the pistons, piston rings and cylinder walls of the engine, and is subjected to the oxidizing action of the compressed gases in the combustion chamber at temperatures of from approximately 425° to 525° F. or above which exist at the upper piston rings of such engines. In this particular application of the invention it should be noted that the hydrocarbons are subjected not only to high temperatures in thin films on the metal surfaces, but also to the high pressures necessary to produce spontaneous ignition of Diesel fuels. These pressures are approximately 400 to 600 lbs./sq. in. at the time of ignition of the fuel, and rise to pressures as high as 750 to 1150 lbs./sq. in. during combustion of the fuel. By the present invention the normal course of reactions occurring in the oil under these conditions may be progressively altered so that formation and/or deposition of adhesive materials is prevented and piston ring sticking is inhibited.

The compositions of this invention are also applicable to the prevention of formation and/or deposition of adhesive materials from hydrocarbon mixtures in those various instances where an oil flows over a metal surface which is heated to high temperatures and where heat transfer is the primary object to be accomplished. For example, oil cooled electric resistances subject the oil to high temperatures at the oil-metal interface of the highly heated electric resistance element. The deposition of adhesive gummy materials on the surface of the resistance element may be inhibited at temperatures as high as 425° to 525° F. and the efficiency of the heat transfer thereby maintained or increased. An oxidizing agent will generally be present in such heat transfer process by reason of dissolved oxygen which is contained in the oil being heated, as well as by reason of air which may be in contact with the oil at one or more points in the system.

The mixed salts of this invention may be added to hydrocarbon oils containing other compounding ingredients, such as pour point depressors, blooming agents, compounds for enhancing the viscosity index of the hydrocarbon oil, etc. The invention in its broader aspects embraces hydrocarbon oils containing, in addition to the mixed salts herein disclosed, thickening agents in grease-forming proportions or in amounts insufficient to form greases, as in the case of mineral castor machine oils or other compounded liquid lubricants.

While the character of this invention has been described in detail and numerous illustrations given, this has been done with the intention that no limitation should be imposed upon the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations of the above disclosures may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

1. A composition of matter comprising a hydrocarbon oil of lubricating viscosity and a small amount each (sufficient to improve the properties of the oil affecting its use as a lubricant, of a metal salt of a phenol and a metal salt of an acid ester of sulfuric acid.

2. The composition of claim 1, wherein said metal salt of a phenol is an oil-soluble polyvalent

metal salt of a phenol and said metal salt of an acid ester is a polyvalent metal salt of a higher alkyl acid sulfate.

3. A compounded lubricant comprising mineral lubricating oil, about 0.1 to 2 per cent by weight of a polyvalent metal salt of a high molecular weight phenol and about 0.1 to 2 per cent by weight of a polyvalent metal salt of a high molecular weight acid ester of sulfuric acid.

4. A compounded lubricant comprising mineral lubricating oil, about 0.1 to 2 per cent by weight of an alkaline earth metal salt of a high molecular weight phenol and about 0.1 to 2 per cent by weight of an alkaline earth metal salt of a high molecular weight acid ester of sulfuric acid.

5. A compounded lubricant comprising a mineral lubricating oil, about 0.1 to 2 per cent by weight of an alkaline earth metal phenate and about 0.1 to 2 per cent by weight of a polyvalent metal salt of an acid ester of sulfuric acid.

6. The lubricant of claim 5, wherein said phenate is the calcium salt of an alkylated phenol wherein the alkyl group contains at least ten carbon atoms.

7. The lubricant of claim 5, wherein said phenate is the barium salt of an alkylated phenol wherein the alkyl group contains at least ten carbon atoms.

8. The lubricant of claim 5, wherein said phenate is the barium salt of an alkylated diphenol disulfide.

9. A compounded liquid lubricant comprising a mineral lubricating oil, about 0.1 to 2 per cent by weight of an oil soluble polyvalent metal phenate and about 0.1 to 2 per cent by weight of an alkaline earth metal salt of a high molecular weight acid ester of sulfuric acid.

10. The lubricant of claim 9, wherein said salt of an acid ester is barium dodecyl sulfate.

11. The lubricant of claim 9, wherein said salt of an acid ester is barium terpinyl sulfate.

12. The lubricant of claim 9, wherein said salt of an acid ester is calcium cetylphenyl sulfate.

13. A compounded liquid lubricant comprising a mineral lubricating oil, about 0.1 to 2 per cent by weight of barium cetylphenate and about 0.1 to 2 per cent by weight of barium dodecyl sulfate.

14. A compounded liquid lubricant comprising a mineral lubricating oil, about 0.1 to 2 per cent by weight of barium salt of diamyl diphenol disulfide and about 0.1 to 2 per cent by weight of barium terpinyl sulfate.

15. A compounded liquid lubricant comprising a mineral lubricating oil, about 0.1 to 2 per cent by weight of calcium cetylphenate and about 0.1 to 2 per cent by weight of calcium cetylphenyl sulfate.

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