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COMPOUNDED LUBRICATING OIL

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This invention relates to compounded mineral oils and more particularly, deals with the addition of a detergent salt together with an antioxidant salt to mineral oils to produce lubricating oils of improved anti-corrosive properties for internal combustion engines, which oils have the property of preventing the sticking of piston rings when running these engines for long periods of time, and which have the ability to properly lubricate the cylinders and pistons under severe conditions of loading.

It is known that in modern internal combustion engines, such as high-speed Diesel engines, aviation gasoline engines, etc., which due to their high power output operate at relatively high temperatures, piston rings have a tendency to become stuck in the grooves. Lacquer and/or carbon formation appear to be the principal reason for this occurrence. The addition of small amounts of certain oil-soluble carboxylic acid salts, such as polyvalent metal salts of fatty acids, naphthenic acids, etc., is known to reduce the ring sticking tendencies. The addition of small amounts of such salts or soaps, however, has the disadvantage that the newer type bearings such as those containing copper-lead, cadmium or silver alloys are corroded. A further disadvantage of such soaps is that many of them tend to settle out of the oil in use. For example, salts of hydroxy aromatic compounds in which the metal is held by a hydroxy group tend to decompose when exposed to the action of water and carbon dioxide under conditions of lubrication in internal combustion engines thereby precipitating oil-insoluble carbonates.

Now in accordance with our invention we have found that polyvalent metal detergent salts and polyvalent metal antioxidant salts, when added together to mineral oils in suitable quantities, produce effective anti-ring sticking lubricants which are relatively free from the above disadvantages, i. e., they are substantially non-corrosive, and phenolates, or the like which, as stated, tend to decompose, are stabilized against decomposition by the presence of the detergent soaps.

The metal salts employed as antioxidant salts in accordance with the invention may be the salts of polyvalent metals with mono-nuclear aromatic hydroxy compounds such as phenol, polynuclear such as naphthol, anthrol, etc., and derivatives thereof. Amino, mono or polynuclear aromatic compounds are effective in the instant invention as long as they contain either a hydroxy or carboxylic group, examples of these compounds being the amino benzoic acids, amino phenols and derivatives thereof.

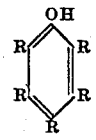
To be effective in the instant invention these salts should be soluble in the lubricating oil to the extent necessary to dissolve the desired amount. While many of the salts of aromatic hydroxy compounds are little soluble in mineral oils, similar salts of the corresponding alkylated compounds are usually much more soluble. However, oil solubility cannot always be predicted from the formula and must be determined experimentally for different compounds. In general, to insure oil solubility it is well that the antioxidant salt employed should have at least three carbon atoms in one or several aliphatic side chains. However, aliphatic side chains containing more than about 20 carbon atoms are not preferred for, though suitable from the point of view of enhancing solubility, they tend to be thermally unstable.

If desired the aromatic hydroxy compounds may contain additional polar substitution radicals, i. e. radicals containing elements other than carbon and hydrogen such as hydroxy, carboxyl, alkoxy, aryloxy, hydrosulfide, amino, imino, halogen, etc., radicals. While, in general, these polar radicals reduce the solubility in hydrocarbon oils considerably rather than enhance it, some of them frequently are advantageous in further reducing corrosiveness. The carboxyl group may be very valuable further to improve the resistance to precipitation due to hydrolysis.

Examples of compounds that may be used to form antioxidant salts with polyvalent metals are alkyl phenols, alkyl naphthols, alkyl amino phenols, alkyl amino benzoic acids, alkyl poly hydroxy phenols, such as alkylated catechol, alkylated resorcinol, alkylated pyrogallol and the like, alkylated oxy carboxylic acids such as alkylated resorcylic acid, alkyl salicylic acids such as diisopropyl salicylic acid and the like.

An especially effective group of antioxidant salts is that comprising the polyvalent metal salts of phenol derivatives containing a total of at least three carbon atoms in aliphatic side chains, which

may be conveniently represented by the general formula



wherein R designates a hydrogen atom, hydrocarbon radical, hydroxy group or carboxylic group and at least one R being an aliphatic hydrocarbon radical. Of such compounds the polyvalent metal salts of alkyl phenols and alkylated salicylic acids have proven to be particularly effective antioxidant salts.

The salts of antioxidants are employed rather than the free antioxidant acids because the former enhance the effect of the detergents employed, have the further advantage of not vaporizing and frequently are stronger antioxidants. Strangely, the antioxidant salts inhibit the corrosiveness of the detergent salts to a far greater extent than true corrosion inhibitors. The reason for this peculiar anomaly may be in the following:

Corrosion inhibitors are believed to be effective by forming a protective film on the metal. An active detergent tends continuously to remove this film, thus exposing the metal surface. Therefore, the only way in which to prevent corrosion is by preventing oxidation of or at the metal which must precede or accompany its being attacked by the relatively weak acids. The presence of strongly corrosive elements such as sulfur, chlorine, etc. should therefore be avoided because, being oxidizing agents themselves, they may cause corrosion even under non-oxidizing conditions.

From the above, it follows that preferred antioxidants are those free from corrosive elements or radicals such as halogen, sulfur, free strong acids such as sulfuric, phosphoric, etc., acid radicals or compounds capable of liberating them under lubricating conditions. For example, it has been found that an antioxidant salt containing a thioether linkage gave good protection against corrosion while fresh. However, an oil containing such an inhibitor and a detergent soap turned highly corrosive after prolonged use in an internal combustion engine.

Suitable detergent salts are the salts of polyvalent metals with petroleum naphthenic acids, fatty acids having at least 10 carbon atoms, equivalent hydroxy fatty acids, aromatic fatty acids, and other aromatic carboxylic acids in which the carboxyl radical is preferably attached to the aromatic nucleus through aliphatic links of varying lengths, rosin acids, paraffin acids produced by the oxidation of paraffin wax, wool fat acids, oil-soluble sulfonic acids such as mahogany sulfonic acids, etc. Of these salts the aromatic fatty acid and oil soluble sulfonic acid salts are preferred. These fatty acids may contain polar substitution radicals similar to those enumerated for the antioxidant salts. However, polar radicals containing corrosive elements are not preferred for the reasons explained above.

The salts may be either the basic or normal salts. Methods of putting the salts in solution may vary. Some can be dissolved cold; others are best added to the lubricating oil at an elevated temperature, for example, in the range of 100° C. to 350° C. Still others can only be formed in the oil, preferably at elevated temperatures by the methods described in the copending application of Bergstrom, Serial No. 331,988, filed April 27, 1940, now U. S. Patent No. 2,226,500. Once they have been dissolved at elevated temperatures, many of the solutions thus obtained tend to remain substantially stable at normal temperatures.

Of the polyvalent metals whose detergent and antioxidant salts are valuable for our purpose are beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum and tin, and of these, calcium, magnesium and zinc appear to be especially effective. It is not well to employ the salts of copper, iron, lead, manganese, chromium, or certain other metals. Because they easily pass through several states of oxidation, these latter metals tend to destroy the beneficial effects of the antioxidant with which they are compounded. Although, in general, it is preferable to employ the same metal in both the detergent and the antioxidant compound, mixtures containing different metals may be used.

In general, we prefer to use about .3 to 1.5% each of the salts in our lubricating oil; however, suitable amounts may be varied from approximately .15% to 2%. In general, it is not well to have a total salt content in the oil of more than 3%, for amounts in excess of this limit tend to cause undue increase in viscosity as well as jelling of the oil.

Crankcase lubricating oils containing the metal salts of the instant invention may contain additional compounding ingredients, such as conventional oxidation inhibitors, pour-point depressors and blooming agents.

The following examples further illustrate our invention:

Example I

About .6% by weight of the zinc salt of diisopropyl salicylic acid and 1.25% of the calcium salt of an oil-soluble petroleum sulfonic acid were dissolved in a S. A. E. 30, 30 V. I. furfural extracted California lubricating oil distillate. A sample of the resulting lubricating oil composition was found to be suitable for internal lubrication of Diesel engines, materially retarding ring sticking, and to have the advantage of the additives not settling out during use and of being substantially non-corrosive to the bearing metals.

To further study the corrosiveness of such an oil another sample was tested in a bearing testing machine. In this machine 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 disks 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 2520 R. P. M. The tests are run for 44 hours. The bearings are weighed before the test, after 20 and 44 hours of operation, and the loss of weight recorded.

The following results were obtained when testing different samples of oil:

	30 V. I., S. A. E. 30, oil compounded with additive	Loss of weight of copper-lead bearing				
		20 hours		44 hours		
		Mg.	Mg./sq. cm.	Mg.	Mg./sq. cm.	Comment
(A)	None	7	0.2	12	0.3	Non-corrosive.
(B)	1.2% zinc diisopropyl salicylate	64	1.6	93	2.4	
(C)	1.5% calcium petroleum sulfonate	8	0.2	32	0.8	
(D)	50% (B)+50% (C)	4.5	0.2	11	0.3	Do.
(E)	(C)+1% commercial corrosion inhibitor (Santolube 36)			80	2.0	

Example II

A sample of a SO_2-extracted clay-treated California lubricating oil distillate, containing dissolved 1% of calcium phenyl stearate, was blended in equal proportions with a SO_2-extracted clay-treated California distillate oil in which about 1% of a salt of calcium with an alkyl phenol was dissolved. The alkyl phenols employed in preparing the oil containing the calcium alkyl phenolate had a boiling range of 240° C. to 260° C. A sample of the resulting blend was found to be suitable for internal lubrication of Diesel engines, materially retarding ring sticking, substantially non-corrosive, and remaining sufficiently soluble during use so as not to settle out in the oil filter.

To determine the resistance of the phenolate towards decomposition under ordinary lubricating conditions in internal combustion engines, a sample of the above blend was mixed with water and blown with carbon dioxide. No precipitate of calcium carbonate was formed. When similarly treating an oil containing the calcium alkyl phenolate only, calcium carbonate was precipitated.

We claim as our invention:

1. An improved compounded mineral lubricating oil, comprising a mineral oil and dissolved therein a small amount of an oil-soluble normally corrosive calcium petroleum sulfonate and a small amount of a zinc salt of diisopropyl salicylic acid.

2. A substantially non-corrosive lubricating composition comprising a mineral oil and dissolved therein between about .3% and 2% by weight each of an oil-soluble salt of a polyvalent metal with a petroleum sulfonic acid and of a normally corrosive polyvalent metal salt of a hydroxy aromatic compound containing a carboxylic acid side chain.

3. A substantially non-corrosive lubricating composition comprising a mineral oil and dissolved therein between about .3% and 2% by weight each of an oil-soluble polyvalent metal salt of a sulfonic acid and of a normally corrosive polyvalent metal salt of an aromatic hydroxy compound.

4. A substantially non-corrosive lubricating composition comprising a mineral oil and dissolved therein between about .3% and 2% by weight each of an oil-soluble polyvalent metal salt of a sulfonic acid and of a normally corrosive oil-soluble polyvalent metal salt of an alkylated phenol.

5. A substantially non-corrosive lubricating composition comprising a mineral oil and dissolved therein between about 3% and 2% by weight each of an oil-soluble polyvalent metal salt of a petroleum sulfonic acid and of a normally corrosive polyvalent metal salt of an alkylated hydroxy thiophenol.

6. A substantially non-corrosive lubricating composition comprising a mineral oil and dissolved therein between about .3% and 2% by by weight each of an oil-soluble calcium petroleum sulfonate and of a normally corrosive oil-soluble salt of calcium with an aromatic hydroxy compound.

7. A substantially non-corrosive lubricating composition comprising a mineral oil and dissolved therein between about .3% and 2% by weight each of an oil-soluble calcium petroleum sulfonate and of a normally corrosive salt of a polyvalent metal of a hydroxy aromatic compound free from carboxylic acid groups.

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