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MINERAL LUBRICATING OIL

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This invention relates to improved lubricants and to a process for their preparation. More particularly, the invention pertains to the preparation of a novel class of compounds which are suitable for use as lubricants or, preferably, as addition agents to mineral lubricating oils. In one of its more specific embodiments, the invention covers a process for the preparation of certain compounds which, when added to a mineral lubricating oil, materially improve its properties, particularly when such compounded oils are used for the lubrication of engines of the compression ignition type.

As is well known, the usual mineral lubricating oils, when subjected to certain conditions of use, such as in internal combustion engines of the Diesel type and spark ignition engines wherein piston temperatures are very high, tend to form sticky carbonaceous deposits which over varying periods of use accumulate in the piston ring grooves, causing the rings to stick and become ineffective. This problem of the piston ring sticking has assumed considerable importance since the advent of high-speed Diesel engines, aviation gasoline engines, and the like. The principal reason for this ring sticking appears to be the lacquer and/or carbon formation during the use of the lubricating oils in such engines.

It has previously been discovered that this ring sticking action may be materially reduced by the addition to the oil of certain selected materials. Thus, it is known that certain naphthenic materials have been compounded with mineral lubricating oils and have been used with varying degrees of success either to inhibit the formation of or to maintain in solution or suspension those materials which lead to the phenomenon of ring sticking. These naphthenic compounds, however, have been found to be unsuitable when used with a certain type of lubricating oils. It is also known that the addition of small amounts of certain metal salts of alkylated aromatic hydroxy monocarboxylic acids in which the carboxylic acid radical is directly attached to the ring, preferably in the ortho position to the hydroxy radical, when added to mineral oils reduces ring sticking tendencies of mineral oils. However, many of the substances which are useful as antiring-sticking agents are difficult to dissolve in lubricating oils in effective quantities.

It is therefore the main object of the invention to obviate the above and other defects, and to provide a product or compound which possesses excellent lubricating properties and which, when added to mineral lubricating oils,

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is readily soluble therein in sufficient amounts to provide excellent antioxidant and/or detergent properties. It is a further object of the invention to provide a novel class of compounds which may be readily dispersed or dissolved in mineral lubricating oils, which compounds possess excellent antiring-sticking properties.

It has now been discovered that the above and other objects may be attained by using as a lubricant, or, preferably, as an addition agent to ordinary mineral lubricating oils, products or compounds which are prepared by heating a salt of a polyvalent metal and of an aromatic hydroxy carboxylic acid in solution or dispersion in a substantially non-polar or only weakly polar fluid, so that the salt decomposes, and continuing the heating until the decomposition products which precipitate (during this first decomposition) are substantially completely redissolved. If desired, these redissolved decomposition products of the above-mentioned salt or salts of a polyvalent metal and an aromatic hydroxy carboxylic acid may then be separated from the fluid medium. In the alternative, a part of the fluid medium may be removed to produce a concentrate of the decomposition product in the remaining part of the fluid medium. It has been discovered that these products of decomposition, when used as lubricants per se or as addition agents to ordinary-lubricating oils, e. g. mineral lubricating oils for internal combustion engines, are exceptionally effective in that the interiors of the cylinders of the engine lubricated thereby, particularly the cylinders of aircraft engines and Diesel engines, remain clean. Additionally, the presence of these novel decomposition products of salts of polyvalent metals and aromatic hydroxy carboxylic acids in lubricants for internal combustion engines prevents, or at least materially inhibits, the deposition of carbonaceous products on the pistons and in the piston ring grooves, and also inhibits the sticking of the piston rings. Furthermore, there is a material decrease in wear when the novel compounds of the present invention are employed as or in lubricants for the lubrication of the specified engines, this wear being normally caused by corrosion.

The salts which are employed as the starting materials for the preparation of the novel compounds possessing excellent antiring-sticking properties are the salts of polyvalent metals and of aromatic hydroxy carboxylic acids which latter may be mono- or poly-nuclear, such as benzoic and naphthoic acids. These acids may be substituted by alkyl, aryl, aralkyl or alkaryl radi-

cals, as well as by alkoxy, hydroxy, aroxy or amino groups which in turn may have other substituents, e. g. halogen atoms or hydrocarbon radicals. As stated, this class of acids comprises the mono- or poly-nuclear aromatic hydroxy carboxylic acids, examples of which are alkyl salicylic, ortho hydroxy naphthoic, or anthracene ortho hydroxy carboxylic acids. Suitable alkyl radicals are particularly those having three or more carbon atoms, examples of such radicals being n-propyl, isopropyl, butyl, amyl, cetyl, and like radicals. One or several monocarboxylic alkyl radicals may be attached to the nucleus. Of the polyvalent metals which may be used to form the salts the metals of the second, third, sixth and iron groups of the periodic table are suitable, examples of these metals being magnesium, calcium, strontium, barium, zinc, nickel, manganese, lead, copper, cobalt and aluminum. Of these metals, those of the second and third groups of the periodic table are preferable, calcium and zinc being typical examples of these metals.

The salts which most readily form the desired decomposition products according to the process of the present invention are those alkylated aromatic hydroxy monocarboxylic acid salts in which the carboxylic acid radical is in ortho position to the hydroxy radical. The best results are obtained with salts of salicylic acid substituted by the mentioned alkyl groups, the zinc and calcium salts of di-isopropyl salicylic acid being preferred embodiments.

It has been pointed out above that the conversion of the herein specified salts of polyvalent metals and of aromatic hydroxy carboxylic acids into the novel compounds which are particularly suitable as addition agents to mineral lubricating oils is preferably effected in the presence of a substantially non-polar fluid. It is preferable to employ as such medium a fluid which is stable at the elevated temperatures employed during the preparation of the compound, i. e. which does not decompose to any substantial degree at such temperatures. Also, in some instances, particularly when it is desired to separate the desired reaction product from such fluid medium, it is preferable, if not essential, to employ as the diluent or solvent a fluid which may be readily separated from the reaction product, e. g. by distillation at ordinary or subatmospheric pressure. Although the conversion according to the process of the present invention of the metal salts may be effected in the presence of any substantially non-polar or weakly polar fluid in which the salt is soluble or dispersible, it is generally preferable to employ as such fluid a hydrocarbon fraction which does not decompose to any substantial degree at the elevated temperatures employed in the decomposition step. For instance, the highly refined oils such as medicinal oils may be used. The conversion may also be effected in the presence of mineral lubricating oils, particularly when the product as such is used as the lubricant or is to be diluted with additional amounts of the same or other lubricating oils. If desired, the mineral oil may be removed from the reaction product of the metal salt, for instance by high vacuum distillation, which leaves the reaction product in the form of a solid substance. When the product has been prepared in a medium of a substantially non-polar or weakly polar fluid other than a mineral lubricating oil, which fluid, as stated, may be a paraffinic hydrocarbon fraction or a high molecular weight ether such as di-n-dodecyl ether, and when it is desired to obtain the substance from such fluid for use as such or for the purpose of adding it to a mineral lubricating oil fraction, it is then possible to separate the fluid medium in part or completely, e. g. by distillation, and to use the resulting solid substance as the antiring-sticking agent or addition product to mineral lubricating oils.

If the starting metal salt of the polyvalent metal and of the specified aromatic hydroxy carboxylic acids is not readily dispersible or soluble in the fluid in which it is decomposed and converted to the desired compound, it is frequently advisable to add to the mixture substances which will promote solution or dispersion of the metal salts. As such, reference is made to high molecular weight alcohols such as wool grease alcohols.

In order to produce the novel antiring-sticking compounds the mentioned salts of polyvalent metals and aromatic monocarboxylic acids, preferably in solution or suspension in substantially non-polar liquids, are subjected to elevated temperatures, preferably while maintaining the reagents in a state of agitation for example by stirring. This heating causes a decomposition of the open salt and the formation first of an internal or basic salt. Further heating, at higher temperatures, results in the decomposition of this internal salt. This latter decomposition is accompanied by the formation of a precipitate. When, however, the reaction product is subjected to still higher temperatures the precipitate is further decomposed producing a compound or compounds which are readily soluble in the solvent and particularly in mineral lubricating oils.

The novel reaction products of the decomposition of the specified salts of polyvalent metals and the aromatic hydroxy carboxylic acids have a relatively very high metal content and at the same time possess a very high solubility in hydrocarbon fractions, e. g. mineral lubricating oil. For instance, as will be pointed out in the examples set forth hereinbelow, the product formed by the decomposition according to the process of the present invention of the zinc salt of di-isopropyl salicylic acid contains not less than 30% of zinc, while the cobalt content of the reaction product obtained by the decomposition of the cobalt salt of di-isopropyl salicylic acid is in the neighborhood of about 21%. The exact composition of the novel compounds formed by the process of the present invention are not known at the present time since it is not seen how it is possible to formulate a compound in which all of the metal dissolving into oil may be bound in the conventional manner.

It has been pointed out that the heating of the starting salts is effected until the decomposition products which precipitate as a result of the first heating are further decomposed and become substantially completely redissolved. Generally speaking, this redissolving occurs at a temperature of about 300° C. Thus, when a mixture of one part by weight of the zinc salt of di-isopropyl salicylic acid and two parts by weight of a hydrocarbon, e. g. mineral lubricating oil, is subjected to heating, the salt at first becomes dissolved in the oil. However, at a temperature of about 230° C. there is noticed the formation of an insoluble decomposition product. At the same time substantial amounts of carbon dioxide are evolved. If the reaction is continued the precipitate thus formed is gradually redissolved so that at a temperature of about 300° C. no pre-

cipitate is noted, the metal salt reaction product (or products) being completely dissolved and in solution. If it is desired to recover this novel composition or compound, the mineral oil may be removed from this compound, for instance, by distillation under a high vacuum. The remaining material has a light yellow color and appears to be somewhat crystalline. When heated to about 150° C. it is miscible with mineral oil in substantially any proportions, and remains dissolved therein even when cooled to an ordinary temperature.

The following examples are presented to illustrate the preferred methods of preparation of the novel compounds possessing the above-mentioned antiring-sticking and other properties, as well as to illustrate the advantages obtained by using said compounds:

Example I

Twenty (20) parts by weight of the zinc salt of di-isopropyl salicylic acid and 80 parts by weight of a highly refined paraffinic hydrocarbon oil having a boiling temperature of between 80° C. and 170° C. at 0.05 mm. of mercury pressure, were placed in a container provided with a stirrer and a condenser. The solution was heated rapidly with stirring. At a temperature of about 200° C. the zinc salt began to dissolve and evolution of gas was noted. The solution of the salt was complete at about 200° C., but a solid precipitate began to appear again when the temperature was raised to about 225° C. With further heating additional amounts of precipitate deposited in the container. This thick paste, however, started to dissolve at about 290° C., the solution of the precipitate being complete at about 300° C. The reddish solution thus formed was further heated for about half an hour at the end of which time the evolution of gas ceased. The reaction mixture thus produced was then subjected to distillation under a vacuum to separate the di-isopropyl phenol. The remaining liquid, after filtration, was subjected to distillation to remove the solvent, and then further heated for purposes of purification. This zinc compound had a light yellow color, was somewhat crystalline and slightly hygroscopic.

Example II

Ten (10) parts by weight of the zinc salt of di-isopropyl salicylic acid and 40 parts by weight of an Edeleanu extracted mineral lubricating oil fraction were heated with stirring and in a current of nitrogen to a temperature of about 300° C., the latter temperature being maintained for about one-and-one-half hours. This results in the production of a clear solution soluble in any proportion in hydrocarbon oils. A mineral lubricating oil containing a small amount of the solution was found to be very effective in maintaining internal combustion engines very clean.

Example III

Ten (10) parts by weight of the zinc salt of di-isopropyl salicylic acid and 15 parts by weight of a highly refined paraffinic lubricating oil were heated rapidly in a current of nitrogen to a temperature of about 295° C. in a container provided with a stirrer and a reflux condenser, this heating being continued until the solution, which at first becomes cloudy or turbid, just clears. The zinc salt formed by this decomposition, when added to a mineral lubricating oil produced a compounded lubricant possessing excellent detergent and antiring-sticking properties.

Example IV

Ten (10) parts by weight of calcium salt of di-isopropyl salicylic acid, 45 parts by weight of a highly refined mineral oil having a boiling temperature of between 80° C. and 170° C. at 0.05 mm. mercury pressure, and 2.5 parts by weight of wool-grease alcohols were heated with stirring in a current of nitrogen. Solution was complete at 195° C. Vigorous evolution of gases occurred at between 210° C. and 220° C., the mixture being heated further to 300° C. and kept at this temperature for about three-quarters of an hour. The solution thus formed remained clear even upon cooling to 50° C. The mineral oil was distilled off under a high vacuum. The calcium content of the residue was found to be equal to 21.4%.

In order to determine the effect of the compounds produced according to the process of the present invention on the lubricating properties or characteristics of mineral lubricating oils, tests were effected in which an Edeleanu extracted mineral lubricating oil was subjected, both in the presence and absence of additives, to the so-called "spiral" test in which a stream of the oil is passed over a metal spiral maintained at an elevated temperature to determine the amount of residue which will adhere to the surface of such spiral. It was found that whereas the use of the undoped mineral lubricating oil resulted in an increase in weight of the spiral by 100 mg. and whereas a light oil containing 1% of the ordinary zinc salt of di-isopropyl salicylic acid, when subjected to the same test, increased the weight of the spiral by 25 mg., the addition of 1% of the zinc salt produced in accordance with the process described in Example I, increased the weight of the spiral by only 15 mg. while the addition of 1% of the compound produced in accordance with the process described in Example III resulted in a lubricating oil which when subjected to the same spiral test increased the weight of the spiral by only 10 mg. It is to be noted that the percentages of the additives set forth herein was calculated with respect to the metal content of the original di-isoproyl salicylate salt, and that in the above tests the greater the increase of the spiral the poorer is the oil in so far as its utility for lubricating internal combustion engines is concerned.

Example VI

A Pennsylvania neutral mineral lubricating oil was employed, both in the absence and presence of 1% of the dope produced in Example III, to an 18-hour test in a Caterpillar Diesel engine, the percentage of the dope being calculated with respect to the metal content of the starting zinc salt. The deposits found in the various parts of the engine are set forth in the following table:

Lubricant	Deposits (in g.)			
	1st groove	Other rings and grooves	Inside of Piston	Lands
Undoped Oil	0.27	0.12	0.15	0.13
Oil and 1% dope	0.09	0.05	0.09	0.09

Although in the above examples the additives of the present invention have been incorporated into the mineral lubricating oils in amounts of 1% (as calculated with respect to the metal content of the original metal salt of the aromatic hydroxy monocarboxylic acid subjected to treatment in ac-

cordance with the present process), these additives may be incorporated into the oils in various amounts. Generally speaking, most if not all of the compounds of the present invention possess the desired antiring-sticking and other properties even when added to lubricating oils in very small amounts, e. g. in the neighborhood of 0.1% by weight (as calculated on the basis of the metal content).

The invention claimed is:

1. A lubricating oil comprising a mineral lubricating oil containing dissolved therein .1% to 1% of an oil-soluble composition produced by subjecting the zinc salt of di-isopropyl salicylic acid in the presence of a stable hydrocarbon oil to a temperature of about 300° C. and for a period of time of from ¾ to 1½ hours sufficient to effect the substantially complete redissolving of the precipitate formed by the decomposition of the salt in said stable hydrocarbon oil.

2. The lubricating oil according to claim 1, wherein the oil-soluble additive is prepared in the presence of a mineral lubricating oil.

3. The lubricating oil according to claim 1, wherein the oil-soluble additive is prepared in the presence of a highly refined mineral oil having a boiling range of between about 80° C. and about 170° C. at 0.05 mm. mercury pressure, and wherein said additive is separated from its solution in said highly refined mineral oil prior to incorporation into the mineral lubricating oil.

4. A lubricating oil composition comprising a mineral lubricating oil containing dissolved therein .1% to 1% of an oil-soluble composition produced by subjecting the zinc salt of an alkyl-substituted salicylic acid said alkyl radical containing from about 3 to about 16 carbon atoms, in the presence of a substantially non-polar fluid, to a temperature of about 300° C. for from ¾ to 1½ hours until the precipitate formed by the decomposition of the salt is substantially completely redissolved in said non-polar fluid.

5. A lubricating oil comprising a mineral lubricating oil containing dissolved therein .1% to 1% of an oil-soluble composition produced by subjecting the cobalt salt of di-isopropyl salicylic acid in the presence of a substantially non-polar stable fluid to a temperature of about 300° C. until the precipitate formed by the decomposition of the salt is substantially completely redissolved in said non-polar fluid medium.

6. A lubricant comprising a mineral lubricating oil containing dissolved therein .1% to 1% of an oil-soluble compound produced by subjecting a salt of a polyvalent metal of the group consisting of the second, third, sixth and iron groups of the periodic table and of an alkyl-substituted salicylic acid said alkyl radical containing from about 3 to about 16 carbon atoms, in the presence of a stable substantially non-polar fluid medium, to an elevated temperature of from 290 to 300° C. for from ¾ to 1½ hours and for a period of time sufficient to effect the substantially complete redissolving in said non-polar fluid of the precipitate formed by the thermal decomposition of the salt.

7. A lubricant comprising a mineral lubricating oil containing dissolved therein .1% to 1% of an oil-soluble salt produced by subjecting a salt of a polyvalent metal of the group consisting of the second, third, sixth and iron groups of the periodic table and of an aromatic hydroxy monocarboxylic acid in which the carboxylic radical is in ortho position to the hydroxy radical, in the presence of a stable substantially non-polar fluid medium, to an elevated temperature of from 290 to 300° C. for from ¾ to 1½ hours for a period of time sufficient to effect substantial redissolving in the non-polar fluid medium of the precipitate formed by the thermal decomposition of the salt.

8. A lubricant comprising a mineral lubricating oil containing dissolved therein .1% to 1% of oil-soluble salt produced by subjecting a salt of a polyvalent metal of the group consisting of the second, third, sixth and iron groups of the periodic table and of an hydroxy aromatic monocarboxylic acid, in the presence of a stable substantially non-polar fluid to an elevated temperature of from 290 to 300° C. for from ¾ to 1½ hours until the precipitate formed by the decomposition of said salt is substantially redissolved in said stable substantially non-polar fluid medium.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,477,913 August 2, 1949

MINTJE VAN LOON

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 7, line 48, after "300° C." insert the words *for from ¾ to 1½ hours;*

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of February, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

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