

UNITED STATES PATENT OFFICE

2,380,685

ESTERS OF SALICYLIC ACID MONO-SULPHIDE AND SALTS THEREOF

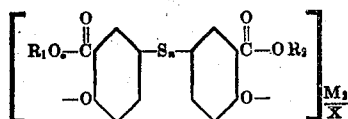
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8 Claims. (Cl. 260-470)

This invention relates to new organic compounds, particularly useful as additives to lubricants because of the detergent, anti-corrosion, film-forming and other valuable properties which they exhibit when dispersed therein, and to their preparation.

The new compounds of our invention to be described and claimed herein may be designated as polyvalent metal salts of alkyl or cycloalkyl salicylate sulphides having the general formula



in which R₁ and R₂ are alkyl or cycloalkyl radicals having 4 or more carbon atoms, n is a positive integer not more than 2, M is a polyvalent metal radical and X is the valence of M.

Although these compounds are useful as foam depressants, fungicides, oxidation inhibitors, etc., they are particularly valuable as additives to lubricating oils used in heavy duty service and under extreme pressure conditions because of the unique detergent, anti-corrosion, film-forming and other properties which they possess. When conventional hydrocarbon lubricating oils are subjected to high operating temperatures for long periods of time, as in heavy duty service, they tend to decompose with the formation of complex oxidation and decomposition products. The acidic oxidation products corrode certain alloy bearings such as copper-lead, silver-cadmium, nickel-cadmium, etc., which are commonly employed in internal combustion engines. These decomposition products also tend to polymerize under the high temperature conditions obtaining in the engine to form sludge which precipitates when the engine is cooled or when fresh oil is added. The precipitated sludge clogs the oil filter and becomes caked on heated metal surfaces to form lacquer-like deposits which may cause the piston rings or even the piston itself to stick.

Attempts have been made to overcome these deficiencies of the lubricating oil by the addition of detergents or anti-corrosion agents, or both. Certain anti-corrosion agents, such as triphenyl phosphite and sulphurized sperm oil, counteract the corrosive effect of the oxidation products formed in the oil. These anti-corrosion agents have no detergent properties, however, and while they cover the bearing surfaces and other corrodable parts of the engine with a passivating

film that prevents corrosion of the metal by the organic acids of the oil, they do not act to disperse the sludge or prevent the formation of the varnish deposits mentioned above.

A number of oil-soluble detergents of the type of metal soaps, phenolates and alcoholates have been proposed and used in crankcase oils to dissolve or disperse the sludge and prevent varnish deposits and piston ring sticking. Unfortunately, however, the greater majority of these substances increase the rate of oxidation in a manner somewhat analogous to the accelerating action of the various metallic soaps or "driers" on the oxidation of varnish films, and their presence results in an increased concentration of acidic oxidation products in the oil. When individual detergents and anti-corrosion agents are used together in the oil the two separate chemicals do not cooperate to reduce corrosion and sludge and varnish formation. The lack of cooperative effect is believed to be due to the action of the detergent in removing from the metal surfaces the passivating film of anti-corrosion agent which is supposed to cover the metal surface and thereby prevent corrosion.

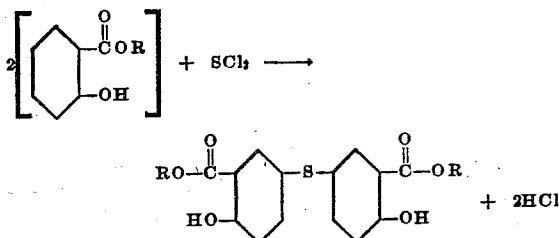
The compounds of the present invention show both excellent detergent and excellent anti-corrosive action when dispersed in lubricating oils and thereby enable us to provide a lubricating oil having a single additive effective to inhibit corrosion, sludge and varnish formation, ring sticking and other difficulties experienced in lubricating oils serving in a heavy duty capacity. The addition of our compounds to lubricating oils also imparts to the oil a high film strength thus enabling the oil to be used under extreme pressure conditions under which the film formed by conventional oils would break and result in seizing of the bearing surfaces.

The extremely high solubility of these compounds in hydrocarbon oils leads to another important advantage, namely, the ease with which they are blended with lubricating oils. This step is further simplified by our practice of dissolving them in ordinary types of lubricating oils to the extent of 50% or more for storage and shipping purposes.

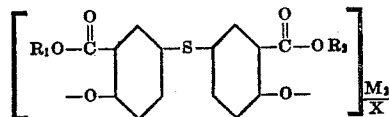
Another advantage to be obtained by the use of our alkyl and cycloalkyl salicylate sulphides is their solubilizing action on certain materials which are known to be good detergents, anti-oxidants, etc., or have good corrosion inhibiting properties but which cannot normally be used in high concentrations on account of their oil insolubility. Certain dithiophosphates, such as

di(para-tertiary amyl phenyl) dithiophosphate; calcium, barium, aluminum, zinc, and magnesium stearates, palmitates, naphthenates, etc., are difficultly soluble in lubricating oils, but because of their solubility in the compounds described herein, it is possible to add them to oils in this way in amounts sufficiently large for them to be effective.

The compounds of the present invention may be prepared by reacting an aliphatic or cyclo-aliphatic ester of salicylic acid with sulphur chloride (S_2Cl_2), sulphur di-chloride (SCl_2), or thionyl chloride (SOCl_2) in the presence of Cu, depending upon whether a mono-sulphide or di-sulphide is desired as the reaction product. We prefer the mono-sulphide compounds because of their greater chemical stability. The monosulphides are prepared by reacting approximately 2 mols of an aliphatic or cyclo-aliphatic ester of salicylic acid with 1 mol of sulphur dichloride in the presence of a small amount, for example 0.2 mol, of anhydrous AlCl_3 as catalyst. Other Friedel-Crafts catalysts, such as SbCl_5 , FeCl_3 , TeCl_4 , SnCl_4 , TiCl_4 , ZnCl_2 and BiCl_3 may also be employed as catalysts in our reaction, but with decreasingly effective results. The disulphides are prepared in the same manner by substituting sulphur chloride in place of sulphur dichloride. The reaction may be illustrated as follows:



The product illustrated is then treated with a metal oxide or hydroxide to prepare salts having the general formula:



in which R_1 , R_2 , M and X are as indicated in the general formula described above.

The metal radicals which we introduce into our alkyl or cycloalkyl salicylate sulphides to form salts thereof, include metal radicals such as aluminum, lead, magnesium, zinc, calcium, barium, strontium, etc. The metal salts of our invention may be prepared by simply neutralizing the alkyl or cycloalkyl salicylate sulphides with an appropriate metal oxide or hydroxide or, if desired, by methods of double decomposition. For purposes of improving lubricants we prefer to employ the alkaline earth metal salts since they possess greater detergency and heat stability.

The salicylic acid ester employed in the above reaction should be an ester of an aliphatic or cyclo-aliphatic alcohol having at least 4 carbon atoms so that R_1 and R_2 in the general formula may be alkyl or cycloalkyl radicals of at least 4 carbon atoms. The size of the alkyl or cycloalkyl radical is important in that the higher molecular weight radicals promote the solubility of our compounds in lubricating oils and the radicals should be of at least the size indicated in order that our compounds may be dissolved in the lubricant without undue difficulty. R_1 and R_2 may therefore be alkyl radicals such as butyl, normal amyl,

tertiary amyl, ethyl hexyl, normal octyl, decyl, dodecyl, hexadecyl, octadecyl, etc., or cyclo-aliphatic radicals such as cyclo-pentyl; cyclo-hexyl, methyl, ethyl, propyl, butyl, and amyl, mono-, di-, and tri-substituted cyclo hexyl radicals, etc.

Ordinarily we carry out the reaction with the reactants dissolved in a suitable solvent such as carbon disulphide, ethylene chloride, petroleum naphtha, nitrobenzene, etc. The reaction mixture with a catalyst present is then heated until the evolution of HCl has substantially stopped. The mixture is then treated with cool dilute hydrochloric acid or other acids such as sulphuric, acetic, etc., and the product recovered by extraction with toluene or other solvents. The product can be further purified by washing with water in which it is insoluble and the solvents removed by evaporation.

It will be understood, of course, that the preparation of the disulphide with sulphur chloride proceeds in the same way under the same reaction conditions. It will also be understood that the cyclo-aliphatic esters of salicylic acid may be employed in place of the aliphatic esters of salicylic acid illustrated in the above illustration in the same manner and using the same molecular proportions.

The preparation of representative compounds of the present invention will now be described in detail in the following examples in which particular parts of the reactants, catalysts, solvents, etc., are indicated merely for purposes of illustration. It will also be understood that our invention is not to be limited to the particular compounds described since as stated above the invention is of broader scope and is to be limited only by the scope of the appended claims. The parts indicated are by weight.

Example 1

150 parts by weight of dodecyl (lauryl) salicylate was condensed with 24 parts of sulphur dichloride in 30 parts of A. S. T. M. naphtha in the presence of 8 parts of AlCl_3 as catalyst. Condensation was carried out by warming the reaction mixture on a steam bath between 60–70° C. with stirring for 30 minutes. The reaction mixture was then cooled and diluted with cold dilute hydrochloric acid, extracted with toluene, washed and the solvent evaporated. Dodecyl salicylate monosulphide was removed as a brownish-yellow liquid.

The barium salt of dodecyl salicylate monosulphide was prepared by neutralizing 40 parts of dodecyl salicylate monosulphide with 18 parts of barium hydrate in a solution of 20 parts of ethyl alcohol and 16 parts of toluene with stirring at 70° C. As the solvent evaporated fresh toluene was added from time to time and the heating increased to a temperature of 110° C. The solution was then filtered from traces of inorganic salts and then evaporated, the last of the solvent being evaporated under reduced pressure. 55 parts of barium dodecyl salicylate monosulphide was obtained which was dissolved in an equal amount of lubricating oil for storage and blending purposes.

Example 2

To 140 parts by weight of decylsalicylate in 140 parts by weight of ethylene trichloride was added 10 parts by weight of anhydrous aluminum chloride. Then, with stirring, 29 parts by weight of sulphur dichloride was slowly added during the course of one-half hour while the reaction mixture was maintained at 40–50° C. When the addi-

tion of all reactants was complete the solution was warmed slowly to 75° C., cooled and stirred with dilute hydrochloric acid, the latter being run in slowly. The water layer was discarded and the lower layer washed once with warm water before being vacuum dried. The product was a light colored liquid.

To 78 parts by weight of decylsalicylate-monosulphide was added 45 parts by weight of barium hydroxide octahydrate, 100 parts by weight of toluene and 100 parts by weight of butanol. The mixture was stirred and distilled at atmospheric pressure, keeping the toluene concentration constant by replacing it as it distilled, until no more water was recovered in the distillate. The inorganic salts were filtered from the solution and the solvents removed by vacuum distillation. The product, the barium salt of n-decylsalicylate-monosulphide, was a brown, wax-like solid having an indefinite melting point. It was easily soluble in toluene but insoluble in water.

Example 3

To 138 parts by weight of n-hexylsalicylate was added an equal weight of ethylene trichloride and 10 parts by weight of anhydrous aluminum chloride. Into this well-stirred mixture was dropped 34 parts by weight of sulphur dichloride at 30° C. When the addition was completed, the solution was warmed slowly to 60° C., cooled and treated with an excess of dilute hydrochloric acid. The water layer was discarded, the lower layer washed once with warm water and then the solvents removed in vacuo.

To 60 parts by weight of hexylsalicylate monosulphide, prepared as just described, was added 17 parts by weight of calcium hydroxide, 120 parts by weight of toluene and 75 parts by weight of butanol. This mixture was stirred and distilled to remove water formed during the reaction. The toluene was replaced in the reaction flask as the distillation progressed. When the reaction was complete, as evidenced by absence of additional water in the distillate, the solids were removed by filtration and the solvents by vacuum distillation, leaving the calcium salt of n-hexylsalicylate monosulphide, a brown solid.

Example 4

To a mixture of 100 parts by weight of n-hexylsalicylate and 100 parts by weight of octadecylsalicylate in 200 parts by weight of ethylene dichloride was added 5 parts by weight of anhydrous aluminum chloride. The flask temperature was maintained at about 50° C. while 36 parts by weight of sulphur dichloride was added, dropwise. The solution was then warmed to 60° C. for a half hour, cooled, and treated with an excess of dilute hydrochloric acid. The acid layer was discarded and the ethylene dichloride layer washed once with warm water. The solvents were removed in vacuo leaving the n-hexyl-octadecylsalicylate as a reddish brown oil. It was diluted with 150 parts by weight of toluene and 150 parts by weight of butanol after the addition of 30 parts by weight of calcium hydroxide. The mixture was stirred in a flask heated by an oil bath while the solvents distilled together with the water formed by the reaction. The toluene was replaced from time to time. When the reaction was complete, the solids were removed by filtration and the solvents removed in vacuo to give the calcium salt of n-hexyl-octadecylsalicylate monosulphide, a brown wax-like solid.

Example 5

To a solution of 110 parts by weight of cyclohexylsalicylate in an equal weight of trichloroethylene was added five parts by weight of anhydrous aluminum chloride. Into this mixture was dropped with stirring thirty parts by weight of sulphur dichloride. The temperature of the reaction was kept between 40–50° C. during the addition of sulphur dichloride. When addition was over, the temperature was raised slowly to 60° C. to complete the reaction. When the mixture had cooled, dilute hydrochloric acid was poured in and, after thorough mixing, the water layer was discarded. The ethylene trichloride solution was washed with warm water and the solvent was then removed by vacuum distillation to give a reddish brown liquid, cyclohexylsalicylate monosulphide.

To a solution of 105 parts by weight of cyclohexylsalicylate monosulphide in 100 parts by weight of toluene and forty parts by weight of n-butanol was added 19 parts by weight of calcium hydroxide. The reaction mixture was stirred and distilled at atmospheric pressure. Fresh toluene was added to the reaction mixture to replace the distillate and the distillation was continued until no more water was recovered. The undistilled mixture was then filtered to remove inorganic salts and the remaining n-butanol and toluene removed in vacuo. There remained in the calcium salt of cyclohexylsalicylate monosulphide, a brownish solid.

The compounds as described above are heat stable and not easily decomposed in the lubricant because of high operating temperatures which may be encountered. They are also practically water-insoluble and are not extracted from the lubricant by contact with water nor do they appreciably promote the formation of emulsions with water in the oil.

The polyvalent metal salts of alkyl and cycloalkyl salicylate sulphides are so very effective as detergents and as corrosion inhibitors that it is possible to improve lubricating oils, particularly those of the crankcase type, to a great extent by the use of very small amounts of the compound. In lubricating oils intended for ordinary purposes where high temperatures occur only occasionally, from 0.1 to 0.8% of the metal salt of the alkyl or cycloalkyl salicylate monosulphide is sufficient. In extreme pressure lubricants and in oils intended for heavy duty service, it is generally advisable to use a little more, as for example 0.5 to 3.0% of the oil.

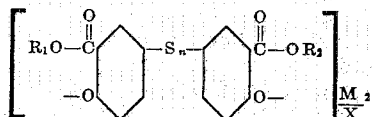
The effectiveness of our compounds in lubricating oils as corrosion inhibitors, detergents and anti-oxidants was demonstrated by the results obtained upon subjecting a No. 30-W grade Mid-Continent solvent refined oil to the Catalytic Indiana test. This test was conducted in an apparatus consisting of a number of large glass test tubes immersed in a constant temperature bath maintained at 341° F. 300 cc. samples of the oil containing dispersed therein 0.4% of barium dodecyl salicylate monosulphide were poured into the tubes and air passed through the oil at the rate of 10 liters per hour. In order to simulate the conditions prevailing in the crankcase of an engine, weighed strips of copper-lead alloy were suspended in the oil. A test tube containing a sample of the same oil without benefit of the barium dodecyl salicylate monosulphide additive was used as a control. After subjecting the oil to the test for 70 hours, the copper-lead alloy strips were removed, washed and weighed.

The copper-lead immersed in the lubricating oil containing no additive showed a bearing loss of 275 mg. per sq. inch. The copper-lead strips immersed in the lubricating oil containing 0.4% of barium lauryl salicylate monosulphide showed, at the end of the 70 hour test, no corrosion loss whatever. After pouring out the oil and rinsing once with kerosene, the two test tubes which had contained the oil with the barium dodecyl salicylate monosulphide additive was very clean, thus indicating that the oil with the additive had a high degree of detergency. The tube containing the oil without additive was very dirty. This test indicated clearly the remarkable corrosion inhibiting and detergent effects of our compounds in lubricating oils.

This a continuation-in-part of our co-pending application, Ser. No. 454,982, filed August 15, 1942.

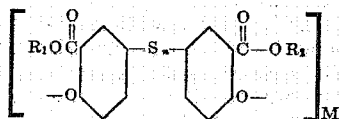
We claim:

1. Chemical compounds having the general formula



in which R₁ and R₂ are members of the group consisting of alkyl and cycloalkyl radicals having at least 4 carbon atoms, *n* is a positive integer not more than 2, M is a polyvalent metal radical and X is the valence of M.

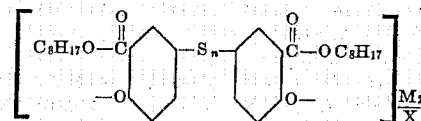
2. Chemical compounds having the general formula



in which R₁ and R₂ are alkyl or cycloalkyl radi-

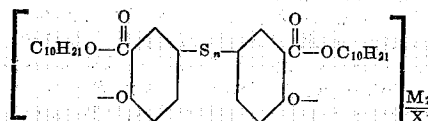
cals having at least 4 carbon atoms, and M is an alkaline earth metal radical.

3. Chemical compounds having the general formula



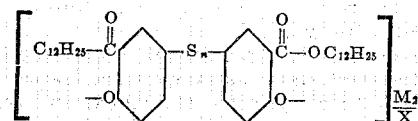
in which *n* is a positive integer not more than 2, M is a polyvalent metal radical and X is the valence of M.

4. Chemical compounds having the general formula



in which *n* is a positive integer not more than 2, M is a polyvalent metal radical and X is the valence of M.

5. Chemical compounds having the general formula



in which *n* is a positive integer not more than 2, M is a polyvalent metal radical and X is the valence of M.

6. Barium octyl salicylate monosulphide.

7. Barium decyl salicylate monosulphide.

8. Barium dodecyl salicylate monosulphide.

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