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2,744,069

COMPOUNDED LUBRICATING COMPOSITIONS

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This invention relates to compounded lubricating compositions. More particularly it deals with mineral lubricating oil compositions containing alkyl phenates, alkyl salicylates and mixtures thereof, as well as to such salts themselves and their preparation.

The addition of various types of metal derivatives of organic compounds to lubricating oils is known and practiced to minimize various deleterious effects of operating internal combustion engines. Thus, various additives which exhibit detergent action in engines are used to minimize deposition of lacquers, resins, carbonaceous materials, and the like, on the engine parts. Basic compounds, such as basic metal compounds, have been used to provide a base reserve to neutralize acidic compounds. Various metal compounds which have been used for such purposes include the metal derivatives of such organic compounds as fatty acids, naphthenic acids, alcohols, phenols, ketones and the like, and where available corresponding basic or hydroxy salts thereof, instead of the neutral (normal) salt, wherein the metal is a polyvalent metal compound.

In some cases, the basic salts are preferred because they retain their activity in lubricating oils longer than do the neutral salts. This may be because sulfur trioxide and other acidic sulfurous gases are formed and converted into sulfuric acid, etc., by the water present in the combustion gases. As a result of this the organic acid radicals of metal organic salts in the lubricating oil would be converted to their corresponding organic acids. These acids have no beneficial effect, but on the contrary may in some cases even contribute to corrosion of the metal parts of the engine or to ring sticking difficulties and the like. When basic salts are added to the lubricating oil, inorganic acids with which they come in contact are neutralized by the conversion of the basic salts to the neutral salts before the latter are converted to the free organic acids.

It is also known that calcium and other polyvalent metal salts of alkyl phenols are beneficial as additives to lubricating oils. The normal (i. e., non-basic) phenates, however, possess the disadvantage of rapid acidification, as mentioned above, thereby soon becoming ineffective. Furthermore, all processes for their preparation heretofore known have involved various difficulties. It has been generally necessary to carry out these methods in the complete absence of water, and/or by the use of expensive starting materials and catalysts. For example, the Denison et al. patent, U. S. 2,228,654 requires a carbide of a metal as a starting material and a non-aqueous environment; the French Patent No. 862,357 requires a medium of absolute alcohol; the Gardiner patent, U. S. 2,211,972, discloses the preparation of an aluminum alkyl phenate using elemental aluminum metal and an iodine catalyst; and the Reiff patent, U. S. 2,197,833, discloses the use of a metallic alkyl metal, or metal alcoholate, or litharge in the presence of a non-oxidizing gas, or anhydrous aluminum chloride. Thus, it may be seen that in spite of intensive effort in this field, heretofore, a con-

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venient and inexpensive method for the preparation of polyvalent metal alkyl phenates has not been developed.

It is also known that calcium and other polyvalent metal salts of alkyl salicylic acids have been used as engine oil detergent addition agents, and corresponding basic (hydroxy) salts have been used additionally for their reserve basicity as neutralizing agents for acidic bodies in the lubricant, regardless of their source. However, previously known methods for their preparation have been able to obtain, at most, a metal content only 50% greater than that which corresponds to the neutral salt.

It is an object of the present invention to provide a new, effective and inexpensive class of addition agents for oils which are to be used as crankcase lubricants for internal combustion engines and which exhibit to a high degree the desirable properties of inhibiting the development of corrosivity in the oil, of improving oxidation stability of the oil, of promoting general engine cleanliness and reducing ring sticking, piston skirt varnish formation and the like, and which exhibit these desirable properties over an extended length of time and under adverse conditions. Another object is to provide an improved highly basic mixture of polyvalent metal alkyl phenates and polyvalent metal alkyl salicylates. Still another object is to provide a simple, direct and inexpensive method for the preparation of such a mixture. A further object is to provide an improved, simple, direct and inexpensive method for the preparation of polyvalent metal alkyl phenates. A still further object is to provide a method for the preparation of very highly basic polyvalent metal alkyl salicylates. Other objects will be apparent from the following description of the invention.

Now, in accordance with the present invention, there is provided an improved oil composition comprising a major proportion of a lubricating oil and a small amount of a mixture comprising an unsubstituted alkyl phenate of a group II metal with an atomic number of from 12 to 56, which phenate contains only alkyl substituents and they contain from 8 to 26 carbon atoms, and an unsubstituted alkyl salicylate of a group II metal with an atomic number from 12 to 56, which salicylate contains only alkyl substituents and they contain from 8 to 26 carbon atoms, and which mixture has a basicity greater than 100% based on the salicylate content of the mixture, and a weight content of salicylate at least equal to that of the phenate.

The term "basicity," as used herein, is defined as the excess of polyvalent metal in the total of the salicylates and phenates (or phenols) over that quantity of polyvalent metal which would be present in the normal (non-basic) salicylates alone. Thus a mixture of 0% basicity would denote a mixture containing the polyvalent metal only in the form of the normal salicylate and a mixture of 100% basicity would denote a mixture containing twice as many equivalents of the polyvalent metal as the number of equivalents of carboxylate in the mixture. If the content of polyvalent metal in a particular mixture is (a) % by weight, and if the content of polyvalent metal the mixture would have if it were present only as the normal salicylate is (b) % by weight then the basicity of the mixture is

$$\frac{(a)-(b)}{(b)} \times 100\%$$

This definition of basicity is related to the salicylates for several important reasons. Firstly, any polyvalent metal in the form of a phenate contributes to the "reserve basicity" of the lubricating oil composition because phenols are relatively weak acids, their salts being easily hydrolyzed. Therefore, any reaction between sulfur acids produced in the combustion process and a mixture of phenates and salicylates will result in the formation of

the relatively innocuous free alkyl phenols to the exhaustion of the phenates before any of the relatively pernicious free salicylic acids are formed. Secondly, whenever a mixture of free alkyl salicylic acids and alkyl phenols are directly treated with an excess of an oxide or hydroxide of a polyvalent metal, only the alkyl salicylic acids are converted into a mixture of neutral and basic salts while the alkyl phenols remain unconverted. Moreover in a mixture of alkyl salicylic acids and alkyl phenols, only the former contribute to the acid number of the mixture.

The new compositions which are the subject of this invention and which are defined in part to contain at least as much salicylate as phenate and the basicity of which is at least 100% as defined above, therefore contain the polyvalent metal in a proportion greater than that which would correspond to a mixture of normal polyvalent metal phenates and normal polyvalent metal salicylates. It should be noted that whenever reference is made herein to a metal salicylate, the term refers to a salicylate wherein the metal is attached to the carboxylate group with the complete replacement of its ionizable hydrogen. Whether the formation of a basic salicylate involves the replacement of the hydrogen of the hydroxy group by a valence of the metal, or whether the basicity is due to the presence of a hydroxy group attached directly to the metal, is not known and, in view of the preceding definition of basicity, is considered immaterial from the standpoint of the effectiveness of the compositions of the present invention.

The terms unsubstituted alkyl phenates and unsubstituted alkyl salicylates refer to the simple mono-cyclic compounds which contain only alkyl substituents and only the elements carbon, hydrogen and oxygen in addition to the metal and wherein the alkyl groups are attached directly to the ring.

The novel highly basic mixtures of polyvalent metal alkyl phenates and polyvalent metal alkyl salicylates of the present invention are conveniently prepared by converting a mixture of alkali metal alkyl salicylates and alkali metal alkyl phenates directly to the corresponding polyvalent metal salts. The alkali metal salt mixture is treated with a quantity of an inorganic salt of a polyvalent metal, which is at least approximately stoichiometrically equivalent to the total alkali metal content of the initial mixture, and with a quantity of a polyvalent metal base (an oxide or its hydrate, which will be equivalent for this purpose) which is at least 90% of the quantity stoichiometrically required for the formation of the mono-basic polyvalent metal alkyl salicylates. The salt and the oxide are applied in the form of alcoholic solutions containing from 1 to 10% of water based on the alcohol. These solutions may be applied separately in a two-step procedure, or they may be applied together in a single-step procedure. There may be diluents present such as xylenes or pentane or any other unreactive non-aqueous solvent.

In connection with the method of preparation of the mixtures of the present invention, it should be noted that it is known to prepare polyvalent metal alkyl salicylates from mixtures of alkali metal alkyl phenates and alkali metal alkyl salicylates. The British Patent No. 586,461 describes such a process: phenol is first alkylated with a mixture of octenes and nonenes, after which the alkyl phenols formed are converted into the sodium compounds and the sodium alkyl phenates are subsequently treated with carbon dioxide to form a mixture of the corresponding sodium alkyl salicylates and unconverted sodium alkyl phenates in accordance with the well-known Kolbe-Schmitt reaction. The mixture of sodium alkyl phenates and sodium alkyl salicylates is then converted to free alkyl phenols and free salicylic acid by acidification with hydrochloric acid. The resulting acidified mixture is then treated with an aqueous solution containing a quantity of

sodium hydroxide and a quantity of calcium chloride which are equivalent to the salicylic acid (carboxyl) content of the mixture. The resulting product is then a mixture of normal calcium alkyl salicylates and free alkyl phenols.

The disadvantages of such a process are obvious. The acidification step is necessary because without it the product would be a mixture of sodium alkyl phenates and calcium alkyl salicylates since the sodium alkyl phenates are not converted to the calcium alkyl phenates in the subsequent treatment with aqueous base and calcium chloride. The sodium alkyl phenates are well known to be undesirable constituents of a lubricating oil. Nevertheless, even with the acidification step, the resulting product is diluted with substantial quantities of free alkyl phenols which contribute no desirable characteristic to the lubricating oil to which the mixture is added.

The process by which the compositions of the present invention are prepared not only results in a new and superior product in that a greater proportion of the polyvalent metal is introduced, but additionally, it is simpler and more direct than that of the British patent.

The fact that the content of polyvalent metal may be even greater than that corresponding to a basicity of 100% may be explained by various factors. In the first place, as has already been indicated, there is an actual conversion of the alkali metal alkyl phenates to polyvalent metal alkyl phenates in the process of this invention. Secondly, this process may involve peptization of free polyvalent metal oxide or hydroxide, thereby increasing the basicity of the mixture. This possibility is wholly advantageous because no precipitation will occur even when the product is very greatly diluted in the finished lubricating oil composition. And finally, by this process the alkali metal alkyl salicylates themselves are converted into basic salts of the polyvalent metal to a much greater extent than when the initial mixture is acidified and subsequently treated as in the process of the British patent.

The process of this invention is applicable in the preparation of polyvalent metal alkyl phenates per se. In contradistinction to the Denison, Gardiner, Reiff and French patents mentioned hereinbefore, the present process is simple and direct and does not require rigid precautions for the exclusion of water from the reacting mass, or the use of expensive starting materials or expensive or hazardous catalyst. For this purpose the addition of the polyvalent metal oxide is unnecessary, as will be shown, because the presence of the salicylates with calcium chloride alone is sufficient for the complete conversion of the alkali metal alkyl phenates to the polyvalent metal alkyl phenates. The polyvalent metal alkyl phenates and/or the polyvalent metal alkyl salicylates, including the highly basic salicylates, may readily be recovered from their mixtures by chromatography or any other of the numerous well known separation techniques which will be determined applicable by those practiced in the art.

Although it is by no means intended to limit the invention other than as defined in the claims, the process of preparing the highly basic mixture of polyvalent metal alkyl phenates and polyvalent metal alkyl salicylates will be exemplified below for the case in which the initial mixture is converted into the basic calcium mixture by means of calcium chloride and calcium oxide. This description will serve as a typical example and the extension of the process to other polyvalent metals, solvents, etc., will thereby be immediately evident to those familiar with the art.

The calcium chloride used for conversion of the initial mixture of alkali metal alkyl phenates and alkali metal alkyl salicylates is applied in the form of a solution in a monohydric, water-miscible, aliphatic alcohol containing from 1 to 5 carbon atoms and from 1 to 10% by weight of water, based on the alcohol. The conversion can be carried out either by first treating the initial mixture with calcium chloride and by adding a calcium base to the

reaction mixture after the salicylates and phenolates of the initial mixture have been converted into the corresponding calcium compounds, or by simultaneously reacting the initial mixture with calcium chloride and the calcium base, such as calcium oxide.

The calcium oxide required for the reaction is suspended in the alcohol. It is also possible to add an alcoholic solution of sodium hydroxide or potassium hydroxide to the alcoholic calcium chloride solution, whereby the calcium oxide, in hydrated form, is formed in situ in a finely dispersed state. In this case the quantity of calcium chloride and the quantity of sodium hydroxide or potassium hydroxide are selected in such a way that the non-converted quantity of calcium chloride and the quantity of calcium oxide formed are the quantities required for the reaction. It is possible and advantageous to add the alcoholic sodium hydroxide or potassium hydroxide solution to the reaction mixture gradually, after the conversion of the initial mixture with aqueous alcoholic calcium chloride has taken place. The further conversion of the mixture into the basic product is then effected by the calcium oxide which is formed in situ with the added alcoholic caustic alkali solution.

As has been already mentioned, for the purposes of this invention the polyvalent metal oxide and its hydrate, the metal hydroxide, are essentially equivalent, and wherever a polyvalent metal oxide is mentioned, the term will be understood to include its hydrate. In some cases the use of calcium oxide results in a product with a higher basicity than does the use of its hydrate. Whether the dry or hydrated calcium oxide is selected in a particular case will depend upon a number of exterior considerations, such as availability, method of addition to the reacting mass, etc. It has been found, however, that when dry calcium oxide is to be used, it is preferable to select a form of that material which is readily reactive with water. A particularly reactive form can, for example, be obtained by heating the hydrate of the oxide for a few hours, say 4 to 8 hours, at about 700 to 750 degrees centigrade.

The initial mixture of alkali metal alkyl phenates and salicylates may further contain a diluent such as xylene or pentane or any other unreactive non-aqueous solvent and be processed in this diluted form.

The reaction of the initial mixture with calcium chloride and calcium oxide or calcium hydroxide generally proceeds smoothly at temperatures of from 70 to 110° C. The upper limit of the reaction temperature is determined by the boiling point of the liquid in which the reaction components have been dissolved or suspended. If the reaction is carried out under pressure, temperatures may be applied which are higher than the normal boiling point of the liquid. This may be particularly advantageous in many cases. The reaction mixture can also be heated in a vessel provided with a reflux condenser, so that the liquid evaporated from the reaction mixture is again recycled to the mixture.

A particularly advantageous embodiment of the process consists in gradually distilling off the alcohol from the reaction mixture during the reaction. In order to retard the distillation of the alcohol during the reaction, a part of the evaporated alcohol can again be added to the reaction mixture by applying the reflux process. If desired, the alcohol may also be distilled off from the reaction mixture at a greater rate during the reaction, and the alcohol distilled off may again be added to the reaction mixture after condensation.

In general, conversion is complete after the reaction mixture has reacted for a few hours, for example 1 to 4 hours at a temperature of 70 to 110° C. with the calcium chloride and calcium oxide. If the conversion of the mixture of alkali metal salicylates and alkali metal phenates into the corresponding calcium compounds by means of calcium chloride, and the further conversion of the product obtained by means of calcium oxide take

place in separate stages, a reaction period of ½ to 1 hour is suitable for the first stage and a period of 1 to 4 hours for the second stage.

The quantity of calcium chloride with which the initial mixture is reacted amounts to at least as much as is required to replace the alkali metal present in the alkyl salicylates and alkyl phenolates of the initial mixture by calcium. Preferably, a slight excess of calcium chloride is used, for example of from 5 to 30% by weight, and more particularly 5 to 10% by weight.

The quantity of calcium oxide which is used for the formation of the basic product, is preferably 90 to 150% and more particularly from 100 to 120% of the theoretical quantity required for the formation of the basic salts of the alkyl salicylic acids. If desired, a greater excess of calcium oxide may be used. In general it has been found, however, that compared with the use of a certain excess of calcium oxide, it is not possible to increase the basicity of the final product any further by applying a still greater excess of calcium oxide.

The desired mixture of calcium alkyl phenates and highly basic calcium alkyl salicylates has at this point been formed. It may be desirable to perform further purification procedures, however, these procedures are immaterial to the invention and may be varied extensively according to many well known methods.

At the end of the reaction any alcohol still present may be removed from the product by distillation, and if desired at reduced pressure. Subsequently the reaction product is freed from the sodium chloride formed during the reaction and from the excess of calcium chloride and calcium oxide. This may be done in various ways, many of which will be immediately apparent to anyone familiar with the art. For example, the inorganic compounds may simply be removed by filtering or centrifuging, preferably after dilution of the reaction mixture with an organic solvent, for example pentane or another light hydrocarbon or mixture of light hydrocarbons. Alternatively, the sodium chloride formed and the excess of calcium chloride may be extracted from the reaction mixture with water or aqueous alcohol at ordinary or elevated temperatures. In general, the extraction may be carried out at temperatures of from 20 to 80° C. A suitable aqueous alcohol is, for example aqueous ethyl alcohol of 50 to 70% concentration. If the extraction is carried out with water it is recommended that at least three times the volume thereof, calculated on the reaction mixture to be treated, should be added and that the reaction mixture should only be stirred for a short time, for example 2 to 5 minutes, with the water added. In this way an emulsion of the oil-in-water type is formed, which again separates easily into the two phases. After removing the sodium chloride formed and the excess of calcium chloride from the reaction mixture by extraction with water or an aqueous alcohol solution or by any other means, the reaction product can be dried. This can be done to advantage by azeotropic distillation by means of a small quantity of an organic liquid, such as for example xylene. After the reaction product has been dried, any calcium oxide or calcium hydroxide present can be removed by filtering or centrifuging, if desired, after dilution of the reaction mixture with an organic solvent, such as xylene, pentane or another light hydrocarbon or hydrocarbon mixture.

After the sodium chloride formed during the reaction and the excess of calcium chloride and calcium oxide have been removed from the reaction mixture, any organic solvents still present in the reaction mixture can be removed by distillation. The product thus obtained is the desired final product, suitable for addition to a finished lubricating oil, or to a lubricating oil additive concentrate for subsequent blending into finished lubricating oils.

Suitable starting materials for practicing the present invention are generally mixtures of alkali metal salicylates

substituted only by alkyl groups and alkali metal phenates substituted only by alkyl groups, in which the salicylates are present in a quantity at least equal to the quantity of phenates. Particularly suitable initial materials are mixtures in which the salicylates and phenates have been formed by alkylation with straight chain hydrocarbons with 8 to 26 and, more particularly, with 10 to 22 carbon atoms; alpha olefins are especially preferred. Such mixtures are obtained, for example, by converting corresponding alkyl phenols into alkali metal phenates, particularly sodium phenates, and subsequently converting these phenates into salicylates by treatment with carbon dioxide according to the well-known Kolbe-Schmitt method. This conversion does not take place completely and at the end of the reaction with carbon dioxide a mixture is obtained which contains, for example, 65 to 80 parts by weight of sodium alkyl salicylates to 35 to 20 parts by weight of sodium alkyl phenates. The resulting mixture will contain phenates with 14 to 32 carbon atoms and salicylates with 15 to 33 carbon atoms in the case of alkylation with olefinic hydrocarbons of 8 to 26 carbon atoms, etc. A preference for the purpose of this invention is the alkylation with alpha olefins containing 14 to 18 carbon atoms. Although the Kolbe-Schmitt method is suitable for the preparation of the initial mixture, many other sources of starting materials are also satisfactory. It is immaterial for the purposes of the present invention how the initial mixture is prepared as long as it contains the required ingredients in the indicated proportions. It has been found, however, that the salicylate content should be at least equal to the phenate content of the mixture and in the usual case it will be desirable that the phenate content be at least 25% by weight of the salicylate content. The salicylates and phenates may contain either one or more alkyl groups. In particular, it is also possible for the salicylates and phenates to contain one or more shorter alkyl groups, in addition to one or more alkyl groups of 8 to 20 carbon atoms, although in general, the compounds containing the single alkyl group will predominate.

The polyvalent metals which are suitable for the practice of the present invention are those of group II of the periodic table of elements having atomic numbers from 12 to 56, inclusive. Preferred polyvalent metals are the alkaline earth metals, calcium, strontium, and barium, particularly calcium and in some cases barium. A single such metal may be utilized in a given case or a mixture of two or more may be used.

As mentioned previously suitable alcohols in which the polyvalent salt and oxide are to be dissolved are those monohydric, water-miscible aliphatic alcohols containing 1 to 5 carbon atoms, namely methanol, ethanol, 1-propanol, 2-propanol, tertiary butyl alcohol, and tertiary amyl alcohol. For a number of reasons ethyl alcohol is preferred in many cases. Similarly in many other cases methanol is preferred. A particularly surprising aspect to this invention is that contrary to the teachings of Denison and the French patent a better conversion of the phenates is obtained in the presence of water than in its absence. Although concentrations of water between 1 and 10% by weight based on the alcohol will be effective, it has been found that especially good results are obtained when the water concentration is between 3 and 7% by weight of the alcohol and particularly from 4 to 6% by weight of the alcohol.

According to the process of the invention it is possible to obtain products having a calcium content which exceeds the calcium content of the corresponding product in which the calcium is only present in the form of the normal calcium alkyl salicylate, by more than 100% by weight, for example 110 to 190% by weight.

The products obtained in the manner indicated have excellent properties as lubricant additives. For example, when using a lubricant which contains a small quantity of these products, deposits of carbonaceous material on

the pistons and in the piston ring grooves are reduced and the interior of engine cylinders, particularly cylinders of aviation engines, automotive engines, and diesel engines, remain clean. Further, by adding small quantities of the products of the invention to lubricating oils, the corrosion which would otherwise occur in the engine, for example on the bearing metals present therein, is suppressed to a great extent. The products of the invention have also great resistance to oxidation.

The quantity in which the products are added to lubricating oils may vary within wide limits. In general the lubricants are already improved to the desired extent by adding the products in small quantities, in general 0.1 to 15% by weight and more particularly 0.5 to 10% by weight. In special cases, however, still greater quantities of the products may be added to lubricating oils. For example, in the preparation of additive concentrates to be used in blending a finished lubricating oil, 50% or even 75% by weight of the products of the invention may be used in lubricating oil stock.

The present products are suitable as additives to lubricants of various types. In the first place mineral lubricating oils of diverse viscosities may be mentioned; synthetic lubricating oils are also suitable, however, as well as lubricating oils which contain fatty oils. Furthermore, they are suitable as additives to lubricants designed for many diverse uses—internal combustion engine lubricants, gear and preservation oils, hydraulic fluids, compressor and motor lubricants, and many others.

The products according to the invention may also be applied to advantage in combination with other lubricant additives, such as in combination with other detergents, for example alkaline earth metal compounds of alkyl phenol formaldehyde condensation products or alkaline earth metal salts of oil-soluble petroleum sulphonic acids; antioxidants, for example the alkyl phenols and arylamines, cycloalkyl thiophosphates or thiophosphites known as antioxidants; anti-corrosives, and extreme pressure dopes.

The invention will be illustrated by the following examples, although it is again emphasized that the invention is not to be limited in any way thereby, other than as set forth in the claims.

Example I

An initial mixture was used consisting of 75 mol per cent of sodium alkyl salicylates and 25 mol per cent of sodium alkyl phenates, in which the alkyl radicals contained from 14 to 18 carbon atoms. The mixture of salicylates and phenates was treated in the following manner to obtain a product with a high calcium content.

Four hundred parts by weight of the mixture, diluted with xylene, was heated to 75°C. while stirring quickly. A saturated solution of calcium chloride in ethyl alcohol containing 4% by weight of water, based on the alcohol, was then added in an excess of 5%, based upon the quantity which is theoretically required for the conversion of the sodium compounds present in the mixture into the corresponding calcium compounds.

Immediately after the addition of the calcium chloride solution, calcium oxide was added in an excess of 10%, based upon the theoretical quantity required for converting the neutral calcium alkyl salicylates into the basic calcium alkyl salicylates. Afterwards such an amount of ethyl alcohol containing 4% of water, based on the alcohol, was added that the total quantity of the reaction mixture was 800 parts by weight.

The alcohol was subsequently distilled off with the temperature at the bottom of the reaction vessel rising to about 105° C. The reaction mixture was diluted with two to three times the quantity by weight of gasoline, after which the sodium chloride formed and the excess calcium chloride and calcium oxide were removed by filtering. Finally, the product was distilled to remove the diluent. In this way a product was obtained having a Ca-content of 6.1% by weight.

For purposes of comparison an experiment was carried out in part by the process of the British patent, No. 586,461, the initial mixture of sodium alkyl salicylates and sodium alkyl phenates being treated with hydrochloric acid, so that a mixture of free alkyl salicylic acids and alkyl phenols was obtained. This mixture was treated with calcium hydroxide in an excess of 100%, based upon the quantity which would theoretically be required for the conversion of the free alkyl salicylic acids into the corresponding basic calcium salts. A product was obtained with a Ca-content of only 4.2% by weight. It will be seen, therefore, that with the process according to the invention it is possible to obtain products having a considerably higher calcium content than that of the products obtained by converting the free alkyl salicylic acids with even a great excess of calcium hydroxide.

Example II

The following experiments were carried out to show that the conversion of alkali metal alkyl phenates into the corresponding phenates of a polyvalent metal by double conversion of the alkali metal phenate with a salt of the polyvalent metal is promoted by the presence of an alkyl salicylate in the reaction mixture:

(1) The conversion of sodium alkyl phenates into calcium alkyl phenates in the absence of alkyl salicylate;

(2) The conversion of a mixture of sodium alkyl phenates and sodium alkyl salicylates into the corresponding calcium compounds;

(3) The conversion of sodium alkyl salicylates into the corresponding calcium salts in the presence of alkyl phenols.

Experiment No. 1.—The sodium alkyl phenate material used during this experiment was a mixture of alkyl phenates which contained alkyl groups of 14 to 18 carbon atoms and had a sodium content of 4.46% by weight.

The mixture, dissolved in xylene, was heated to 50° C., after which such a quantity of a 20% by weight solution of calcium chloride in 95% aqueous methanol was added to this solution that 1.05 equivalents of CaCl_2 , calculated on the sodium content of the sodium alkyl phenates, was present in the reaction mixture. The reaction mixture was heated while distilling off the methanol; heating was continued until the bottom temperature of the reaction mixture had risen to 105° C. Subsequently, the reaction mixture was filtered to remove the excess of calcium chloride and the sodium chloride formed during the conversion, after which the xylene was removed from the filtrate by distillation at reduced pressure.

The reaction product thus obtained was found to have a calcium content of only 0.50% by weight while with complete conversion of the sodium alkyl phenates into the corresponding calcium alkyl phenates a calcium content of 3.90% by weight should have been obtained. The very incomplete conversion may possibly be explained as being due to hydrolysis of the phenates as a result of the water present in the 95% methanol. This would bear out the prior art's insistence upon the use of absolute alcohol (Fr. 862,357) or of carbides (Denison, U. S. 2,228,654).

Experiment No. 2.—The mixture of sodium alkyl phenates and sodium alkyl salicylates used in this experiment had been obtained by converting a portion of the mixture of sodium alkyl phenates used in Experiment 1 into the corresponding sodium alkyl salicylates by the Kolbe-Schmitt method. The reaction product thus obtained consisted of 80 mol per cent of sodium alkyl salicylates and 20 mol per cent of sodium alkyl phenates. The mixture had a sodium content of 4.16% by weight.

A solution of the mixture of salicylates and phenates in xylene was heated to a temperature of 50° C., after which a solution of calcium chloride of 20% by weight in aqueous 95% methanol was added; 1.05 equivalents of CaCl_2 , calculated on the sodium content, was thus added. Subsequently, the reaction mixture was further heated

while distilling off the methanol. Heating was continued until the bottom temperature of the reaction mixture had risen to 105° C. The reaction mixture was filtered to remove the excess of calcium chloride and the sodium chloride formed during the conversion. The filtrate was finally subjected to distillation at reduced pressure to remove the xylene.

The reaction product thus obtained had a calcium content of 3.75% by weight while the theoretical quantity for the calcium content at complete replacement of sodium by calcium in the initial mixture amounted to 3.64% by weight.

Thus in accordance with the invention, in the presence of alkyl salicylates the alkyl phenates are completely transformed into the calcium compounds, so that in this case the phenates are not hydrolyzed. To prove that the calcium content of the end product obtained during this experiment may only be ascribed to calcium compounds formed during the conversion and not to peptization of calcium chloride by the alkyl salicylate whereby possible hydrolysis of the phenates would more or less be compensated, the following experiment was performed, in which sodium alkyl salicylates were converted in the presence of free alkyl phenols into the corresponding calcium alkyl salicylates. The free alkyl phenols are so weakly acid that they do not react with calcium chloride.

Experiment No. 3.—In this experiment an initial mixture was used consisting of 80 mol percent of sodium alkyl salicylates and 20 mol percent of free alkyl phenols, which as far as the nature of the alkyl radicals and the number thereof per molecule is concerned was entirely analogous to the initial mixture of Experiment No. 2. The mixture had a sodium content of 3.51% by weight. A solution of this mixture had been obtained by acidifying a xylene solution of the mixture of sodium alkyl salicylates and sodium alkyl phenates applied in Experiment No. 2 with hydrochloric acid, separating off the aqueous phase formed thereby, and treating the other phase, consisting of a xylene solution of a mixture of free alkyl salicylic acids and free alkyl phenols, with an equivalent quantity, calculated on the salicylic acid content, of a solution of 6% by weight NaOH in 95% methanol. In this case only the alkyl salicylic acids were converted into the sodium salts, and the alkyl phenols did not react. The caustic soda solution phase was removed and the mixture thus obtained, consisting of 80 mol percent of sodium alkyl salicylates and 20 mol percent of alkyl phenols (dissolved in xylene and the methanol from the alcoholic NaOH), was used for the present experiment.

The solution was heated to a temperature of 50° C., after which a 20% by weight solution of calcium chloride in aqueous 95% methanol was added, to contain 1.30 equivalents of calcium, calculated on the sodium content of the sodium alkyl salicylates. The reaction mixture was further heated, while the methanol was distilled off, until the bottom temperature of the reaction mixture had risen to 105° C. The mixture was then filtered to remove the excess of calcium chloride and the sodium chloride formed during the conversion. Finally the xylene was removed from the reaction mixture by distillation at reduced pressure.

The reaction product thus obtained had a calcium content of 3.19% by weight while the value calculated theoretically from the sodium content of the initial mixture, taking into account the fact that only the sodium alkyl salicylates react with calcium chloride, was 3.07% by weight, the difference being within the unavoidable errors of analysis. From this it follows that the alkyl salicylates had not peptized any of the excess calcium chloride.

By comparing the results of Experiments 1, 2 and 3, it is seen, therefore, that the conversion of alkali metal alkyl phenates in an aqueous alcoholic medium into compounds of a polyvalent metal is promoted by the presence of alkyl salicylates.

Example III

In order to show that a lubricating oil, in which a highly basic product has been incorporated according to the present invention, is more resistant to the action of acids (determined as the acid number of the lubricating oil after an acid has acted upon the lubricating oil for a specific time under specific conditions) than a lubricating oil in which the same content of a polyvalent metal has been incorporated in the form of a product having a lesser basicity, the following experiment was carried out.

As highly basic lubricating oil additive, a product was used which had been obtained by starting from a mixture of about 80 mol percent of sodium alkyl salicylates and 20 mol percent of sodium alkyl phenates. The sodium alkyl salicylates contained alkyl groups of 14–18 carbon atoms, while the sodium alkyl phenates also contained alkyl groups of 14–18 carbon atoms. The mixture of sodium alkyl salicylates and sodium alkyl phenates was reacted with a 6% by weight solution of calcium chloride in 96% methyl alcohol (the quantity of calcium chloride amounted to 1.05 equivalents, calculated on the sodium content of the mixture to be converted), and with calcium oxide in an excess of 10% in respect of the theoretical quantity required for the conversion of the neutral calcium alkyl salicylates to the mono-basic calcium alkyl salicylates. The product obtained had a basicity of 128%.

The product having a lesser basicity used for purposes of comparison was a product which had been obtained by treating a mixture of 80 mol percent of free alkyl salicylic acids (alkyl groups of 14–18 carbon atoms) and 20 mol percent of free alkyl phenols (alkyl groups also of 14–18 carbon atoms) with 2.0 equivalents of calcium hydroxide, calculated on the free alkyl salicylic acids. The product obtained had a basicity of 55%.

The highly basic product of 128% basicity was dissolved in a lubricating oil in such a quantity that the lubricating oil had a calcium content of 0.099% by weight. This lubricating oil was a selective solvent refined distillate having a viscosity of 24 centistokes at 50° C. and a viscosity index of about 100. The product with lesser basicity (55%) was dissolved in a second sample of the same lubricating oil and also in such a quantity that the lubricating oil had a calcium content of 0.099% by weight.

Each of the two lubricating oil samples was treated in the following manner with hydrochloric acid:

A 100 gram sample of the lubricating oil was stirred for 30 minutes at room temperature with 13.5 cc. of 0.19 N hydrochloric acid. Subsequently the mixture was diluted with 80 cc. of pentane and centrifuged, the oil phase and the water phase being separated. The separated oil phase was washed with water, after which the pentane was finally removed from the lubricating oil by distillation at reduced pressure.

The lubricating oil sample which contained the product with a basicity of 55% was found to have attained an acid number of 0.48 mg. of KOH/g. On the other hand, the acid number of the lubricating oil in which the product with the basicity of 128% had been dissolved was only 0.09 mg. of KOH/g.

It will be seen, therefore, that with the same content of polyvalent metal, the lubricating oil containing the highly basic additive is more resistant to the action of acid than the lubricating oil containing the additive of lesser basicity.

Example IV

This example is given to show that in the engine, too, lubricating oils containing the highly basic products obtained according to the present process are more resistant to the action of the acids formed when operating the engine than lubricating oils which contain additives having a lesser basicity. For this purpose two samples

of lubricating oils were compared with each other. In both cases the lubricating oil base consisted of an oil which had been obtained by subjecting a residual lubricating oil fraction to an extraction with a selective solvent to remove aromatic compounds. The oil had a viscosity of 60 centistokes at 50° C. and a viscosity index of about 100. The one sample contained the product having a basicity of 128%, described in Example 3, in such a quantity that the calcium content of the lubricating oil amounted to 0.20% by weight. The other sample contained a product similar to the one described in Example 3, having a basicity of 55%, with the slight difference, however, that the basicity of the product now employed was 59%. The second lubricating oil sample contained an amount of the product so that the calcium content of the oil was 0.15% by weight. Although the calcium content of the first lubricating oil sample was greater than that of the second sample, the content of additive, calculated as salicylic acid, was essentially the same in both cases.

The two samples of lubricating oil were tested in a Caterpillar single-cylinder 4-stroke engine. The experiments were carried out at an average effective pressure of 5.2 kg. per sq. cm. The engine was allowed to run at a rate of 850 revolutions per minute. The temperature of the water applied as cooling liquid was 80° C. The motor fuel used in these experiments had a sulphur content of 1.4% by weight.

After the engine had run for 96 hours in the manner indicated, the oil from the crankcase was analyzed with respect to the calcium content and the acid number. The results obtained were as follows:

Additive	Additive having a basicity of 59%	Additive having a basicity of 128%
Percent by weight of Ca in the initial oil.....	0.15	0.20
Percent by weight of Ca after the 96-hour test.....	0.012	0.032
Acid number after the 96-hour test, mg. KOH/gram.....	1.94	1.46

Thus, the used oil containing the additive having the basicity of 59% had an acid number which was 33% higher than the acid number of the used oil in which the additive having the basicity of 128% had been dissolved.

Example V

The following comparative experiment was carried out to show that, when the additives having a high basicity are applied in a lubricating oil, there is considerably less corrosion in engines in which this lubricating oil is used than when a lubricating oil additive is used which is also of the alkyl salicylate type but which has, however, been obtained by treating the free alkyl salicylic acids with an excess of calcium hydroxide. The first-mentioned lubricating oil additive, which will be referred to as lubricating oil additive A, was obtained in the manner indicated in Example I, from a mixture of 75 mol per cent of sodium C₁₄–18-alkyl salicylates and 25 mol percent of sodium C₁₄–18-alkyl phenates and had a basicity of 185%. The lubricating oil additive applied for purposes of comparison, which will be indicated by the letter B, was obtained by converting a mixture of sodium C₁₄–18-alkyl phenates into the corresponding salicylates by treating the sodium alkyl phenates with carbon dioxide, releasing the resulting C₁₄–18-alkyl salicylic acids therefrom by means of hydrochloric acid, and treating the alkyl salicylic acids with an excess of calcium hydroxide, whereby the alkyl phenates not converted during the treatment with carbon dioxide were left in the mixture and were present as free alkyl phenols in the end product. This additive B had a basicity of 50%.

Additive A was dissolved in a lubricating oil base having a viscosity of 59 centistokes at 50° C., to give a cal-

cium content of 0.15% by weight. Additive B was dissolved in another portion of the same lubricating oil base to give a calcium content of 0.11% by weight. The weights of the additives in the two cases were approximately the same.

The two samples of lubricating oil were tested in a Caterpillar single-cylinder 4-stroke engine. The tests were carried out at an average effective pressure of 5.2 kg. per sq. cm. The engine was allowed to run at a rate of 850 revolutions per minute. The temperature of the water applied as cooling liquid amounted to 80° C. In the tests a motor fuel with a sulphur content of 0.96% by weight was used.

After the engine had run for 96 hours in the manner indicated, the corrosivity of the oil used was determined. To this end an apparatus was used consisting of a journal fitting into two Ford V-8 half bearings provided with a lining consisting of a Cd-Ni alloy. The bearing is enclosed in a casing of cast iron. The half bearings are pressed against the journal by means of a system of levers. The force pressing the half bearings against the journal can be regulated by means of a steelyard.

Corrosion is determined as follows. The journal and the two half bearings are first cleaned by applying kerosene and a little Carborundum to the journal and, while the half bearings are being pressed against the journal, rotating the journal back and forth for a few minutes. The journal and the half bearings are then cleaned with gasoline and dried with a cloth. The dry half bearings are then weighed to an accuracy of 1 milligram. A little of the oil to be examined is applied to the journal and the bearing. After the apparatus has been assembled, an amount of the oil to be examined is added, until the journal is at least half-submerged (200 cc. of oil are needed for this), after which the shaft is allowed to rotate for a few minutes. The steelyard is then adjusted to 3 kg. This corresponds to a total force of 150 kg. and a load of 7 kg. per sq. cm. of projected surface. During the test the temperature is maintained at $160^{\circ} \pm 3^{\circ}$ C. by means of an electric heating element. The rate at which the journal rotates during the test is 1400 revolutions per minute. After 3 hours the oil is drained off; the half bearings are then washed with gasoline, dried and weighed. The loss of weight is a measure of the corrosive action of the oil.

In this way a loss of weight of the Cd-Ni bearings of 90 mg. was measured for the lubricating oil used with the additive A, while the corrosion caused by the lubricating oil used with additive B was 285 mg., expressed in the manner indicated. From this it will be seen that the lubricating oil additives having a high basicity, which are obtained according to the process of the invention, possess considerably better anti-corrosion properties than the corresponding lubricating oil additives, which, however, are obtained by releasing the smaller amount of sodium alkyl phenates and treating the product thus obtained with an excess of calcium hydroxide.

It was also found that the anti-corrosion properties of the lubricating oil may be further improved by adding a small quantity of sulphurized wax olefines or a small quantity of a cyclo-alkyl thiophosphate or cyclo-alkyl thiophosphite to the lubricating oil, in combination with the product of this invention.

I claim as my invention:

1. A process for preparing lubricating oil additives which comprises reacting a mixture containing unsubstituted alkali metal alkyl phenates of from 14 to 32 carbon atoms and unsubstituted alkali metal alkyl salicylates of from 15 to 33 carbon atoms, wherein the weight ratio of the phenates to the salicylates is from 1:4 to 1:1, with a halide of a metal of group II of the periodic table of elements having an atomic number from 12 to 56 in a monohydric water-miscible aliphatic alcohol of from 1 to 5 carbon atoms and containing water from 1 to 10%

by weight of said alcohol, said halide being present in a quantity from 100 to 130% of that which is stoichiometrically equivalent to the total alkali metal content of said mixture of phenates and salicylates, and with an oxide of a metal of group II of the periodic table of elements having an atomic number from 12 to 56 in a monohydric water-miscible aliphatic alcohol of from 1 to 5 carbon atoms and containing water from 1 to 10% by weight of said alcohol, said oxide being present in a quantity from 90 to 150% of that stoichiometrically required for the formation of the mono-basic salts of said salicylates and said group II metal.

2. A process for preparing lubricating oil additives which comprises reacting a mixture containing unsubstituted alkali metal alkyl phenates of from 16 to 28 carbon atoms and unsubstituted alkali metal alkyl salicylates of from 17 to 29 carbon atoms wherein the weight ratio of the phenates to the salicylates is from 1:4 to 1:1, with an alkaline earth metal chloride in a monohydric water-miscible aliphatic alcohol of from 1 to 2 carbon atoms and containing water from 1 to 10% by weight of said alcohol, said chloride being present in a quantity from 105 to 130% of that which is stoichiometrically equivalent to the total alkali metal content of said mixture of phenates and salicylates, and with an oxide of an alkaline earth metal in a monohydric water-miscible aliphatic alcohol of from 1 to 2 carbon atoms and containing water from 1 to 10% by weight of said alcohol, said oxide being present in a quantity from 105 to 130% of that stoichiometrically required for the formation of the mono-basic salts of said salicylates and said alkaline earth metal.

3. The process of claim 2 wherein the alcohol is ethyl alcohol.

4. The process of claim 2 wherein the alcohol is methyl alcohol.

5. The process of claim 2 wherein the unsubstituted alkali metal alkyl phenates contain from 20 to 24 carbon atoms and the unsubstituted alkali metal alkyl salicylates contain from 21 to 25 carbon atoms.

6. The process of claim 2 wherein the mixture containing unsubstituted alkali metal alkyl phenates and unsubstituted alkali metal alkyl salicylates is diluted with a hydrocarbon solvent.

7. The process of claim 2 wherein the alcohol is distilled off from the reaction mixture during the course of the reaction.

8. The process of claim 2 wherein the alkaline earth metal chloride is calcium chloride and the alkaline earth metal oxide is calcium oxide in a form reactive to water.

9. The process of claim 2 wherein the alkaline earth metal chloride is barium chloride and the alkaline earth metal oxide is barium oxide.

10. The process of claim 2 wherein the unsubstituted alkali metal alkyl phenates are unsubstituted sodium alkyl phenates and the unsubstituted alkali metal alkyl salicylates are unsubstituted sodium alkyl salicylates.

11. The process of claim 2 wherein alkaline earth metal chloride is present in a quantity from 105 to 110% of that which is stoichiometrically equivalent to the total alkali metal content of said mixture of phenates and salicylates and the alkaline earth metal oxide is present in a quantity from 100 to 120% of that stoichiometrically required for the formation of the mono-basic salts of said salicylates and said alkaline earth metal.

12. A process for preparing lubricating oil additives which comprises reacting a mixture containing unsubstituted sodium alkyl phenates of from 20 to 24 carbon atoms and unsubstituted sodium alkyl salicylates of from 21 to 25 carbon atoms wherein the weight ratio of the phenates to the salicylates is from 1:4 to 1:1, with calcium chloride in ethyl alcohol containing water from 4 to 6% by weight based on the alcohol, said calcium chloride being present in a quantity from 105 to 110% of that which is stoichiometrically equivalent to the total sodium

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content of said mixture of phenates and salicylates, and with calcium oxide in a form reactive to water in ethyl alcohol containing water from 4 to 6% by weight based on the alcohol, said oxide being present in a quantity from 100 to 120% of that stoichiometrically required for the formation of the mono-basic calcium salts of said salicylates.

13. In a process of preparing unsubstituted alkyl phenates of a metal of group II of the periodic table of elements having an atomic number from 12 to 56, said phenates containing from 14 to 32 carbon atoms, the improvement comprising reacting unsubstituted alkali metal alkyl phenates in the presence of at least an equal quantity of unsubstituted alkali metal alkyl salicylates containing from 15 to 33 carbon atoms with a halide of a metal of group II of the periodic table of elements having an atomic number from 12 to 56 in a monohydric water-miscible aliphatic alcohol of from 1 to 5 carbon atoms and containing water from 1 to 10% by weight of said alcohol, said halide being present in a quantity from 100 to 130% of that which is stoichiometrically equivalent to the total alkali metal content of the said phenates and said salicylates.

14. In a process of preparing basic unsubstituted alkyl salicylates of a metal of group II of the periodic table of elements having an atomic number from 12 to 56, said salicylates containing from 15 to 33 carbon atoms, the improvement comprising reacting unsubstituted alkali metal alkyl salicylates in the presence of from 25 to 100% by weight based on the said salicylates of unsubstituted alkali metal alkyl phenates with a halide of a metal of

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group II of the periodic table of elements having an atomic number from 12 to 56 in a monohydric water-miscible aliphatic alcohol of from 1 to 5 carbon atoms and containing water from 1 to 10% by weight of said alcohol, said halide being present in a quantity from 100 to 130% of that which is stoichiometrically equivalent to the total alkali metal content of the said salicylates and said phenates, and with a quantity of an oxide of a metal of group II of the periodic table of elements having an atomic number from 12 to 56 in a monohydric water-miscible aliphatic alcohol of from 1 to 5 carbon atoms and containing water from 1 to 10% by weight of said alcohol, said oxide being present in a quantity from 90 to 150% of that stoichiometrically required for the formation of the mono-basic salts of said salicylates and said group II metal.

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