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LUBRICATING OILS

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10 Claims. (Cl. 252—56)

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This invention relates to a new and improved lubricating oil, consisting of a petroleum lubricant to which certain organic chemical compounds, commonly referred to as additives, have been added. Attention is directed to my prior U. S. Patent No. 2,375,516, dated May 8, 1945. Said aforementioned patent discloses an improved lubricating oil, in which there is present as an additive, a relatively small amount of a saturated alcohol-alpha-beta unsaturated polybasic carboxylic acid-unsaturated aliphatic alcohol condensation polymer; said saturated alcohol containing at least 8 and not more than 32 carbon atoms; said acid having less than 10 carbon atoms and said unsaturated alcohol containing less than 32 carbon atoms and having at least 3 intervening carbon atoms between the carbon atoms to which the hydroxyl group was attached and the nearest ethylenic carbon atom; said polymer being present in an amount varying from 0.025% to about 5%, on the basis of the lubricating oil with which it is admixed.

The main object of my present invention is to provide an improved lubricating oil of the general type or kind above mentioned, in which the additives employed consist of polymeric compounds alone, or polymers, in admixture with monomeric compounds, or monomeric compounds alone. My preference is to use polymeric compounds in which there is admixed a significant portion of monomeric compounds, for instance, 10% to 65% by weight of monomeric compounds.

The additives described in said aforementioned U. S. Patent No. 2,375,516 are obtained from alcohols having at least 8 and not more than 32 carbon atoms, and such alcohols may be cycloaliphatic as well as aliphatic. In contradistinction, the additives contemplated in the present invention are derived solely from aliphatic alcohols in which the upper carbon atom limit is 22 carbon atoms and the lower limit is 8 carbon atoms. Similarly, the additives employed in the aforementioned U. S. Patent No. 2,375,516 are obtained from alpha-beta unsaturated polycarboxy acids which may contain as many as 10 carbon atoms, or even more, whereas, the additives herein contemplated are derived from polycarboxy acids having not more than 5 carbon atoms. Furthermore, there is a very restricted limitation as to the proportion of the reactants, particularly the ratio of unsaturated alcohol to saturated alcohol, in comparison to an analogous limitation appearing in my aforementioned U. S. Patent No. 2,375,516. Briefly, then, the previously mentioned patent describes a process of preparing

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new polyester products having particular utility as additives for lubricating oils, and especially effective as pour-point depressants or wax crystallization modifiers. These products were derived by an esterification reaction, in which two different types of alcohol enter into combination with a polycarboxy alpha-beta unsaturated acid or anhydride. The two types of alcohols consisted of:

(*a*) Unsaturated aliphatic or cycloaliphatic alcohols; and

(*b*) Saturated long chain aliphatic alcohols.

The proportions of reactants were chosen, so that the total moles of (*a*) and (*b*) should approximately equal the equivalents of alpha-beta unsaturated acid or anhydride, and the ratio of moles of (*a*) to moles of (*b*) should be between 0.2 and 5.0.

The additives of the present invention are prepared from the more restricted type of reactant previously referred to, as exemplified by unsaturated alcohols, saturated alcohols, and alpha-beta unsaturated polycarboxy acids or anhydrides. The products of the present invention are prepared from the same reactants as described above. I have discovered that particularly effective reagents are obtained when the proportions of reactants are so chosen that the ratio of moles of alpha-beta unsaturated acid to unsaturated aliphatic or cycloaliphatic alcohol, is between the limits of about 1.5 to 2.5, preferably 2.0. The moles of saturated alcohol should then be chosen, such that the total moles of alcohols are approximately equal to the equivalents of alpha-beta unsaturated acid.

In recapitulation, the raw materials employed in the manufacture of the herein described new additives, are best described in terms of their method of preparation. The required reactants are:

(1) A dicarboxy alpha-beta unsaturated acid or anhydride having not more than 5 carbon atoms;

(2) An unsaturated aliphatic alcohol having at least 8 and not more than 22 carbon atoms;

(3) A saturated aliphatic alcohol having at least 8 and not more than 22 carbon atoms.

The total moles of (2) and (3) used, should approximately equal the equivalents of (1) with respect to carboxylic acid groups, while the ratio of mole of (1) to moles of (2) may vary from about 1.5 to 2.5.

Examples of suitable reactants of class (1), above, are alpha-beta unsaturated, carboxylic acids and anhydrides, such as: maleic acid, fu-

maric acid, citraconic acid, aconitic acid, itaconic acid, mesaconic acid. maleic anhydride, citraconic anhydride, itaconic anhydride, and the like. Because of their availability, relatively low cost, and marked reactivity, maleic anhydride, fumaric acid, and citraconic anhydride, are especially useful, and products obtained with these reactants will be used below to illustrate the present invention.

Alcohol reactants of class (2), above, which are suitable for use in preparing the present products, are the aliphatic monohydric alcohols, in which the ethylenic carbon atom nearest to the hydroxyl group, is separated from the carbon atom attached to said hydroxyl group by at least three singly bonded carbon atoms. Such alcohols may contain one or more carbon-to-carbon double bonds, but all must satisfy the above requirement as to proximity to the hydroxyl group. When the alcohol contains two or more double bonds, these may be either conjugated or non-conjugated. My preferred class of unsaturated aliphatic alcohols is exemplified by the following: Octene-3-ol-8, decene-1-ol-10, oleyl alcohol, erucyl alcohol, linoleyl alcohol, eicosene-10-ol-1, crude sperm oil alcohols, crude jojoba oil alcohols, and the like. My preferred unsaturated alcoholic reactant is monoethylenic.

Alcohol reactants of class (3), above, which are suitable for preparing products of the present invention, are exemplified by various alcohols, and particularly, the normal, primary alcohols. Examples of suitable alcohols are: 2-ethyl hexanol, 5-ethylnonanol-2,7-ethyl-2-methylundecanol, 3,9-diethyltridecanol-6, and the like. Examples of the most preferred alcohols are: n-octanol, n-decanol, lauryl alcohol, myristic alcohol, cetyl alcohol, stearyl alcohol, 1-eicosanol, 1-docosanol. My preferred saturated alcohol has not over 18 carbon atoms.

One method of preparing the new products used to produce the improved lubricating oil constituting my present invention, is to mix the three desired reactants of the kind described above in the desired proportions, keeping these proportions within the limits previously specified. This mixture is then heated and stirred at a temperature in the range from about 100° C. to about 250° C. for a period of several hours. The exact temperatures and heating periods employed will depend upon the specific reactants employed, as well as upon the use to which the product is to be put. During the heating period the viscosity and average molecular weight of the product increase. For certain purposes, as, for example, use as a pour-point depressant for lubricating oils, a material of average molecular weight in the range of 1,200 to 5,000 may be desirable; so the reaction may be stopped when a sample removed from the reaction mass is found to have this molecular weight. Actually, for control purposes, measurements of viscosity at some standard temperature can be used, instead of molecular weight, as these two properties may be correlated for a given combination of reactants reacted under specific conditions.

Although the present compounds may be prepared by reacting at temperatures of from about 100° C. to about 250° C., I generally prefer to carry out the reaction in the temperature range from about 150° C. to about 210° C. The reaction involved is not completely understood, but appears to involve both esterification and addition of the unsaturated constituents. Conventional esterification catalysts such as sulfuric acid, beta camphor sulfonic acid, paratoluene sulfonic acid, hydrochloric acid, etc., may be employed. Also olefine condensation catalysts such as sulfuric acid, benzoyl peroxide, hydrogen peroxide, etc., may also be employed. However, none of these catalysts is necessary for preparation of the compounds, as appreciable reaction and polymerization may be obtained simply by heating the reactants at the proper temperature, for a period of several hours.

To obtain the highest rate of reaction and polymerization, I have found that certain conditions of reaction are particularly desirable. The discovery of the reaction conditions actually constitutes an invention within an invention, in that it makes possible the preparation of the most desirable products with the minimum of time and effort. In particular, I have found that reaction is prompted by passing through the mixture, during reaction, a slow stream of oxygen or oxygen-containing gas, such as air. The beneficial effect of this operation appears to arise directly from the oxygen in the gas used. If nitrogen, hydrogen, or other inert oxygen-free gas is passed through the reaction mixture, the rate of reaction appears not to be appreciably increased. When oxygen or an oxygen-containing gas is passed through the reaction mixture, the temperature may be maintained at any point over a rather wide limit; but as remarked above, I obtain best results using a temperature of reaction in the range from about 150° C. to about 210° C. With reactants that boil within the temperature range, it is desirable that the materials be reacted under pressure, or that the reaction be conducted for a while at a lower temperature until esterification of the reactants has produced an intermediate of higher boiling point. The temperature may then be gradually increased to a higher value, in order to increase the rate of the reaction. At extremely high temperatures, however, decomposition and oxidation of the product may occur to an objectionable degree.

The time of reaction will depend, of course, upon the reactants themselves and upon the temperature at which the reaction is carried out, as well as upon the use to which the material is to be put. Ordinarily, this time of reaction will be several hours, and perhaps as much as 48–72 hours. To prepare pour-point depressants, I have found that a typical set of conditions may involve a reaction temperature of about 200° C. and a reaction time of about 24 hours. If the product is to be used as a viscosity index improver, a material of higher molecular weight is required and the reaction in this instance might be maintained for as long as 48 hours, or even longer.

Although the present compounds have been described in terms of their preparation from three classes of reactants, it should be pointed out that the reaction may be carried out in a series of steps. The first step might involve reacting only two of the reactants; and this product then may be further reacted with the third material. For example, in preparing a pour-point depressant from reactants such as maleic anhydride, oleyl alcohol, and stearyl alcohol, the maleic anhydride and oleyl alcohol may be condensed first to give a semi-resinous polymer ester of the type described in my co-pending application Serial No. 489,237, filed May 31, 1943. This product may then be mixed with stearyl alcohol about equivalent to the free carboxylic acid content of the polymer, and further heated and esterified to complete esterification. Ordinarily, however, it is more

convenient and simpler to combine all of the reactants at once to prepare the desired compound.

The following examples will serve to illustrate the methods of preparation which may be employed.

EXAMPLE 1

1.47 moles of commercial oleyl alcohol (iodine No. 54 and hydroxyl value 205; consisting of about 68% oleyl alcohol and 32% stearyl alcohol) was mixed with 1.27 moles of stearyl alcohol, 1.27 moles of lauryl alcohol and 2.0 moles of maleic anhydride. This mixture was stirred and heated for 3 hours at 190° C. during which time about 1.3 moles of water was evolved. A gas inlet tube was then introduced into the mixture and a slow current of air was passed through the reactants which were held at 200° C. Heating at 200° C. with air passing through the mixture, was continued for 48 hours.

The product was a viscous, reddish oil, completely soluble in lubricating oil.

EXAMPLE 2

One mole of pure oleyl alcohol was mixed with 3 moles of lauryl alcohol and 2 moles of maleic anhydride, and the combination was reacted as in Example 1. The product was an extremely viscous, oil-soluble liquid.

EXAMPLE 3

2.54 moles (based on hydroxyl value) of commercial oleyl alcohol (79% oleyl content, the remainder a mixture of saturated, long chain alcohols), 2.46 moles of stearyl alcohol, and 3.00 moles of n-decanol and 4.20 moles of maleic anhydride, were placed in a reactor fitted with gas inlet tube, viscometer tube, thermometer, water trap, and condenser. The whole was heated by vapors of boiling m-cresol (200±2° C.). The mixture was heated for 2 hours, after which water evolution had become very slow. A slow air stream was then started through the reactants. Viscosity determinations were made at intervals and the following values obtained:

Hours of Heating	Viscosity at 200° C. in Centipoises
6	8.2
20	11.2
36	12.7
48	14.6

The final product was a viscous oil having a strong pour depressant action on a number of lubricating oils.

EXAMPLE 4

3.0 moles of n-octanol were substituted for the n-decanol in Example 3. Viscosity of the product was determined at various times after the start of air introduction, with the results shown below:

Hours of Heating	Viscosity at at 200° C. in Centipoises
36	11.9
60	14.7
84	29.2

The product was an efficient pour-point depressant, but not as generally effective as the product of Example 3.

EXAMPLE 5

Fumaric acid was substituted for the maleic anhydride in Examples 1 to 4, inclusive.

EXAMPLE 6

Citraconic anhydride was substituted for maleic anhydride in Examples 1 to 4, inclusive, and heating was continued for 84 hours while passing a slow air current through the reactants.

The molecular weights of the present products may vary over a wide range, depending upon the extent of reaction brought about, but the most effective pour depressants appear to be those within the molecular weight range 1200 to 5000 and having viscosities (at 200° C.) between about 13 and 30 centipoises.

The time of reaction required to obtain effective reagents varies with the reactants and the rate at which air is passed through the reaction mass, as well as upon the scale of the reaction (that is, the total weight of reactants). The role of the air or oxygen containing gas is not clear, but it is definitely known that the presence of oxygen and its rate of passing through the reactants, greatly effects the rate of viscosity and molecular weight increases.

It is believed, on the basis of this experimental evidence, that the effect of air or oxygen-containing gas, other than its effect in removing water, probably arises from an oxidation of the unsaturated alcohol which results in the formation of one or more additional double bonds therein. It is believed that the maleic anhydride or other alpha-beta ethylenic acid then adds at or near the original and new-formed double bonds by a proton transfer reaction, to form a polycarboxylic acid (or anhydride) which is simultaneously or subsequently esterified by the saturated alcohols present. It appears possible that maleic acid esters may, themselves, condense with the unsaturated alcohol in a manner similar to maleic anhydride, as it seems to make little or no difference in the nature of the products, whether the saturated alcohol is added before or after reaction of maleic anhydride with the unsaturated alcohols. A practical advantage arises from the early addition of the saturated alcohols, due to the fact that they form esters with maleic anhydride and prevent its partial loss in the oxygen-containing gas stream.

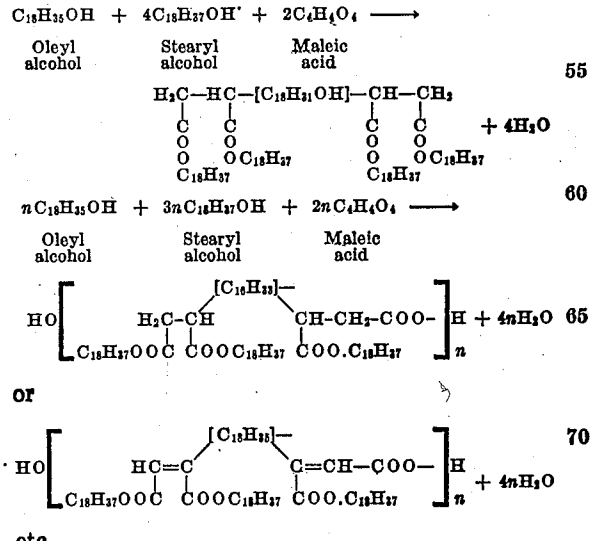
The products may range in acid numbers from about 40 down to practically zero, depending upon the extent of reaction, and the exact ratio of acid to alcohol equivalents employed. By using a slight excess of alcohol to the equivalents of alpha-beta ethylenic acid, very low acid number products are obtained. In actual plant manufacture, a small amount of acid is usually lost in volatilization in the gas stream, which results in a small increase in the ratio of alcohol equivalents to acid equivalents. Where this effect is not desired, a fractional excess of alpha-beta ethylenic acid is sometimes used in the starting materials. (E. g. see Example 3.)

Where the final product does contain free carboxyl groups, these may be reacted with further amounts of alcohol to yield complete esters, or may be neutralized with amines, alkalies or heavy metal oxides to yield salts, which, in some instances, may have beneficial properties in addition to those of the original compound. For example, salts such as those of sodium or zinc, have sludge-dispersing as well as pour-depressing properties in lubricating oils. In general, however, the desired products will have acid numbers below about 10 and preferably below 2.

It will be noted that in some of the examples mixtures of saturated alcohols have been em-

ployed instead of a single species of saturated alcohol. The use of such mixtures is considered the equivalent of using a single species of alcohol. If desired, mixtures of unsaturated alcohols may also be employed, instead of one unsaturated alcohol; and the analogous conditions apply to the use of the alpha-beta unsaturated polycarboxylic acid.

As pointed out above, the nature of the reaction which results in the formation of the present products, is not clearly understood, but it is believed that the alpha-beta unsaturated carboxylic acid esterifies the hydroxyl groups of the alcohols and also adds, by proton transfer to the unsaturated alcohol, two molecules of such alpha-beta unsaturated acid or ester adding to the chain of each unsaturated alcohol under the influence of oxygen or oxygen-containing gas. The present products are distinguished from those disclosed in my aforementioned U. S. Patent No. 2,375,516, by the fact that they may contain large amounts of monomer, as evidenced by the molecular weight of the desired products. However, these products, in most instances, will also contain considerable amounts of polyesters. These probably arise from the fact that the unsaturated alcohol which undergoes condensation with two molecules of ethylenic acid, is often times esterified by a different molecule of ethylenic acid which leads to the formation of a kind of linear polyester. Since the saturated alcohols employed in the reaction mixture are also esterified by the polybasic acid, the final products are thus a type of linear polyester having long chain hydrocarbon branches attached thereto through ester linkages. This postulated reaction and the products resulting may be exemplified in part by the reaction between oleyl alcohol, stearyl alcohol, and maleic anhydride. Conceivable reaction products are shown below. In these formulae the number of hydrogens remaining in the oleyl radical after completion of the reaction is uncertain and the number of double bonds remaining in this radical or in the maleic acid radical are uncertain. For these reasons, the figures given for the number of hydrogen atoms in these radicals are to be understood as being subject to some possible variation. It is known that the final products have a small iodine number, and thus, therefore, must contain unsaturation. The location of this unsaturation is unknown:



In the above formulae, no attempt has been made to define the carbon atoms of the oleyl radical to which the maleic anhydride residue becomes attached. From theoretical considerations, it appears likely that the maleic anhydride residue becomes attached to a double bond carbon atom, or to a carbon atom alpha to a double bond. During the course of the reaction and in the presence of oxygen, further unsaturation probably occurs and condensation of these new-formed double bonds may take place. Here again, however, I believe that the maleic anhydride residue attaches itself to a carbon atom of the new double bond, or at a carbon atom near this new double bond.

Because of the uncertainty as to the mechanism of the reaction, as well as the large variety of possible reactions which could be postulated, no effort will be made to describe the present products in terms of conventional chemical formula.

As has previously been mentioned, the ratio of equivalents of acid to alcohols employed may not be exactly one to one. When a predominantly monomeric product is desired, a slight excess of either alcohol or acid is usually employed, as exemplified in the first reaction formula above. However, the ratio of acid equivalents to alcohol equivalents should be kept within the approximate range of 0.8 to 1.2.

It may be well to emphasize what has been said previously. The reactions can be conducted and controlled by the viscosimeter method previously indicated, so that the reaction is stopped when substantially all of the products of reaction are present in monomeric form. The reactions are preferably conducted in the manner described, so that a sizeable amount of polymeric material is formed, but there is still present a significant amount of monomeric material, for instance, 10 to 65%. If desired, however, the reaction can be conducted to such a stage that the entire reaction mass is polymeric. Therefore, the additives herein employed may be either monomeric or polymeric, or a mixture, but preferably, a mixture, in which a significant proportion is monomeric.

My present invention consists in using products of the kind previously described to lower the pour-point, or increase the viscosity or viscosity index of lubricating oils, or consists of a new composition of matter, composed of a relatively small amount of such compounds and a lubricating oil. The following are examples of my improved lubricating oil.

EXAMPLE I

The product of Example 1 was dissolved in varying proportions in a Mid-Continent solvent refined motor oil of SAE 10 grade. A. S. T. M. pour-points of the various mixtures are shown in the table below:

Conc. of Product in Oil, (Per Cent)	A. S. T. M. Pour Point, ° F.
0	+15
0.025	+10
0.050	−10
0.10	−35
0.20	−40

EXAMPLE II

The product of Example 2 was dissolved in varying amounts in Mid-Continent, 100 vis., high

VI neutral oil. Pour-points of these solutions were as follows:

Conc. of Product in Oil, Per Cent	A. S. T. M. Pour Point, ° F.
0	+20
0.025	+20
0.050	−10
0.10	−25
0.25	−45

EXAMPLE III

The product of Example 2 was added in the amount of 2.5% to a Gulf Coast lubricating oil having a viscosity index of 50. The resulting blend was a clear, light red oil having a viscosity index of 88.

EXAMPLE IV

The product of Example 3 was dissolved in varying amounts in a conventionally refined, SAE 20 motor oil. The pour-points and "stable" pour-points (by A. S. T. M. "Proposed method of test for determining maximum pour-points") were determined on these blends with the results shown below.

Conc. of Product in Oil, percent	A. S. T. M. Pour Point, ° F.	"Maximum" Pour Point, ° F.
0	10	10
0.0625	−10	5
0.125	−20	5
0.188	−25	−10
0.250	−35	−10

In general, the percentage of the herein described compounds which will be required to depress the pour-point of oils sufficiently to be of practical interest, will vary from as little as 0.025% to as much as 2%, or even 5% for low "maximum" pour-points. The amounts required to increase the viscosity index by appreciable amounts, will vary from as little as 0.025% to as much as 5%, or even more, depending upon the compound and the character of the oil to which it is added.

Thus, one object of my invention is the preparation of improved lubricating oils or lubricating oil compositions, adding not less than about 0.025% or more than about 5%, by weight, of the herein described compounds, to lubricating oils which are used in an internal combustion engine, or as lubricants for moving machinery.

The outstanding effectiveness of the herein described compounds, in comparison with those mentioned in my aforementioned U. S. Patent No. 2,375,516, is illustrated in the following table, where the comparative effectiveness as pour-point depressants of the best previously described compounds, is compared with some of the present reagents.

TABLE I

Pour-points of solvent refined SAE 10 oil with additives

Compound added to oil	Concentration in Oil	
	0.0625%	0.125%
Product of Example 5 in U. S. Pat. 2,375,516	−15° F.	−30
Product of Example 1 herein	−30	−40

TABLE II

Pour-points of Pennsylvania 200 viscosity neutral oil with additives

Compound Added to Oil	Concentration in Oil	
	0.075%	0.150%
Product of Example 3 in U. S. Pat. 2,375,516	−5° F.	−10° F.
Product of Example 3 herein	−5° F.	−25° C.

The herein contemplated reactions employed for producing the additives, invariably result in more than one chemical compound. It has been pointed out that the reactions may produce various monomers, various polymers, or a mixture thereof. The reaction products are referred to as condensation products, to include both monomeric and polymeric forms. The dicarboxy acid anhydrides are the obvious functional equivalents of the dicarboxy acids.

The present products are in general unsaturated, as reaction does not remove all of the olefinic groups of the unsaturated reactants. If desired, these products may be hydrogenated to remove olefinic double bonds. Other chemical reactions may also be employed to modify the properties of the compounds. For example, they may be treated with sulfur at elevated temperatures to form sulfurized polymers; or they may be treated with chlorine to remove the unsaturation and otherwise modify their properties; or they may be treated with sulfur chloride to give products of somewhat different properties. The introduction of sulfur into the present compounds does not appear to change their pour-point depressant properties, while at the same time it improves their resistance to oxidation and also imparts to them film strength improving properties.

Reference is made to my co-pending application Serial No. 489,238, filed May 31, 1943.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A composition of matter, consisting of a mineral lubricating oil and a relatively small amount of an aliphatic saturated alcohol-alpha-beta unsaturated dicarboxy acid-unsaturated aliphatic alcohol condensation product; said alcohols containing at least 8 and not more than 22 carbon atoms; said acid having not over 5 carbon atoms and said unsaturated alcohol having at least 3 intervening carbon atoms between the carbon atom to which the hydroxyl group is attached and the nearest ethylenic carbon atom; said condensation product resulting from a reaction in which the molal proportions of the alpha-beta unsaturated dicarboxy acid to the unsaturated alcohol are within the range of about 1.5 to 2.5 and the saturated alcohol reactant is such that the total equivalents of alcoholic reactants is about equal to the equivalents of dicarboxy acid used; said additive being present in amount varying from 0.025% to about 5%, by weight, on the basis of the lubricating oil with which it is admixed.

2. A composition of matter, consisting of a mineral lubricating oil and a relatively small amount of an aliphatic saturated alcohol-alpha-beta unsaturated dicarboxy acid-unsaturated aliphatic alcohol condensation product; said alcohols being normal straight chain containing at

least 8 and not more than 18 carbon atoms; said acid having not over 5 carbon atoms and said unsaturated alcohol having at least 3 intervening carbon atoms between the carbon atom to which the hydroxyl group is attached and the nearest ethylenic carbon atom; said condensation product resulting from a reaction in which the molal proportions of the alpha-beta unsaturated dicarboxy acid to the unsaturated alcohol are within the range of about 1.5 to 2.5 and the saturated alcohol reactant is such that the total equivalents of alcoholic reactants is about equal to the equivalents of dicarboxy acid used; said additive being present in amount varying from 0.025% to about 5%, by weight, on the basis of the lubricating oil with which it is admixed.

3. A composition of matter, consisting of a mineral lubricating oil and a relatively small amount of an aliphatic saturated alcohol-alpha-beta unsaturated dicarboxy acid-unsaturated aliphatic monoethylenic alcohol condensation product; said alcohols being normal straight chain containing at least 8 and not more than 18 carbon atoms; said acid having not over 5 carbon atoms and said unsaturated alcohol having at least 3 intervening carbon atoms between the carbon atoms to which the hydroxyl group is attached and the nearest ethylenic carbon atom; said condensation product resulting from a reaction in which the molal proportions of the alpha-beta unsaturated dicarboxy acid to the unsaturated alcohol are within the range of about 1.5 to 2.5 and the saturated alcohol reactant is such that the total equivalents of alcoholic reactants is about equal to the equivalents of dicarboxy acid used; said additive being present in amount varying from 0.025% to about 5%, by weight, on the basis of the lubricating oil with which it is admixed.

4. A composition of matter, consisting of a mineral lubricating oil and a relatively small amount of an aliphatic saturated alcohol-alpha-beta unsaturated dicarboxy acid-unsaturated aliphatic monoethylenic alcohol condensation product; said alcohols being normal straight chain containing at least 8 and not more than 18 carbon atoms; said acid having not over 5 carbon atoms and said unsaturated alcohol having at least 3 intervening carbon atoms between the carbon atom to which the hydroxyl group is attached and the nearest ethylenic carbon atom; said condensation product resulting from a reaction in which the molal proportions of the alpha-beta unsaturated dicarboxy acid to the unsaturated alcohol are within the range of about 1.5 to 2.5 and the saturated alcohol reactant is such that the total equivalents of alcoholic reactants is about equal to the equivalents of dicarboxy acid used; with the proviso that 10% to 65%, by weight, of the condensation product be monomeric; said additive being present in amount varying from 0.025% to about 5%, by weight, on the basis of the lubricating oil with which it is admixed.

5. A composition of matter, consisting of a mineral lubricating oil and a relatively small amount of an aliphatic saturated alcohol-alpha-beta unsaturated dicarboxy acid-unsaturated aliphatic monoethylenic alcohol condensation product; said alcohol being normal straight chain containing at least 8 and not more than 18 carbons; said acid having not over 5 carbon atoms and said unsaturated alcohol having at least 3 intervening carbon atoms between the carbon atom to which the hydroxyl group is attached and the nearest ethylenic carbon atom; said condensation product resulting from a reaction in which the molal proportions of the alpha-beta unsaturated dicarboxy acid to the unsaturated alcohol are within the range of about 2.0 and the saturated alcohol reactant is such that the total equivalents of alcoholic reactants is about equal to the equivalents of dicarboxy acid used; with the proviso that 10% to 65%, by weight, of the condensation product be monomeric; said additive being present in amount varying from 0.025% to about 5%, by weight, on the basis of the lubricating oil with which it is admixed.

6. The composition of matter defined in claim 5, wherein the saturated alcoholic reactant employed in the condensation reaction is stearyl alcohol.

7. The composition of matter defined in claim 5, wherein the saturated alcoholic reactant employed in the condensation reaction is stearyl alcohol, and the unsaturated alcohol is oleyl alcohol.

8. The composition of matter defined in claim 5, wherein the saturated alcoholic reactant employed in the condensation reaction is stearyl alcohol; the unsaturated alcohol is oleyl alcohol, and the dicarboxy reactant is maleic anhydride.

9. The composition of matter defined in claim 5, wherein the saturated alcoholic reactant employed in the condensation reaction is stearyl alcohol; the saturated alcohol is oleyl alcohol, and the dicarboxy reactant is citraconic anhydride.

10. The composition of matter defined in claim 5, wherein the saturated alcoholic reactant employed in the condensation reaction is stearyl alcohol; the saturated alcohol is oleyl alcohol, and the dicarboxy reactant is fumaric acid.

CHARLES M. BLAIR, JR.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,101,227	Werntz	Dec. 7, 1937
2,062,917	Lawson	Dec. 1, 1936
2,375,516	Blair	May 8, 1945