

1

3,071,546

LUBRICANT COMPOSITION

Robert W. Van Tuyle, Cincinnati, Ohio, assignor to Emery Industries, Inc., Cincinnati, Ohio, a corporation of Ohio

No Drawing. Filed Sept. 26, 1958, Ser. No. 763,461
1 Claim. (Cl. 252-39)

This invention is directed to materials adopted to be added to the lubricating oils used in internal combustion engines for the purpose of promoting engine cleanliness and reducing the corrosive effects of combustion products. This application is a continuation in part of my co-pending application for "Lubricant Additive," Serial No. 505,033, filed April 29, 1955, and now abandoned.

The more precise designs of internal combustion engines, the higher horsepower ratings and the greater use of diesel engines has made it necessary to improve the properties of petroleum lubricants to provide longer engine life and more trouble-free performance. These improvements are achieved by incorporating in the base petroleum lubricants, quantities ranging from a trace to two to three percent of specific chemical compounds designed to enhance certain desired properties. For example, extreme pressure additives may be used to increase the film strength and adhesion at bearing surfaces and thereby improve lubricating properties.

Another class of additives in common use are termed detergents and are added to decrease the formation of adhesive deposits on internal working parts and to keep sludge materials which may form in suspension in the lubricating oil. Likewise, materials are added for the purpose of neutralizing acidic products formed during the combustion of the fuel. The need for such additives, generally termed alkali reserve agents, is greater in diesel lubricating oils as diesel fuels often contain sulfur compounds which, after combustion, result in the formation of sulfuric or sulfurous acids in the crank case oil. Such acid formation not only corrodes engine parts but also increases the formation of sludge and/or carbon deposits on operating parts, particularly the piston rings.

Materials employed as additives must be soluble in the petroleum lubricant and must remain in solution under the extremes of temperature which may be encountered in an engine crank case. Dissolving the additive in the oil should not radically change the physical characteristics of the oil, for example, its viscosity. Additives are employed to improve the temperature viscosity relationships of lubricants, but obviously a product which, although soluble, converted a lubricating oil into a grease-like material, would not be usable.

Additives must also be so chemically constituted as to be resistant to deterioration when subjected to the heat of engine parts and the oxidizing conditions encountered in a crank case.

It is the purpose of this invention to provide compositions which are soluble in petroleum lubricating oils, resistant to oxidation, capable of neutralizing acidic products of combustion and which contribute to engine cleanliness.

It is more specifically the purpose of this invention to provide certain salts, as hereinafter described, of fatty acids which have been structurally modified to increase the oil solubility of the salts and also to improve their resistance to oxidation and heat deterioration. The salts of the normal fatty acids of commerce, such as oleic acid, stearic acid and mixtures of these have previously been used in lubricants as gelling agents in the production of

2

lubricating greases. The ability of the calcium aluminum barium, sodium and similar soaps of fatty acids to form a grease when properly constituted with a petroleum lubricant is the very property which has prevented the use of normal fatty acid salts as lubricating oil additives. The unsaturated fatty acids have less-pronounced gelling tendencies than the saturated acids, but this advantage is more than offset by their lack of stability towards oxidation.

I have found that unsaturated fatty acids which have first been modified by heat treatment, either in the presence or absence of catalyst, to effect a structural rearrangement and then hydrogenated, yield metal salts which are soluble in petroleum oils, are resistant to oxidation and deterioration, and are effective alkaline reserve agents when added to lubricating oils. The structurally modified acids are conveniently obtained from the monomeric acids obtained as by-products from the production of dibasic fatty acids such as dimer acids. A process for the production of dimer acids is described in United States Patent No. 2,482,761. In this process fatty acids containing polyunsaturated acids are heated to temperatures in excess of 260° C. in the presence of water which is retained in the reaction mixture by the application of pressure. The heating is continued until polymerization of the polyunsaturated acids is substantially complete and the polymerized acids then separated from the unpolym-
 25 erized acids, most conveniently by distillation. The acids employed in this invention are derived from the mono-
 30 meric unpolymerized acids.

Investigation has shown that these acids consist of saturated fatty acids contained in the original fatty acids which are essentially unchanged by the treatment, unsaturated acids which have not been polymerized and have
 35 not been structurally modified, and unsaturated acids which have not been polymerized but have become structurally modified.

It has not been possible to determine the molecular configuration of the structurally modified acids nor to explain the mechanism by which they are formed. The acids contain approximately one double bond per molecule, as shown by iodine value determinations, and these double bonds can be saturated by hydrogenation. The double bonds do not hydrogenate as readily as do the
 45 double bonds in normal straight-chain acids and the hydrogenation appears to become increasingly more difficult as the hydrogenation progresses. It is possible, therefore, that the structurally modified acids are not composed of a single compound but rather of a series
 50 of closely related compounds. Hydrogenation and the saturation of the double bonds increase the stability of the acids but, surprisingly, does not cause their conversion into solid acids as is the case of normal unsaturated acids. In other words, these structurally modified acids,
 55 whatever they may be, can be hydrogenated to attain the inertness of saturated acids without losing their liquid character. The salts of these acids not only retain the solubilities of the liquid acids, but the solubility actually is enhanced by the structural modification which has
 60 occurred.

The hydrogenation step is preferably carried out on the mixed monomeric products prior to attempting the separation of the structurally modified acids from the saturated acids and unchanged unsaturated acid with
 65 which it is contaminated. By hydrogenating first, the unchanged oleic acid or oleic isomers are converted to solid stearic acid. The separation is thereby simplified as it is then only necessary to separate solid acids from

the liquid structurally modified acids. This can be done conveniently by solvents, for example, by the process disclosed in United States Patent No. 2,293,676 as the structurally modified acids, although saturated by hydrogenation, retain the solubilities of liquid acids.

In place of the structurally modified monomeric acids which are the co-products of the practice of the polymerization process described in U.S. Patent 2,482,761, the other co-products of other polymerization methods may be employed such as those produced by heating the methyl and ethyl esters or by heating the esters or acids in the presence of various clays. U.S. Patents 2,793,219 and 2,793,220, both issued May 21, 1957, described dimerizing or polymerizing processes which utilize clays and produce as co-products structurally modified acids of the type in question. All of these structurally modified acids may be hydrogenated and solvent separated to produce the hydrogenated liquid, structurally modified acids which are suitable for the production of the soaps which are used as the lubricant additives of this invention.

These structurally modified, hydrogenated, liquid acids are specifically disclosed and claimed in U.S. Patent 2,812,342, issued November 5, 1957. As pointed out in this patent, neither the nature of the raw material which is polymerized nor the process used greatly affects the physical or chemical characteristics of the co-products remaining after hydrogenation and solvent separation.

The hydrogenated liquid, structurally modified acids which are obtained by the methods which have been described, are slightly yellow liquids having the general appearance of a light-colored oleic acid. The iodine value (Weiss) of these acids may be from 3 to 10 depending upon the degree of hydrogenation. The titer of these acids may be 3° to 15° C., depending upon the efficiency of the solvent separation. When pure, the acids titrate 99% free fatty acid as oleic, and their boiling point under a vacuum is practically the same as that of oleic acid.

The acids are carboxylic acids having 18 atoms per molecule but, obviously, the structure of the molecule must be different from that of stearic acid or oleic acid because the iodine value is about that of a good stearic acid whereas the titer is about that of a good oleic acid. Spectrographic tests suggest that these acids are neither straight chain acids nor cyclic acids but perhaps a mixture of branch chain acids. In any event, and for all practical purposes, these acids may be considered to be liquid stearic acids inasmuch as they are 18 carbon, carboxylic, saturated acids and differ in properties from normal stearic acid only in that they are liquid at room temperature whereas stearic acid is solid at room temperature. Therefore, for the purpose of describing this invention, these structurally stabilized fatty acids, which have an iodine value of substantially 3-10 and a titer below 15° C. will be referred to as "isostearic acid."

In the following examples involving comparative tests, isostearic acid was used which resulted from the polymerization of refined tall oil containing substantially 50% oleic acid and 50% linoleic acid. The tall oil was polymerized in the presence of clay to produce a yield of substantially 50-60% polymer. However, the degree of treatment does not determine the character of the pertinent end product, inasmuch as all unmodified oleic and linoleic acids are saturated and converted to "normal" stearic acid by the hydrogenation process, and eliminated by solvent separation leaving only the liquid or isostearic acid as the end product. The term "normal" stearic acid as used above is intended to distinguish from both the liquid isostearic acid and the common or commercial stearic acid which is in fact 45% "normal" stearic acid and 55% palmitic acid. Further, the identity of the starting material is not critical as the isostearic acids produced from tall oil, oleic acid, cotton seed oil, soy bean oil, etc., are all substantially alike and are not subject to independent identification.

The alkaline earth soaps of the isostearic acid may be

prepared by first preparing an aqueous solution of the sodium soap and then adding inorganic salts of calcium, barium and magnesium to precipitate the corresponding soaps of the isostearic acid. The soaps may also be prepared by reacting with the aid of heat a solution of the isostearic acid in mineral oil with oil suspensions of the appropriate metal oxides. The concentrated solutions prepared in this manner may then be further diluted with lubricating oil to the desired concentrations.

The solubilities of the soaps in lubricating oils, particularly those which are highly paraffinic in nature, may be increased if required by the addition of a proportion of free unneutralized acids or alternatively by only partially neutralizing the acids during the preparation of the soaps. The presence of the small amount of unneutralized carboxylic acid in a lubricating oil is not generally objectionable for most lubricating uses because carboxylic acids are relatively inert in relation to most metals which are exposed to the lubricating oils. These metals are, however, not inert to sulfurous, sulfuric or sulfonic acids which are much stronger and more corrosive acids than carboxylic acids, particularly the long chain fatty acids. The salts of the isostearic acid serve as an alkaline reserve agent in relation to these stronger acids which react with the salts of the weaker acid as the stronger acids are formed, thus converting the stronger acids to salts and the salts of the isostearic acid to the less corrosive isostearic acid.

The solubilities of the metal soaps of stearic, oleic and the isostearic acid were determined in 100 second paraffin oil containing 1% of the corresponding free acid by the following method:

The metal soap was added in excess to the fatty acid paraffin oil solution which was heated to 130-140° C. The mixture was allowed to settle at 125° C. and the undissolved soap removed by filtration at this temperature. Under these conditions the magnesium soaps showed infinite solubility. The calcium and barium soaps of stearic acid yielded cloudy gels. The oleic and isostearic acids gave clear solutions in the oil. Portions of the oil solutions were then ashed and the content of dissolved soap calculated from the ash content. The following results were obtained:

	Stearic Acid, Percent	Oleic Acid, Percent	Isostearic Acid, Percent
Barium.....	1.5	2.7	10.2
Calcium.....	3.6	4.6	5.1

These results show that under equal conditions the soaps of the isostearic acid are more soluble than the soaps of either stearic or oleic acids.

To demonstrate resistance to oxidative deterioration, 10 gram samples of the acids were exposed to an atmosphere of oxygen at 60° C. and the time required for the absorption of 10 cc. of oxygen was determined. The following results were obtained.

Material	Time to absorb 10 cc. of oxygen
Stearic acid.....	days... 65
Oleic acid.....	hours... 5
Isostearic acid.....	days... 65

In another test the barium soaps were placed in a pressure bomb and subjected to 110 pounds' pressure of pure oxygen at 100° C. for a period of 15 days. At the end of this period, the oxygen pressure remaining was measured as an indication of the amount of oxygen unabsorbed. This test showed:

Barium Soap of	Initial Pressure, lbs.	Pressure after 15 days, lbs.
Stearic Acid.....	110	109.5
Oleic Acid.....	110	68.5
Isostearic Acid.....	110	103.0

5

Both of the above tests show that the isostearic acid and the soaps are far superior in oxidation resistance to oleic acid and about equal to stearic acid in this characteristic.

The effectiveness of the calcium, barium and magnesium salts of the isostearic acid in oil additives was determined by running standard engine tests, using a diesel engine to determine the effect on cleanliness of engine parts and a spark ignition engine primarily for the purpose of determining that the additive did not adversely affect the operation of an engine of this type.

In conducting the tests, the oxidation inhibitors and detergent additives usually employed were used and in addition 2% of the salts of the structurally modified acids. In the diesel test, a fuel containing 2% of sulfur was employed in order to accelerate the formation of ring deposits. The engine was operated for 50 hours under controlled conditions and at the end of this time the pistons and rings were examined for sludge and carbon deposits. It was found that the pistons and rings were remarkably clean when the salts of the isostearic acid were added in comparison to the control runs employing the same oil and additives but without the salts of the isostearic acid. The calcium and barium salts were found to be somewhat better than the magnesium salts. For example, employing a scale of demerit points, the control oil was given a rating of 56, the oil containing 2% of magnesium salts of isostearic acid 11, and the oil containing the calcium or barium salts ratings of 3.8 and 4.0 respectively.

The same oils were used in a gasoline engine operated on a standard leaded reference gasoline for a period of 40 hours. In these tests, the salts of the isostearic acid had no adverse effects on operation. Upon examination, the engine operating on the control oil was found to be quite clean. The engine operated with lubricant to which the salts of isostearic acid had been added in some cases were slightly but not significantly cleaner. These tests demonstrated that the detergents normally employed were adequate for this usage, but also indicated that the salts of the isostearic acid could be employed for the type of service where alkaline reserve agents are not normally required without detracting from the functioning of the other additives.

My invention is more completely illustrated by the following examples:

EXAMPLE 1

Preparation of Salts by Precipitation

An aqueous solution of the sodium soaps of isostearic acid is prepared by mixing 10 parts of the acid and approximately 100 parts of water, heating the mixture almost to boiling and while stirring continuously adding a concentrated solution of sodium hydroxide containing a slight excess of alkali over that required to neutralize the acids (about 7.5 to 8.5% excess). A solution of the appropriate metal salt, i.e., barium chloride, calcium chloride or magnesium sulfate, is then added to the aqueous solution of sodium soap until no further precipitate is formed. Ten percent excess of the metal salt is adequate to insure complete precipitation. The aqueous liquid is removed either by decantation or filtration, the precipitates washed with water to remove inorganic salts and then dried in an oven at 110° C. The original white precipitates become light brown in color during the drying operation.

EXAMPLE 2

Preparation of Soaps by Direct Reaction of Acids and Appropriate Oxides in Mineral Oil

The barium, calcium and magnesium soaps are prepared by heating the oxides and the isostearic acid to temperatures of 110° C. to 125° C. for from ½ to 2

6

hours. Some variations in procedure are desirable with the various oxides in order to avoid gel formations. With barium oxide, about 20% excess of the oxide should be employed and the oxide suspended in about ½ of the volume of oil added over a period of about ½ hour to the acids dissolved in the remaining oil. The temperature is held at 100° C. during the addition and then raised to 110° C. for an additional two hours.

With calcium oxide, a 10% excess of oxide, is ample and the oil oxide and acid may be slurried together and then heated to 110° C. during about ½ hour and heating then continued at 110° C. for 1 hour or at 125° C. for ½ hour.

A similar procedure is employed with magnesium oxide, except that 40% excess magnesium oxide is required if the "heavy" form of oxide is used.

The resulting solutions of salts of isostearic acid in oil are filtered while hot through a bed of filter aid to remove any excess oxide or other insoluble material. In this manner, it was possible to prepare solutions containing as high as 35% of the barium salt, 40% of the calcium salt and 50% of the magnesium salt. The magnesium salts are almost completely neutral, but it was not possible to secure over 80 to 85% neutralization with the calcium and barium oxides.

EXAMPLE 3

Diesel Engine Tests

A Witte single cylinder diesel engine was operated on a fuel containing 2% sulfur to accelerate piston and ring deposits. The engine was operated for 50 hours at 1800 r.p.m. with a 4-5 brake horsepower load, an oil temperature of 140-150° F. and a cooling jacket temperature of 175 to 180° F. After 50 hours of operation, the pistons and rings were examined for cleanliness and assigned demerit points for presence of sludge or carbon deposits.

Tests were run on control oils and on the same oils to which 2% of the salts of isostearic acid had been added. The composition of the oils and the results of the piston examinations are shown in the following chart:

Salt of Isostearic Acid	Oxidation Inhibitor	Detergent Calcium Sulfonate	Barium Sulfonate	Piston Rating
None	1.31	3.0		56
2% Barium Salt	1.31	3.0		19.0
2% Mg Salt	2.18	3.0		11.0
None	1.31	5.5	2.5	28.0
2% Barium Salt	1.31	5.5	2.5	4.0
2% Barium Salt (check)	1.31	5.5	2.5	3.8

Oil used S.A.E. 30.

Oxidation Inhibitor—Wax olefin reacted with P₂S₅.

Detergent—Di-wax benzene sulfonates.

It will be noted that the pistons and rings were uniformly clean as shown by the lower demerit ratings when the salts of the isostearic acid were used regardless of the type or amount of detergent employed.

EXAMPLE 4

Gasoline Engine Tests

The gasoline engine tests were run on 4-cylinder (International) engines for 40 hours at 2500 r.p.m. under 11 brake horsepower load, oil sump at 280° F. and cooling jacket at 200° F. using a straight run cracked blend leaded gasoline. At the end of the test run, the engines were examined for piston varnish, total varnish and sludge and assigned demerit ratings. The results obtained with the control oils and with oils to which salts of the

isostearic acid were added are shown in the following table:

Salt of Isostearic Acid	Other Detergent	Total Detergent Additives	Oxidation Inhibitor	Demerit Rating
None.....	5.5 Calcium Sulfonate.	5.5	1.31	13.0
2% Barium Salt.....	3.0 Calcium Sulfonate.	5.0	1.31	14.5
2% Calcium Salt.....	do.....	6.0	1.74	12.5
2% Mg Salt.....	do.....	5.0	2.18	11.0
2% Mg Salt Check.....	do.....	5.0	2.18	12.0

Other detergents and oxidation inhibitors were the same as in Example 3. The results show that the differences, if any, are slight but show that if an oil compounded for diesel operation, i.e. by adding the salts of isostearic acid, were used in a spark ignition engine, there would be no adverse effects. The results tend to indicate that the salts of the isostearic acid can replace a part of the detergent normally employed so that the total amount of additives of this class is not increased.

Having described my invention, I claim:

A lubricant composition consisting essentially of a petroleum lubricating oil and a minor amount, sufficient to increase the detergent activity of the composition and to provide the latter with an alkaline reserve, of at least one salt selected from the group consisting of the calcium, magnesium, and barium salts of a structurally stabilized, C₁₈ monocarboxylic fatty acid having an iodine value of substantially 3-10 and a titer below 15° C., said fatty acid representing the normally liquid fraction of the product obtained on hydrogenation of the unpolymerized acid portion of the reaction mixture obtained by the polymerization of C₁₈ unsaturated, fatty acids.

References Cited in the file of this patent

UNITED STATES PATENTS

2,215,955	Cox	Sept. 24, 1940
2,231,168	Lazar et al.	Feb. 11, 1941
2,343,737	Beerbower et al.	Mar. 7, 1944
2,860,151	Lamson	Nov. 11, 1958

OTHER REFERENCES

"The Condensed Chemical Dictionary," 5th Ed., 1956, Reinhold Pub. Corp., pages 130, 131, 210, 675 and 676.