Patented Apr. 16, 1940 2,197,153

UNITED STATES PATENT OFFICE

2,197,153

LUBRICATING OIL CONTAINING ARYL FATTY ACID SOAP

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No Drawing. Application February 23, 1937, Serial No. 127,199

12 Claims. (Cl. 87—9)

This invention relates to hydrocarbon oils, such as petroleum oils, particularly adapted for use as lubricants, but also for use as transformer oils, switch oils, agricultural spray oils, and the like. The oils of this invention are characterized by their stability or resistance to change of characteristics on exposure to oxidizing conditions, as by contact with air at ordinary or elevated temperatures, with or without the presence of light. A particular object of the invention is to provide a stabilized lubricating oil, adequate to prevent the sticking of rings and valves in engines where the oils receive severe service, as in Diesel engines. A further object of the invention is to provide petroleum oils which, on exposure to air and light, have unusually slight tendency to darken in color, to become cloudy, or to deposit finely divided, oil-insoluble carbonaceous materials, commonly referred to as sludge. Such formation of dark colors and deposition of sludge is undesirable, as it makes the oil less readily salable and useful for the various intended purposes.

In the case of severe service conditions such as encountered in Diesel engines and the like there is a strong tendency on the part of lubricating oils to develop bodies which cause particularly a sticking of piston rings, and this may extend also to sticking of valves. Even in other service uses where the conditions are less severe, similar results are sometimes encountered due perhaps more to the character of the lubricating oil as in the case of more modern, very heavily refined lubricants such as very highly paraffinic oils from which substantially all non-paraffinic constituents have been removed. In many instances these oils also tend to the development of corrosive conditions which are especially objectionable in the case of certain modern alloy bearings such as cadmium silver bearings and the like. Heretofore, attempts have been made to introduce various substances including various soaps into lubricating oils to stabilize them from the standpoint of severe service conditions such as result in the sticking of rings in Diesel engines and also from the standpoint of bearing corrosion. For example, metallic naphthenates and oleates have been employed, but these have not been entirely satisfactory, due to further tendency toward bearing corrosion in the case of naphthenates, and due to frequent development of sludge conditions resulting from oxidation in the case of unsaturated fatty acids such as oleic acid. Again, in the case of saturated fatty acids such as stearic acid, solubility of soaps may be inadequate unless a common solvent is employed, but the use of such solvent is objectionable in view of the hazard of the loss of solvent by evaporation and consequent separation of the soap from solution or the development of excessive "body" or viscosity.

However, I have found that there are types of oil-soluble soaps which will stabilize mineral oils including stabilizing lubricating oils to overcome sticking of piston rings and valves in Diesel engines and the like and also to overcome development of corrosive conditions with respect to special bearings. These may be developed from unsaturated fatty acids in which one or more phenyl (C_6H_5) or other aryl groups have been introduced at the double bonds. Various soaps of these phenylated or arylated fatty acids may be employed, such as alkali metal soaps, alkaline earth metal soaps, heavy metal soaps and soaps of organic bases. Other suitable materials are such soaps of all compounds obtained by condensing aromatic hydrocarbons with unsaturated fatty acids as when accomplished under the influence of aluminum chloride as a catalyst.

Broadly stated, the invention resides in the addition to mineral oils such as lubricating oils of small quantities of a soap of a compound obtained by the condensation of aromatic hydrocarbons with unsaturated fatty acids having at least ten carbon atoms. The invention more particularly includes the use in lubricating oils of oil-soluble soaps of alkali metals, alkaline earth metals, heavy metals and organic bases with the heavier unsaturated fatty acids in which at least one aromatic hydrocarbon group has been introduced at a double bond, especially a phenyl group. The invention particularly extends to the use of such soaps in quantity sufficient to produce the desired ends, and in the case of lubricating oils in quantity insufficient to thicken or increase the viscosity of the oils unduly so that they will remain sufficiently fluid for use at the temperatures for which they are intended. In general this will average about 1% based on the total lubricant and will range between about ½% and 3% for most uses.

In practicing the invention, oil-soluble soaps of any of the various unsaturated fatty acids of sufficient molecular weight may be employed. This applies to all unsaturated fatty acids having ten or more carbon atoms including naturally occurring unsaturated fatty acids regardless of whether they contain 1, 2 or 3 or more double bonds. For example, I may use the unsaturated fatty acids having only one double bond, such as

oleic acid ($C_{18}H_{34}O_2$), both of the isomers of myristoleic acid ($C_{14}H_{26}O_2$), palmitoleic acid ($C_{16}H_{30}O_2$), ricinoleic acid ($C_{18}H_{34}O_3$), petroselenic or petroselic acid ($C_{18}H_{34}O_2$), which is an isomer of oleic acid and erucic acid ($C_{22}H_{42}O_2$); also the unsaturated fatty acids having two double bonds such as linolic (linoleic) acid ($C_{18}H_{32}O_2$), and elaeo-stearic acid ($C_{18}H_{32}O_2$); as well as the unsaturated fatty acids having three double bonds such as linolenic acid ($C_{18}H_{30}O_2$). Also fatty acids having four double bonds such as clupanodonic acid ($C_{18}H_{28}O_2$) may be used. Such acids and their structural formulas may be found in such publications as Fryer and Weston, "Oils, Fats and Waxes" (1920) and Lewkowitsch "Chemical Technology and Analysis of Oils, Fats and Waxes," sixth edition (1921).

All of these acids when condensed with aromatic hydrocarbons to include an aromatic nucleus such as a phenyl group (C_6H_5) are within the scope of the invention, and from them various oil-soluble soaps may be made including the soaps of the alkali metals sodium and potassium, soaps of the alkaline earth metals such as calcium and magnesium, soaps of aluminum, heavy metal soaps such as zinc, tin, iron and manganese, and other metals in the same groups of the periodic system, as well as soaps of organic bases such as triethanolamine, morpholine, ethylene polyamines such as triethylene tetramine, quaternary ammonium bases such as tetra-ethyl ammonium hydroxide, quinoline bases, nitrogen bases from petroleum and the like. The modified acids to be employed in preparing the soaps hereof may be readily made by condensation of the organic acid and benzene or other appropriate aromatic hydrocarbon such as toluene, xylene and naphthalene, using aluminum chloride as the catalyst. Such processes are well understood. For example the unsaturated oleic acid may be condensed with benzene in the presence of aluminum chloride to produce phenyl stearic acid which will contain one phenyl group. Again, linolic acid may be condensed with benzene to introduce two phenyl groups and form a diphenyl stearic acid, or to introduce a single phenyl group forming a phenyl oleic acid. Similarly the triple double-bonded linolenic acid may be condensed to introduce 1, 2 or 3 phenyl groups, thereby forming a phenyl linolic acid or a di-phenyl oleic acid or a triphenyl stearic acid. Actually mixtures are probably formed in most cases but these are satisfactory for the intended purpose.

For example in the production of a phenyl stearic acid from oleic acid, two parts of oleic acid may be dissolved in four parts of benzene and one part of powdered aluminum chloride added slowly. A very vigorous action will take place promptly. After a time this action will have moderated, at which time the mixture may be slowly heated with mild agitation up to a temperature of as high as about 170–180° F. for a period of about six hours or until hydrochloric acid is no longer evolved. The mixture is then poured into seven parts of 20% hydrochloric acid, and the excess benzene removed by steam distillation. The oily layer is fractionated under reduced pressure to remove uncombined oleic acid and the product is then recovered as a distillate in the nature of a yellowish oil having a boiling point of about 480° F. at 4 mm. and an iodine number of less than 5.

From the acid so prepared, soaps of metals or bases herein mentioned may be made by conventional methods, such as (1) formation of a sodium soap followed by metathesis to yield the other desired soap, or (2) formation of the hydroxide or hydrated oxide of the metal to be employed and neutralization of such hydroxide with the phenyl stearic acid above described, this taking place either in the presence of a solvent or otherwise as may be desirable. The oil in which the soap is to be used may itself be used as the solvent.

The other modified acids and their corresponding soaps will be formed in similar fashion to that above described.

Having produced the soaps and recovered them in such state of purity as may be appropriate, they will be added to lubricating oils in proportions to attain the ends herein sought. For lubricating oils for Diesel engines and the like, the range ordinarily will be from about 0.5% to 3% or preferably between about 0.8% and 1.5%. However, these proportions may be increased to as much as 4% without increasing the viscosity of the oil objectionably, nor do they increase the ash content undesirably. For Diesel engines it may be preferable to employ a lubricating oil having in itself some tendency toward elimination of ring and valve sticking, for instance a naphthenic or Western type oil. Again, these materials may be used with highly paraffinic oils. The percentages may depend to some extent upon the severity of the use and the effects desired.

Not only may these soaps be employed in ordinary lubricating oils as above indicated, but it may be desirable in some instances to use them in thickened oils or so-called liquid greases, and possibly in other connections such as solid or semi-solid greases, for purpose of stabilization towards oxidation.

In the case of the phenyl stearic acid soap hereof, the phenyl stearic acid employed is commonly known as "Nicolet and De Milt's" acid, inasmuch as its composition is not definitely known and it was first described by Nicolet and De Milt. Apparently the phenyl group is attached to either the ninth or tenth carbon or possibly both of these isomers are present. Similar conditions doubtless exist in the case of all of the other modified acids here disclosed.

In addition to benzene, other suitable aromatic hydrocarbons as above mentioned may be used such as toluene, xylene, ethyl benzene, naphthalene and alkyl naphthalenes.

The soaps herein produced to be used for the purposes of the present invention are soluble in mineral lubricating oils, and in such blends of lubricating oil as may be employed, to the extent required for the desired purposes.

A soap of special value in oils such as Diesel engine lubricating oil is calcium phenyl stearate, which may be employed in quantities within the ranges above mentioned, or on the average in amount of the order of about 1% soap.

It is to be understood that the disclosures above are given for purposes of illustration and not as limitations, inasmuch as many variations will be apparent to those skilled in the art.

I claim:

1. A normally fluid mineral oil lubricant comprising an oil containing an oil-soluble organic base soap of an unsaturated fatty acid of at least ten carbon atoms condensed with an aryl compound.

2. A normally fluid mineral lubricating oil containing a morpholine soap of an unsaturated fatty acid of at least ten carbon atoms condensed with

an aryl compound, the soap being present in amount between about 0.5% and 4%.

3. A lubricant comprising a major proportion of mineral lubricating oil containing a minor proportion of an oil-soluble organic base soap of an unsaturated fatty acid of at least ten carbon atoms condensed with an aryl compound and thereby containing an aryl group.

4. A normally fluid mineral lubricating oil for the lubrication of severe service internal combustion engines containing an oil-soluble, organic base soap of an unsaturated fatty acid containing at least ten carbon atoms per molecule which has been condensed with an aryl compound to introduce an aryl group, the soap being employed in proportion between about 0.5% and 4% based on the mineral oil and being present in quantity to control ring sticking and avoid appreciable viscosity increase in the product over that of the original oil.

5. A lubricant according to claim 4 wherein the amount of soap is in the order of one percent.

6. A lubricant according to claim 4 wherein the organic base is triethanolamine.

7. A lubricating oil according to claim 1 wherein the soap is a phenyl stearate.

8. A lubricating oil according to claim 3 wherein the aryl group is a phenyl group.

9. A lubricant according to claim 4 wherein the soap is a phenyl stearate.

10. An oil according to claim 2 wherein the soap is a phenyl stearate.

11. A lubricant according to claim 3 wherein the soap is a triethanolamine phenyl stearate.

12. A lubricant according to claim 3 wherein the soap is a morpholine phenyl stearate.

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