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IMPROVED LUBRICANTS AND METHODS OF MANUFACTURING THE SAME

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The present invention relates to the production of improved oils for lubricating purposes and, especially, of low pour point oils. The invention will be fully understood from the following description of the oils and their methods of manufacture.

It has been found that certain oxygen-containing substances such as acids, soaps, esters and the like when present in small quantities in viscous lubricating oils make valuable addition agents suitably modifying the lubricating film so as to increase its strength and the load bearing capacity, reducing friction and generally improving lubricating quality. It has also been found that there are certain classes of substances which have the power of modifying crystal form or growth of the waxy constituents of lubricating oils so as to prevent solidification or congelation of the oil at its normal pour point. In this way an oil which normally becomes solid at say 30, or 40 or 50 or even 75° F. may be caused to remain liquid even as low as 15 or 10, or 0 or below, without removal of any of the wax therefrom. The present invention relates to a new class of substances which possess both of the two enumerated properties to a more or less substantial degree.

The materials which form the basis of the present invention are condensation products of various compounds. The condensation is carried out with the assistance of aluminum chloride, zinc chloride, boron fluoride or other known condensation agents of this class and ordinarily at room temperatures such as 70 to 100° F. and generally not above say 125 or 150° F., although the allowable limits may vary somewhat when different materials are used. If desired, solvents may be used during the condensation and for that purpose highly saturated kerosene or heavy naphtha, or other solvent may be used.

In general, oxygen-containing aliphatic materials of the class of esters, ethers, acids, alcohols and ketones serve the present purpose. The substances of these classes which are used are those which contain relatively long hydrocarbon chains, say containing 10 or 12 carbon atoms at least, and preferably even more. The hydrocarbon chains are preferably straight or, at least, should be substantially so. If these materials are olefinic themselves they may be condensed as such by means of aluminum chloride or its equivalents; or, on the other hand, if the chains are saturated they may be chlorinated or otherwise halogenated by bubbling chlorine, for example, through the liquid material until it is increased in weight by 10 or 14% due to the addition of chlorine. The chlorinated derivatives may then be used as such and the condensation is carried out in the same way as indicated above with the aluminum chloride type of catalysts at substantially the same temperatures mentioned. During this process a considerable amount of hydrochloric acid may be evolved. If preferred, the chlorine may be removed from the material prior to condensation in any known manner such as by application of heat, preferably in the presence of such materials as barium chloride so as to split off hydrochloric acid leaving unsaturated material for condensation. Unsaturated or an already partially unsaturated material may be increased by this or by other suitable means before condensation.

As to the particular materials which may be used, acids of the type of stearic or palmitic are suitable, but since these are saturated they should be treated as above indicated either to render them unsaturated or to make their halogen derivatives. Generally speaking, straight chain saturated acids produced by the oxidation of paraffin wax by blowing with air, preferably in presence of catalysts of the siccative type which range from C_{10} to C_{22} or more, may all be used, or mixtures may be used just as the natural fatty acids would be used. Naturally, unsaturated acids may also be used such as oleic, erucic, elaïdic or crotonic, and highly unsaturated acids can also be used such as linoleic, or their hydroxy derivatives such as naphtholic. Likewise, the acetylenic acids such as behenolic or stearolic are suitable.

The esters of all of these acids such as methyl, ethyl or propyl esters may be used, or even higher alkyl esters such as the drying or semi-drying oils, but the reaction of such materials is so sluggish that they are not nearly so desirable as the lower alkyl esters for the present purposes. In fact, the lower alkyl esters are probably more desirable than the acids themselves. Alcohols, ketones or ethers are useful for the present purpose exactly as the esters, and the substances of this class should contain straight hydrocarbon chains of, at least 10 or 12 carbon atoms, as indicated above. If they are already unsaturated they may be used as such as indicated before, but if saturated they may be first halogenated or rendered unsaturated by the methods indicated above, or by similar suitable means.

The materials which have been listed above falling in the classes of acids, esters, alcohols, ethers and the like may be used alone, but it is preferable to carry out the condensation in the presence of a cyclic compound such as benzol or naphthalene or their hydrogenated or alkylated derivatives such as toluol or xylol or ethylnaphthalene. The presence of a hydroxy group in the cyclic substances is permissible although not specially desirable, as illustrated by the phenols and naphthols. Nitrated aromatics can be used as well as amines such as aniline and naphthylamine. In addition to the cyclic compounds listed above, cyclic terpenes may also be used.

The condensation which is described above is more than a simple union of two molecules since very heavy polymers are sought to be produced and these materials are particularly desirable. The polymers which are to be used are those having molecular weights well above 600 and since the method produces materials of a series of molecular weights, it is difficult to say which are those responsible for this specific action. It has been found that materials of molecular weights of 1000 or 2000 and even higher are present. The crude reaction product may be purified by the ordinary methods known in the art, for example, by washing with water or alkali to remove traces of the aluminum chloride, or treated with sulphuric acid of a strength insufficient to carbonize or sulphonate, and the lighter fractions which do not possess pour depressing properties may be removed by distillation, preferably under vacuum up to a boiling point of say 475 to 575° F. (1 millimeter vacuum) so as to concentrate the valuable heavy polymers. Distillation with steam can also be used and care should be taken not to crack the product.

The exact structure of these materials after condensation is, of course, unknown but oxygen is still present in the final product in addition to carbon and hydrogen and this can be demonstrated by analysis. If acids or esters are used the oxygen remains in an acidic form, that is to say, the carboxyl group is not destroyed since acid or saponification values can be obtained. This acid group may also be esterified, neutralized or otherwise modified.

The heavy polymers produced by the methods indicated above may be added to lubricating oils in order to increase their film strength on the one hand, and to reduce pour point caused by the presence of waxy constituents. The polymers can be used in wax free oils if desired, but it is generally preferred to use the material in a waxy oil with a pour point of 30° or higher. A part of the wax, of course, may be removed if desired, and in the case of naturally low pour oils I have found it desirable even to add substantial quantities of wax along with the addition agent so as to improve the oil in regard to its viscosity-temperature curve and at the same time maintain a low pour point. For the present purpose the amount of polymer to be added is always below 10% and generally below even 5% depending on whether a more or less concentrated material may have been produced. If a heavy polymer having an average molecular weight of say 600 to 700 is produced by distilling off light fractions, then 1 to 4% is generally sufficient to materially increase the lubricating value of the oil and to reduce its pour point by some 30 to 50° F., and in this concentration the material does not greatly increase the viscosity of the oil with which it is blended. While many methods have been disclosed above, the preferred method is illustrated by the following examples in which the preferred materials and the most satisfactory conditions are used.

About 100 parts of methyl oleate is mixed with 50 parts of naphthalene and 50 parts by weight of anhydrous aluminum chloride. The reaction is vigorous at room temperature and a sludge is separated after reaction and heat evolution have substantially subsided. Traces of the aluminum chloride are removed with water and about 50% of the total product is distilled under vacuum which is largely the methyl ester of naphthalene stearic acid, although it contains lower polymers. The heavier residue remaining is a viscous oily liquid with an average molecular weight of 600 and on analysis showed 82% of carbon, 10.4% hydrogen; the balance is presumably oxygen since no nitrogen or sulphur was present in the initial materials, and only a trace of chlorine is detectable. The material has a saponification value of 142 milligrams of KOH per gram and it is stable to light and heat at moderate temperatures. Substantially the same product can be produced by using 200 grams of oleic acid ester, 250 grams of naphthalene and 105 grams of aluminum chloride in the presence of 500 cc. of carbon disulphide which merely acts as a solvent and may be removed afterwards.

When 1% of the polymer such as is produced as the heavy residue of Example 1 is added to a Bayonne engine oil having a viscosity of 50 seconds Saybolt at 210° F. and a pour point of 30° F., it is found that the pour point is reduced to 15° F. and if 4% of the same polymer is added to a second sample of oil the pour point is reduced to —20° F. This blended oil is a highly satisfactory lubricant and its increased film strength can be noted on the Mougey testing machine described in the National Petroleum News of November 11, 1931 at page 47. This oil is particularly valuable, giving high film strength when used in bearings of aluminum to steel or aluminum to cast iron.

As a second example 200 grams of oleic acid is dissolved in 400 grams of dry benzol and 100 grams of aluminum chloride is added to effect a reaction which becomes violent quickly and subsides in a short time. The mixture is refluxed for several hours and is then distilled at 1 millimeter pressure taking off an overhead cut to 480° F. The heavy residue left in the still comprising 35% of the charge is a powerful pour inhibitor and the light oil is largely phenyl stearic acid.

In the following claims the term "polymerization" is used to describe an effective combination of the materials so as to produce heavy molecular weight substances in substantial quantities, that is to say, with molecular weights well above 600 and ranging through 1000 to 2000. These heaviest materials cannot be vaporized or, only with very great difficulty, without decomposition. When "polymerization of oxygen-containing materials of the class of acids, esters, alcohols, ethers and ketones containing straight chained hydrocarbon groups of at least 10 carbon atoms" is used, it is to be understood that if the materials are saturated they must be rendered unsaturated or else must be halogenated, or if they are unsaturated originally they may be polymerized as such.

My invention is not to be limited by any theory of the operation of the condensation, nor to the use of any particular starting materials, but only to the claims in which I wish to claim all novelty inherent in the process.

I claim:

1. A composition of matter comprising a viscous lubricating oil containing waxy constituents and a small quantity of a high boiling polymer produced by the reaction of an aliphatic oxygen-containing compound with an unsaturated hydrocarbon chain of at least 10 carbon atoms and selected from the class consisting of esters and acids on the one hand, and on the other cyclic compounds selected from the class consisting of aromatic hydrocarbons, their hydrogenated, alkyl, oxy, hydroxy, nitro and amino derivatives.

2. A composition of matter comprising a viscous waxy mineral oil containing a minor quantity of a heavy polymer produced by the condensation of a non-drying ester of an unsaturated aliphatic acid of more than 10 carbon atoms, such reaction being produced by the agency of a condensation catalyst of the aluminum chloride type.

3. A composition according to claim 2 in which the polymer is produced by the reaction of an oleic acid ester and an aromatic hydrocarbon.

4. A composition of matter comprising a viscous mineral oil containing waxy constituents and a small quantity of a high boiling polymerized fraction of the reaction product of a non-drying ester of an aliphatic acid with an unsaturated chain of at least 10 carbon atoms, and an aromatic hydrocarbon, and formed under the influence of a catalyst of the class of aluminum chloride, such high boiling polymer having a molecular weight of at least 600 being present in tensionizing and pour inhibiting proportions.

5. A composition of matter comprising a viscous mineral oil containing waxy constituents and a small quantity of a high boiling polymerized fraction of the reaction product of an oleic acid compound and an aromatic hydrocarbon and formed under the influence of a catalyst of the aluminum chloride type, such fraction being present in pour reducing proportions.

6. A composition of matter according to claim 5 in which a polymer produced from a monoalkyl ester of oleic acid and an aromatic hydrocarbon are used.

7. A composition according to claim 5 in which a polymer produced from a monoalkyl ester of oleic acid and naphthalene are used.

8. A composition of matter comprising a viscous mineral oil containing wax in a small quantity and high boiling polymerized fractions of the product of reaction of a non-drying unsaturated acid compound selected from the group consisting of acids and esters having a chain of at least 10 carbon atoms and a cyclic carbon compound.

9. A composition of matter comprising a waxy mineral oil and a minor quantity of a polymer produced by the reaction of a chlorinated oxygen-containing aliphatic compound containing a chain of at least 10 carbon atoms selected from the class consisting of acids and esters and a cyclic carbon compound.

10. A composition of matter comprising a viscous waxy oil and a minute quantity of a high boiling polymer produced by the aluminum chloride condensation of a chlorinated organic aliphatic acid compound containing at least 10 carbon atoms, and a cyclic carbon compound.

11. A composition according to claim 10 in which the aliphatic acid compound is a lower alkyl ester.

12. A composition according to claim 10 in which the cyclic carbon compound is an aromatic hydrocarbon.

13. An improved lubricating oil comprising a viscous waxy hydrocarbon containing a small quantity of a polymer produced by the condensation of an oxygen containing aliphatic compound with a chain of at least ten carbon atoms and selected from the class consisting of esters and acids.

14. The combination, with oil containing waxy material in solution, of a quantity, sufficient to depress substantially the pour point of said oil, of the acid condensation product constituting the principal result of the reaction between naphthalene and oleic acid, as hereinbefore described.

15. The combination with oil containing waxy material in solution, of a quantity, sufficient to depress substantially the pour point of said oil, of the condensation product, having a molecular weight above about 600, obtained by reacting oleic acid with an aromatic hydrocarbon in the presence of aluminum chloride.

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