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LUBRICANT

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This invention embodies improvements in the lubricating compositions and methods of lubricating disclosed in our co-pending application Serial No. 618,704, filed June 22, 1932, now Patent No. 2,106,554 of January 25, 1938. It is particularly concerned with providing new lubricating compositions and new methods of lubrication for relatively moving metallic surfaces under conditions of extreme pressure.

By "extreme pressures" are meant pressures of or in excess of 10,000 lbs. per square inch, such pressure being often attained in hypoid gears, bearings, and contact surfaces of cylinder and piston rings in internal combustion engines, and an increasingly large number of other points in modern machine design. It is well known that mineral lubricating oils are deficient in oiliness characteristics which is an important defect when the lubricant is employed under conditions of boundary lubrication where the viscosity of the lubricant plays little or no part in lubrication.

Boundary lubrication conditions are obtained when engines are operating at heavy load, low speeds or, if for any reason, the supply of lubricant is cut off or not sufficient. This last condition may exist when for mechanical reasons the lubricant pump is not functioning properly or when the lubricant feed line is clogged with foreign matter.

It has been known that hydrocarbons of the aliphatic series, such as are found in petroleum oils or distillates, and cyclic hydrocarbons, for example, the aromatic hydrocarbons having an aliphatic side chain attached to the nucleus such as the hydrocarbons occurring in the products of the destructive distillation of coal or wood, may be oxidized under properly controlled conditions of pressure and temperature by means of oxygen, air or other oxidizing agents, with or without the use of a catalytic agent, to produce economical yields of certain oxidation products. These products usually contain organic acids containing the carboxyl group and the hydroxy acids, that is, acids containing both the carboxyl group and one or more hydroxyl groups, as well as esters, alcohols, lactones, aldehydes, ketones, etc.

The oxidation process may be carried on by treating the hydrocarbon to be oxidized with an oxidizing gas under pressure at an elevated temperature. The temperature and pressures, in this case, vary depending upon the hydrocarbon being treated and upon the speed with which the reaction is to take place, and whether or not a catalyst is used to promote the reaction. It is to be remembered that these oxidation processes are known to the art and are not to be considered part of our invention.

One object of our invention is to provide a lubricant of high oiliness character, low coefficient of friction, and one which will act as a safety factor in lubrication when abnormal conditions, such as unusually high pressures between the rubbing surfaces, exist for one reason or another.

Another object of our invention is to provide a lubricant which will maintain a very low coefficient of friction when diluted with light hydrocarbons such as are obtained in an automobile crank case by incomplete combustion of the fuel.

A further object of our invention is to provide a lubricant having penetrative lubricity characteristics. It has been found that our lubricant does not drain off the rubbing surfaces when idle, thereby providing a lubricating film on the rubbing surfaces at all times and being of great value to the life of the machine in cold weather starting when the lubricant is very viscous and sluggish.

It has been demonstrated a number of times that hydrocarbon lubricants of the very best quality are not constant in coefficient of friction with slightly changing loads or speeds, and in some cases the coefficient of friction varies over rather wide limits with some lubricants when all operating conditions are held constant.

Another object of our invention is therefore to provide a lubricant which shows a more nearly constant coefficient of friction, thereby insuring smoother engine operation.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail one approved method of carrying out the invention, such disclosed method, however, constituting but one of the various ways in which the principle of the invention may be used.

Broadly stated, our invention contemplates the addition to mineral lubricating oils of relatively small quantities of the product derived from the halogenation of the product obtained by the controlled oxidation of hydrocarbons, the free acids and alcohols present in such product being esterified either before or after the halogenation process.

Since the addition agent of our invention is unusually effective in increasing the extreme pressure characteristics of the lubricating composition to which it is added it has been found necessary to employ only small percentages, less than 20% by weight based on the amount of mineral oil, of such addition agent, and amounts as low as 0.1%, and sometimes even less, may often be employed with effect. As a general rule, we have found that percentages of from about 0.1% to about 5% of the addition agent are satisfactory for most oils for most uses and very seldom is there any occasion to employ more than 10%.

The following is a description of one method of carrying out the present invention. It should be understood, however, that this example is not to be considered a limitation upon our invention but is merely given by way of illustration to aid those skilled in the art to practice our invention.

We oxidize hydrocarbons and wax to form acids, alcohols and esters by any of the methods shown in the following patents: Burwell, 1,690,769; Mackenzie et al., 1,705,298; Pungs et al., 1,787,951; McCoull, 1,767,147; Burwell, 1,690,768. The oxidation product thus obtained, as for example according to the Burwell process, in which a petroleum hydrocarbon oil is oxidized in the presence of a manganese compound in the neighborhood of 120° C. under about 300 pounds pressure, is then treated with chlorine at room temperature. Excess free chlorine and hydrogen chloride are removed by warming and washing with solvents.

The free organic acidity of the composition is then determined in the usual manner and the acids and alcohols present are esterified. It is believed that any lactones resulting from the oxidation step will be hydrolyzed during the esterification and will themselves be esterified.

The alcohols which are employed to form esters may be of the open-chain or closed-chain type. Among the aliphatic alcohols those containing six carbon atoms or less and those having from twelve to eighteen carbon atoms are generally preferred due to the fact that they are available in commercial quantities. Typical examples of suitable alcohols are:

A. Cyclic hydroxy compounds.
  Aromatic hydroxy compounds.
    I. The hydroxyl group attached to the ring.
      Phenol and the substituted phenols:
        Methyl phenol.
        Ethyl phenol.
        Octadecyl phenol.
      Naphthol and the substituted naphthols:
        Methyl naphthol.
        Ethyl naphthol.
      Cresol and the substituted cresols:
        Ethyl cresol.
      Polyhydroxy benzenes such as:
        Catechol.
        Phloroglucinol.
    II. The hydroxyl group attached to a side chain; the aromatic alcohols.
      Benzyl alcohol.
      Ortho-tolyl alcohol.
      Meta-tolyl alcohol.
      Para-tolyl alcohol.
  Naphthenic alcohols and their substitution products.
    Cyclohexanol.

B. Aliphatic alcohols.
  Methyl alcohol.
  Ethyl alcohol.
  Propyl alcohol.
  Iso-propyl alcohol.
  Butyl alcohol.
  Iso-butyl alcohol.
  Lauryl alcohol.
  Octa-decyl alcohol.

To esterify the alcohols found present in the oxidation product acids such as the following are satisfactory:

A. Aromatic acids.
  Benzoic acid and the substituted benzoic acids:
    Methyl benzoic acid.
    Ethyl benzoic acid.
    Propyl benzoic acid.
    Octadecyl benzoic acid.
  Phthalic acid and the substituted phthalic acids:
    Methyl phthalic acid.
    Ethyl phthalic acid.
    Propyl phthalic acid.
    Octadecyl phthalic acid.
B. The naphthenic acids, such as those which may be obtained from the oxidation of petroleum hydrocarbons.
C. Aliphatic acids.
  Acetic acid.
  Propionic acid.
  Butyric acid.
  Lauric acid.
  Oleic acid.
  Ricinoleic acid.
  Stearic acid.

When selecting the particular alcohols and acids to be employed consideration should be given to the characteristics especially desired in the product of esterification. For instance, an ester of a low molecular weight acid, such as acetic acid, and a high molecular weight alcohol is notable for its aid in forming stable lubricating films while an ester of a high molecular weight acid and a high molecular weight alcohol, such as octadecyl alcohol, has unusual properties which aid in the protection of metallic rubbing surfaces. The low molecular weight acids have another practical advantage since they are more reactive than those containing a large number of carbon atoms. While in the process outlined above the oxidation product was halogenated prior to esterification of the acids and alcohols present it is to be understood that such halogenation may be performed subsequent to the esterification if such should be desired. In some cases it may also be possible to cause the mutual esterification of the acids and alcohols present in the oxidized mass without the addition of further amounts of either if proper equivalents are already present.

All of the halogens are satisfactory for use in accordance with this invention but chlorine is the most desirable since it is by far the cheapest and most easily available. Fluorine and bromine are also very effective but somewhat less easily handled while iodine is relatively expensive and the supply limited.

The product thus prepared is added to a sample of high quality lubricating oil and tested on the Timken machine, a machine developed and manufactured by the Timken Roller Bearing Company and well known in the art, where it is compared to a sample of the same oil to which no

addition agent has been added. It is found that the addition agent approximately doubles the film-strength of the lubricant. The coefficients of friction of the lubricant with and without the addition agent are also compared by testing on the Herschel Friction Testing Machine which was developed by Dr. W. H. Herschel of the United States Bureau of Standards and is well known to the art. The reduction in the coefficient of friction found when the addition agent is employed indicates a marked increase in the lubricating qualities of the composition.

Particular advantages resulting from the esterification of the acids and alcohols are an increase in the stability of the composition and higher boiling points which render the composition more suitable for uses where high temperatures are encountered, as, for instance, when used as an addition agent to a lubricant intended for use in the crank-case of internal combustion engines, especially Diesel or airplane engines. Another important advantage is the removal of acid hydrogen and alcohol hydroxyl hydrogen from the composition which reduces the chemical activity of the composition and renders it more suitable as an addition agent to lubricating oils, especially those intended for use with bearings including a characterizing content of tin, cadmium, silver, copper, or lead.

With this end in view it will quite generally be desirable to reduce the acid number of the lubricating composition to below 5.00 and for most uses below 2.00, while an acid number of below 1.00 is preferable. This may generally be accomplished when the addition agent of this invention is treated as above indicated.

While mineral oil generally is the principal ingredient of the lubricant, it is not essential that it be the only ingredient other than the addition agent, provided that there should be no additional ingredient which is incompatible with said addition agent. It is within the contemplation of this invention to include, if necessary or desirable, such other addition agents as are commonly added to improve the viscosity index or cold test of the lubricant, and the like.

In summary, a lubricating composition prepared in accordance with the present invention has the following important advantages:

1. Extreme pressure characteristics providing adequate lubrication over a wider range of working conditions.

2. Increased lubricity tending to decrease the coefficient of friction.

3. Improved stability and higher boiling point of the addition agent.

4. Greater safety when employed in the lubrication of any of the new bearing metals and alloys.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the composition and method herein disclosed, provided the ingredients or steps stated by any of the following claims or the equivalent of such stated ingredients or steps be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation product of a hydrocarbon, the alcohols and acids in such product having been converted by esterification.

2. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 5% by weight, based on the amount of mineral oil, of the halogenated oxidation product of a hydrocarbon, the alcohols and acids in such product having been converted by esterification.

3. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation products of a mixture of hydrocarbons, the acid number of which has been substantially decreased by esterification of the acids in such product.

4. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation products of a mixture of hydrocarbons, the acid number of which has been substantially decreased by esterification of the alcohols in such product.

5. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation products of a mixture of hydrocarbons rich in cyclic hydrocarbons, the acid number of which has been substantially reduced by the esterification of the acids and alcohols in such products.

6. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation products of a mixture of hydrocarbons rich in acyclic hydrocarbons, the acid number of which has been substantially reduced by the esterification of the acids and alcohols in such products.

7. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation product of a hydrocarbon, the acid number of which has been decreased to below 5.00 by esterification of the alcohols and acids present in such product.

8. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation product of a hydrocarbon, the acid number of which has been decreased to below 2.00 by esterification of the alcohols and acids present in such product.

9. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the halogenated oxidation product of a hydrocarbon, the acid number of which has been decreased to below 1.00 by esterification of the alcohols and acids present in such product.

10. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 20% by weight, based on the amount of mineral oil, of the chlorinated oxidation product of a hydrocarbon, the alcohols and acids in such product having been converted by esterification.

11. A lubricating composition comprising a major proportion of mineral oil and from about 0.1% to about 5% by weight, based on the amount of mineral oil, of the chlorinated oxidation

product of a hydrocarbon, the alcohols and acids in such product having been converted by esterification.

12. A lubricating composition comprising a major proportion of mineral lubricating oil and a minor proportion of a halogenated oxidation product of a hydrocarbon prepared by oxidizing a hydrocarbon to produce a complex mixture of various hydrocarbon oxidation products including those of the class consisting of alcohols and acids and esterifying such last-named oxidation products.

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