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LUBRICATION

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7 Claims. (Cl. 252—54)

This application is a continuation in part of our co-pending application Serial No. 610,988, filed May 12, 1932 and application Serial No. 615,462, filed June 4, 1932.

This invention relates, as indicated in my above-mentioned co-pending application of which this is a continuation in part, to lubrication and more particularly to the improvement of those properties such as increased film strength, reduction in friction, reduction in wear, increased stability, etc., which may be deficient in plain mineral lubrication oils, especially when employed for the purpose of lubricating under extreme conditions, such as those imposed by elevated temperatures, extreme pressures and the like.

It is a principal object of our invention, therefore, to provide lubricating compositions and a method of lubricating characterized by the aforementioned improvements.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain approved combinations of ingredients embodying our invention, such disclosed means constituting, however, but certain of various forms in which the principle of the invention may be used.

Broadly stated, this invention comprises the discovery that lubricating compositions of improved characteristics may be produced by the addition to lubricating oils, such as mineral oil, of various amounts of halogenated organic acids.

Further objects of this invention are to provide a lubricant with high oiliness character and high film strength without introducing the objectionable features of lubricating oil sludging, gumming, rancid odor and perceptible corrosion. The application of this invention realizes these objects very economically.

Under conditions of boundary lubrication the viscosity of the lubricant plays only a minor part in lubrication. With slow speeds and heavy loads contributing to boundary lubrication, the lubricant to be efficient must have a high degree of oiliness or unctuosity and must have a high film strength. The very best mineral oils are, as a rule, very deficient in oiliness character and film strength, resulting in considerable wear, low efficiency, and at times seizure of metals in machines lubricated with mineral oils only. For these particular duties lubricating engineers have used animal and vegetable oils with some success, but the changes occurring in the animal and vegetable oils during use have made them very unsatisfactory for general use, as well as uneconomical due to the expense of the fatty oils and the quantities required.

Mineral oils having low film strength allow seizure of the rubbing surfaces when, for one reason or another, pressures are increased or the rubbing speed is slow.

It has been found that commercial stearic acid as found on the market and other saturated fatty acids, when blended with mineral lubricating oil, will greatly reduce the coefficient of friction. As an example, a good grade mineral oil had a coefficient of friction of 0.135 to 0.140 when tested on the Herschel friction testing machine with a 40% lead disc. (The Herschel friction testing machine is a development by Dr. W. H. Herschel of the U. S. Bureau of Standards.) When 0.5% commercial stearic acid was added to the above mineral oil, it had a coefficient of friction of only 0.055. Thus, by adding a very small amount of stearic acid, the coefficient of friction was only 39 to 41% as great as with the original oil.

The melting point of commercial stearic acid is around 100–170° F., depending upon the impurities present in the commercial acid. (These impurities do not affect the value of this invention, it being found that any of the commercial stearic acids are suitable.) Stearic acid is completely soluble in mineral oil at high temperatures, but due to its high melting point, the stearic acid starts solidifying as the temperature goes below say 100° F. and at low temperatures, say around 15 to 30° F., will in time settle out of the solution. This is a common characteristic of the saturated fatty acids of high melting point, which requires their use in warm weather and prohibits storage and use of lubricants prepared in this manner during cold weather. With this knowledge, the use of saturated fatty acids in mineral oil may be economically and efficiently applied in a number of places.

It has been found, however, that the solubility and film strength of atty acids can be greatly improved by halogenation. The halogenated fatty acids will remain in solution over long time storage during cold weather and will not cause sludging of the lubricant, gumming or other objectionable features. Addition of halogen to the fatty acid molecule lowers the melting point and accomplishes this very beneficial result and makes them available for economical use under any kind of temperature conditions.

As an example of this, ordinary commercial

stearic acid (a saturated acid) with a melting point around 120–140° F. was chlorinated direct with chlorine until the chlorinated product had a melting point of 62° F. Excess free chlorine and hydrochloric acid are removed by any of the ordinary means and the chlorinated product added to mineral oil lubricants in small quantities. The poorer the quality of the original lubricating oil, the more the chlorinated acid required. The Herschel friction tssting machine was used to determine the increased oiliness. The original mineral oil showed a coefficient of friction of 0.135 to 0.140%. Chlorinated stearic acid was added in quantities of from .05% to .5% with the following results:

Amt. of chlor. stearic acid added to mineral lubricant	Coefficient of friction on Herschel friction machine
Original mineral lubricant	0.135 to 0.140
.05%	0.072 to 0.077
.1%	0.070 to 0.075
.25%	0.070 to 0.075
.50%	0.070 to .075

Another sample of commercial stearic acid was chlorinated until the chlor acid had a melting point of 9° F. This product was added to the same mineral oil with the following results:

Amt. of chlor. stearic acid added to mineral lubricant	Coefficient of friction on Herschel machine
Original mineral lubricant	0.135 to 0.140
.05%	0.075 to 0.080
0.10%	0.075 to 0.080
0.5%	0.115 to 0.120

Both of the above examples clearly show that the maximum reduction in coefficient of friction is obtained with small quantities of the chlor fatty acid. In the case of the fatty acid chlorinated at 9° F. melting point, the coefficient of friction increased when the amount of acid added reached 0.5%. As previously stated, with a poorer quality original mineral oil as much as 2% or more acid may be required to get the same reduction in coefficient of friction.

It has been found that unsaturated free fatty acids will reduce the coefficient of friction when used in small quantities. For example, 0.5% of oleic acid in a mineral oil having an original coefficient of friction of 0.135 to 0.140 gave a product with a coefficient of friction of 0.055 to 0.060.

Commercial oleic acid representing the field of unsaturated fatty acids was chlorinated to partial saturation and sufficient chlorine added to prevent acid sludging or polymerization of the unsaturated acid. This product, when added to a mineral lubricant having an original coefficient of friction of 0.135 to 0.140, gave the following result:

Chloroleic acid added	Coefficient of friction Herschel machine
0.5%	0.065 to 0.070
Original mineral oil	0.135 to 0.140

It is a particular object of this invention to provide safe and efficient lubrication for relatively moving metallic surfaces acting with inter-surface pressures which may be considerably in excess of 10,000 pounds per square inch. Such pressures are now commonly encountered in hypoid gears, bearings, and contact surfaces of cylinders and piston rings in internal combustion engines, and are becoming more prevalent with advances in modern machine design.

It is believed that the halogenated organic acids react chemically or physico-chemically with the metallic surfaces to form a non-fluxing surface which will not seize or score. This invention is not intended to be limited, however, by any particular theory or explanation of the action upon the metallic surfaces.

When used in conjunction with a lubricant an amount from about 0.1% and sometimes less to about 20% of the addition agent, based on the amount of oil, and often from about 0.5% to about 2% or less is all that is required to render the finished lubricant efficient under conditions of extreme pressure. In the case of gear lubricants, for example, somewhat larger quantities, from about 5% to about 10%, may often be preferred, but ordinary crankcase oils generally require no more than the lesser quantities indicated above, viz., about 0.1% to about 2%. When, however, the particular use makes advisable a higher percentage of the so-called addition agent, the halogenated organic acids may be employed with any such proportion of lubricating oil as may be required to afford the characteristics desired. It is, of course, obvious that generally only such amounts of the addition agent may be included as are soluble in the specified amount of oil. By the term "soluble" as herein used, we intend to indicate the ability to form not only true solutions but also any form of substantially permanently homogenous solution when incorporated in mineral oil. With most of the compounds there is usually little difficulty, especially if the incorporation is effected in the manner described in Cornell Patent No. 2,042,880, and since quite small percentages often give remarkably improved results it is seldom of extreme importance that the addition agents be oil-soluble in all proportions. Also, certain compounds are of value as gelling or bodying agents when used in amounts greater than are strictly soluble; for example, certain compounds such as halogenated acids of the type which contain an anthracene nucleus and a plurality of side chains.

It is also desirable for many uses that the addition agent have a vapor pressure less than atmospheric at 140° C. and where high operating temperatures are encountered as in the combustion chambers of internal combustion engines it is preferable that the addition agent have a vapor pressure less than atmospheric at 170° C.

All of the various halogens are effective when employed in accordance with the present invention but chlorine is generally preferred inasmuch as it is the least expensive and one of the most effective of the halogens. Bromine and fluorine are more expensive and the latter is difficult to handle but they are each satisfactory. Iodine is not so easily obtainable as the other halogens and has been quite expensive but it also may be used to provide effective addition agents in accordance with the present invention.

It should also be noted that two or more different halogens may be present on the same molecule. The brom-chlor compounds and the fluorinated chlorine or bromine compounds give especially satisfactory results.

The following is a table including various examples of the halogenated carboxylic acids which may be employed in accordance with this invention:

Halogenated aliphatic acids (fatty acids):
- Saturated, e. g.—
  - Halogenated lauric acid
  - Halogenated palmitic acid
  - Halogenated stearic acid
- Unsaturated, e. g.—
  - Halogenated acrylic acid
  - Halogenated oleic acid
  - Halogenated linoleic acid
  - Halogenated hypogaeic acid
- Straight chain, e. g.—
  - Halogenated lauric acid
  - Halogenated palmitic acid
  - Halogenated stearic acid
  - Halogenated oleic acid
- Side chain, e. g.—
  - Halogenated iso-butyric acid
  - Halogenated iso-caproic acid
  - Halogenated meta crylic acid
- Long chain (10 or more C atoms) e. g.—
  - Halogenated lauric acid
  - Halogenated palmitic acid
  - Halogenated stearic acid
  - Halogenated oleic acid
- Short chain (less than 10 C atoms) e. g.—
  - Halogenated acetic acid
  - Halogenated propionic acid
  - Halogenated butyric acid
  - Halogenated caproic acid
  - Halogenated acrylic acid
- Hydroxy aliphatic acids, e. g.—
  - Halogenated lactic acid
  - Halogenated glyceric acid
  - Halogenated mannitic acid
  - Halogenated malic acid
  - Halogenated saccharic acid
  - Halogenated citric acid
  - Halogenated ricin-oleic acid

Aromatic substituted fatty acids:
- Halogenated mandelic acid
- Halogenated phenyl-lactic acid
- Halogenated phenyl-acetic acid
- Where the aromatic hydrocarbon is selected from the group of benzene or its homologs—
  - Halogenated phthalic acid
  - Halogenated phenyl-acetic acid
  - Halogenated tolyl-acetic acid
  - Halogenated xenyl-acetic acid
  - Halogenated phenyl-stearic acid
  - Halogenated tolyl-lauric acid
  - Halogenated xenyl-palmitic acid
  - Halogenated cinnamic acid
- Where the aromatic hydrocarbon is selected from the group of naphthalene and its homologs
- Where the aromatic hydrocarbon is selected from the group of phenanthrene, anthracene, and their homologs
- Compounds where the aliphatic radicle has more carbon atoms than the aromatic radicle
- Where the compound contains a hydroxyl radicle—
  - (a) Attached to the aliphatic radicle:
    - Halogenated mandelic acid
    - Halogenated phenyl-lactic acid
  - (b) Attached to the aromatic radicle:
    - Halogenated hydroxy phenyl lactic acid
  - Where the halogen is attached—
    - (a) To the aliphatic radicle
    - (b) To the aromatic radicle
    - (c) To both radicles

When the halogen is attached to a carbon of the benzenoid ring structure it is especially stable and not readily hydrolysed.

To determine the film strength of lubricants under high pressure, two testing machines have been developed. One is called the Mougey machine and was perfected by Dr. H. G. Mougey of the General Motors Corporation and has been described by the inventor in various literature. The other machine is known as the Timken machine and was developed by the Timken Roller Bearing Company, which has also been described in the literature. The primary object of these machines is to give very high pressure per unit area of rubbing surfaces under conditions resembling those found in commercial use but probably a little more severe. The lubricant is placed between the friction surfaces and used with increasing pressure or load at the friction point until seizure of the metal surfaces occurs. With the Mougey machine the pressure or load may be held constant and one may determine the time required for seizure of the metal surfaces. By the use of these machines it is easy to compare the film strength of two oils.

Using the Mougey machine a good grade mineral oil allowed seizure of the friction surfaces in 30 minutes with a load of 2000# per square inch. Using another sample of the same mineral oil blended with 0.5% of chlorstearic acid of 9° F. melting point and operating the Mougey machine at 2000 pounds per square inch pressure, there were no signs of seizure after a period of 45 minutes, providing a decided superiority of film strength in the lubricant blended with chlorstearic acid. With higher pressures, larger quantities of the chlorstearic acid should be used—as much as 5% or more being required.

Using the Timken machine with the original lubricant seizure of metal surfaces occurred when 18.2 pound weight had been added, which represent a pressure of approximately 10,500 pounds per square inch. To a sample of this same lubricant 0.25% of chlorstearic acid of 9° F. cold test was added, and when this blended lubricant was used in the Timken machine seizure did not occur until a 32.2 pound weight had been added representing a pressure of approximately 19,000 pounds per square inch.

Repeating the test on the Timken machine with the same original lubricant containing 0.5% of chlorstearic acid of 9° F. melting point, metal seizure did not occur until 38.0 pound weights had been added, which represents a pressure of approximately 22,000 pounds per square inch. Thus, by adding 0.5% of the product of this invention to a high quality lubricant, its film strength is more than doubled.

The above tests clearly demonstrate the economy and efficiency of the process and show that by this invention it is possible to prepare a lubricant for practically any duty by either varying the percentage of product blended and/or varying the degree of halogenation of the product to be blended.

It has also been found that lubricants prepared

by this invention do not lose their oiliness characteristics when diluted with small amounts of unburned motor fuel, making this type of lubricant of unusual value in actual commercial lubrication conditions.

The addition of halogenated fatty acids in the manner of our invention reduces sludging or polymerization in the oil. For example, using the Tidewater oxidation test, which consists in determining the amount of sludge formed in an oil after heating for seven hours at 392° F., the following results were obtained:

300 reduced oil—0.5% oleic acid gave a sludging number of 91.6 while the same oil with 0.5% of halogenated oleic acid gave a sludging number of 72.4 or a reduction in sludging number of 19.2.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

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

1. A lubricating composition comprising a major proportion of lubricating oil and a minor proportion of a halogenated aromatic substituted fatty acid.

2. A lubricating composition comprising a major proportion of lubricating oil and a minor proportion of a halogenated aromatic substituted aliphatic acid.

3. A lubricating composition comprising a major proportion of lubricating mineral oil and a minor proportion of halogenated organic acid containing an aromatic group in the molecule.

4. A lubricating composition comprising a major proportion of lubricating mineral oil and a minor proportion of halogenated organic acid containing an aromatic group in the molecule, which aromatic group is selected from the group of benzene and its homologs.

5. A lubricating composition comprising a major proportion of lubricating mineral oil and a minor proportion of a halogenated aromatic substituted fatty acid of the type in which a hydroxyl group is attached to a chain structure.

6. A lubricating composition comprising a major proportion of lubricating oil and a minor proportion of a halogenated hydroxy aromatic acid.

7. A lubricating composition comprising a major proportion of lubricating mineral oil and a minor proportion of halogenated organic acid containing a benzene group in the molecule.

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