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UNITED STATES PATENT OFFICE

2,213,804

LUBRICATING OIL

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No Drawing. Application February 23, 1938, Serial No. 191,955

16 Claims. (Cl. 252—45)

Our invention relates to lubricating oils and more particularly to a lubricating oil of high quality containing an addition agent improving its film strength and oiliness.

This application is a continuation in part of our co-pending application, Serial No. 65,090, filed February 21, 1936.

Present-day mechanical devices require lubricating oils of high film strength and of high oiliness characteristics. It has been found that the present-day hydrocarbon lubricants of the very highest quality are deficient in these two very important characteristics. These two properties are of vital importance under conditions of thin film lubrication where the lubricant has been squeezed from between the friction surfaces due to high pressure, slow speeds, and other causes. It is readily seen that the viscosity or the body of the lubricant plays no part in this type of lubrication and that the remaining film of oil must have a very high film strength and be of high oiliness value to prevent rupture of the film of the lubricant, which would cause seizure, and tend to keep the coefficient of friction as low as possible.

Mechanical devices are being designed for higher pressure operation and the film strength of the best quality straight hydrocarbon lubricant has been found to be too low. It will be obvious that an invention which provides the means of improving the film strength of these lubricants is of great importance to the art of lubricant manufacture and to the designer and fabricator of mechanical devices.

Substantially all machines operate in part or at times totally under conditions of boundary or thin film lubrication, under which conditions the oiliness or unctuosity of the lubricant is the first and primary requisite of efficient operation. Those skilled in the art of lubricant manufacture or machine manufacture will readily appreciate the value of an invention that will improve the oiliness of these otherwise high quality lubricants.

In starting idle mechanical equipment which is lubricated from a sump by pumping or circulating the lubricant, there is always a short period of time in which the rubbing surfaces must operate under conditions of dry friction if ordinary hydrocarbon lubricants are used. With dry friction, the wear on friction surfaces is extreme; and during cold weather when the lubricant is sluggish or during periods when the lubricating system is not functioning properly for one reason or another, rubbing surfaces may not only suffer considerable wear but may be damaged to the point where they must be replaced. The product of our invention has a very important property of reacting with the metal surfaces, penetrating or absorbing on the metal surfaces, and leaving a film of lubricant with high oiliness character, which remains on the metal surface irrespective of the length of time the machine has been idle.

This high oiliness film gives very even and smooth operation, which may be easily discerned by the experienced operator and lubricating engineer.

When the hydrocarbon lubricants are diluted with unburned fuel or with other light hydrocarbons the small degree of oiliness of the original hydrocarbon lubricant is greatly decreased. We have found that the addition of the products of our invention to hydrocarbon lubricants more than compensates for the loss in oiliness and load-carrying ability from dilution.

Most oils and greases change color and/or deteriorate when exposed to light or the oxygen of the air during use or storage. Deterioration during use of a hydrocarbon oil in an internal combustion engine takes the course of sludge formation and the production of soluble acids and/or corrosive materials. Furthermore, ordinary lubricants are low in film strength.

In the prior art, it has been suggested that oxidation inhibitors or antioxidant materials such as weakly basic nitrogen compounds including the aliphatic amines and the like, or metallic compounds including compounds of tin, chromium, zinc and the like, be employed.

One object of our invention is to provide a lubricant which has a reduced tendency to oxidize and form sludge and soluble oxidation products.

Another object of our invention is to provide a lubricant of increased film strength.

A further object of our invention is to provide a stabilized lubricant which produces in use less material corrosive to the parts being lubricated.

A still further object of our invention is to provide a lubricant which may be used from five to ten times as long as ordinary lubricants before it is necessary to discard the lubricant on account of its corrosive action on the parts being lubricated.

Other and further objects of our invention will appear from the following description.

In general, our invention comprises the addition of relatively small amounts of stable, heterocyclic sulphur compounds to hydrocarbon lubricants. The hydrocarbon portion of our compound may be comparatively viscous or nonviscous, refined or unrefined, natural or synthetic. In other words, any hydrocarbon oil may be used within the scope of our invention.

In practicing our invention, we use only stable organic sulphur compounds which may contain other inorganic elements, as for example, oxygen, hydrogen, phosphorus, etc. We are aware

of the use of sulphur-treated and sulphur-chloride-treated oils in the improvement of lubricating oils. An example of such sulphur chlorinated oils is shown in U. S. Patent No. 461,513 issued to Sommer, dated October 20, 1891. Sulphuretted lard oil and other oils have been used, but all these oils treated with sulphur or sulphur chloride and the like contain sulphur in a relatively loose, unstable or chemically corrosive condition. In our invention, on the contrary, the sulphur compounds designed to be used as addition agents contain sulphur in a very stable form; that is, firmly bound in a chemical combination. Furthermore, none of the compounds included in our invention may be made by direct treatment of any material with sulphur, or sulphur chloride with or without the aid of heat.

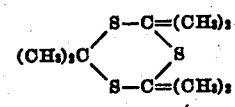
We have discovered that certain heterocyclic compounds of sulphur, when added in small quantities to an otherwise finished lubricant, form mixtures having corrosion inhibiting properties, improved film strength and long life. In addition, it has been found that these compounds inhibit the formation of finely divided oil-insoluble carbonaceous material commonly known as "sludge." This sludge inhibiting property prevents lubricants to which our compounds have been added from darkening in use or storage.

Furthermore, the addition of our compounds to a lubricant increases its load carrying capacity, thus affording an increased lubricating safety factor in reducing friction and preventing metal to metal contact in bearing and other rubbing surfaces.

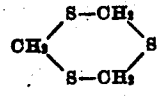
Our invention consists in adding to an otherwise finished lubricant, a suitable amount of a heterocyclic organic compound containing at least one ring consisting of carbon and other atoms but including in such ring at least two sulphur atoms. Other atoms beside carbon and sulphur such as oxygen, nitrogen, and other inorganic elements may be present in the ring with the two or more atoms of sulphur or in other rings or parts of the molecule. Various substituting groups may be present without impairing the effectiveness of the two sulphur atom rings. Thus, groups such as alkyl, aryl, aryl-alkyl, hydroxyl, amino, nitro, carboxyl, cyano, aldehyde, ether carbinol, and others may be present in any part of the molecule. Selenium and tellurium are to be considered equivalents of sulphur in those cases in which the corresponding compounds exist.

Specific examples of compounds which may be used in our invention are:

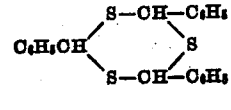
Trithioacetone,



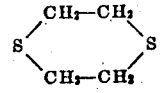
1,3,5-trithiane,



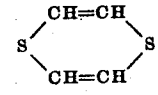
and its other derivatives such as trithiobenzaldehyde



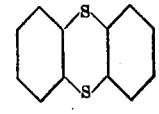
1,4-dithiane,



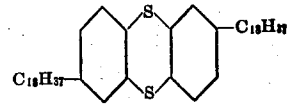
1,4-dithiine,



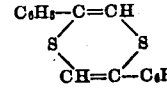
and their derivatives such as thianthrene,



dioctadecyl thianthrene,

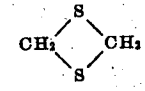


and 2,5-diphenyl-1,4-dithiine,

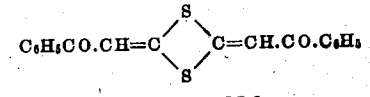


Examples of other compounds which may be used are:

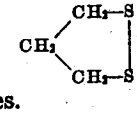
1. Dimethylene disulfide,



and its derivatives, such as desaurin:

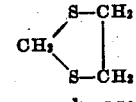


2. Trimethylene-1,2-disulfide,

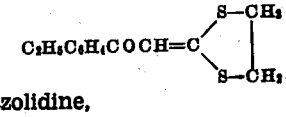


and its derivatives.

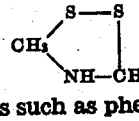
3. Trimethylene-1,3-disulfide,



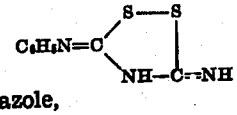
and its derivatives, such as:



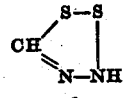
4. Dithiazolidine,



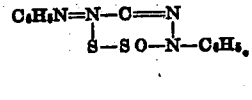
and its derivatives such as phenyl thiuret:



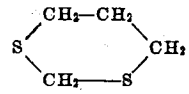
5. Dithiodiazole,



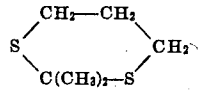
and its derivatives such as thionyl diphenyl pseudo thiocarbazone



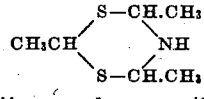
6. 1,3-dithiane,



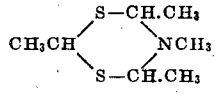
and its derivatives such as 2,2-dimethyl-1,3-dithiane:



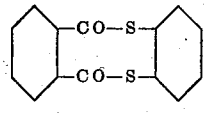
7. Thialdine,



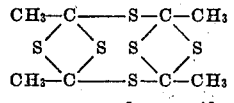
and its derivatives such as methyl thialdine:



8. Compounds containing larger than six membered rings with at least two sulphur atoms in the ring such as dithio disalicylide



tetraethenyl hexasulphide:



Any of these compounds or other members of the classes represented or their derivatives are used within the scope of our invention. Preferably we use from .5 to 2 per cent of one or more of these addition agents to lubricating oil; but in some cases we may use as low as .01 of 1 per cent or as high as 15 per cent or more.

In practicing our invention, oil soluble stable sulphur compounds are to be selected. Such compounds as are insoluble in the hydrocarbon oil may be used in colloidal suspension or emulsion in the hydrocarbon oil accompanied by suitable stabilizing agents for rendering the emulsion or suspension permanent. The selection of a particular compound or combination of compounds to be used as an addition agent to hydrocarbon oil is to be made considering the use to which the blend is put. Thus if water is likely to be present during use, a stable sulphur compound or combination of compounds is selected which are not affected by water. If a particular added stable sulphur compound proves too volatile for its application, a higher boiling stable sulphur compound should be used and the more volatile compound used for blending in a hydrocarbon oil intended for duty at lower temperature. In general, we prefer to use compounds having boiling points over 150° F. Some of these stable sulphur compounds may be too odoriferous for certain purposes. In such cases the odor is covered by a suitable perfuming agent. Such details of practice will be apparent to anyone skilled in the art.

It is sometimes advantageous to combine more than one of these compounds in a blend to obtain particular properties. We accomplish this by mixing two or more of these compounds together and blending the mixture with the hydrocarbon oil or by blending one in the hydrocarbon oil, blending the second into this mixture and so on until the composition is complete.

The various sulphur compounds may give improvement other than film strength to the hydrocarbon oil. For example the sludging tendencies may be decreased by as little as 0.01 per cent of some sulphur compounds. The oxidation characteristics of lubricants is very important in some services, and such is improved by sulphur compounds as a rule. The ability to reduce friction is another feature contributed to lubricating oils by some sulphur compounds.

To test the effectiveness of these heterocyclic sulphur compounds as corrosion inhibiting agents, we employed a corrosion testing apparatus which comprised an oil container, an electric motor, an electric heater, and a clamp shaft. The oil container comprised an iron cup about four inches in diameter and eight inches deep, equipped with vanes at the sides and bottom thereof. The electric motor was a $\frac{1}{10}$ H. P., operating at 1700 R. P. M. The motor was mounted directly over the oil container. The oil heater was mounted within the oil container and equipped with a temperature control apparatus. The clamping shaft is directly connected to the motor. The other end of the clamping shaft is provided with a bearing in the bottom of the oil container. Adjustable clamps are provided for holding specimen bearings while rotating in the oil container. Test bearings were prepared by sawing automobile half bearing inserts into two one-half width pieces. The test bearings were prepared for test by polishing the bearing surfaces with number 100 emery paper and weighing. Eight hundred cubic centimeters of the oil to be tested were placed in the cup and agitated by rotating the shaft with half of the bearing clamp attached until the oil reached the test temperature of 350° F., being raised to this temperature by the heater. The shaft was then removed and the shaft with test bearings clamped in place and the motor started. Air at a measured rate of 200 cubic centimeters per minute was bubbled through the oil. The motor was stopped at intervals and the test bearings inspected. This process was continued until it was noted that corrosion had commenced. The corroded test bearings were then washed with gasoline and then with a solution containing one part toluene, one part ethyl acetate and one part 96 per cent ethyl alcohol. They were then wiped with a soft cloth, dried in an oven and weighed. The weight loss of the test bearings was plotted against the time on cross section paper, showing the time elapsing before corrosion began.

A number of bearings were tested by this method, with various lubricating oils by themselves and various lubricating oils with various amounts of thianthrene or other heterocyclic sulphur compounds added. The amount of the addition agent added varied between .05 of one per cent and two per cent. As a result of these tests, it was found that, if a mineral oil without the addition agent could be run for about four hours before corrosion began, a small amount such as $\frac{1}{10}$ of one per cent of thianthrene could be run for about ten hours before corrosion commenced and that, in general, lubricants to which thianthrene had been added were twice as resistant to corrosion and deterioration as the same lubricants to which no addition agent had been added.

This corrosion resisting and inhibiting effect obtained, too, in hydrocarbon oils which were thickened with various soaps to form greases.

It will be understood that certain features and

sub-combinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, what we claim is:

1. A lubricant comprising in combination a hydrocarbon oil and a small quantity of an organic compound containing at least two sulphur atoms in a heterocyclic ring.

2. A lubricant comprising in combination a hydrocarbon oil and from 0.05 to 2.0 per cent by weight of an organic compound containing at least two sulphur atoms in a heterocyclic ring.

3. A lubricant comprising a major proportion of hydrocarbon oil and from 0.05 to 2.0 per cent of thianthrene.

4. A lubricant comprising a major proportion of hydrocarbon oil and from 0.05 to 2.0 per cent of a substituted thianthrene.

5. A lubricant comprising in combination a hydrocarbon oil and a small quantity of an organic compound containing at least two non-adjacent sulfur atoms in a heterocyclic ring.

6. A lubricant comprising in combination a hydrocarbon oil and from 0.05 to 2.0 per cent by weight of an organic compound containing at least two non-adjacent sulfur atoms in a heterocyclic ring.

7. A lubricant comprising in combination a hydrocarbon oil and a small quantity of a cyclic mercaptal.

8. A lubricant comprising in combination a hydrocarbon oil and from 0.05 to 2.0 per cent by weight of a cyclic mercaptal.

9. A lubricant comprising in combination a hydrocarbon oil and a small quantity of a cyclic mercaptol.

10. A lubricant comprising in combination a hydrocarbon oil and from 0.05 to 2.0 per cent by weight of a cyclic mercaptol.

11. A lubricant comprising in combination a hydrocarbon oil and a small quantity of thianthrene.

12. A lubricant comprising in combination a hydrocarbon oil and a small quantity of a substituted thianthrene.

13. A lubricant comprising in combination a hydrocarbon oil and a small quantity of trithioacetone.

14. A lubricant comprising in combination a hydrocarbon oil and from 0.05 to 2.0 per cent by weight of trithioacetone.

15. A lubricant comprising in combination a hydrocarbon oil and a small quantity of 2,2-dimethyl-1,3-dithiane.

16. A lubricant comprising a major proportion of hydrocarbon oil and from 0.05 to 2.0 per cent of 2,2-dimethyl-1,3-dithiane.

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