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LUBRICATING OIL

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Our invention relates to lubricating oil and specifically comprises such products as new compositions of matter.

This is a continuation in part of our copending application, Serial No. 330,950, filed April 22, 1940.

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 between the friction surfaces because of 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 should tend to keep the coefficient of friction as low as possible and 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.

Mechanical devices are being designed for higher pressure operation, and the film strength of the best quality straight hydrocarbon lubricants has been found to be too low and not sufficient; therefore 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 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. Under some conditions, a very small amount of an addition agent will stabilize a hydrocarbon oil against formation of corrosive oxidation products or sludge forming compounds; and as little as 0.001 per cent is often sufficient.

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 during 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

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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 the very important property of reacting with the metal surfaces, penetrating or adsorbing on the metal, and leaving a film of lubricant with high oiliness character which remains on the metal surface irrespective of the length of time the machine is idle.

This high oiliness film is very even and results in 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, this small degree of oiliness of the original hydrocarbon lubricant is greatly decreased. We have found that the addition of the product of our invention to hydrocarbon lubricants more than compensates for the loss of oiliness and load-carrying ability by dilution.

One object of our invention is to provide a lubricating composition having improved film-strength and extreme-pressure characteristics.

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

We have found that certain compounds are adsorbed or absorbed by metals forming a plurality of layers or films on the surface of the metal, which films are very tenacious (they have a high film strength) and have the property of reducing the coefficient of friction to a marked degree. The compounds which are most readily absorbed by metals are ones consisting of polar molecules, that is, molecules of unsymmetrical electrical character which contain an atom or group of atoms exhibiting a secondary or residual valence. These polar compounds tend to produce regimentation of the molecules of hydrocarbon oil when added thereto. If a metal is immersed in a strongly polar compound, a regimentation or cybotaxis of the molecules will take place in the adsorbed film, the molecules being oriented with respect to the surface of the metal by which they are adsorbed. The films of polar compounds, adsorbed by a metal, can be plainly seen and the orientation of the polar molecules on the metal surface ascertained by X-ray diffraction methods, in which a monochromatic X-ray beam is passed through the adsorbed films at an angle. The series of films act as a diffraction grating, and a diffracted beam will be reflected from the planes of the films and

can be recorded photographically. The X-ray photographs will clearly show the orientation of the molecules by characteristic pictures.

The X-ray investigation has shown that strongly polar molecules form adsorbed films of unusual thickness and regularity of arrangement. Thickness of films of 9,000 Angstrom units have been obtained, which are of enormous magnitude when compared with molecular dimensions.

In general our invention comprises the addition of relatively small amounts, suitably from 0.001 to 10 per cent, of certain boron compounds to hydrocarbon lubricants. For some purposes, we use from 0.1 to 2 per cent of the organic boron compound in the hydrocarbon oil. For other purposes, we use from 0.001 to 0.1 per cent of the organic boron compound in a lubricant. The hydrocarbon portion of our lubricant 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 certain organic boron compounds which contain certain other inorganic elements such as halogen, nitrogen, oxygen, sulfur, phosphorus, metals, etc. The boron compounds particularly suited to our invention are of two classes, as follows:

R_2BOR^1, in which R and R^1 are organic radicals at least one of which contains a carboxylic ester group, $—CO_2R^{11}$, and at least one of the said R and R^1 contains one or more substituents, said substituents being atoms or combination of atoms in organic or inorganic radicals, selected from the group of halogen, nitrogen, sulfur, phosphorus, oxygen, metals, etc.

$RB(OR^1)_2$, in which R and R^1 are organic radicals, at least one of which contains a carboxylic ester group, $—CO_2R^{11}$, and at least one of which contains one or more substituents, said substituents being atoms or combinations of atoms in organic or inorganic radicals, selected from the group of halogen, nitrogen, sulfur, phosphorus, oxygen, metals, etc.

These two types of substituted organo-boron esters have the general formula

$$(Y_nR)_mB(OR^1Z_p)_{3-m}$$

in which R and R^1 are organic radicals, at least one of which contains carbon, hydrogen, and oxygen, the latter in the form of the carboxylic ester group, $—CO_2R^{11}$; Y and Z are substituents containing at least one atom from the group of oxygen, halogen, sulfur, phosphorus, nitrogen, metals, etc., said substituent being either an organic or inorganic radical; n and p are integers, the sum of which is at least one; m is an integer less than 3, the valence of boron. They contain at least one carbo-boron bond and at least one organic radical is removable by saponification.

The organo-boron esters, to which we add substituents from the group set out in the next preceding paragraph to produce the compounds that are added to hydrocarbon oil to form new compositions of matter which comprise the present invention, are described in our copending application, Serial 330,950, filed April 22, 1940.

We have found that the organo-boron esters that contain a carboxylic ester group in an organic radical are superior to the less complex organo-boron esters. We have found that the desirable characteristics of our organo-boron esters containing carboxylic ester groups are appreciably improved by chemically incorporating a radical made up of or containing an atom or atoms from

the group hereinabove set forth. The film strength of the blend made up of hydrocarbon oil and a small quantity of our substituted organo-boron ester is higher than that of a similar blend in which the addition agent is an organo-boron ester containing no substituted atoms from the group we have tried and tested and herein claim.

The addition agents of our invention impart to a hydrocarbon oil a greater resistance to oxidation than do the organo-boron addition agents of the prior art; thus lubricants prepared by adding even minute quantities of the products within the ambit of our invention prevent or greatly reduce the deterioration of the oil while it is stored or while it is in use. The lubricants produced by blending a hydrocarbon oil and our additives are especially suitable for use in crankcases of modern internal combustion engines and Diesel engines. Their stability, film-strength, noncorrosiveness, and particularly oiliness characteristics designate them as very effective and efficient lubricants for all rubbing surfaces requiring a lubricant with a viscosity that may be obtained in a blend made up of hydrocarbon oil and our addition agents.

Examples of the compounds which we add to a hydrocarbon oil to produce new and improved lubricants are the following:

I. $C_5H_{11}B(OCH_2COSC_5H_{11})_2$
Di-thiocarboxyamylmethyl amylborate

II. $C_5H_{11}B(OCH_2P(C_5H_{11})_2)_2$
Di(bis-amylphosphinomethol) amylborate

III. $C_5H_{11}B(OCH_2N(C_5H_{11})_2)_2$
Di(bis-amylaminomethyl) amylborate

IV. $C_5H_{11}B(OCH_2CO_2)_2Ca$
Calcium di(carboxymethyl) amylborate

V. $C_5H_{11}B(OC_{24}H_{48}Cl)_2$
Di(chlorotetracosyl) amylborate

The above compound and compounds of the same type, when added even in small quantities to hydrocarbon oils, form a more stable, more effective lubricant.

It is sometimes more 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 hydrocarbon oil, or by blending one in the hydrocarbon oil, blending the second into this mixture, and so on until the composition is complete.

We have found that the substituted carboxylic ester containing organo-boron compounds may be more effective in some proportions if a small amount of halogen-free, oxygen-containing carbon compound is included in the composition. The oxygen-containing carbon compound may be of aliphatic, aromatic, or hetero-cyclic nature and may be blended with the substituted organo-boron compound in amounts ranging from 5 to 50 per cent. Such compounds include esters of oxidized petroleum hydrocarbons such as wax, methyl ricinoleate, diphenyl ether, diphenylene oxide (dibenzofuran), and many others.

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

ot to be limited to the specific details shown nd described.

Having thus described our invention, we claim:

1. A lubricant comprising in combination a ıajor proportion of hydrocarbon oil and a minor roportion, sufficient to stabilize the oil against ormation of corrosive oxidation products or ludge forming compounds, of a boron compound elected from the class consisting of compounds ıaving the general formulas R_2BOR' and $RB(OR')_2$ in which R and R' are organic radials, at least one of which contains a carboxylic ster group.

2. A lubricant comprising in combination a najor proportion of hydrocarbon oil and a minor roportion, sufficient to stabilize the oil against ormation of corrosive oxidation products or ludge forming compounds, of a boron compound elected from the class consisting of compounds ıaving the general formulas R_2BOR' and $RB(OR')_2$ in which R and R' are organic radials, at least one of which contains a carboxylic ster group, and at least one of which contains hosphorus.

3. A lubricant comprising in combination a najor proportion of hydrocarbon oil and a minor proportion, sufficient to stabilize the oil against formation of corrosive oxidation products or

sludge forming compounds, of a boron compound selected from the class consisting of compounds having the general formulas R_2BOR' and $RB(OR')_2$ in which R and R' are organic radicals, at least one of which contains a carboxylic ester group, and at least one of which is sulphur bearing.

4. A lubricant comprising in combination a major proportion of hydrocarbon oil and a minor proportion, sufficient to stabilize the oil against formation of corrosive oxidation products or sludge forming compounds, of thiocarboxyamylmethyl amylborate.

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