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LUBRICANT COMPOSITION

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This invention relates to an improved lubricant for use on bearing surfaces which are subjected to high pressures, elevated temperatures and high rubbing velocities during use.

The present day trend in automotive design is toward smaller rear axles and consequently smaller gears. On account of the small gears, tooth pressures and rubbing velocities are rapidly approaching a point where rear axles cannot be lubricated satisfactorily with the ordinary mineral lubricating oils. Improved lubricants are also needed in the crank-case of automobiles on account of the use of alloy bearings such as the copper-lead and cadmium-silver bearings. The trend toward increasing loads on gear teeth in other fields has developed an urgent need for special lubricants. When hypoid gears, worm gears, heavy duty bearings, alloy crank-case bearings, planetary automatic shifts, and the like are used under conditions of high pressure and high rubbing velocities, special types of lubricants such as those having extreme-pressure properties and/or non-corrosive properties must be provided in order to reduce the wear upon such moving parts. Extreme-pressure lubricants are likewise important in cutting and drawing operations where the oil must withstand high pressures encountered under those conditions of use.

The object of our invention is to provide a lubricant which will give satisfactory lubrication to bearing surfaces which are subjected to high pressures and/or high rubbing velocities as well as alloy bearings which tend to corrode on account of the action of the oil upon the bearing. A further object is to provide a lubricant which will maintain a lubricant film on bearing surfaces at all times. We have found that if small amounts of certain types of organic sulfur compounds are added to the lubricating oils and soft greases, the lubricant will enable the bearing surfaces to withstand the high pressures and high rubbing velocities without noticeable wear or corrosion. Similarly, these sulfur compounds may be incorporated into drawing lubricants and cutting oils.

We have found that the improved lubricants can be prepared by adding a small quantity of an alkyl disulfide, high molecular weight alkyl sulfides, aryl thiocyanates and aryl isothiocyanates, xanthic disulfides, or xanthates to mineral lubricating oils, preferably, those lubricating oils having a viscosity from about 90 to 200 seconds Saybolt at 210° F. These compounds may be used in oils designated as S. A. E. 20, 30, 40, 50, and 60 oils. The oils designated by S. A. E. viscosity number have Saybolt viscosities ranging from 90 to 300 seconds at 130° F. These sulfur compounds are added in very small quantities. Amounts ranging from 0.1–1.0% to 5–7% may be used but generally amounts ranging from ½ to 5% are satisfactory. The organic sulfur compounds may be dissolved in the oil by any conventional mixing means. If desired, calcium and aluminum soaps or other soaps of high molecular weight fatty acids may be added to the composition to increase the viscosity or consistency of the lubricant. These lubricants have substantially no corrosive action upon metal surfaces.

The sulfur-bearing compounds which may be added to mineral lubricating oils or greases to impart improved lubricating properties thereto are as follows:

I $R—S—R_1$ (Sulfides) $R_2—S—S—R_3$ (Disulfides)

wherein R and R_1 represent alkyl groups containing at least 5 carbon atoms each or aromatic groups such as phenyl radicals and tolyl radicals, however, when R represents a phenyl group, R_1 may represent any alkyl group; and R_2 and R_3 represent alkyl groups or phenyl groups. The term alkyl is intended to include the saturated cyclic radicals also, such as the cyclohexyl group. Examples of the sulfides are amyl sulfide, hexyl sulfide, cyclohexyl sulfide, phenyl sulfide, ethyl phenyl sulfide, methyl phenyl sulfide, tolyl sulfide, and butyl phenyl sulfide. Examples of the disulfides are ethyl disulfide, n-propyl disulfide, n-butyl disulfide, secondary butyl disulfide, tertiary butyl disulfide, cyclohexyl disulfide, ethyl propyl disulfide, amyl disulfide, heptyl disulfide, tolyl disulfide, and phenyl disulfide.

II $R_4—S—C\equiv N$ (Aryl thiocyanic esters) $R_4—N=C=S$ (Aryl isothiocyanic esters)

wherein R_4 represents aryl groups such as phenyl, tolyl and naphthyl groups. Examples of the hydrocarbon thiocyanic esters are phenyl thiocyanic ester, tolyl thiocyanic ester, and naphthyl thiocyanic ester. Examples of the aryl isothiocyanic esters or aryl isosulphocyanic esters are phenyl isosulphocyanic ester, tolyl isosulphocyanic esters, and naphthyl isosulphocyanic ester. Other hydrocarbon thiocyanic esters and isothiocyanic esters may be used, particularly those hydrocarbon derivatives containing six or more carbon atoms in the hydrocarbon radical. The hydrocarbon radical may be of the straight chain

type and may contain from six, ten, twelve or more carbon atoms. The hydrocarbon esters of isothiocyanic acid impart excellent extreme-pressure lubricating properties to mineral oils.

III $R_5—O—CS—S—R_6$ $R_7—O—CS—S$ / $R_7—O—CS—S$

Xanthic acid esters Xanthic disulfides

Wherein R_5, R_6, and R_7 represent alkyl groups. Examples of the xanthic esters are ethyl xanthate ethyl ester, methyl xanthate ethyl ester, ethyl xanthate methyl ester, ethyl xanthate butyl ester and ethyl xanthate propyl ester. Examples of the xanthic disulfides are methyl xanthic disulfide and ethyl xanthic disulfide.

The load-carrying capacity of these improved lubricants when used as extreme-pressure lubricants may be determined by the extreme-pressure testing machines such as the "Almen Extreme-Pressure Lubricant Testing Machine" described by Wolf and Mougey in their paper on extreme-pressure lubricants given at the 13th annual meeting of the A. P. I. at Houston, Texas, November 17, 1932.

The following table illustrates the load-carrying capacity of the compositions when used as extreme-pressure lubricants as determined by an extreme-pressure lubricant testing machine designed and operated on the same principle as the Almen extreme-pressure lubricant testing machine. These lubricants may also be used to lubricate alloy bearings which are corroded by used mineral lubricating oils.

TABLE I

Sample.—5% of the following compounds dissolved in zero bright stock (mineral oil having a viscosity of 150 Saybolt at 210° F.).
Speed of pin.—150 R. P. M.

Compounds	Pressure applied per projected sq. in. in lbs. before failure	Comments
Control	About 5,000	Failed.
Amyl sulfide	20,000	O. K.
n-Propyl disulfide	25,000	O. K.
n-Butyl disulfide	25,000	O. K.
Diphenyl sulfide	20,000	O. K.
Amyl mercaptan	25,000	O. K.
Ethyl xanthate methyl ester	20,000	O. K.
Phenyl isothiocyanic ester	25,000	O. K.

As stated hereinbefore, the sulfur compounds may be added to the viscous mineral oil by any suitable means. Generally the sulfur compounds are added to the mineral oil and stirred until a homogeneous mixture is obtained. Coastal oils, Mid-Continent oils and paraffin mineral oils may be used in the preparation of our improved lubricants.

Example I

Our improved lubricants may be prepared by mixing a small amount of one of the organic sulphur compounds with a mineral oil having a viscosity suited for the particular use of the lubricant. A concentrated mineral oil solution of the particular sulphur compound may be added to a large portion of mineral oil or the desired amount of the organic sulphur compound may be mixed with the body of mineral oil to be treated.

The hydrocarbon derivatives of the compounds herein disclosed may be prepared by any of the conventional means. The disulfides, for example, may be prepared from the mercaptans occurring in petroleum distillates boiling within the gasoline or kerosene range. A petroleum distillate, preferably one containing a high percent of mercaptans, is agitated with caustic. The caustic solution is separated from the hydrocarbon material by decantation and then oxidized with any suitable chemical reagent, for example air, or oxygen. The alkyl disulfides are then removed from the oxidized caustic solution by boiling and are collected by absorption in a mineral oil solution; if desired, they may be absorbed in the mineral oil used in the preparation of the extreme-pressure lubricant. The oxidation with air or oxygen is preferably performed under pressure and at a temperature below the boiling point of the mercaptans in the petroleum distillate. Generally this temperature is below 80 to 100° C. Other oxidizing agents such as hydrogen peroxide or potassium permanganate may be used instead of the oxygen. Also the high molecular weight alkyl disulfides may be prepared by treating hydrocarbon distillates with sodium plumbite solution and sulfur, separating the plumbite solution from the oil containing the dissolved disulfide and recovering the alkyl disulfides by distilling the hydrocarbon oil from the dissolved disulfides.

The present application is a continuation-in-part of our copending application Serial 718,438, filed March 31, 1934, now Patent No. 2,110,281 issued March 8, 1938. While we have described our invention with reference to particular examples, it should be understood that our invention is not limited thereby, except as set forth by the claims.

We claim:

1. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an organic sulfur compound selected from the group consisting of hydrocarbon thiocyanic esters having the formula R—S—C≡N, wherein R represents a hydrocarbon radical containing at least 6 carbon atoms; and hydrocarbon isothiocyanic esters having the general formula

R—N=C=S,

wherein R represents a hydrocarbon radical containing at least 6 carbon atoms.

2. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an organic sulfur compound selected from the group consisting of hydrocarbon thiocyanic esters having the general formula

R—S—C≡N,

wherein R represents a hydrocarbon radical; and hydrocarbon isothiocyanic esters having the general formula R—N=C=S, wherein R represents a hydrocarbon radical.

3. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an aryl thiocyanic ester.

4. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an aryl isothiocyanic ester.

5. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an organic compound having the formula R—S—C≡N, wherein R represents an aromatic hydrocarbon radical.

6. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an organic compound having the formula R—N=C=S, wherein R represents an aromatic hydrocarbon radical.

7. An improved lubricant composition comprising a mineral lubricating oil and a small

amount of an organic compound having the formula R—S—C≡N, wherein R represents a hydrocarbon radical containing from 6 to 12 carbon atoms.

8. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an organic compound having the formula R—N=C=S, wherein R represents a hydrocarbon radical containing from 6 to 12 carbon atoms.

9. An improved lubricant composition comprising a mineral lubricating oil and a small amount of an organic compound selected from the group consisting of hydrocarbon thiocyanic esters having the general formula R—S—C≡N, wherein R represents a hydrocarbon radical containing at least 6 carbon atoms; and hydrocarbon isothiocyanic esters having the general formula R—N=C=S, wherein R represents a hydrocarbon radical containing at least 6 carbon atoms.

10. An extreme-pressure lubricant comprising a mineral lubricating oil and a small amount of a sulfur-containing organic compound selected from the group consisting of hydrocarbon thiocyanic esters and hydrocarbon isothiocyanic esters.

11. An extreme-pressure lubricant comprising a mineral lubricating oil and a small amount of a sulfur-containing organic compound selected from the group consisting of aryl thiocyanic esters and aryl isothiocyanic esters.

12. An extreme-pressure lubricant comprising a mineral lubricating oil and a small amount of an organic compound having the formula

$$R—N=C=S,$$

wherein R represents a hydrocarbon radical containing from 6 to 12 carbon atoms.

13. An improved lubricant composition comprising a mineral lubricating oil and from ½ to 7% of phenyl isothiocyanate.

14. An improved lubricant composition comprising a mineral lubricating oil and from ½ to 7% of a hydrocarbonphenyl isothiocyanate.

15. A composition of matter as defined in claim 1 wherein the said organic sulfur compound is present in amounts ranging from ½ to 7%.

16. An improved lubricant composition comprising a mineral lubricating oil and from ½ to 7% of an organic compound having the formula R—S—C≡N, wherein R represents a hydrocarbon radical containing from 6 to 12 carbon atoms.

17. Composition of matter comprising a viscous mineral lubricating oil and a small amount of an ester selected from the class of alkyl and aryl esters of isothiocyanic acid.

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