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3,133,020

## EXTREME PRESSURE LUBRICANTS

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4 Claims. (Cl. 252—33.6)

This invention relates to extreme pressure lubricants having improved properties and particularly lubricants adapted for heavy duty service. In one aspect, the invention relates to lubricating oils and in another aspect to lithium base greases.

The prior art discloses numerous additives which are employed to provide E.P. (extreme pressure) properties to lubricating oils and greases. For example, Langner, U.S. Patent No. 2,785,130, discloses extreme pressure lubricants comprising lubricating oils containing a lead soap, polyhydric alcohol, and extreme pressure agent selected from halogenated an sulfohalogenated organic compounds. It is taught in this patent that it is essential to provide an extreme pressure agent containing a portion of a halogenated or sulfo-halogenated organic compound; thus the patentee in this instance derives at extreme pressure properties through the combined use of lead, alcohol, active halogen, and in some instances active sulfur. The patentee further teaches that extreme pressure properties are reduced by use of the alcohol in the absence of active halogen.

In U.S. Patent No. 2,858,273, impartation of E.P. properties to calcium soap greases is provided by incorporating as additives a polyhydric alcohol, a metal organodithiocarbamate, and an alkanol amine. The patentee teaches that the alkanol amine is essential to his greases in order to provide good mechanical stability. He further teaches that only those alcohols containing 3 or 4 hydroxyl groups are operative in his compositions.

The applicant has found that certain specific greases and lubricating oils in general can be considerably improved in E.P. properties by the use of a particular combination of additives not disclosed by the prior art.

It is therefore an object of this invention to provide improved lithium soap greases having high E.P. properties.

It is another object of this invention to provide improved lithium 12-hydroxy stearate greases having improved E.P. properties.

Still another object of this invention is to provide improved lithium soap greases containing small amounts of an aliphatic polyhydric alcohol and a metal organodithiocarbamate.

Yet another object of this invention is to provide improved lubricating oils having high E.P. properties and containing small amounts of an aliphatic polyhydric alcohol and a metal organodithiocarbamate.

The foregoing objects are realized broadly by providing lithium base lubricating greases comprising a mineral lubricating oil thickened with a lithium soap and having incorporated therein an aliphatic polyhydric alcohol and a metal organodithiocarbamate.

In one aspect, the invention is directed to lubricating oils containing an aliphatic polyhydric alcohol and a metal organodithiocarbamate.

The mineral lubricating oils which are employed in the compositions of this invention can be derived from naphthene or paraffin base crude and can be either residual or distillate oil or a mixture thereof, depending on the particular grease or lubricant which is being prepared. For example, in an automotive gear lubricant, a blend of a residual oil with a distillate oil has been found particularly suitable in meeting the viscosity requirements for the various grades.

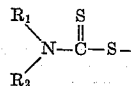
The lithium base lubricating greases, which are well

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known in the art, comprise a dispersion of a lithium soap in a mineral oil. Usually, a calculated amount of soap, between about 5 percent and about 25 percent or higher by weight, is dispersed in the mineral oil base followed by heating at an elevated temperature, for example, from about 350 to about 450° F. until the mixture thickens. Subsequently the hot grease is cooled to provide the final product. Mixing or milling can be provided as desired during any of the preparation steps. Various soaps or admixtures of soaps can be employed in the lithium base greases; however, preferably, the soaps are hydroxy fatty acid soaps of lithium. A particularly desirable grease is obtained through the employment of soaps derived from mixtures of a hydroxy fatty acid and a hydrogenated fatty material, for example, hydrogenated fish oil, castor oil, and the like. Further details concerning the latter greases and their method of preparation are set forth in U.S. Patent 2,475,589.

The polyhydric alcohol and metal organodithiocarbamate which are added to the lubricants of this invention can be incorporated in the grease at any stage in its preparation; however, preferably, these materials are added during the final steps of preparation. Any of the aliphatic polyhydric alcohols can be employed in the lubricating compositions, including alcohols containing 2, 3, or 4 hydroxy groups. Specific examples of alcohols which are used include glycerin, pentaerythritol, hexylene glycol, ethylene glycol, polypropylene glycol, polybutylene glycol, diethylene glycol, and the like. The preferred alcohols are those containing 3 or 4 hydroxy groups; however the other alcohols also provide a substantial E.P. effect.

The dithiocarbamate compounds added to these mineral oils have in their molecular structure one or more dithiocarbamate groups which may be represented by the formula:



in which  $R_1$  and  $R_2$  represent hydrogen or organic groupings similar or dissimilar in nature, and present in the molecule so that the sum  $R_1 + R_2$  contains at least eight carbon atoms in alkyl groups, and the structural relationship indicated by the relative positions and linkages of the respective atoms in the formula. The organic groupings represented by  $R_1$  and  $R_2$  can be alkyl, aryl, alkylaryl, mixture of alkyl and aryl, cycloalkyl and heterocyclic groupings. These groupings can contain inorganic substituents, such as sulfur, oxygen, phosphorus and nitrogen, when special properties are sought. Particularly important to the proper functioning of these compounds is that they possess adequate solubility in the mineral base stock and for this reason it is generally required that the combined  $R_1$  and  $R_2$  groups, when wholly organic, contain a total of at least 8 carbon atoms in alkyl groups. Considerable improvement in this regard is effected by increasing the number of carbon atoms in alkyl groups to 10, 12, and 16, preferably.

The preferred dithiocarbamates are those in which the organo groups are alkyl groups and particularly the lead dialkyl dithiocarbamates, for example, lead diamyl dithiocarbamate. Illustrative examples of metal organodithiocarbamates which can be employed are zinc dibutyl dithiocarbamate, nickel dicyclohexyl dithiocarbamate, nickel dibutyl dithiocarbamate, sodium dicyclohexyl dithiocarbamate, lead dicyclopentyl dithiocarbamate, lead diphenyl dithiocarbamate, and the like. Although polyvalent metals generally are used in the metal organodithiocarbamates, the alkaline earth metals, cobalt, iron, nickel, aluminum, tin, chromium, copper, manganese, mercury, zinc, and lead are more often used, with lead being pre-

ferred as stated previously. Although very minor amounts of the polyhydric alcohol and the metal organodithiocarbamate provide improvement in E.P. properties, these materials are ordinarily employed within certain percentage ranges, namely, from about 0.1 to about 5.0 percent by weight of the alcohol based on the grease and preferably from about 0.3 to about 1 percent; and from about 0.4 to about 10 percent of the metal organodithiocarbamate based on the grease and preferably from about 1.0 to about 4 percent. The compositions can also contain small amounts of the conventional additives which are incorporated for specific purposes, including anticorrosive agents, pour depressants, viscosity improvers, oxidation inhibitors, dyes, and the like.

The combination of the polyhydric alcohol and metal organodithiocarbamate is found to give substantial improvements in the extreme pressure properties of the lithium soap greases without a corresponding adverse effect on the mechanical stability of the greases and without limitation as to the type of polyhydric alcohol which is employed. This combination of additives also provides a similar effect in lubricating oils.

The following examples are presented in illustration of the invention:

#### Example 1

The following is given as an example of a base lubricant composition having extreme pressure properties:

	Percent by weight
Mineral lubricating oil	97.5
50 percent lead diamylthiocarbamate and 50 percent mineral oil	2.5

Several blends were prepared in which various polyhydric alcohols were added to the above lubricating base. The following table shows the data obtained:

Polyhydric Alcohol Added	Weight Percent Addition	Timken Test <sup>1</sup> "OK" Load, Pounds
None		45
Glycerin	0.2	60
Glycerin	0.3	70
Ethylene glycol	0.3	55
Polypropylene glycol <sup>2</sup>	0.6	50
Polybutylene glycol <sup>3</sup>	0.6	50
Polybutylene glycol <sup>4</sup>	0.6	50

<sup>1</sup> The Timken Test was run according to the direction given by the A.S.T.M. Committee D-2 (A.S.T.M. Bulletin No. 181, page 43, April 1952). Special Timken steel blocks No. T-4349 and Timken cups No. T-4351 were used. Ten-minute runs are made at various load levels. These levels are increased until failure occurs which is indicated by obvious scoring of the test specimens. The maximum load without failure and the unit pressures existing at this maximum safe load are considered as the performance criteria.

<sup>2</sup> Average molecular weight 1,950-2,100.

<sup>3</sup> Average molecular weight 1,000.

<sup>4</sup> Average molecular weight 1,500.

The above data illustrate the effectiveness of the combination of the polyhydric alcohol with a metal organodithiocarbamate, glycerin being particularly effective as the alcohol.

#### Example 2

This example shows the co-operative effect exerted by polyhydric alcohols on the extreme pressure properties of a lithium soap grease containing an additive consisting of 50 percent lead diamylthiocarbamate and 50 percent mineral oil. The particular grease used was a 10,000-pound batch (approximately) of commercially produced grease prepared by open kettle saponification of a mixture of hydrogenated castor oil and 12-hydroxy stearic acid in a mineral lubricating oil. Its finished approximate composition was as follows:

	Percent by weight
Lithium soap	5.5
Mineral lubricating oil	94.5

The above base grease was blended with an additive consisting of 50 percent lead diamylthiocarbamate and 50 percent mineral oil and various polyhydric alcohols. The following data were obtained:

Polyhydric Alcohol Added	Weight Percent Addition	Weight Percent Dithiocarbamate-Mineral Oil Mixture	Timken Test "OK" Load, Pounds
None		2.5	40
Glycerin	0.3	None	8
Do	0.2	2.5	65
Do	0.3	2.5	70
Do	0.5	2.5	70
Ethylene Glycol	0.3	2.5	55
Hexylene Glycol	0.3	2.5	45

The above data illustrate the effectiveness of the combination of the polyhydric alcohol with a metal organodithiocarbamate, glycerin being particularly effective as the alcohol. Addition of the alcohol and dithiocarbamate in each instance had no adverse effect on the mechanical stability of the base grease.

#### Example 3

The following data were obtained to illustrate the effect of glycerin on the mechanical stability of lithium greases similar to the base grease employed in Example 2:

BATCHES WITH GLYCERIN ADDED  
(10,000-POUND BATCHES)

Grease Batch	Timken	A.S.T.M. D 217-52T Penetration	
		60 Stroke	10,000 Stroke <sup>1</sup>
A	70	310	310
B	70	320	305
C	75	320	310

BATCHES WITHOUT GLYCERIN

D	40	310	315
E	40	300	315
F	40	320	320

<sup>1</sup> 10,000 strokes in five-hole worker.

The above data show that glycerin when added to the base grease does not reduce the mechanical stability of the grease and, in some instances, may even improve mechanical stability.

Having thus described the invention by providing specific examples thereof, it is to be understood that no undue limitations or restrictions are to be drawn by reason thereof and that many variations and modifications are within the scope of the invention.

I claim:

1. A lithium base lubricating grease consisting essentially of a mineral lubricating oil thickened with lithium fatty acid soap and containing between about 0.1 and about 5.0 percent glycerin and between about 0.4 and about 10.0 percent lead diamylthiocarbamate.

2. A lithium base lubricating grease consisting essentially of a mineral lubricating oil thickened with between about 1 and about 25 percent of the lithium soap of a hydroxy fatty acid and hydrogenated castor oil and containing from about 0.1 to about 5.0 percent glycerin and from about 0.4 to about 10.0 percent lead diamylthiocarbamate.

3. The grease of claim 4 in which the hydroxy fatty acid is 12-hydroxy stearic acid.

4. A lithium base lubricating grease consisting essentially of a mineral lubricating oil thickened with between about 1 and about 25 percent by weight of the lithium soap of a hydroxy fatty acid and hydrogenated castor oil

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and containing from about 0.3 to about 1.0 percent by weight glycerin and from about 1.0 to about 4.0 percent by weight lead diamylidithiocarbamate.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,133,020

May 12, 1964

William P. Scott

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 20, for "an" read -- and --; column 4, line 70, for the claim reference numeral "4" read -- 2 --.

Signed and sealed this 10th day of November 1964.

(SEAL)

Attest:

ERNEST W. SWIDER  
Attesting Officer

EDWARD J. BRENNER  
Commissioner of Patents

