

UNITED STATES PATENT OFFICE

2,504,672

LITHIUM GREASE

Bruce B. Farrington, Berkeley, and Frank A. Leyda, La Crescenta, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Application November 1, 1948,
Serial No. 57,834

8 Claims. (Cl. 252—33.6)

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This invention relates to lithium base greases stabilized against deterioration by the presence of small quantities of stabilizing agent.

Lithium base greases, that is, greases of the soap-mineral oil type wherein the soap or a substantial part of the soap component is a lithium soap, are described and methods of making them are set forth in several patents to Clarence E. Earle, Nos. 2,274,673, 2,274,674, 2,274,675, 2,274,676 and 2,293,052. As set forth in these patents, lithium soaps or salts of various organic acids, such as the higher fatty acids (for example, stearic, oleic and palmitic acids), acetic acid, butyric and ethyl butyric acids, ethyl hexoic acid and caproic acid may be incorporated in mineral lubricating oils, nondrying vegetable oils, chlorinated diphenyl or chlorinated diphenyl oxide to produce greases. The lithium soap or salt may be the only soap or salt component of the grease or there may be incorporated in the grease another soap, such as a soda soap or lime soap or both, together with the lithium soap. An agent such as polymerized esters of methacrylic acid may be incorporated in small amount in the grease to improve thixotropic properties. Proportions of lithium soap ranging from 4 to 40 per cent by weight of the grease are disclosed by Earle.

Lithium base greases so made are water resistant, resistant to structural deterioration induced by high and low temperatures and have good plastic properties at high and low temperatures. They are, however, particularly subject to oxidative deterioration, which is especially disadvantageous when such greases are used at inaccessible lubrication points or in sealed bearings, etc.

Inhibition of oxidation of lithium greases involves inhibiting the catalytic action of lithium soap on the oxidation of oil as well as inhibiting the destructive oxidation of the lithium soap itself, which latter oxidative deterioration destroys the grease character causing hardening or softening, among other adverse effects. While inhibition of lithium soap greases primarily involves the above factors, it is highly important that the inhibition be attained without adversely affecting the desirable properties of the grease such as the low and high temperature characteristics and water resistance of lithium soap greases.

It is an object achieved by this invention to improve lithium base greases.

It is a further object achieved by this invention to stabilize lithium base greases against deterioration caused by oxidation.

It is a particular object achieved by this invention to stabilize lithium soap-mineral oil greases against oxidation.

These and other objects achieved by the inven-

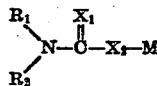
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tion will be apparent from the following description and the appended claims.

We have discovered that oil-soluble polyvalent metal salts or organo-substituted thiocarbamic acids are particularly effective to inhibit the deterioration of lithium base greases. These agents do not have deleterious effects on the desirable properties of the finished lithium soap grease composition. For example, they do not adversely affect the low temperature properties of lithium base greases, whereas other agents suitable for inhibiting oxidation of lubricating oils considerably raise the minimum temperature at which lithium base grease can be satisfactorily employed. The inhibited lithium base greases of the present invention are unctuous, smooth, buttery greases of good appearance and having no tendency to bleed.

The present lithium soap grease compositions have long, useful life which make them particularly suited for use at inaccessible lubrication points, in sealed bearings and the like, especially where extremes of high and low temperature are encountered. Their long life permits longer periods between inspection and replacement of grease in bearings, etc., thus cutting maintenance costs. In addition, such grease compositions are stable during storage, i. e., are free from changes such as hardening, bleeding, etc.

The polyvalent metal dithiocarbamates may be represented by the formula



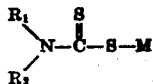
wherein R_1 and R_2 are hydrogen or organic groups, at least one R being an organic group; X_1 and X_2 are oxygen or sulfur, at least one X being sulfur; and M represents a polyvalent metal. Where the complete formula is not given it will be understood that the remaining valences of the polyvalent metal are satisfied by the same or different acid radicals or by the hydroxyl radical as in the basic salts.

For the purpose of inhibiting oxidative deterioration of lithium soap grease the polyvalent metal dithiocarbamates are found to be unexpectedly far superior to the monovalent metal dithiocarbamates. Preferably, the dithiocarbamate salts are of the polyvalent metals above hydrogen in the electromotive series and within that class, especially those of groups II—b, IV and VIII of the periodic table. Suitable metals include zinc, iron, lead, cadmium, tin, aluminum, calcium, strontium and barium. The heavier metals, for instance, those having an atomic weight above 100 are preferred. Especially preferred are zinc, cadmium and lead.

The preferred group of agents are the oil-solu-

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ble polyvalent metal dithiocarbamates represented by the formula.



wherein both R_1 and R_2 are groups of hydrocarbon structure and M is a polyvalent metal. These preferred compounds, from the usual method of obtaining them (which is by reacting a secondary amine with carbon disulfide in the presence of aqueous or alcoholic caustic alkali to form the water-soluble alkali metal dithiocarbamates and adding to an aqueous solution thereof a water-soluble polyvalent metal salt to precipitate the water-insoluble polyvalent metal dithiocarbamate) may be looked upon as derivatives of a secondary amine, carbon disulfide and a polyvalent metal. Such inhibitors are greatly preferred to the thio carbamates which are derived from or may be regarded as derived from primary amines, or from carbon monosulfide (COS) or from monovalent metals. Thus, the preferred inhibitors are as a class, oil-soluble and water-insoluble, they are easily prepared, they are stable at temperatures of the order of 300° F., and they are powerful grease stabilizers.

Among the polyvalent metal dithiocarbamates the calcium and zinc dithiocarbamates, more particularly the zinc dithiocarbamates, are preferred, and it is preferred to use dithiocarbamates in which R_1 and R_2 are sufficiently large hydrocarbon groups (e. g., 4 to 20 carbon atoms each) to render the polyvalent metal salt soluble to the extent of 1% by weight or more in mineral lubricating oil. Examples of preferred oil-solubilizing groups are the butyl and amyl groups; other examples are given hereinafter.

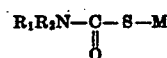
As stated, polyvalent metal dithiocarbamates derived from secondary amines are preferred. Cyclic compounds such as piperidine and its homologues, which are secondary amines and in which the secondary amino nitrogen constitutes part of a heterocyclic ring, may be advantageously used to prepare dithiocarbamates for use according to the invention. In that case, the R_1 and R_2 groups of the formulae illustrated above are joined, forming a single chain, both ends of which are attached to the nitrogen and whose carbon atoms may carry one or more alkyl or other hydrocarbon substituents. The most useful grease inhibitor of the invention is a mixture of such salts, being the product of extracting cyclic nitrogen bases from certain cracked naphthas, reducing the extracted bases, reacting the reduced bases with carbon disulfide in aqueous or alcoholic caustic alkali and adding a water-soluble zinc salt to an aqueous solution of the alkali metal salts to precipitate the desired mixture of zinc salts. Other polyvalent metal salts may be similarly produced, such as the lead, cadmium, aluminum, iron and barium salts, but the zinc salts are preferred. Such mixtures of dithiocarbamates derived from petroleum bases are sometimes referred to hereinafter as "petroleum base dithiocarbamates."

Illustrative examples of thiocarbamates from which grease additives or oxidation inhibitors may be chosen are zinc dibutyl dithiocarbamate; zinc methyl octyl dithiocarbamate; zinc dicetyl dithiocarbamate; zinc diamyl thiolcarbamate; zinc diamyl thioncarbamate; zinc monocetyl dithiocarbamate; zinc butyl amylphenyl dithiocarbamate; zinc dibenzyl dithiocarbamate; zinc di-(cetylphenyl) dithiocarbamate; zinc di-(amyl-

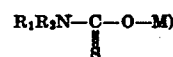
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piperidyl) dithiocarbamate; calcium, zinc, cadmium and tin "petroleum base" dithiocarbamates (produced as described in Example 1 of said co-pending application Serial No. 441,964, which issued on November 21, 1944, as Patent No. 2,363,012); lead dibutyl dithiocarbamate; lead dicyclohexyl dithiocarbamate; lead diamyl dithiocarbamate; lead amyl ethylphenyl dithiocarbamate; cadmium dibutyl dithiocarbamate; cadmium diamyl dithiocarbamate; cadmium dicyclohexyl dithiocarbamate; cadmium dibenzyl dithiocarbamate; cadmium dicetylphenyl dithiocarbamate; calcium dibutyl dithiocarbamate; calcium dioctyl dithiocarbamate; calcium di-(cyclohexylphenyl) dithiocarbamate; barium dibutyl dithiocarbamate; tin dicyclohexyl dithiocarbamate; iron dibutyl dithiocarbamate, iron diamyl dithiocarbamate; aluminum dibutyl dithiocarbamate and aluminum methyl ethylhexyl dithiocarbamate.

General methods of preparing thiocarbamates are available in the literature. The best method presently available for preparing dithiocarbamates is that method in which a primary or secondary amine is moderately heated with carbon disulfide and aqueous or alcoholic caustic potash, producing an alkali metal dithiocarbamate. This may be recovered by crystallization, but since the polyvalent metal salts are preferred, it will be the usual practice to add an aqueous solution of a water-soluble polyvalent metal salt, such as calcium chloride or zinc sulfate, to the reaction mixture (diluted with water if necessary) containing the alkali metal dithiocarbamate, thereby precipitating the desired polyvalent metal dithiocarbamate. This may be purified by crystallization from a suitable solvent, such as a light hydrocarbon thinner. General methods of preparing monothiocarbamates (which are of two types: thiolcarbamates,



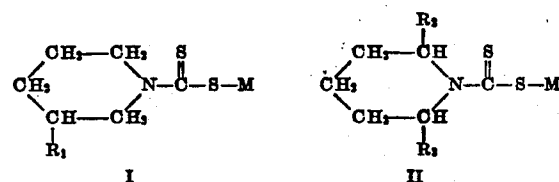
and thioncarbamates,



are available in the literature, e. g., thiolcarbamates from amines and COS.

The preparation of petroleum base dithiocarbamates is described in detail in Miller and Rutherford patent application Serial No. 441,964, filed May 6, 1942, which issued on November 21, 1944, as Patent No. 2,363,012.

From the properties and reactions of the petroleum base dithiocarbamates as well as those of the cracked petroleum nitrogen bases from which they are derived, it is deduced that the "petroleum base" dithiocarbamates are predominantly one or more, probably a mixture, of substances having the following structural formulae:



In the above formulae, R_1 , R_2 and R_3 represent alkyl groups, which may be attached at the points shown or at other points on the piperidine ring, and R_1 and the sum R_2+R_3 each contains an average of 5 carbon atoms. M represents a poly-

valent metal. Although the petroleum base dithiocarbamates are piperidine derivatives, with one or more alkyl groups on the carbon part of the ring, dithiocarbamates derived from other ring type amines, such as trimethylene imine, tetramethylene imine and hexamethylene imine, preferably containing one or more alkyl groups on the carbon part of the ring, may also be used according to the invention.

The grease additives of the present invention exert antioxidant and other desirable effects when incorporated in grease in amounts as low as 0.1 or lower and as high as 5 or higher but amounts ranging from about 0.4 to 1 are preferred, all amounts being percentages by weight based on the finished grease containing the dithiocarbamate additive. These additives may be incorporated in the grease in various ways, as by addition to the mineral oil component of the grease before compounding the grease, by addition dur-

a more stable grease than a grease which drops equally in pressure in a shorter time.

A lithium base grease was prepared as follows:

The formula was 15 parts lithium stearate; 2.5 parts of a mineral oil concentrate consisting of 80% low V. I. naphthenic type lubricating oil and 20% zinc petroleum base dithiocarbamate; and 82.5 parts of the same oil as used in the concentrate. (All parts and percentages by weight.) The lithium stearate was mixed at room temperature with the mineral oil and the mixture was then heated to about 410° F. The heated mixture was a uniform liquid. The concentrate of zinc petroleum base dithiocarbamate was then added and mixed in to assure homogeneity. The mixture was then drawn from the mixture kettle and allowed to cool.

This grease was subjected to the oxidation test described above with results as shown in the table below.

Oxidation test

Main Soap Constituent, Percent	Minor Soap Constituent, Percent	Oxidation Inhibitor, Percent	Test Temperature	Hours for Oxygen Pressure to Drop			Appearance of Grease After Test
				5 lbs.	10 lbs.	20 lbs.	
16% Li Stearate	Nil	Nil	210	1.1	1.6	2.4	Oil separated. Same as before test.
15% Li Stearate	do	1% Zn petroleum base dithiocarbamate.	210	100+	-----	-----	
12% Li Stearate	0.3% Zn stearate	0.1% Zn petroleum base dithiocarbamate.	210	2.5	-----	-----	
15% Li Stearate	0.2% Zn stearate	0.5% Zn petroleum base dithiocarbamate.	210	400+	-----	-----	No change except slightly lighter color. Same as before test.
Do	do	0.5% Zn dibutyl dithiocarbamate.	210	100+	-----	-----	

ing the compounding of the grease or by addition to the finished grease. Generally some degree of heating is advisable during incorporation of the dithiocarbamate in the grease or its components to hasten the solution or dispersion of the dithiocarbamate. Preferably the dithiocarbamate is purified before incorporation into the grease, since impurities may cause the grease to be corrosive. This purification may be accomplished by dissolving the crude dithiocarbamate in alcohol, filtering and crystallizing the dithiocarbamate. Or the crude dithiocarbamate may be purified by dissolving it in mineral lubricating oil to produce a concentrated solution (e. g., about a 20% solution) of the same in oil and filtering the concentrate. The filtered concentrate may then be used in compounding the grease.

The antioxidant effect of the grease additives of the invention has been demonstrated by tests in an oxidation bomb carried out as follows: 20 grams of grease are distributed equally among five shallow glass dishes placed on a rack and placed in a pressure-proof vessel fitted with an inlet for oxygen and connected with a pressure gauge. The bomb, after being thoroughly flushed with oxygen to free it of air, is filled with oxygen to an initial pressure of 110 pounds per square inch gauge. Temperature inside the vessel is maintained throughout the test at 210° F. (in some cases, 250° F.). The drop in oxygen pressure is recorded. As the grease becomes oxidized, oxygen is absorbed and the pressure drops. This drop in pressure is a measure of oxidation, hence of oxidation stability of the grease, and a grease which sustains a longer exposure for a given drop in oxygen pressure is

The zinc stearate present in several of the greases served as a plasticizer.

The marked oxidation inhibiting effect of the dithiocarbamates is apparent from the table.

In another series of experiments the long inhibitory effect on oxidation of lithium base greases was demonstrated by carrying out the above-described oxidation bomb test in the same manner except that the runs were continued until the pressure drops quite rapidly (e. g., 5 to 10 or more points per day). The time in hours at which the sudden pressure drop takes place is called the inhibition period. No sudden pressure drop was obtained for very long periods in many cases, which are indicated by "plus" following the time at which the test was discontinued. The inhibition periods obtained are given below in Table II.

Table II

Inhibitor:	Inhibition period
Zinc dibutyl dithiocarbamate	480 plus
Cadmium dibutyl dithiocarbamate	576 plus
Lead dibutyl dithiocarbamate	648 plus
Sodium dibutyl dithiocarbamate	150

The above data illustrates the unexpectedly high superiority of polyvalent metal dithiocarbamates over the monovalent metal dithiocarbamates as oxidation inhibitors in lithium soap greases.

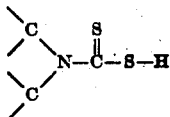
This is a continuation-in-part of our copending application Serial No. 521,434, filed February 7, 1944, now abandoned.

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We claim:

1. A lubricating grease comprising: a mineral lubricating oil, a lithium soap in quantity sufficient to substantially thicken said oil, and an amount of a zinc dialkyl dithiocarbamate between about 0.1% and about 1%.

2. A lubricating grease comprising: a mineral lubricating oil, a lithium soap in quantity sufficient to substantially thicken said oil, and about .1% to about 1% of an oil-soluble zinc salt of a dithiocarbamic acid having the structure.



in the molecule and wherein any substituent on the nitrogen is a non-aromatic hydrocarbon.

3. A grease comprising mineral lubricating oil, lithium soap and about 0.1 to 5% by weight based on finished grease of zinc dialkyl dithiocarbamate containing at least 8 alkyl carbon atoms.

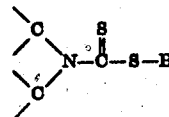
4. A grease comprising mineral lubricant oil, lithium soap and about 0.1 to 5% by weight based on finished grease of zinc petroleum base dithiocarbamate.

5. A grease comprising mineral lubricating oil, lithium soap and about 0.1 to 5% by weight based on finished grease of zinc diaryl dithiocarbamate.

6. A lubricating grease comprising: a mineral lubricating oil, a lithium soap in quantity sufficient to substantially thicken said oil, and about

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0.1 to about 1% of an oil-soluble metal salt of a dithiocarbamic acid having the structure



in the molecule and wherein any substituent on the nitrogen is a non-aromatic hydrocarbon and said metal is selected from the group consisting of zinc, cadmium and lead.

7. The grease of claim 6 wherein the metal is cadmium.

8. The grease of claim 6, wherein the metal is lead.

BRUCE B. FARRINGTON.
FRANK A. LEYDA.

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