Patented Nov. 18, 1952

2,618,598

UNITED STATES PATENT OFFICE

2,618,598

HIGH-TEMPERATURE LUBRICATING GREASE

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No Drawing. Application February 8, 1950, Serial No. 143,171

17 Claims. (Cl. 252—33.6)

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The present invention relates to high temperature lubricating greases and, particularly, to greases which contain as thickeners the combined soaps of high molecular weight fatty acids and low molecular weight thio ether acids. The improved composition is particularly useful for the lubrication of antifriction bearings, especially where such bearings are to be operated at abnormally high temperatures.

It has been suggested in the prior art, that it is advantageous, in cases where improved high temperature performance is requisite, to combine with conventional metal soaps of long chain fatty acids the salts of certain low molecular weight acids. Thus, the addition of such salts as metal acetates, acrylates, crotonates, furoates, and the like, has been found in the prior art to improve the high temperature stability of soda base greases, calcium base greases and certain other common grease compositions.

The particular reasons why the low molecular weight salts improve the high temperature performance of conventional greases are not entirely clear. It has been suggested that a complex of salt and soap is formed which has superior thickening effect in a given quantity of lubricating oil. Whatever may be the phenomena involved, the addition of low molecular weight salts is often advantageous, particularly in connection with alkali and alkaline earth metal greases. It does not follow, however, that all low molecular weight acids are useful and, as a matter of fact, some have been found to be definitely objectionable.

According to the present invention, it is advantageous to use in combination with conventional fatty acid soaps, the metal salts of low molecular weight thio ether acids. The alkali metal salts of such acids are particularly useful, especially in combination with alkali metal soaps. However, certain other metal salts and soaps such as those of alkaline earth metals can be combined. Barium soaps and salts are very satisfactory. Also, alkali metal salts can be combined with alkaline earth metal soaps or vice versa. It is usually preferable to use the same metal base for forming both the salt and the soap. For purposes of the present invention, the salts and soaps of sodium and of barium are specifically preferred, but the invention is not limited thereto. Potassium soaps make softer products and calcium base greases may be prepared in the same manner.

The low molecular weight thio ether acids suitable for forming the salts used in the present invention have the general formula R_1SR_2COOH,

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wherein R_1 and R_2 are each aliphatic hydrocarbon groups or radicals of 1 to 2 carbon atoms. In other words, the thio ether acid is a relatively short chain aliphatic acid having a thio ether linkage. The salts of such acids as ethyl thioglycolic acid, also known as ethyl mercapto acetic acid, are particularly preferred and the close homologs such as ethyl mercapto propionic acid salts appear to be equally useful, within the limits of the above formula. A lubricating grease of good properties is prepared by using about 2 to 10% by weight, based on the total composition, of the salt in combination with 5 to 35% of a conventional soap of the C_{12} to C_{24} fatty acids. The preferred proportions are about 3 to 6% of the salt and 15 to 25% of the soap. Any lubricating oil may be used, but the mineral base oils are preferred because the soaps and the salts may be formed in situ therein without objectionable side reactions. Where synthetic oils are used, the soaps and salts should be formed under such conditions that there is no hydrolysis of the synthetic oils. In this case, as is now well understood in the art, the salts and/or soaps may be preformed or may be prepared in a neutral diluent, such as mineral lubricating oil, to form a concentrate. This concentrate then may be extended by blending in the appropriate synthetic oil, such as an ester of dibasic acid, a polyglycol or other suitable lubricating fluid.

The preferred process is carried out by first adding about 5 to 35 parts by weight of saponifiable fatty acids, preferably substantially saturated, of the C_{12} to C_{24} range, to about 25 parts of mineral base lubricating oil. The oil preferably has a viscosity between about 35 and 70 S. S. U. at 210° F. This mixture is stirred and heated gently to melt the fatty acids, e. g. heated to about 135° to 150° F., and then the thioether acid is added. If another low molecular weight acid such as acetic acid is also to be added, this may also be stirred into the oil and fatty acid blend. Since the low molecular weight acids are quite insoluble, they should be continuously stirred while the saponification and neutralization step is being carried out.

The metal base, e. g. an aqueous solution or a slurry of NaOH, barium octahydrate, or the like, is stirred into the mixture described above while heating and stirring are continued. Saponification of the fatty acids and neutralization of the low molecular weight acids takes place spontaneously. The product is dehydrated by further heating above 212° F. Then 25 to 75 parts of additional lubricating oil (preferably but not neces-

sarily of mineral base) are blended in with further heating and continued stirring. The grease is cooked to a final temperature between about 350 and 475° F., preferably about 400 to 450° F. Thereafter antioxidants and any other desired modifiers may be added and the product is packaged and cooled.

The invention will be more fully understood by reference to the following specific examples.

EXAMPLE 1

Ingredients	Wgt. percent
Ethyl thioglycolic acid	6.0
Hydrogenated fish oil acids ("Hydrofol Acids 54")	15.0
Sodium hydroxide	4.4
Mineral Oil 55 S. S. U. viscosity at 210° F	73.6
Phenyl alpha naphthylamine	1.0

The fatty acids and ⅓ of the mineral oil were charged to a fire heated grease kettle and warmed to 140° F. When all the acid was melted, the ethyl thioglycolic acid was charged and the combined acids co-neutralized with a 33⅓% aqueous solution of sodium hydroxide. The combined soaps in mineral oil were then heated to 225° F. where they were dehydrated. When dry, the temperature was raised to 300° F. where ½ of the balance of the mineral oil was slowly added. The temperature was then raised to 425° F.; during this heating period the balance of the mineral oil was added. The grease was cooled to 400° F. and the phenyl alpha-naphthyl amine inhibitor added. The grease was then drawn into pans for cooling and the cold grease milled. The resulting product was smooth, of short fiber structure.

Properties

Per cent free alkalinity as NaOH	0.16
Worked penetration—mm./10	330
Stability to mechanical working—penetration after 100,000 strokes in a mechanical grease worker, employing a 325 1/16" hole worker plate—mm./10	335
Dropping point, °F	386

As mentioned above, it has been considered desirable in the prior art to use the salts of certain low molecular weight carboxylic acids. Acetic acid has been considered particularly desirable for economic reasons. The acetic acid greases have shown good structural and oxidation stability, but in order to obtain satisfactory soap dispersions with the use of a minimum quantity of thickener for good structural stability it has been necessary to cook the acetic acid greases to very high temperatures, commonly in excess of 500° F. Cooking to such temperatures tends to produce a grease of hard consistency which is difficult to dispense in commercial and industrial grease dispensing equipment. Such greases, furthermore, are often too hard for some important anti-friction bearing services.

A further aspect of the present invention is the discovery that a small amount of a low molecular weight sulfur-bearing aliphatic acid, such as ethyl thioglycolic acid, may be combined with acetic acid, and with conventional soaps, to form a soft smooth and structurally stable grease which can be manufactured at considerably lower temperatures. This is illustrated in Example II and should be compared with the prior art product, shown in Example III, both of which appear below in the table.

TABLE

Formulation (per cent weight)	Example II	Example III
Oleic acid	20.0	20.0
Acetic acid	4.0	4.0
Ethyl thioglycolic acid	0.5	
NaOH	6.4	6.4
Mineral oil, 55 S. S. U. viscosity at 210° F	68.1	68.6
Phenyl alpha-naphthyl amine	1.0	1.0
Maximum manufacturing temperature, °F	410	510
Properties:		
Per cent free alkalinity as NaOH	0.58	0.78
Penetrations mm./10:		
Unworked	269	126
Worked 60 strokes	291	146
Worked 100,000 strokes (325 1/16" hole worker plate)	346	315
Dropping point, °F	460	482
Corrosion test: Cu strip inserted in grease for 24 hours at 210° F	(1)	(1)
Norma Hoffman oxidation test: Hours to a 5 p. s. i. drop in oxygen pressure	235	226
Dispensing test (hand gun)	(2)	(3)
10,000 R. P. M. spindle test at 300° F. hours of operation	339	334

[1] No discoloration.
[2] Easily dispensed.
[3] Too hard to feed into pump.

The greases of Examples II and III were prepared in exactly the same manner as that of Example I except that it was necessary to heat the grease of Example III to a considerably higher temperature, about 500° F., in order to obtain a satisfactory dispersion of the soap and the acetate. The greases of both Examples II and III were milled after manufacture. Example II gave a smooth product, while that of Example III was slightly grainy in appearance.

EXAMPLE IV

Formulation

Ingredients	Percent weight
"Hydrofol acids" 54	14.00
Acetic acid (glacial)	3.00
Ethyl thioglycolic acid	.50
Barium octohydrate $Ba(OH)_2.8H_2O$	15.40
Phenyl alpha-naphthyl amine	.50
Mineral oil, 55 S. S. U. vis. at 210° F	66.60

Procedure

The "Hydrofol acids" 54 and one-third of the mineral oil were charged to a fired heated, grease kettle and warmed to 150° F. The ethyl thioglycolic acid and acetic acid were then added and the combined acids immediately neutralized with an aqueous solution of the barium hydroxide. The mass was heated to 225–230° F. and dehydrated at this temperature, whereupon the mass was further heated to 420° F. During this heating period the balance of the mineral oil was added. The phenyl alpha naphthylamine was incorporated into the grease, and the mass stirred while cooling, forming a smooth, soft short fibered product.

Evaluations

Dropping point °F	430
Penetrations mm./10:	
Unworked	340
Worked 60 strokes	345
Worked 60,000 strokes	311

Solubility in boiling water (10 grams of grease placed in boiling water for 30 minutes)—insoluble with no disintegration of grease.

EXAMPLE V

(Use of ethyl mercapto propionic acid)

Formulation

Ingredients	Percent weight
Oleic acid (commercial red oil)	20.00
Glacial acetic acid	3.00
Ethyl mercapto propionic acid	2.00
Sodium hydroxide	6.25
Phenyl alpha-naphthyl amine	1.00
Mineral oil, 55 S. S. U. vis. at 210° F	67.75

Procedure: Similar to that employed in Example II

Dropping point ° F ---------- 475
Penetrations mm./10:
Unworked ---------- 300
Worked 60 strokes ---------- 320
Worked 60,000 strokes ---------- 332
Corrosion test:
Cu strip inserted in grease for 24 hours at 210° F ----------None (no discolorations).

Where the sulfur bearing acids are to be combined with a simple low molecular weight acid to form the low molecular weight salt, the proportions of sulfur bearing acids may be very small, for example from 0.1 to 1 or 2%. In such case, it is common to use about 4% by weight, based on the total composition, of the other low molecular weight salt but these proportions may be varied considerably, for example from 1 to about 10%.

It will be understood that other conventional additives such as antioxidants, tackiness agents, extreme pressure additives, metal deactivators, and the like, may be incorporated in usual proportions where desired without substantially modifying the properties of the grease compositions of this invention.

What is claimed is:

1. A lubricating grease composition comprising a lubricating oil thickened to a grease consistency with a salt-soap complex which comprises the reaction product of 0.1 to 10% by weight based on the total composition of a metal base with a low molecular weight acid of formula R_1SR_2COOH, wherein R_1 and R_2 are each aliphatic hydrocarbon groups of 1 to 2 carbon atoms, said thickener comprising also 5 to 35% by weight, based on the total composition of a soap of a long chain fatty acid having between 12 and 24 carbon atoms.

2. Composition according to claim 1 wherein the metal base is selected from the group consisting of alkali and alkaline earth metals.

3. Composition according to claim 1, wherein the low molecular weight acid comprises ethyl thioglycolic acid.

4. Composition according to claim 1, wherein the low molecular weight acid comprises ethyl mercapto propionic acid.

5. Composition according to claim 1, wherein the metal base is an alkali metal base.

6. Composition according to claim 1, wherein the metal base is a sodium base.

7. Composition according to claim 1, wherein the metal base is an alkaline earth metal base.

8. Composition according to claim 1, wherein the metal base is a barium base.

9. Composition according to claim 1, wherein the metal base is a mixed base selected from the metals of the group consisting of alkali and alkaline earth metals.

10. A lubricating grease composition comprising a lubricating oil thickened to a grease consistency with 2 to 10% by weight, based on the total composition, of a metal salt of an acid of general formula R_1SR_2COOH, wherein R_1 and R_2 are each aliphatic hydrocarbon radicals of 1 to 2 carbon atoms, and 5 to 35% of a metal soap of fatty acid having 12 to 24 carbon atoms per molecule.

11. A lubricating grease composition consisting essentially of about 73 parts by weight of mineral base lubricating oil, about 8% soda salt of ethyl thioglycolic acid, about 17.5% of soda soap of substantially saturated C_{12} to C_{24} fatty acids, and about 1% antioxidant.

12. A composition according to claim 10, wherein the salt is present in proportions of 3 to 7% and the soap in proportions of 15 to 25%.

13. A lubricating grease composition comprising a mineral base lubricating oil thickened to a grease consistency with 0.1 to 2%, based on the total composition, of an alkali metal salt of an acid of formula R_1SR_2COOH, wherein R_1 and R_2 are each hydrocarbon radicals of 1 to 2 carbon atoms, 1 to 10% of another low molecular weight salt of low molecular weight organic acid, and 5 to 35% of a metal soap of fatty acid having between 12 and 24 carbon atoms per molecule.

14. Composition according to claim 13, wherein the low molecular weight salt is an acetate.

15. Composition according to claim 13, wherein the low molecular weight salt is sodium acetate.

16. Composition according to claim 13, wherein all salts and soap are of sodium.

17. A lubricating grease composition consisting essentially of mineral base lubricating oil, thickened to a grease consistency with a complex thickener consisting of barium soap of fatty acids of the C_{12} to C_{24} range, barium salt of low molecular weight fatty acid, and a small amount, between 0.1 and 2%, based on the total composition, of the barium salt of an acid of formula R_1SR_2COOH wherein R_1 and R_2 are each aliphatic hydrocarbon radicals of 1 to 2 carbon atoms.

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