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WATER-RESISTANT SODIUM GREASES CONTAINING AMIDES

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10 Claims. (Cl. 252—42.1)

This invention relates to sodium base lubricating greases having improved water resistance. It relates also to a method of producing such water-resistant sodium base greases.

Although greases thickened with sodium soaps are of great value for certain lubrication utilizations because of their high melting point, they are notably lacking in water resistance and therefore cannot be used where water may get into the bearings where the grease is employed. It has been found, however, that the usual sodium soap greases can be modified by the addition of an N-alkyl substituted amide of a higher molecular weight hydroxy or keto fatty acid or an amide product as defined hereinbelow, to the sodium base grease either during or following its preparation imparts the property of water resistance to a great extent.

It is an object of this invention, therefore, to prepare a water-resistant sodium base grease.

It is a further object of this invention to provide a method of preparing a water-resistant sodium base grease.

It is another object of this invention to provide a water-resistant sodium base grease by incorporating in the grease an amide product which has the properties of imparting water resistance to the grease.

According to this invention, a sodium base grease is prepared following the usual procedure for preparing such greases and at some point in the preparation of the grease or following the normal procedure, between about 0.5% and 5% by weight of the total grease of an amide or amide product is added and dispersed in the grease. Upon completion of the preparation of the grease or completion of the dispersion of amide following the preparation of the grease, the resulting product is found to have substantially the same properties as a typical sodium base grease with respect to melting point, penetration, stability, and the like, but it also has the ability to resist the washing effects or emulsifying effects of water on the grease.

In a typical preparation, to a grease kettle is charged the soap stock, for example stearic acid, tallow fatty acid, tallow or hydroxy fatty acids, or a mixture of two or more of these materials together with approximately 5 to 10 or 15% by weight, based on the soap stock, of a mineral lubricating oil. This mixture is stirred and heated to approximately 160° F. and sufficient sodium hydroxide, as a 50% solution of NaOH in water, is added to completely neutralize the fats and/or fatty acids employed. The mixture is then heated to complete the saponification, the temperature reaching 260–270° F. at this time. To the soap mixture present in the kettle, mineral lubricating oil is added slowly with mixing until approximately one-third to one-half of the total amount required for the batch has been added. At this point, the free alkalinity is adjusted so that there will be present approximately 0.1% of free alkalanity calculated as sodium hydroxide. The amide or amide product is added and the mixture heated to 310–320° F. with agitation

to complete dehydration, and the remainder of the oil is then added. During the addition of the oil oxidation inhibitors such as those normally added to greases may be incorporated. During the addition of the final amounts of oil, the batch is permitted to cool. Substantially the same results are obtained if the grease is completed without the addition of amide and following this, the grease then reheated to a point sufficient to melt the amide, the amide then added and dispersed by mixing and the product cooled.

As a modification of the above method of preparation, the sodium grease may be made following the above procedure with the change that the final heating to complete dehydration is effected by heating the mass to 400–420° F. to produce a melt and following completion of the addition of lubricating oil at about this temperature, the product is drawn into pans to cool. The cooled grease is then returned to the kettle where it is reworked. In this instance the amide may be added during the heating to effect dehydration.

Lubricating oils to be used in preparing the greases of this invention include those oils which are useful in preparing ordinary sodium soap greases. These include naphthenic and paraffinic type oils ranging in V. I. from 15–20 to 100 or over. Preferably dewaxed and solvent treated paraffinic mineral oils of lubricating viscosity are used. Particularly satisfactory oils are the dewaxed and solvent-treated Western mineral lubricating oils having viscosity indices between about 80 and 90 and viscosities between about 30 and about 100 SSU at 210° F.

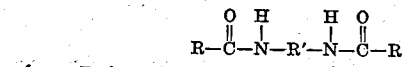
The amides or amide products which are useful in preparing water-resistant sodium base greases are preferably those prepared by reacting a diamine, such as ethylene diamine, with a hydroxy or keto fatty acid, as for example 12-hydroxy stearic acid or 12-keto stearic acid, under dehydration conditions to effect amidation. Amides produced in this manner will be referred to herein as diamides. Similar products equally useful are prepared by reacting diamines with hydroxy fatty acid chlorides. The diamines which may be employed in the preparation of these additives will contain from 2 to 6 or 8 carbon atoms per molecule. The hydroxy or keto fatty acids which may be employed to produce useful additives for the purpose described will contain from 12 to 22 carbon atoms and preferably one hydroxy or keto group, although dihydroxy or diketo substituted acids may be employed.

Another class of amides which may be employed are the simple N-alkyl substituted hydroxy or keto fatty acid amides produced by reacting alkyl monoamines with hydroxy or keto fatty acids of the class described hereabove. The alkyl group of the alkyl monoamines will contain from 1–10 carbon atoms. This latter class of amides, which will be referred to herein as monoamides, are not the full equivalent of the diamides described above, however, they do impart a certain degree of water resistance and therefore are to be considered as being encompassed by this invention.

Methods of preparing the mono- and diamides of this invention are well known. A typical method of preparing these compounds is as follows.

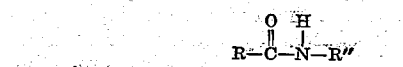
A chemical equivalent mixture of a diamine such as ethylene diamine and a hydroxy or keto fatty acid such as 12-hydroxy stearic acid is converted into the corresponding diamide by heating this mixture of reactants in the presence of a solvent such as hexane or petroleum naphtha under reflux using a water trap in the reflux line. Heating is continued until the production of water ceases. Following this treatment the solvent may be removed by distillation. By this or other means of

amidation there is produced a compound having the following formula:



where R is a hydroxy or keto fatty acid radical of 12 to 22 carbon atoms, preferably 16 to 20 carbon atoms, and R' is the bivalent hydrocarbon portion of the diamine of 2 to 8 carbon atoms and preferably 2 to 4 carbon atoms.

The simple amides are prepared by substantially the same process, using, however, a mono-amine such as propylamine in place of the diamine. Thus when an alkylamine is reacted with a hydroxy or keto fatty acid under dehydrating conditions, the resulting product will be a compound of the formula



where R is the hydroxy or keto fatty acid radical having 12 to 22 carbon atoms and preferably 16 to 20 carbon atoms and R'' is a saturated alkyl radical of 1 to 10 carbon atoms and preferably 2 to 6 carbon atoms.

It is possible, and in fact particularly with the higher diamines it is known that side reaction products are formed during the amidation reaction. The reaction mixture containing any such side reaction products may be used and will impart substantially the same degree of water resistance to the sodium greases as the pure amides and diamides. For this reason the terms amide and diamide will be used herein to cover the pure materials as well as the amidation products which may or may not be pure.

In order to determine the water resistance of greases described a test has been employed which will be referred to herein as the bearing test. In this test a ball bearing assembly is packed with grease and operated at a speed of 600 R. P. M. while directing a stream of water against the bearing for a period of one hour. The size and rate of the water stream is constant throughout the testing of all samples. In some tests the water is maintained at 100° F. and in others the temperature is maintained at 180° F. The bearing is weighed before the test and following the test the bearing is dried and weighed again to determine the loss of grease.

This method of determining loss of grease has been found in most cases to check results obtained by weighing the amount of grease applied to the bearing and determining the loss by removing and weighing the grease remaining in the bearing following the test. When the grease is found to emulsify badly with water the amount of grease left in the bearing at the end of the test is more accurately determined by removing the grease as with a solvent and vaporizing water and solvent from the removed grease before weighing.

The following examples illustrate the important aspects of this invention.

Example I

A typical sodium soap grease is prepared from the following ingredients:

	Grams
Tallow fatty acids	360
Tallow	319
Aqueous NaOH (50%)	216
Mineral lubricating oil[a]	3932
Oxidation inhibitor[b]	1.9

[a] A solvent treated and dewaxed western paraffinic oil having a viscosity at 210° F. of 80 SSU at 210° F. and a V. I. of 85.

[b] A commercial inhibitor.

The tallow and tallow fatty acids are charged to a grease kettle having means for heating and cooling and means for mixing or stirring the kettle contents. To the soapstock in the kettle is added 105 grams of lubricating oil and after melting and mixing at 140–160° F. the aqueous NaOH is added slowly with stirring. When the addition of caustic is complete the temperature of the batch is increased to about 260–270° F. to effect reaction between the soap stock and the caustic. About one-half of the remaining lubricating oil is then added slowly and mixed into the batch while gradually increasing the temperature to about 320° F. to complete saponification. When this temperature has been reached the remainder of the oil is added slowly while stirring and during this addition the batch is cooled. When the temperature reaches 200–250° F. the antioxidant is added. Cooling and mixing is continued until the temperature reaches about 150–160° F. and the batch is then drawn.

The above grease has the following characteristics:

ASTM worked penetration at 77° F	280
Dropping point ASTM, ° F	360
Sodium soap, percent by weight	15

Example II

A 1000 gram portion of the sodium soap grease of Example I is placed in a grease kettle and heated with stirring to 285° F. Twenty-six grams of Paricin 285, a diamide obtained by reacting ethylene diamine with 12-hydroxy stearic acid and obtainable from Baker Castor Oil Company, is added and stirring continued for 30 minutes. The product is cooled with slow stirring.

Example III

A grease is prepared according to the method outlined in Example I except that following saponification and addition of one-half the lubricating oil, 95 grams (2% by weight of the total batch) of Paricin 285 is added. This material is described in Example II. This grease is substantially the same as the product of Example I with regard to consistency, melting point and percent soap.

Example IV

A 1000 gram portion of the grease produced in Example I is heated in a grease kettle with stirring to a temperature of 300° F. and to it is added 20 grams of an amide product obtained by reacting chemically equivalent amounts of propyl amine with 12-hydroxy stearic acid under dehydrating conditions as described hereinabove. This product is considered to be N-propyl 12-hydroxystearamide.

Example V

A grease is prepared following the method outlined in Example I except that after completion of the neutralization and after adding about one-half of the oil, 95 grams of the amide product described in Example IV is added. The product grease is substantially identical in penetration, melting point and percent soap with the product of Example I.

Example VI

A 500 gram portion of the grease produced in Example I is heated to 270° F. and 15 grams of the diamide obtained by reacting 1,5-diamino pentane with 12-keto stearic acid in chemically equivalent proportions and the product mixed and cooled.

Example VII

Example VI is repeated using the diamide product obtained by reacting hydroxy palmitic acid with ethylene diamine in place of the amide compound there described.

Example VIII

Example VI is repeated using the diamide product obtained by reacting hydroxy arachidic acid with butylene diamine in place of the amide described in that example.

Example IX

A grease is prepared according to Example I using the chemically equivalent amount of 12-hydroxy stearic acid

in place of the tallow and tallow fatty acids. This product has a penetration of 300 at 77° F. and a melting point of 380° F.

Example X

Example IX is repeated except that following complete saponification and addition of about one-half of the total oil 47.5 grams of Paricin is added.

Example XI

To 500 grams of the grease produced in Example IX is added 15 grams of Paricin and the mixture heated and stirred to a temperature of 290° F. Cooling is then effected while stirring.

Example XII

To 500 grams of the grease produced in Example IX is added 25 grams of the product obtained by reacting 12-keto stearic acid with a chemically equivalent amount of octyl amine. The reaction product containing as a major ingredient N-octyl-12-keto-stearamide is added after heating the grease to 270° F. and the resulting mixture then cooled with stirring.

Example XIII

A sodium stearate grease containing about 13.5% soap is prepared from the following ingredients:

	Grams
Stearic acid	30
Sodium hydroxide	4.8
Paricin 285	4
460 oil[a]	200

[a] This is a naphthenic oil having a V. I. of 28 and a viscosity at 100° F. of 600 SSU.

The stearic acid and a small amount of oil is heated to 140° F. and the caustic added. After heating to 260° F. approximately half the oil is added as the batch temperature is gradually increased. At a temperature of 290° F. the diamide, Paricin 285, is added and the heating continued to 220° F. The remainder of the oil is added as the batch cools. The product has a penetration of 153 at 77° F.

Results of bearing tests to determine water resistance of the greases of the above examples are shown in the following table.

Product of Example No.	Amide Product		Percent Water Loss in Bearing Test at—	
	Reaction Product of—	Percent by Wt.	100° F.	180° F.
I			100	
II	Ethylene diamine+12-hydroxy stearic acid.	2.6	18.5	57.5
III	do	2.6	19	56
IV	Propyl amine+12-hydroxy stearic acid.	2.0	25	61
V	do	2.0	25	63
VI	1,5-diamino pentane+12-keto stearic acid.	3.0	22	59
VII	Ethylene diamine+hydroxy palmitic acid.	3.0	19	55
VIII	Butylene diamine+hydroxy arachidic acid.	3.0	18	53
IX			100	
X	Ethylene diamine+12-hydroxy stearic acid.	1.3	20	60
XI	do	3.0	5	35
XII	Octylamine+12-keto stearic acid.	5.0	5	28
XIII	Ethylene diamine+12-hydroxy stearic acid.	1.7	7.5	45.5

In the above table it will be observed that the products of Examples I and IX are ordinary sodium soap greases without added amides. Example I grease is made with tallow and tallow fatty acids and thus contains saturated and unsaturated fatty acid soaps and Example IX grease is made with 12-hydroxy stearic acid. Both of these products were completely washed from the bearing at 100° F.

The greases of Examples II to VIII, inclusive, are greases like the product of Example I but each contain an amide product added either during preparation of the grease or added to the simple sodium soap grease after it has been completely prepared. It appears to make little difference when the amide product is incorporated as indicated by the results of Examples II and III. It will be observed that an amount less than about one fourth of any of these greases is washed from the bearing at 100° F. and even at 180° F. a good portion of the grease remains in the bearing.

Greases of Examples X, XI and XII are sodium 12-hydroxy stearate greases of the type produced in Example IX but containing amide product. These products show even greater resistance to water than those based on sodium soaps of tallow and tallow fatty acids.

The grease of Example XIII being made from stearic acid, a saturated acid and containing an amide product is similar to the preceding group of greases in water resistance.

It is to be noted that the bearing test is very severe compared with conditions encountered in ordinary service even where water or moist conditions are encountered so that even though some grease is washed from the bearing in the above test these greases containing amide product are successfully used in service where the ordinary sodium soap greases have been found to fail in a relatively short period of time.

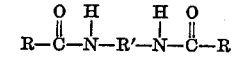
As would be understood by one skilled in the art when the term sodium soap grease is used it is meant to include those products consisting essentially of lubricating oil containing thickening proportions of sodium soap with or without added oxidation inhibitors.

The foregoing description and examples are illustrative of the invention but are not to be taken as limiting the invention since many variations may be made without departing from the spirit and the scope of the following claims.

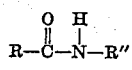
I claim:

1. A water resistant sodium soap grease consisting essentially of mineral lubricating oil and thickening proportions of sodium soap and containing between about 0.5% and about 5% of an amide product obtained by reacting under dehydrating conditions an amine selected from the class consisting of alkylene diamines having 2–8 carbons per molecule and alkyl monoamines having 1 to 10 carbon atoms per molecule with a fatty acid selected from the class consisting of hydroxy and keto fatty acids having 12 to 22 carbon atoms per molecule.

2. A water resistant sodium soap grease consisting essentially of mineral lubricating oil and thickening proportions of sodium soap and containing between about 0.5% and about 5% of an amide product selected from the class consisting of (1) diamides having the formula



in which R is a fatty acid radical of 12 to 20 carbon atoms having at least one substituent of the class consisting of hydroxyl and ketone substituents and R′ is the bivalent hydrocarbon portion of the alkylene diamine and (2), monoamides having the formula



in which R is the same as R in the diamide formula and R″ is a saturated alkyl radical of 1 to 10 carbon atoms.

3. A grease according to claim 1 in which said amide product is a diamide obtained by reacting ethylene diamine with 12-hydroxy stearic acid.

4. A grease according to claim 1 in which said amide product is a diamide obtained by reacting butylene diamine with 12-hydroxy stearic acid.

5. A grease according to claim 1 in which said amide product is a diamide prepared by reacting ethylene diamine with 12-keto stearic acid.

6. A grease according to claim 1 in which the amide product is a monoamide obtained by reacting propyl amine with 12-hydroxy stearic acid.

7. A grease according to claim 2 in which said amide product is a diamide in which R' is an ethylene radical and R in each instance is a 12-hydroxy stearic acid radical.

8. A grease according to claim 2 in which said amide product is a diamide in which R in each instance represents a 12-keto stearic acid radical.

9. A grease according to claim 2 in which said amide product is a monoamide in which R represents a 12-hydroxy stearic acid radical.

10. A grease according to claim 2 in which said amide product is a monoamide in which R'' represents a propyl radical.

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