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PRODUCTION OF LUBRICATING GREASE

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The present invention relates to the production of lubricating greases and particularly to the production of greases which are thickened with metal soaps and also are modified by including therein certain acidogenic materials and/or the salts thereof.

Various suggestions have been made in the prior art for the improvement of high temperature properties and the modification of other properties of lubricating greases by modifying the characteristics of the material used to thicken lubricating oil to grease-consistency. The thickener commonly used is a soap or a mixture of soaps of the fatty acids. Soaps of calcium, barium, sodium, lithium, wax, and the like, have long been used as thickeners for mineral base lubricating oils. The soda soap greases are widely used, and are particularly preferred for the lubrication of anti-friction bearings which operate at fairly high temperatures. There is a tendency in the industries gradually to increase the operating temperatures of anti-friction bearings as lubricants become available to maintain such bearings. A number of suggestions have been made recently that the dropping point or melting point of soda base greases can be raised appreciably by incorporating therein a salt of a low molecular weight acid.

In the co-pending application of Morway, one of the present inventors, Serial No. 777,328, filed October 1, 1947, now Patent No. 2,468,099, there is disclosed a superior high temperature lubricating grease of the soda base type prepared by incorporating into the grease composition a small amount, from about 0.1 to 5%, of an acid or acidogenic material, preferably acrylic acid, methacrylic acid, crotonic acid, or the like. The application of Morway and Daniels, Serial No. 9,315, filed February 18, 1948, now Patent No. 2,468,098, also mentions the use of certain saturated acids such as glycolic or hydroxyacetic acid, alpha or beta hydroxy butyric acid, acetoacetic acid, and the like. These acids are added to the grease ingredients prior to saponification and the sanponifying agent, usually sodium hydroxide, is added in sufficient quantity not only to form the soap with the fatty materials which are present but also to neutralize or substantially neutralize and form a salt with the acid or acidogenic material.

Although the products described in the applications referred to above have desirable characteristics, it is desirable for several reasons to modify the methods of manufacture to overcome certain difficulties. Acrylic acid in particular is

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a highly toxic material and its handling is attended with some difficulties and with some danger. It is also a costly material since it is ordinarily prepared from an ester. Thus, acrylic acid may be obtained by first preparing a hydroxy nitrile, e. g. $CH_2OH—CH_2CN$. This nitrile dehydrates spontaneously to leave acrylonitrile $CH_2=CHCN$. The acrylonitrile is esterified by treating it with a suitable aliphatic alcohol, preferably a lower aliphatic alcohol such as methyl, propyl, isopropyl, butyl or isobutyl alcohol. Thus, with ethyl alcohol, $CH_3CH_2OH+CH_2=CHCN \rightarrow CH_2=CH—COOC_2H_5+NH_3$.

This ester, according to the present invention, and related analogous esters, may be used directly in lieu of acrylic acid, in the preparation of grease following the general procedure described in the aforesaid application of Morway, Serial No. 777,328. If it were desired to use acrylic acid rather than the ester, such acid would be derived ordinarily from the same ester and its cost would be considerably higher than that of the ester. This particular ester has the very important advantage of being relatively harmless to the human skin, whereas the acid is highly toxic and the simplicity of the present process, and the economy of the ingredient represent a distinct improvement over the process of the aforesaid application.

Although various esters may be employed, as noted above, the esters of low molecular weight monobasic acids, e. g., acrylic, crotonic, benzoic, and the like, are preferred because they are more readily available, much less expensive and also may readily be reacted in the desired manner. The by-products, usually alcohols which are released upon neutralization, are readily disposed of either by evaporation or by recovery in the case of the lower aliphatic esters. Higher esters may be used, however, particularly where the alcohols which are released upon treatment with alkali may be permitted to remain in the grease composition as plasticizers. In general, the C_1 to C_4 aliphatic esters of the lower aliphatic acids are preferred, and the C_1 to C_4 esters of benzoic acid, but other esters of higher chain length, up to 10 or 12 carbon atoms in the alcohol radical, may be utilized in some cases.

The esters of unsaturated acids such as acrylic acid, methacrylic acid, and crotonic acid, and the lower esters (C_1 to C_4, preferably) of the other related acids mentioned above including such as those referred to in Patent No. 2,468,098, e. g. glycolic, alpha or beta hydroxy butyric, and acetoacetic acid may be used. The acids from

which the esters may be derived, or on which the esters may be based are numerous, but in general they should have not more than 6 or 7 carbon atoms, preferably 3 to 6 carbon atoms per molecule. Heterocyclic acid esters also may be used, for example, the lower aliphatic esters of furoic acid and the corresponding thio acids and their homologs.

Greases according to the present invention are prepared in much the same general way as those described in the aforesaid applications of Morway and Morway et al., except that equivalent molar quantities of ester are substituted for the acids. Thus, instead of using 0.1 to 5% by weight of acid, based upon the total composition, a similar or slightly larger quantities, depending upon the molecular weight, of the ester may be used. The ester is added to the mineral oil and fatty material prior to saponification. Thereafter, saponifying agent, preferably sodium hydroxide, is added and the grease is cooked in the conventional manner to a temperature which may be as high as 500° F. or more, but usually is within the range of 250° to 450° F.

In this process the ester is hydrolyzed. In order to prevent polymerization, when an acrylic, methacrylic or other polymerizable ester is used, a polymerization inhibitor should be used. Hydroquinone, thymol, phenyl naphthylamine and the polyalkylated phenols, e. g. 2,4,6 tri-tertiary butyl phenol, alkylated alkoxyphenols, and the like, are suitable. Aromatic amines may also be used. Small quantities of such inhibitors, e. g. 0.01 to 1 or 2% are quite adequate. By proper choice of the polymerization inhibitor, the grease may also be inhibited at the same time and for this purpose hydroquinone or phenyl α or phenyl β naphthylamine are usually preferred. A combination may be used, since hydroquinone is a particularly preferred polymerization inhibitor whereas the phenyl naphthylamines are superior oxidation inhibitors.

Where the acid is used as in the above mentioned Morway application, water is evaporated whereas with the use of esters as in the present case an alcohol is given off, the type of alcohol depending upon the esterifying group. The following examples indicate the manner in which the ingredients may be combined and, in general, they represent the replacement of acids with esters, with suitable control to prevent polymerization or other undesirable reactions. The process otherwise is quite similar to that described in the aforesaid Morway Patent No. 2,468,099.

Example I

A grease composition was prepared of the following ingredients:

	Per cent
Hydrogenated fish oil acids (hydrofol acids 54)	14.00
NaOH	4.25
Methyl ester of acrylic acid	3.96
Mineral lubricating oil of 500 S. S. U. viscosity at 100° F	76.75
Phenyl alpha naphthylamine	1.00
Hydroquinone	0.04

The methyl ester of acrylic acid (containing 1.0% of hydroquinone as a polymerization inhibitor) and approximately an equal quantity of mineral oil, were charged to a cold fire heated grease kettle equipped with means for adequate agitation. A 40% aqueous solution of sodium hydroxide was added and the ingredients were stirred together without heating for one hour. The hydrogenated fish oil acids were then added and the mixture was slowly heated to 200° F. Mineral oil equal to the first charge was then added and the ingredients heated further to 300° F. Heating was also continued while adding the balance of the mineral oil to a maximum temperature of 490° F. At this point the phenyl alpha naphthylamines was added and the batch was next cooled, while stirring, to a temperature of 160° F. Agitation was discontinued overnight and the next morning the cold grease was stirred to a smooth homogeneous product. It showed the following inspection:

Percent free alkalinity, as NaOH	0.53
Dropping point °F	440
Worked penetration:	
(60 strokes) mm./10	250
(6000 strokes)	280
(75000 strokes)	327
Water resistance (AN-G-15 method) °F	125
Water temperature, percent loss, none	

Example II

	Per cent
Hydrogenated fish oil acids	15
NaOH	4.2
Methyl methacrylate	3
Phenyl alpha naphthylamine	1
Mineral lubricating oil as in Example I	76.8

Example III

	Per cent
Oleic acid	15
NaOH	4
Ethyl ester of glycolic (hydroxyacetic) acid	3.5
Phenyl alpha naphthylamine	1
Mineral lubricating oil as in Example I	76.5

Preferred proportions of the ingredients are 10 to 20% of fatty material based on the total composition, although the weight of these ingredients may vary from as little as 5 to as much as 30%. The esters may be used in proportions of 0.1 or 0.2 up to about 7 or 8%, and the quantity of saponifying agent required should be enough to completely saponify the fatty materials and to completely or substantially completely hydrolyze the ester. A small excess of acidity or alkalinity may be permitted, however.

Conventional anti-oxidants such as phenyl alpha naphthylamine, phenyl beta naphthylamine, and the like, in quantities of about 0.1 to 1% may be used both as anti-oxidants and as polymerization inhibitors or they may be used with other polymerization inhibitors where the esters are polymerizable as the acrylic type esters are. Various other additives such as extreme pressure compounds, tackiness or stringiness agents, metal deactivators, corrosion inhibitors, and the like, may be employed as is well understood in the art. Unless the polymerization inhibitor is itself an anti-oxidant, an oxidation inhibitor should be added when cooking has been completed.

The lubricating oil is preferably a mineral oil of lubricating grade having a viscosity of 200 to 1,000 S. S. U. or more at 100° F. Mineral oil should be used in the preparation of the grease, but a synthetic ester type lubricant may be prepared by using only a sufficient quantity of mineral oil to cook the soap-forming ingredients properly after which an ester oil such as di-2-ethylhexyl sebacate, and the like, may be used in lieu of the remainder of the mineral oil, as is also well understood in the art.

What is claimed is:

1. The process of preparing lubricating grease containing an alkali metal salt of a low molecular weight monocarboxylic acid which comprises the steps of adding 0.1 to 8% by weight, based on the final composition of a C_1 to C_4 aliphatic alcohol ester of said monocarboxylic acid to a hydrocarbon lubricating oil and 5 to 30% of a saponifiable fatty material, thereafter adding saponifying agent at an elevated temperature of 150 to 200° F., in quantity sufficient to substantially hydrolyze and neutralize said ester and said fatty material, and finally cooking the ingredients to evaporate water and other volatile ingredients and to form a grease structure.

2. Process as in claim 1 wherein the ester is a C_1 to C_4 aliphatic ester of an unsaturated monocarboxylic aliphatic acid having 3 to 5 carbon atoms.

3. Process as in claim 1 wherein the ester is a C_1 to C_4 aliphatic ester of an acrylic acid.

4. Process according to claim 1 wherein the ester is a C_1 to C_4 aliphatic ester of crotonic acid.

5. Process according to claim 1 wherein the ester is a C_1 to C_4 aliphatic ester of glycolic acid.

6. Process according to claim 1 wherein the ester is a C_1 to C_4 aliphatic ester of methacrylic acid.

7. Process as in claim 1 wherein said ester is a polymerizable ester of an unsaturated acid of 3 to 5 carbon atoms and a polymerization inhibitor is employed during said grease formation.

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