

2,801,969

LUBRICATING GREASES THICKENED WITH SOAPS OBTAINED BY ALKALI FUSION OF AMINO ALCOHOLS

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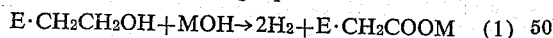
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11 Claims. (Cl. 252—33.6)

The present invention relates to an improved method of preparing lubricating greases and to grease compositions produced by this method. More specifically, the invention pertains to improvements in the manufacture of grease thickeners and to greases containing such thickeners. In its broadest aspect, the invention provides an improved method of preparing amino acids and grease thickeners by fusing high molecular weight amino derivatives having a primary alcohol group, particularly amino ether alcohols, with caustic alkali, producing a metal soap from the amino acid so formed and incorporating this metal soap into a lubricating oil in grease making proportions. In a preferred embodiment of the invention, the fusion is carried out in the presence of lubricating oil.

Lubricating greases normally consist of lubricating oils thickened by alkali and alkaline earth metal soaps or other thickeners to a solid or semi-solid consistency. The soaps may be prepared by the neutralization of high molecular weight fatty acids or by the saponification of fats which is usually carried out in a portion of the oil to be thickened.

The present invention pertains to highly valuable, stable lubricating greases in which the high molecular weight fatty acids are replaced or at least supplemented by a new grease making material. It has now been found that such greases may be prepared by incorporating into lubricating oils a grease thickener obtained by fusing high molecular weight amino derivatives having a primary alcohol group, particularly amino ether alcohols, with alkali, particularly caustic soda or potash at temperatures of about 400°–620° F., preferably about 500°–575° F. for a time sufficient to form the alkali metal salt of the acid corresponding to the amino alcohol used. The chemical reaction taking place during the fusion process may be illustrated by the following equation:



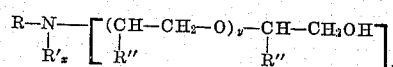
wherein E may be an amino or an amino ether radical containing 1 or more carbon atoms and M is an alkali metal, such as sodium or potassium. The amino or amino ether alcohol should contain a total of at least 10 carbon atoms per molecule.

The discovery of the utility of alkali fusion of high molecular weight amino alcohols for grease making greatly increases the wealth of raw materials available for grease production. Heretofore, ester-type fats, oils or high molecular weight fatty acids have been used almost exclusively in the manufacture of soap-thickened greases and these starting materials have been believed indispensable for the purpose. All these materials have numerous other industrial uses, a situation conducive to the development of shortages forcing undesirable variations in grease making procedures and grease characteristics. The discovery of an entirely new and large class of suitable raw materials eases this situation considerably.

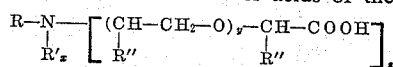
The use of high molecular weight amino alcohols as grease making materials introduces no complication into the grease making procedure. While alkali fusion of the

amino alcohol may be carried out in a separate preliminary acid-forming stage, the greases are preferably produced essentially in a single process step in which the high molecular weight amino alcohol is fused with alkali in the lubricating oil base in grease making proportions and at grease making conditions, although at somewhat higher temperatures. At the conclusion of the fusion process a finished grease is obtained.

Quite generally, amino alcohols, particularly amino ether alcohols, may be used which have about 10–50 or more carbon atoms per molecule and a sufficiently high boiling point to prevent excessive volatilization during the fusion process. The amino alcohols suitable for the invention have the general formula



and yield upon alkali fusion ether acids of the formula



wherein

R=a hydrocarbon group containing from 1–40 carbon atoms selected from the group consisting of alkyl, alkylene, naphthyl, aryl, alkaryl and aralkyl

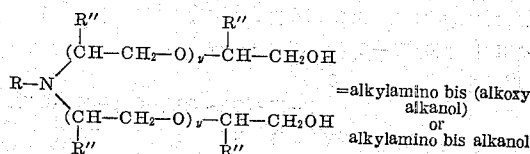
R' and R''=H or one of the groups represented by R

y=an integer from 0–50

x=0 or 1, z=1 or 2, and x+z=2.

These amino alcohols include the amino derivatives of alkylene or polyalkylene (e. g. ethylene, propylene, polyethylene, polypropylene) glycols. Specific examples of these compounds are:

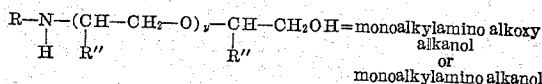
TYPE A



Examples:

Ethylamino—bis (decaethoxyethanol)
Octylamino—bis (decaethoxyethanol)
Laurylamino—bis (octaethoxyethanol)
Stearylaminobis (pentapropoxyethoxyethanol)
Behenylaminobis (octapropoxypropanol)
Laurylamino—bis (tetrapropoxytetraethoxyethanol)
Hexadecylamino—bis (ethanol)
Cyclohexylamino—bis (decaethoxyethanol)

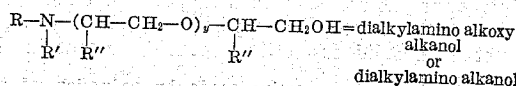
TYPE B



Examples:

Monoethylamino—decapropoxypropanol
Monolaurylamino—octadecapropoxydecaethoxyethanol
Mono-coco-amino¹—eicosaethoxyethanol
Mono-stearylamin—ethanol
Toluino—pentadecaethoxyethanol

TYPE C



¹Derived from mono-cocoamine made by reduction of the nitriles of coconut oil acids.

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² Derived from di-coco-amine made by reduction of the nitriles of coconut oil acids.

used alone or in addition to mineral lubricating oil to bring the grease to the desired consistency. The oil base preferably comprises about 50 to about 95% of the total weight of the finished grease.

As indicated above, the alkali fusion of the invention may be carried out in two stages. When so operating, the amino alcohol to be fused may be added in the initial charge or over a period of 1-8 hours to a molten mixture of alkali and mineral oil, maintained at fusion temperatures of, say, about 400°-620° F. The amount of alkali employed may be substantially stoichiometric or somewhat higher, for example from 1-3 mols of alkali per mol of amino alcohol. When all the amino alcohol has been added, heating may be continued at these temperatures until gas evolution substantially ceases. The acid formed may be recovered from the reaction mixture after cooling, by dilution with water or with 50% isopropanol, followed by extraction of the oil and any unreacted alcohol with a suitable solvent, such as heptane or the like, and acidification. If desired, the free acid may be purified by vacuum distillation.

The acid so prepared may then be introduced into a lubricating oil base stock, other high and/or low molecular weight fatty acids as well as other grease additives may be added and the mixture may be converted into a grease by the addition of at least sufficient caustic alkali, preferably in aqueous solution, to neutralize the acids present. Conventional grease making conditions including temperatures of about 350°-500° F. may be used in this stage. The soap derived from the amino alcohol by alkali fusion should form at least 20 wt. percent and preferably about 30-50 wt. percent of the grease thickener or about 2.0-20 wt. percent of the finished grease. The remainder of the grease thickener is preferably made up by a suitable soap-salt complex of the type described above. The proportion of soap derived from amino alcohol to soaps and salts derived from other acids may be about 1:4 to 4:1 and preferably is about 1:1.

The free amino polyether acids and also their soaps may be used as additives in lubricating oils. By controlling the length of the alkyl group and the polyether groups, the resulting acids may be valuable in the production of oil soluble chelates and the soaps may be valuable as detergents.

In order to prepare a grease by alkali fusion of the amino alcohol in situ in accordance with a more desirable embodiment of the invention, the grease making procedure may be quite generally as follows. A mineral lubricating oil base is mixed with the amino alcohol and the mixture is heated to about 130°-180° F. The alkali is added preferably in the form of an aqueous solution of about 30-50% concentration. The mass is then dehydrated at temperatures of about 300°-400° F. for about 1-6 hours, depending upon the size of the batch. Thereafter, the temperature is increased to a fusion temperature of about 400°-620° F. and maintained within this range until gas formation has receded appreciably, which takes place usually after about 1-2 hours. The grease may then be allowed to cool under stirring to about 200°-250° F. at which level further additives may be introduced. Finally, the grease may be poured into pans to be cooled to room temperature.

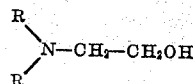
A similar procedure is employed when the amino alcohol is subjected to alkali fusion in situ in the presence of suspending agents, such as soaps of high molecular weight fatty acids or complexes of such soaps with salts of low molecular weight acids in accordance with the preferred embodiment of the invention. In this case, the high molecular weight acids are added to the mineral oil together with the amino alcohol while the low molecular weight acid may be added after the initial heating stage immediately prior to the alkali addition. Thereafter, sufficient caustic alkali to neutralize the acids

and convert the amino alcohol to soap is added, preferably in the form of an aqueous solution of about 40-50% and the mixture is heated at a saponification temperature of about 300°-400° F. until the acids are converted to soaps and salts and all the water is volatilized. Alkali fusion is then carried out substantially as described above, except that less violent stirring is required.

The invention will be best understood by reference to the following specific examples which represent preferred modifications of the invention.

Example I

Dicocoaminoethanol having the formula



(average molecular weight approximately 425) was prepared by reacting ethylene oxide with dicocoamine manufactured by Armour and Company by reduction of the nitriles of coconut oil acids. The dicocoaminoethanol was used in grease manufacture as follows:

Ingredients:	Weight percent
Dicocoamino ethanol	10.00
Hydrofol acids 54 ¹	10.00
Glacial acetic acid	4.00
Sodium hydroxide	6.50
Phenyl alpha-naphthylamine	1.00
Naphthenic type lubricating oil distillate having a viscosity of 50 S. S. U. at 210° F.	68.5

¹ Hydrogenated fish oil acids, having a degree of unsaturation corresponding approximately to commercial stearic acid.

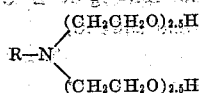
PREPARATION

The dicocoaminoethanol, the Hydrofol acids 54 and ½ of the mineral oil were charged to a fire heated kettle equipped with means of good agitation. The ingredients were warmed to 170° F. and the acetic acid was charged thereto, followed immediately by a 40% aqueous solution of the sodium hydroxide. Heating was continued at 400° F. until the mixture was dehydrated. The balance of the mineral oil was added and heating continued to 560° F. At this temperature a sudden large expansion in the kettle contents occurred, which slowly subsided. Heating at 560° F. was continued for 120 minutes. The grease was solid at this temperature. Heating was discontinued but stirring continued while cooling to 250° F. where the phenyl alpha-naphthylamine was added. Cooling was then continued to 200° F. Properties:

Dropping point, ° F.	500+.
Penetration, mm./10; 77° F:	
Unworked	136.
Worked 60 strokes	160.
Worked 100,000 strokes	240.
Water washing test, percent loss	None.
Norma Hoffmann oxidation test, hours to 5 p. s. i.	
Drop in oxygen pressure	175.
Appearance	Excellent smooth uniform grease—slight fiber before homogenization.
A. F. B. M. A. test, 80°, 150°, 250° F. (operation of an open 204 ball bearing at given temperatures)	Excellent lubrication-channeling type grease. No leakage through bearing seals.

Example II

The amino alcohol used in this example was Ethomeen T/15 a product of Armour and Company. Ethomeen T/15 has the approximate general formula



(mol wt. 491) wherein R stands for a hydrocarbon radical derived from tallow and consisting of about 25% saturated C_{18} groups, 70% saturated C_{18} groups and 5% unsaturated C_{18} groups. This amino alcohol is made by reacting tallow acids with ammonia to form the ammonium salt of these acids, heating to dehydrate the salt to the amide, further dehydrating the latter to form the nitrile, reducing the nitrile to the amine and reacting this amine with 5 mols ethylene oxide per mol of amine.

Ingredients:	Weight percent
Ethomeen T/15	10.00
Hydrofol acids 54	10.00
Acetic acid (glacial)	4.00
Sodium hydroxide	6.50
Phenyl alpha-naphthylamine	1.00
Blend of naphthenic type mineral oil distillate having a viscosity of 55 S. S. U. at 210° F.	68.50

PREPARATION

The Hydrofol acids 54, Ethomeen T/15, and $\frac{1}{2}$ the mineral oil were charged to a fire heated grease kettle and warmed to 150° F. The acetic acid was added, followed immediately by a 40% aqueous solution of NaOH. The temperature was raised to 400° F., volatilizing water. Then the balance of the mineral oil was added. Heating was continued to 560° F. and the temperature held above 500° F. for 2 hours. Then heating was discontinued and the mass allowed to cool while agitating. When a temperature of 275° F. was reached the inhibitor (phenyl alpha-naphthylamine) was added and the mass cooled to 200° F. A portion of this grease was then pumped through a homogenizer, filtered and packaged.

Properties:

Dropping point, ° F.	500+
Penetrations, 77° F. mm./10:	
Unworked	199
Worked 60 strokes	210
Worked 60,000 strokes	235
Water washing test, percent loss	None
Appearance	Excellent smooth uniform grease

The balance of the grease left in the kettle was diluted as follows:

50% above described product	
50% solvent extracted Mid-Continent distillate + solvent extracted Bright Stock, having a viscosity of 57 S. S. U. at 210° F. and a V. I. of 102.	

This product was homogenized, filtered and packaged.

Properties:

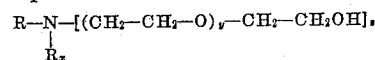
Dropping point, ° F.	472
Penetrations, 77° F. mm./10:	
Unworked	310
Worked 60 strokes	320
Worked 100,000 strokes	332
Water washing test, percent loss	20
Norma Hoffmann oxidation test, hours to 5 p. s. i. drop in oxygen pressure	214

The invention is not limited to the specific figures of the foregoing examples. The relative proportions of the grease constituents may be varied within the limits indicated above to obtain greases of different consistency and varying characteristics.

What is claimed is:

1. A lubricating grease comprising a lubricating oil

and a grease making proportion of a grease thickener comprising an alkali metal soap of an organic acid produced by fusing an amino alcohol with alkali at a temperature in the range of 400 to 620° F. until gas evolution substantially ceases, said alcohol having about 10 to 50 carbon atoms per molecule and having the general formula



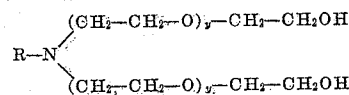
wherein R is an alkyl hydrocarbon group containing from 1-40 carbon atoms, y is an integer from 0-50, x is an integer from 0 to 1, z is an integer from 1 to 2, and $x+z$ is 2.

2. A grease according to claim 1 wherein the said grease thickener is made up of about 30 to 50 wt. percent of the alkali metal soap derived from the amino alcohol, and the remainder is made up of an alkali metal soap of a high molecular weight fatty acid.

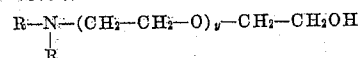
3. A grease according to claim 1 wherein said grease thickener is made up of about 30 to 50 wt. percent of the alkali metal soap derived from the amino alcohol and the remainder is made up of a complex of a high molecular weight fatty acid soap with a low molecular weight fatty acid salt.

4. A grease according to claim 1 which contains a minor amount of a suspending agent, which is solid at the conditions of fusion, sufficient to prevent the alkali from settling out of the reaction mixture during said fusion.

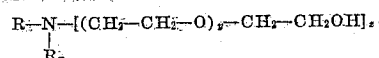
5. A grease according to claim 1 in which said alcohol has the general formula



6. A grease according to claim 1 in which said alcohol has the general formula

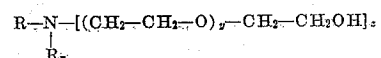


7. The process of preparing a lubricating grease composition which comprises admixing a major proportion of a mineral lubricating oil with an amino alcohol having about 10 to 50 carbon atoms per molecule and having the general formula



wherein R is an alkyl hydrocarbon group containing from 1-40 carbon atoms, y is an integer from 0-50, x is an integer from 0 to 1, z is an integer from 1 to 2, and $x+z$ is 2, heating said mixture to a temperature of about 130° to 180° F., then adding an amount of alkali sufficient for fusing said amino alcohol, dehydrating the resulting mixture at a temperature of about 300° to 400° F., continuing heating at a temperature of about 400° to 620° F. until gas evolution substantially ceases and then cooling the resulting grease composition, said amino alcohol being employed in an amount sufficient to form about 2 to 20 wt. percent of a grease thickening alkali metal soap.

8. The process for preparing lubricating grease compositions which comprises admixing a major proportion of a mineral lubricating oil, about 2 to 30 wt. percent, based on the finished grease composition, of a high molecular weight fatty acid and an amino alcohol having about 10 to 50 carbon atoms per molecule and having the general formula



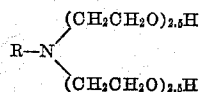
wherein R is an alkyl hydrocarbon group containing from 1-40 carbon atoms, y is an integer from 0-50, x is an integer from 0 to 1, z is an integer from 1 to 2, and $x+z$ is 2, heating said mixture to a temperature of about 130° to 150° F., adding to the heated mixture about 1 to 10% by weight, based on the finished grease composition, of a

low molecular weight carboxylic acid, then adding sufficient alkali for fusing said amino alcohol and for neutralizing said high and low molecular weight carboxylic acids, dehydrating the resulting mixture at a temperature of about 300° to 400° F., continuing heating at a temperature of about 400° to 620° F. until gas evolution substantially ceases and then cooling the resulting grease composition, said amino alcohol being employed in an amount sufficient to form about 2 to 20 wt. percent of a grease-thickening alkali metal soap.

9. The process of claim 8 wherein the high molecular weight fatty acid is a hydrogenated fish oil acid and said low molecular weight carboxylic acid is acetic acid.

10. The process of claim 8 wherein said amino alcohol is dicocoamino ethanol.

11. The process of claim 9 wherein said amino alcohol has a molecular weight of 491 and the approximate formula



wherein R is a hydrocarbon radical of tallow acid.

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