The present invention relates to an improved method of preparing lubricating greases and to lubricating 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 alkyl group, particularly amino ether alcohols, with caustic alkali, forming a metal soap from the amino acid so formed and incorporating this metal soap into a lubricating oil in the presence of the 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 thickeners may be prepared by neutralizing 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 thickening 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 alkyl group, particularly amino ether alcohols, with alkali, particularly caustic soda or potash at temperatures of about 400° to 620°F., preferably about 500° to 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:

\[
E\cdot CH_2CH(OH)\cdot MOH + 2H_2 + E\cdot CH_2COOM \rightarrow 2
\]

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 in 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 alcohol, 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

\[
R-N\left[\left(CH-CH-O\right)_{n-1}CH-CH_{2}OH\right]_{n}
\]

and yield upon alkali fusion ether acids of the formula

\[
R-N\left[\left(CH-CH-O\right)_{n-1}CH-COOH\right]_{n}
\]

wherein

- \( R = \) hydrocarbon group containing from 1-40 carbon atoms selected from the group consisting of alkyl, alkylenyl, naphthenyl, aryl, alkyaryl and aralkyl
- \( R' = H \) or \( R' = R'' \)
- \( y = \) 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 alkylenyl or polyalkylene (e.g. ethylene, propylene, polyethylene, polypropylene) glycols. Specific examples of these compounds are:

**TYPE A**

- Ethylamino-bis (decaethoxyethanol)
- Octylamino-bis (decaethoxyethanol)
- Laurylaminobis (octaethoxyethanol)
- Stearylaminobis (pentapropoxyethoxyethanol)
- Behenylaminobis (octapropoxypropanol)
- Laurylaminobis (tetrapropoxytetraethoxyethanol)
- Hexadecylaminobis (ethanol)
- Cyclohexylaminobis (decaethoxyethanol)

**TYPE B**

- Monoethylamino-decapropoxypropanol
- Monolaurylamino-octadecaproxydodecaethoxyethanol
- Mono-coco-amino-octaethoxyethanol
- Mono-stearylaminobis-ethanol
- Toluino-pentadecaethoxyethanol

**TYPE C**

- 1-Dimethylenediamine (alkoxy alkyl)
- dialkylamino alcohols

\[1^{\text{Derived from mono-concomine made by reduction of the nitriles of coconut oil acids.}}\]
Examples:
Diethylamino-pentadecaethoxyethanol
Diocetylaminodecaethoxyethanol
Octyl laurylamino-decaethoxyethanol
Diphenylnalma-triacontaethoxyethanol
Dicetylaminotetraethoxyethanol
Dilaurylamino-dipropoxypropanol
Di-coco-amino-ethanol
Di-coco-amino-pentapropyoxidiethoxyethanol
Di-coco amino-triethoxypentapropyoxetriethoxyethanol
Diododecylamino-ethanol

Particularly desirable starting materials are the amino and amino ether alcohols obtained from primary or secondary aliphatic amines, particularly straight chain amines, such as octadecyl amine, lauryl amine, etc.

The amino and amino ether alcohols to be subjected to alkalai fusion in accordance with the invention may be prepared from these starting materials quite generally by a reaction with alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide, oxynylene oxide, hexa-decylene oxide, butadiene monoxide, styrene monoxide, etc., at temperatures of about 200° to 250°F. In the presence or absence of catalysts, for example an alkali type catalyst, to form monoglycol or polyglycol ethers having a primary alcohol group. The amount of alkylene oxide used may be as high as 50 or more mols for each mol of the amino compound used as the starting material.

The water and oil solubility of this end product may be controlled to a certain degree by a proper choice of the molecular weight of the alkylene oxide used. In general, the higher the molecular weight of the alkylene oxide the lower the water solubility and the higher the oil solubility of the end product. Thus, water insoluble, oil soluble end products may be produced by combining the low molecular weight amino compounds with high molecular weight alkylene oxides.

The reactions involved in the formation of suitable amino alcohols from amino compounds and alkylene oxides may be illustrated by the following equations:

\[ R{-NH} + (g+1) R^1{-OH} \rightarrow R{-NH}+g R^1{-OH} \]

\[ R{-N}-(CH_{2}CH_{2}O)_{n}CH{-OH} \rightarrow R{-N}-(CH_{2}CH_{2}O)_{n}CH{-OH} \]

(3)

The amino or amino ether alcohols produced in this manner may then be converted into the corresponding carboxylic acids or their soaps by fusion with alkali as described above and illustrated with reference to Equation 1.

While the acids and soaps may be produced in a separate process step and the preformed products incorporated into lubricating oils in grease making proportions, a particular advantage of the present invention resides in the fact that the new greases thickeners may be prepared in situ in the lubricating oil as an integral stage of the grease making process. In other words, the amino alcohols may be converted into soaps by alkali fusion in the grease kettle using the lubricating oil base of the grease as a reaction medium.

When carrying out this preferred embodiment of the invention, it has been observed that the alkali has a strong tendency to settle out of the reaction mixture to the bottom of the reactor in the form of a cake which does not fully participate in the reaction. Highly efficient stirring or agitation will counteract this tendency. However, in many cases more efficient stirring is required than may be obtained in conventional grease kettles and special equipment is necessary.

This settling tendency of the alkali in the lubricating oil amino alcohol mixture is negligible when a sufficient amount of a solid suspending agent is present in the reaction mixture. Most desirable suspending agents are those which serve simultaneously as grease thickeners, such as soap of high molecular weight fatty acids, silica gel, carbon black, bentonites, Attapulgus clay modifications, etc.

Soaps, particularly sodium soaps of high molecular weight fatty acids, are preferred for this purpose. However, the melting points of most of these soaps in lubricating oil is rather low, usually below 400° F. Thus, at the high reaction or fusion temperature of about 500° F. or thereabove, these soaps are liquid when used as such and do not entirely counteract the settling tendencies of the alkali. This difficulty may be overcome in accordance with a specific embodiment of the invention by using the salt, preferably the alkali metal salt, of a low molecular weight acid in addition to the high molecular weight fatty acid soap. In this manner, soap salt complexes are formed which melt well above 500° F. and thus form an excellent suspending agent.

These soaps or soap-salt complexes are preferably formed in situ by neutralization of the corresponding acids in the amino alcohol-oil mixture with alkali added in amounts sufficient for this neutralization and the subsequent fusion which takes place at higher temperatures. High molecular weight acids useful for this purpose include hydrated fish oil acids, C18-C22 naturally occurring acids of animal or vegetable origin, etc. These acids may be used in amounts ranging from about 2-30 wt. percent based on the finished product. Suitable low molecular weight acids include acetone, furic acid, acrylic acid and similar to be used in proportions of about 1-10 wt. percent based on the finished product. Esters, e.g., glycerides of the high and/or low molecular weight acids, particularly those containing mono basic acid esters may be used in place of the free acids in corresponding proportions.

In this case, the alkali portions of the esters are converted into acids and the corresponding soaps by alkali fusion. If esters of low molecular weight alcohols are used, elevated pressures may be employed to prevent volatilization of the products. Esters, of course, of esters of low molecular weight alcohols, such as polyhydric alcohol esters, e.g., sorbitol acetate, glycol acetate, etc., may be used. Particularly the high molecular weight type of acids or their esters used for this purpose may also be prepared by alkali fusion of amino alcohols. In this case, a portion of the product of the alkali fusion process in which the principal grease thickener is prepared in accordance with the invention may be returned to the fusion stage to serve as an agent preventing settling of the alkali.

Soaps of high molecular weight fatty acids and/or soap-salt complexes of the type specified may be incorporated in the greases of the present invention to improve high temperature or other characteristics even no suspending agents are required. Thus, when soaps derived from branched chain amino alcohols are employed it is often desirable to incorporate soaps derived from straight-chain fatty acids in order to obtain greases having particular structure characteristics.

The soaps formed by alkali fusion of amino alcohols in the presence of other fatty acid soaps yield excellent smooth greases. Other conventional thickeners, anti-oxidants, corrosion inhibitors, tackiness, considerents, and carrying compounds, viscosity index improvers, oiliness agents, and the like may be added prior, during and/or after the fusion process as will be apparent to those skilled in the art.

The base oil used as menstruum during the fusion process should be a mineral lubricating oil. After the fusion is completed, synthetic lubricating oils, such as a dibasic acid ester (e.g. di-2-ethyl hexyl sebacate, adipate, etc.), polyglycol type synthetic oils, esters of dibasic acids and polyhydric alcohols, etc., as well as alkyl silicates, carbonates, formals, acetals, etc., may be
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 alkaline 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 temperature 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 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. It is the high molecular weight fatty acids are added to the mineral oil together with the amino alcohol while the low molecular weight fatty acids in accordance with the preferred embodiment of the invention.

And convert the amino alcohol to soap, 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 1**

**Dicocoaminoethanol having the formula**

```
R               H
OCH2CH2OH
```

(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
  - Glacial acetic acid 4.00
  - Sodium hydroxide 6.50
  - Phenyl alpha-naphthylamine 1.00

**Naphthenic type lubricating oil distillate having a viscosity of 30 S.S.U. at 210° F.**

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

**PREPARATION**

The dicocoaminoethanol, the Hydrofol acids 54 and 1/2 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 and 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: 136
- Worked strokes: 160
- W o r k e d 1 , 0 0 , 0 0 0 strokes: 240
- Norma Hoffmann oxidation, hours to 5 p. s. i: None.
- Water washing test, percent loss: None.
- Drop in oxygen pressure: 175
- Appearance: Excellent smooth uniform grease—slight fiber before homogenization.
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

\[ (\text{C}_2\text{H}_4\text{CH}_2\text{O})_n \text{R} \]

(mol wt. 491) wherein \( R \) stands for a hydrocarbon radical derived from tall oil and consisting of about 25% saturated \( \text{C}_16 \) groups, 70% saturated \( \text{C}_18 \) groups and 5% unsaturated \( \text{C}_18 \) groups. This amino alcohol is made by reacting tall oil 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:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethomeen T/15</td>
<td>10.00</td>
</tr>
<tr>
<td>Hydrophilic acids 5-9</td>
<td>10.00</td>
</tr>
<tr>
<td>Acetic acid (glacial)</td>
<td>4.00</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>6.50</td>
</tr>
<tr>
<td>Phenyl alpha-naphthylamine</td>
<td>1.00</td>
</tr>
<tr>
<td>Blend of naphthenic type mineral oil distillate having a viscosity of 55 S. S. U. at 210° F.</td>
<td>68.50</td>
</tr>
</tbody>
</table>

**PREPARATION**

The Hydrophilic acids 5-9, 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 360° 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-isolvent-extracted Bright Stock, having a viscosity of 57 S. S. U. at 210° F. and a V. L. 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

\[ \text{R-N-}[(\text{C}_2\text{H}_4\text{CH}_2\text{O})_n\text{R}], \]

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 \( x+y+z \) 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 condition 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

\[ \text{R-N-}[(\text{C}_2\text{H}_4\text{CH}_2\text{O})_n\text{R}], \]

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 \( x+y+z \) is 2.

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

\[ \text{R-N-}[(\text{C}_2\text{H}_4\text{CH}_2\text{O})_n\text{R}], \]

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 \( x+y+z \) is 2.

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

\[ \text{R-N-}[(\text{C}_2\text{H}_4\text{CH}_2\text{O})_n\text{R}], \]

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 \( x+y+z \) 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

\[ \text{R-N-}[(\text{C}_2\text{H}_4\text{CH}_2\text{O})_n\text{R}], \]

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 \( x+y+z \) 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 di coco amino ethanol.

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

\[
\text{R} - \overset{(\text{CH}_2\text{CH}_2\text{O})_m}\text{N} - \overset{(\text{CH}_2\text{CH}_2\text{O})_n}\text{H}
\]

wherein \( \text{R} \) is a hydrocarbon radical of tallow acid.