This invention relates to the preparation of an improved detergent mixture. More particularly, the invention has to do with the preparation of an improved detergent mixture having important properties and containing the reaction products of an alkylamino, a polyalcohol such as phosphoric, fatty acids containing about 16 to 20 carbons and an acylating substance.

One embodiment of this invention involves the preparation of complex mixtures of surface-active materials from natural products containing fats and oils. This invention can be used to create the utilization of inorganic phosphates and large quantities of water. The process of treating such materials and the valuable products obtained provides a means for upgrading low-priced fats or fatty acids such as tallow grease, acidulated vegetable oil foils or still bottoms. Also, the relatively cheap C₁₄-C₁₈ fatty acids are used.

Derivatives of amino acids have been proposed heretofore as detergents and in other areas of use where the compositions have the ability of altering surface properties of liquids and solids are required. The compositions of this invention, while derivatives of amino acids, provide many advantages not exhibited by previously known amino acid derivatives.

The compositions, irrespective of the particular alkylamino or acylating substance, possess the property of modifying surface behavior of liquids in which they are incorporated. This modification of surface behavior is observed in aqueous solutions containing large quantities of electrolytes. This is an important advantage when it is realized that the majority of previously known amino acid derivatives are not compatible with aqueous solutions containing more than small amounts of electrolytes. These solutions tend to salt out many of the known alkylamidines resulting in a substantial reduction in effectiveness of these compositions. Moreover, the normally used detergents have limited solubility in the presence of electrolytes which results in an impaired detergent action. On the other hand, the compositions of this invention are quite soluble in such electrolytes. The coconut oil detergent, for example, is used in wool fulling when there is present a high soda ash concentration.

It is an object of this invention to provide new chemical compositions.

Another object is the provision of a method for the utilization of inexpensive fats and oils in large quantities. Another object is to provide detergents which will function satisfactorily in high concentrations of electrolytes.

Additional objects, if not specifically set forth herein, will be readily apparent to those skilled in the art from the detailed description of the invention which follows.

The liquid detergent compositions of this invention are prepared by heating together (with agitation under vacuum at a temperature of about 230° F.) a mixture of (1) an alkylamino, (2) an acylating substance, (3) C₁₄-C₁₈ fatty acids or their alkyl esters, and (4) an inorganic acid. The mixture is usually heated until most of the volatile products come off.

A neutralizing agent such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, potassium carbonate, sodium carbonate, or ammonia is added and the batch is agitated for around fifteen minutes to one-half hour at a temperature of about 140-170 degrees F. Then more acylating substance is added to form a reaction and a miscible solvent are added and agitated for another half-hour or so to reduce the viscosity of the finished composition.

The alkylamines are usually employed in an excess (1 to 10 moles per 1 equivalent of fatty acids) and react with the fatty acids to form alkylamides which in turn are reacted with the inorganic acid to form what is believed to be esters. In the case of phosphoric acid enough is added to make the product soluble and a phosphate ester linkage is believed to be formed. The unreacted acid is neutralized with a base such as sodium hydroxide. A soap is formed by adding additional acylating fatty acids to the unreacted amine present in the reaction mixture.

The purpose of the solvent and water is to provide the desired viscosity and concentration.

The compositions of this invention are believed to be compounds comprising aliphatic amide alcohols bridged by means of an ester linkage such as a phosphate-ester. The actual structure appears to be immaterial, however, as long as the phosphoric acid is attached. Considerable variation in structure of the composition is possible inasmuch as any of a large number of acyl groups may be present in the alkyl amide and any of a number of alkyl amines may be employed in the alkyl amine portion of the mixture. Similarly, diverse combinations of alkyl amine radicals may be present in the alkyl amine and alkyl amide portions of the mixture.

More specifically, the compositions are complex mixtures obtained by reacting primary, secondary, or tertiary alkyl amine and fatty alkylamides with a polyalcohol such as phosphoric acid.

Polyalcohols are meant to be those which contain and HO— group attached to the nonmetal portion and may or may not contain an O═ group. Polyalcohols also are meant to cover the alkyl esters thereof. For example—

wherein R is hydrogen or an alkyl radical are the most preferred inorganic acids. The alkyl radicals usually contain 1 to about 8 carbons such as methyl, ethyl, propyl, butyl, hexyl, octyl, etc., however, higher alkyl esters may also be used. Specific examples include H₂SO₄, H₂SO₃, H₂SO₄, H₂SO₄, wherein x is 3, 4, 5, 6, 7, and 8, H₃PO₄, H₃PO₄, H₃PO₄, H₃PO₄, H₃PO₄, H₃PO₄, and the methyl, ethyl, propyl, butyl, etc., esters thereof.

Amino alcohols which may be used include primary, secondary, and tertiary amino aliphatic alcohols. The lower alkyl amines of two to eight carbon atoms are very satisfactory, but higher alkyl amines can also be used. Typical alkyl amines which may be reacted with the inorganic acid are monoethylamine, monoethylamine, diethylamine, triethylamine, monoiso-octylamine, dilo-octylamine, N,N-dimethylamine, N-ethyl, N,N-dihexylamine, N,N-diisopropyl ethanolamine, etc. The amino alcohols may also be dialkyl compounds and may be unsubstituted or substituted with noninterfering substituents.

The acylating substances used in this invention are the fixed fats and oils. The fatty acids which are taken
from the animal and vegetable oils can be straight chain, branched chain, saturated and unsaturated such as caprylic, capric, palmityl, oleic, linoleic, laurie, etc. One of the main features of this invention is the utilization of inexpensive fats and oils in large quantities. Tall oil, crude or refined, which contains minor amounts of resin acids; or any low-priced fat or fatty acid such as tallow, grease, aciduluted vegetable oil foots or still bottoms may be used. Other examples include butter, mutton tallow, castor oil, olive oil, palm oil, coconut oil, peanut oil, corn oil, cottonseed oil, linseed oil, red oil, soybean oil, tung oil, etc. The fatty acid portion usually contains 4–26 carbons and may be unsubstituted or substituted with non-interfering substituents. A mixture of the fatty acids wherein at least some C18 unsaturated acids are present is preferred along with acids in the range of C8–C18.

The other acylating ingredient is a fatty acid of about 8–10 carbons or a mixture of any combination of C8–C18 fatty acids or their esters. Specific examples include a 50–50 mixture of methyl caprylate and capricate, and mixtures of methyl, ethyl, propyl, butyl, etc., esters of pelargonic acid. The lower esters or the free C8–C18 fatty acids are preferred due to their relatively cheap cost. Pelargonic acid is a specific preferred ingredient.

Preferred solvents which may be used to reduce viscosity of the composition are diethylene glycol mono-ethyl ether, ethyl alcohol, methyl alcohol, isopropyl alcohol, glycerine, propylene glycol, ethylene glycol monobutyl ether, or other H2O miscible solvents. The constituents can usually be varied in the amounts stated below:

<table>
<thead>
<tr>
<th></th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Alkylamine</td>
<td>25 to about 60</td>
</tr>
<tr>
<td>(2) Acylating substance</td>
<td>1 to about 20</td>
</tr>
<tr>
<td>(3) C8–C18 acids or esters</td>
<td>1 to about 20</td>
</tr>
<tr>
<td>(4) Inorganic acid (H3PO4)</td>
<td>1 to about 15</td>
</tr>
<tr>
<td>(5) Neutralizing agent (sodium hydroxide)</td>
<td>0 to about 10</td>
</tr>
<tr>
<td>(6) Acylating substance</td>
<td>0 to about 20</td>
</tr>
<tr>
<td>(7) Coconut fatty acids</td>
<td>0 to about 20</td>
</tr>
<tr>
<td>(8) Solvent</td>
<td>0 to about 15</td>
</tr>
<tr>
<td>(9) Water</td>
<td>0 to about 50</td>
</tr>
</tbody>
</table>

As can be seen from the above table, the amounts of ingredients can vary greatly. Generally, however, the composition should contain the C8–C18 and C10–C18 acids in a combination total of at least 10–20%.

The following examples are given to illustrate the invention. It will be understood, however, that these examples are illustrative and not to be taken in any manner as limiting the invention as defined in the appended claims.

**Example I**

180 grams of diethanolamine, 58 grams of tall oil fatty acids (3–5% resin acids), 22 grams of methyl esters of capric and caprylic acids (a 50–50 mixture) and 23.4 grams of phosphoric acid (85%) are heated together in a reactor with agitation under vacuum of 3–5 inches of mercury at a temperature of 310 to 320° F. After a period of heating for 3½ to 4½ hours, the temperature is raised to 240 to 245° F. and is maintained at this level for a period of 1½ to 2 hours. The temperature is then lowered to 140° F.–170° F. and 30 grams of aqueous sodium hydroxide (11%) is added and the batch is agitated for 15 minutes to ½ hour. Then 60 grams of tall oil fatty acids, 20 grams of coconut oil fatty acids, 22.2 grams of diethylene glycol monoethyl ether and 44.5 grams of water are added in this order and the batch agitated for another half hour, at which time manufacture of the composition is complete.

The temperatures, times and the vacuum disclosed above are important for the manufacture of this specific material.

**Example II**

The use of the free C8–C18 acids in place of the esters of caprylic and capric in the above example eliminates the problem of methyl alcohol recovery. The alcohol which is freed, being volatile, will come off and should be collected. Also the amount of foaming is decreased when the free acids are used.

As mentioned above, the use of coconut oil fatty acids as the acylating agent results in a product having outstanding properties in that it will function in a satisfactory manner in wool fulling where there is a high electrolyte concentration.

An example of the procedure to form the coconut detergent is as follows:

**Example III**

Dietanolamine (420 g.), coconut oil fatty acids (132.5 g.), pelargonic acid (51.6 g.), and 54.8 g. of 85% phosphoric acid are heated together in a reactor with agitation under 28 inches of vacuum and reacted for around 2½ hours at about 300° F. The clear amber mixture is cooled under vacuum for clear color. The mixture is cooled to around 140° F. and 70 g. of 11% sodium hydroxide is added and agitated for about 4½ to 5½ hours. After the NaOH has been thoroughly mixed in the batch, 186.8 g. of additional coconut fatty acids is added to form a soap. The solution becomes thicker on addition of the coconut oil fatty acids, and 81.6 g. of diethylene glycol monoethyl ether is added to provide the desired viscosity.

**Example IV**

The procedure is the same as Example II, and 290 grams monoethanolamine was also substituted for the diethanolamine. The above example was also carried out with red oil (oleic acid) replacing all the tall oil fatty acids.

**Example V**

300 grams of diisopropanolamine, 42 grams of coconut oil, 16.5 grams pelargonic acid and 17.2 grams of 85% phosphoric acid are placed together in a reactor equipped with heating and stirring apparatus and also with vacuumizing equipment. The mixture is heated to a temperature of about 285–305° F. with agitation under full vacuum for about 3 hours. The clear amber mixture is cooled under vacuum in order to maintain a clear solution. The mixture is cooled to around 140° F. and 21.4 grams of 11% sodium hydroxide is added and the mixture is agi-
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After the NaOH has been thoroughly mixed into the batch, 42.8 grams of coconut oil and 14.4 grams of coconut oil fatty acids are added to form a soap. In order to reduce the viscosity of the finished composition, 15.5 grams of diethylene glycol monoethyl ether and 31.7 grams of water are added.

It will be appreciated that the details and examples hereinbefore set forth are illustrative only and are in no way to be considered as limitations of the invention.

We claim:

1. A process for preparing an improved liquid detergent which comprises simultaneously reacting at an elevated temperature and under vacuum (1) a stoichiometric excess of an alkylolamine having about 2 to 8 carbon atoms per alkyl group, (2) a member selected from the group consisting of ternary polypropionic inorganic acids and the C₃-C₈ alkyl esters thereof, said ternary polypropionic inorganic acid consisting of hydrogen, oxygen and a member selected from the group consisting of sulphur, phosphorus and boron, and (3) an aliphatic fatty acylating substance containing 4 to 26 carbons in the acyl portion thereof, said aliphatic fatty acylating substance containing C₁₅-C₂₀ and C₂₅-C₃₂ aliphatic fatty acylating substances in an amount of at least about 10%, by weight, based upon the total weight of ingredients (1), (2) and (3).

2. A process for preparing an improved liquid detergent which comprises simultaneously reacting at a temperature above about 280° F. and under vacuum (1) a stoichiometric excess of an alkylolamine having about 2 to 8 carbon atoms per alkyl group, (2) a member selected from the group consisting of ternary polypropionic inorganic acids and the C₃-C₈ alkyl esters thereof, said ternary polypropionic inorganic acid consisting of hydrogen, oxygen and a member selected from the group consisting of sulphur, phosphorus and boron, (3) a C₁₅-C₂₀ aliphatic fatty acid, and (4) a member selected from the group consisting of C₁₅-C₂₀ fatty acids, the lower alkyl esters of said C₁₅-C₂₀ fatty acids and mixtures thereof.

3. A process for preparing an improved liquid detergent which comprises simultaneously reacting at a temperature between about 280° F. and 360° F. and under vacuum (1) about 25 to 60%, by weight, of an alkylolamine having about 2 to 8 carbon atoms per alkyl group, (2) about 1 to 20%, by weight, of a member selected from the group consisting of fixed fats and oils having free aliphatic fatty acids, the acyl portion of said fixed fats and oils and said free aliphatic fatty acids having about 4 to 26 carbon atoms, (3) about 1 to 20%, by weight, of a member selected from the group consisting of C₁₅-C₂₀ fatty acids, the lower alkyl esters of said C₁₅-C₂₀ fatty acids and mixtures thereof, and (4) about 1 to 15%, by weight, of a member selected from the group consisting of ternary polypropionic inorganic acids and the C₃-C₈ alkyl esters thereof, said ternary polypropionic inorganic acid consisting of hydrogen, oxygen and a member selected from the group consisting of sulphur, phosphorus and boron.

4. A process for producing an improved liquid detergent which comprises heating to a temperature between about 280° F. and 360° F. and simultaneously reacting under vacuum (1) a to 10 mol excess per equivalent of fatty acids of an alkylolamine having 2 to 8 carbon atoms per alkyl group, (2) a member selected from the group consisting of ternary polypropionic inorganic acids and the C₃-C₈ alkyl esters thereof, said ternary polypropionic inorganic acid consisting of hydrogen, oxygen and a member selected from the group consisting of sulphur, phosphorus and boron, (3) an aliphatic fatty acid having 12 to 26 carbon atoms, and (4) a member selected from the group consisting of C₁₅-C₂₀ fatty acids, the lower alkyl esters of said C₁₅-C₂₀ fatty acids and mixtures thereof, cooling the reaction mixture and thereafter reacting said mixture with an aliphatic fatty acid having from 8 to 26 carbon atoms whereby said excess alkylolamine reacts with said fatty acids having 8 to 26 carbon atoms to form soaps.

5. A process for preparing an improved liquid detergent which comprises simultaneously reacting, at a temperature between about 310° F. to 320° F. with agitation under vacuum for about 3½ to 4½ hours, a mixture in the ratio of about 180 grams of diethanolamine, about 58 grams of tall oil fatty acids, about 22 grams of the methyl ester of caprylic acid and capric acid, and about 23.4 grams of 85% phosphoric acid; raising the temperature of said mixture to about 340° F. to 345° F. and maintaining said temperature for about 1½ to 2 hours; lowering the temperature of said mixture to about 140° F. to 170° F.; adding to said mixture about 30 grams of 11% aqueous sodium hydroxide, about 60 grams of tall oil fatty acids, about 20 grams of coconut oil fatty acids, about 22.2 grams of diethylene glycol monoethyl ether, and about 44.5 grams of water and agitating the mixture for about ½ hour.

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