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DIAMIDE TEXTILE LUBRICANTS

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This invention relates to textile lubricants and softeners, and more particularly to textile lubricants and softeners comprising mixed fatty diamides. This application is a continuation-in-part of the copending application of Robinson and Kelley Serial No. 274,808, filed May 20, 1939, now Patent No. 2,345,632.

It has been proposed to use higher fatty amides, such as oleic acid amide, oleic acid methyl amide and oleic acid ethylene diamide, as softeners and lubricants for textile materials. Such amides are ordinarily prepared by reacting a fatty acid or fatty ester with a mono- or polyamine. The reaction of monoamines with higher fatty acids or fatty esters yields products which are not readily dispersible in water and hence these products cannot be advantageously applied to textile material. It has been proposed, therefore, to react polyamines with higher fatty acids or fatty esters to produce amides having free amino groups capable of reacting with weak acids so as to solubilize the products and render them readily dispersible or soluble in water. However, the monoamides formed from such polyamines by reaction thereof with higher fatty acids or fatty esters cause yellowing of textile material upon application thereto and hence are highly unsuitable for use as textile lubricants and softeners. On the other hand, polyamides formed by the reaction of higher fatty acids or fatty esters with polyamines are much less desirable as softeners and lubricants than the corresponding monoamides because of their relatively poor softening and lubricating properties.

It has also been proposed to prepare textile lubricants and softeners by reacting unsymmetrical dialkyl ethylene diamines with higher fatty acids such as oleic acid. Such unsymmetrical dialkyl amines are, however, relatively expensive and difficult to obtain and hence, while amides thereof have been used to some extent as textile lubricants and softeners, there is a great demand in the textile industry for cheaper products which may be used in place of these amides.

It is an object of this invention to provide inexpensive and highly effective textile lubricants and softeners.

It is a further object of this invention to provide a process for the preparation of textile lubricants and softeners from polyamines.

We have now found that diamides having the general formula:

(1) $$R_1-\overset{O}{\overset{\|}{C}}-\overset{R_3}{\overset{|}{N}}-X-\overset{R_3}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R_2$$

wherein:

$$R_1-\overset{O}{\overset{\|}{C}}-$$

represents a fatty acyl radicle containing from 8 to 22 carbon atoms;

$$-\overset{O}{\overset{\|}{C}}-R_2$$

represents a fatty acyl radicle containing from 2 to 5 carbon atoms: R_3 in each occurrence, and independently of its other occurrence, represents a hydrogen atom or an alkyl radicle; and X represents an aliphatic linking chain which may be branched or interrupted by ether or keto groups, may be applied to textile materials so as to impart thereto excellent softness, drape and pliability. These diamides are also highly useful as synthetic waxes and as ingredients in cosmetics, defoaming compositions and the like. The diamides of this invention are readily prepared by reacting a diamine such as ethylene diamine, N-methyl ethylene diamine, 1,6 diamino hexane, etc., with a fatty acid containing from 8 to 22 carbon atoms, or an ester or acid halide thereof, and with a short-chain fatty acid containing from 2 to 5 atoms, or an ester, anhydride or acid halide thereof. The foregoing reactions may be carried out in either order or simultaneously, i. e., the higher fatty acid material may be condensed with the diamine to form a monoamide after which the lower fatty acid material is condensed with the monoamide; or the lower fatty acid may be condensed with the diamine and the resultant monoamide condensed with the higher fatty acid material; or all the reagents may simultaneously be condensed. The first method will usually be preferred for manipulative reasons. The resultant diamides, although they are less readily dispersible than the acid-solubilizible secondary-amino-group-containing polyamides of the parent application above referred to, may, nevertheless, be dispersed in water, by the use of suitable emulsifiers, if necessary, and may be applied to textile in that form. Moreover, the diamides of this invention may likewise be applied to textiles in solvent solution. Textiles so treated have admirable softness but are not adversely affected as to color. The products are also useful as ingredients in synthetic wax compositions, defoaming compositions, emulsifying agents for water-in-oil emulsions, and the like.

Diamines which may be used as starting materials in the process of this invention are any aliphatic compounds containing two amino groups (primary or secondary) joined by an aliphatic group, which may optionally be interrupted by ether groups, having the formula:

$$H-\overset{R_3}{\overset{|}{N}}-X-\overset{R_3}{\overset{|}{N}}-H$$

under the notation of formula (1) supra. Such diamines are exemplified in ethylene diamine, N-methyl ethylene diamine, N,N' diethyl ethylene diamine, symmetrical diamino ethyl ether, 1,6 diamino hexane, and the like.

The long chain fatty acid compound reacted with the polyamine in accordance with our invention may be any of the fatty acids containing from 8 to 22 carbon atoms, preferably from 12 to 18 carbon atoms, or the esters or acid halides thereof; the following higher fatty acids may be mentioned by way of examples: caprylic acid, nonylic acid, capric acid, undecylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, ricinoleic acid, mixtures of these acids, etc. In place of the higher fatty acids, derivatives thereof such as glycerides and other esters may be employed. Actually, we prefer to use glycerides of the fatty acids since products are obtained having superior softening properties to those resulting from the reaction of the polyamines with the free fatty acids. Products particularly suitable as textile lubricants and softeners are obtained by employing coconut oil to react with the polyamines in accordance with our invention, since these products are more readily dispersible in water and possess excellent lubricant and softening properties. As examples of other glycerides that may be employed in place of the long chain fatty acids, there may be mentioned teaseed oil, castor oil, hydrogenated castor oil, etc.

The short chain acids employed in accordance with our invention contain from 2 to 5 carbon atoms; thus, for example, acetic acid, glycollic acid, lactic acid, propionic acid, butyric acid and valeric acid may be employed; derivatives thereof such as esters, acid halides and anhydrides may be employed in accordance with procedures well known to the art. We prefer to use acetic acid or acetic anhydride in the preparation of our novel products because of their ready availability and the excellent softening properties of the amides prepared from these compounds.

In carrying out the reaction in accordance with our preferred method, approximately equimolecular quantities of a polyamine and a fatty acid containing from 8 to 22 carbon atoms are mixed; if a glyceride of a fatty acid is employed, e. g., coconut oil, approximately ⅓ mol of the glyceride per mol of polyamine is used. The compounds are then permitted to react at a temperature sufficiently high to cause the formation of the monoamide; this temperature may vary from about 120° C. to about 200° C. but preferably is between about 150° C. and about 170° C. The time of this reaction may vary widely depending somewhat upon the particular reactants and somewhat upon the temperature; generally, 8 hours or more are required. The pressure under which the reaction is carried out is preferably atmospheric; however, pressures above or below atmospheric may be employed. The product of the reaction is then mixed with a suitable quantity of a short chain fatty acid containing from 2 to 5 carbon atoms; as above mentioned, anhydrides, esters or acid halides of these acids may also be employed. The conditions under which this reaction is carried out may vary widely, but we have found that the constituents may be reacted at atmospheric pressure and at a temperature of about 135° C. for about 3 to 5 hours, the mixture then raised to between about 150° C. and about 170° C. and the reaction continued for about 5 to about 8 additional hours with excellent results. However, it is to be understood that these conditions may be varied somewhat without affecting the course of the reaction, e. g., pressures above or below atmospheric may be used, the temperatures may vary widely so long as they are sufficiently high to effect acylation, and the time of reaction may differ from the time above set forth.

The products of this invention may be liquids or solids, but generally they are solids. The products are in general insoluble in water; however, they may readily be dispersed in water by the use of suitable emulsifiers. Our novel products may be marketed as such or in the form of an aqueous dispersion or paste, or in the form of a solvent solution thereof. They may be applied to textile materials by any of the well known methods, e. g., in the form of an aqueous dispersion, or solvent solution thereof, and in every case impart excellent softness, drape, flexibility and handle to the textile material. The products are further adapted for use as synthetic waxes or ingredients in synthetic wax. Further, the products may be used in cosmetics, defoaming compositions, emulsifying agents for water-in-oil emulsions, as plasticizers and the like.

The following examples are illustrative of our invention, all parts given being by weight:

Example I

Coconut oil	230 parts (⅓ mol)
Ethylene diamine	60 parts (1 mol)
Acetic anhydride	50 parts (½ mol)

The ethylene diamine and coconut oil were mixed in an open kettle and agitated at temperatures between 150° and 170° C. for 8 hours. The acetic anhydride was then added to the reaction product and the mixture agitated at a temperature of 135° C. for 3 hours, after which the temperature was raised and the reaction continued at temperatures between 150° and 170° C. for an additional 5 hours. A solid product relatively insoluble in water was thereby obtained which was suitable as a textile dressing or as a synthetic wax.

Example II

Hydrogenated tallow (iodine value 10)	82 parts (⅓ mol)
Ethylene diamine	18 parts (1 mol)
Glycollic acid (70% aqueous)	30 parts (1 mol)

The hydrogenated tallow and ethylene diamine were reacted together at 125° C. for 8 hours. Thereafter the temperature was elevated and held between 160° and 165° C. for a further 8 hours. The temperature was lowered to 150° C. and the glycollic acid was added. Reaction was continued at 150° C. for 3 hours, at the end of which time the total alkali was 0.5 calculated as ethylene diamine. The resultant product solidified over the range 115°–125° C. to form a mixture which was admirably adapted as a hard wax substitute.

Example III

Oleic acid	282 parts (1 mol)
Ethylene diamine	166 parts (1 mol)
Acetic anhydride	51 parts (½ mol)

The oleic acid and ethylene diamine were condensed together at 125° C. for 24 hours, the water evolved being allowed to escape. The mixture was then cooled, the acetic anhydride added and stirred in and the temperature raised to 135° C.; the mixture was agitated for 3 additional hours, after which the temperature was raised and reaction continued at temperatures between 150° C. and 170° C. for 5 hours. A solid amide condensation product was obtained.

Example IV

Stearic acid	284 parts (1 mol)
Symmetrical diethyl ethylene diamine	156 parts (1 mol)
Lactic acid (85% aqueous)	106 parts (1 mol)

The stearic acid and diethyl ethylene diamine were agitated together at temperatures between 150° C. and 170° C. for 12 hours. Thereafter the mixture was cooled down to 70° C., the lactic acid stirred in and the temperature again raised to 150° C. for 3 hours. The resultant product was a solid at room temperature.

From the foregoing general discussion and specific examples, it will be apparent that this invention provides novel diamide products suitable for a wide range of uses, notably as textile lubricants, synthetic waxes, ingredients in defoaming agents, emulsifiers for water-in-oil emulsions, and the like. The products may be prepared from the readily and cheaply procurable higher fats and fatty acids and lower fatty acids and aliphatic diamines and are synthesized by a process which may be carried out by relatively unskilled operatives in conventional equipment.

We therefore claim:

1. Diamides having the general formula:

$$R_1-CO-\overset{R_3}{\overset{|}{N}}-X-\overset{R_3}{\overset{|}{N}}-OC-R_2$$

wherein R_1—CO— represents an aliphatic acyl radicle containing from 8 to 22 carbon atoms; —OC—R_2 represents a fatty acyl radicle containing from 2 to 5 carbon atoms; R_3 in each occurrence, and independently of its other occurrence, represents a substituent chosen from the group consisting of hydrogen atoms and alkyl radicles; and —X— represents an aliphatic linking chain selected from the group consisting of bivalent hydrocarbon chains and bivalent hydrocarbon chains interrupted by an ether linkage.

2. Diamides according to the general formula of claim 1, wherein —X— more particularly represents an aliphatic hydrocarbon chain.

3. Diamides according to claim 1, wherein —X— more particularly represents the group —CH_2—CH_2—.

4. Diamides according to the formula of claim 1, wherein R_1—CO— more particularly represents the fatty acyl radicles contained in a fatty glyceride oil.

5. Diamides according to the formula of claim 1, wherein R_1—CO— more particularly represents the fatty acyl radicles contained in coconut oil.

6. Diamides according to the formula of claim 1, wherein R_1—CO— more particularly represents the fatty acyl radicles contained in hydrogenated tallow.

7. Diamides according to claim 1, having the more particular formula:

$$R_1-CO-\overset{R_3}{\overset{|}{N}}-X-\overset{R_3}{\overset{|}{N}}-OC-CH_3$$

under the notation of claim 1.

8. Diamides according to claim 1, having the more particular formula:

$$R_1-CO-\overset{R_3}{\overset{|}{N}}-X-\overset{R_3}{\overset{|}{N}}-OC-CH_2-OH$$

under the notation of claim 1.

9. Diamides having the general formula:

$$R_1-CO-\overset{R_3}{\overset{|}{N}}-CH_2-CH_2-\overset{R_3}{\overset{|}{N}}-OC-R_2$$

wherein R_1—CO— represents the fatty acyl radicles contained in a glyceride oil; —OC—R_2 represents an aliphatic acyl radicle containing from 2 to 5 carbon atoms; and R_3 in each occurrence, and independently of its other occurrence, represents a substituent chosen from the group consisting of hydrogen and alkyl radicles.

10. Diamides according to claim 9, wherein R_1—C—O— more particularly represents the fatty acyl radicles contained in coconut oil.

11. Diamides according to claim 9, wherein R_1—C—O— more particularly represents the fatty acyl radicles contained in hydrogenated tallow.

12. A diamide having the general formula:

$$R_1-CO-\overset{H}{\overset{|}{N}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{H}{\overset{|}{N}}-OC-CH_3$$

wherein R_1—CO— represents the fatty acyl radicles contained in a glyceride oil.

13. A diamide having the general formula:

$$R_1-CO-\overset{H}{\overset{|}{N}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{H}{\overset{|}{N}}-OC-CH_2-OH$$

wherein R_1—CO— represents the fatty acyl radicles contained in a glyceride oil.

14. A diamide having the general formula:

$$R_1-CO-\overset{H}{\overset{|}{N}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{H}{\overset{|}{N}}-OC-CH_3$$

wherein R_1—CO— represents the fatty acyl radicles contained in coconut oil.

15. Process which comprises condensing by heating at a temperature between about 120° C. and about 200° C. a diamine having the formula:

$$H-\overset{R_3}{\overset{|}{N}}-X-\overset{R_3}{\overset{|}{N}}-H$$

wherein R_3 in each occurrence, and independently of its other occurrence, represents a substituent chosen from the group consisting of hydrogen atoms and alkyl radicles, and —X— represents an aliphatic linking chain selected from the group consisting of hydrocarbon chains and hydrocarbon chains interrupted by an ether linkage with approximately a fatty acid molecular equivalent of a substance chosen from the group consisting of higher fatty acids containing from 8 to 22 carbon atoms and the esters and acid halides thereof; and with approximately an acid molecular equivalent of a substance chosen from the group consisting of lower aliphatic acids containing from 2 to 5 carbon atoms and the esters, anhydrides, and acid halides thereof.

16. Process according to claim 15, wherein the substance chosen from the group consisting of higher fatty acids and the esters and halides thereof is a fatty glyceride oil.

17. Process according to claim 15, wherein the substance chosen from the group consisting of higher fatty acids and the esters and halides thereof is coconut oil.

18. Process according to claim 15, wherein the substance chosen from the group consisting of higher fatty acids and the esters and halides thereof is hydrogenated tallow.

19. Process according to claim 15, wherein the condensations between the several ingredients are effected in stages, the diamine being first condensed with the substance chosen from the group consisting of higher fatty acids and esters and acid halides thereof to form a monoamide, and in which the resulting monoamide is then further condensed with the substance chosen from the group consisting of lower fatty acids and the esters and acid halides thereof.

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