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(54) **Acylated polyamines, compositions containing them and their use as fabric softeners.**

(57) Diethylene triamine or a higher homologue thereof reacted with two molar proportions of fatty acid, mono-ethoxylated and, optionally, wholly or partially neutralised with a lower organic acid and/or sulphur dioxide, provides an effective and fluid fabric softener.

Croydon Printing Company Ltd.

This invention relates to novel fabric softeners, compositions containing them and the use thereof for the treatment of fabrics.

It has been proposed that certain quaternised amido amines, quaternised imidazolines prepared by cyclising amido amines, quaternised mixtures of imidazolines and amido amines, and quaternised tertiary amines impart good softening and rewetability properties to fabrics when applied after washing, and especially after washing in non-soap detergents.

The more effective of the known fabric softening compounds, those that have hitherto actually been used commercially, are all relatively expensive and inconvenient to make. The majority are quaternary ammonium salts which are quaternised by means of reagents such as dimethyl sulphate or methyl chloride. These reagents are highly toxic, so that their use is hazardous and requires expensive precautions both to protect workers and to avoid contamination of the product with toxic residues.

According to R.R. Egan in J. American Oil Chemists Society January 1978 Vol. 55, p 118 to 121, the five most commonly found active softening agents in consumer products purchased in the U.S.A. are all quaternary nitrogen compounds:-(I) a methyl chloride quaternised tertiary amine,(II) a dimethylsulphate quaternised tertiary amine,(II) a dimethyl sulphate quaternised polyethoxylated di amido amine, (IV) a dimethyl sulphate quaternised polypropoxylated diamido amine and (V) a diemthyl sulphate quaternised alkyl amido alkyl imidazoline.

German Patent Application No. 2520150 (Brit. Pat. 1,483,984) for example describes the preparation of a quaternised mixture of a diamido diethylenetriamine and an imidazoline. The presence of the quaternised diamido diethylenetriamine is said to lower the softening effect of the mixture compared with the quaternised imidazoline alone but to improve the rewettability of the fabric after washing, which most known fabric softeners reduce. The patent implies that quaternised diamido diethylenetriamines alone are not effective fabric softeners.

We have now discovered that when unquaternised diamidoamines are partially neutralised, they provide salts which are surprisingly more effective as fabric softeners than any of the fabric softeners in common commercial use, including the quaternised imidazoline softeners and the quaternised imidazoline/amido amine mixtures. They are moreover considerably more convenient to make, and potentially safer, since they do not require the use of highly toxic reagents. Surpisingly we have also found that they perform better in tests for skin irritancy than current commercially available fabric softeners.

However, unquaternised diamido amines, their salts and partial salts tend to be intractable solids at room temperature, which even on dilution with a suitable solvent e.g. 25% of a lower alkanol such as isopropanol, hexylene glycol, propylene glycol or mixtures thereof, are still too viscous for convenient handling.

We have now further discovered that certain novel unquaternised hydroxyalkyl diamido amine salts, can be obtained as mobile pastes in the presence of the aforesaid solvents, and exhibit much improved handling characteristics, while retaining the desirable softening properties which we have found to be characteristic of the unquaternised diamido amines. The novel salts also perform well in rewettability tests, which is unusual for such effective softeners. We have not found that the compounds of this invention cause significantly more yellowing of fabric than quaternary softeners.

Our invention therefore provides a novel composition which comprises a water dispersible amido amine of the average formula:

$$RNH\left[(CH_2)_n\ NR\right]_m\ R$$

wherein an average of from 20% to 80% of the R groups per molecule are acyl groups having an average of from 12 to 22 and preferably 16 to 18 carbon atoms, at least 20% of the R groups are $-CH_2CH_2OH$ or $-CH_2CH(OH)CH_3$ or mixtures of these groups and any other R group is hydrogen, n is 2 or 3 and m is an integer from 2 to 5. Where R groups are acyl they can be saturated, e.g. stearoyl, monounsaturated, e.g. oleoyl, polyunsaturated or may be mixtures of these types.

The preferred compounds are those wherein n and m are each 2. Preferably the acyl groups are derived from tallow or lard.

The products of our invention optionally but preferably contain a compatible amount, up to 70%, preferably 10 to 50%, e.g. 25% by weight, of a fluid, water miscible hydroxyaliphatic solvent.

Typically, any water miscible hydroxy-, or polyhydroxy-, alkane or alkylether having a viscosity of less than 30 centipoises at 20°C may be used. Preferred examples include isopropanol, hexylene glycol, propylene glycol, ethylene glycol monomethylether and mixtures thereof.

Preferably the hydroxyalkyl amido amine is partially (e.g. from 10% to 80%, preferably 20 to 60%) neutralised with a lower carboxylic or hydroxycarboxylic acid, e.g. acetic, formic, propionic, lactic or glycollic acid. The product may additionally contain a minor proportion of salts of inorganic acids especially sulphites, which help to stabilise the product against oxidation.

The novel amido amines of our invention may be obtained by controlled alkoxylation of an amido amine prepared by amidating a polyalkylene polyamine, e.g. by heating it with the necessary amount of a glyceryl ester to provide the desired alkyl groups in the correct proportions. Alternatively, the polyamine may be heated with a fatty acid or methyl ester thereof while distilling off water or methanol respectively. Preferably the heating is carried out at temperatures above 100°C but not sufficiently high to decompose any glycerol formed.

To avoid cyclisation and maintain the product as an amido amine the temperature should be maintained below 180°C and preferably at 120 to 160°C, e.g. 140°C.

Higher temperatures, up to 300°C, particularly with the application of a purge gas or vacuum will cause the amido amine to cyclise to the imidazoline with the loss of water.

Heating is preferably carried in an inert atmosphere to prevent colour degradations, e.g. under nitrogen for from 2 to 6, preferably 4 hours. The product may then be reacted with ethylene or propylene oxide at a temperature between 100 and 200°C. The presence of a catalyst should generally be avoided in order to prevent formation of polyoxyalkylene chains. The solvent may be added after alkoxylation to facilitate dispersion of the product in water.

The invention provides softening compositions comprising the novel amido amine, any glycerol remaining from the preparation of the diamide and the added solvent. The novel products of our invention maybe used in conventional manner, e.g. as a post-rinse after washing.

The substantially monoethoxylated products of our invention are significantly more fluid in the presence of organic solvent than corresponding non-ethoxylated diamidoamines.

Examples

Example 1

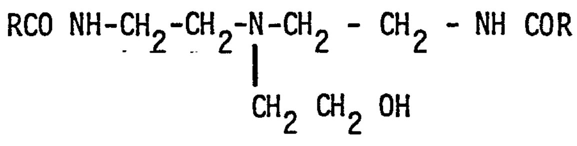
Example of a preparation of the subject of our patent

To a reactor fitted with a heating/cooling jacket, stirrer and nitrogen purge 1560 kg of deodourised tallow glyceride, mole weight 872, was added and heated to 50°C.

The vessel was evacuated and flushed with nitrogen to displace most of the air.

287 kg of diethylene triamine, 98% purity, was added over 5 minutes, no exotherm was observed, and the charge was heated to 140°C over 60 minutes. This temperature was maintained for 240 minutes whilst a slow stream of nitrogen was passed into the charge. A determination of base value and free ester value of the charge showed that the reaction to form the diamido amine was complete.

The reactor charge was then cooled to 120°C and 132 kg of ethylene oxide fed in slowly cooling to maintain 120°C. The product, substantially



$$RCO\ NH{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CH_2\ CH_2\ OH}}{N}{-}CH_2 - CH_2 - NH\ COR$$

where R = tallow alkyl

was found to be pumpable at 60 to 65°C without the addition of solvents.

To the product of the reaction above at 60 - 65°C was added propylene, glycol and isopropyl alcohol, the solution cooled to 36°C and sulphur dioxide and acetic acid added.

The product then contained

Sulphur dioxide	0.75%
Acetic acid	2.12%
Isopropyl alcohol	24.64%
Propylene glycol	14.96%
Ethoxylated diamido amine	57.53%
	100.00%

The product is a hazy, mobile, pumpable liquid at 20°C.

Example 2

The above preparation was repeated but without the addition of solvents. The product was a waxy solid which was fluid at 40 to 45°C. On dilution to 75% with isopropanol the product became pourable at 20°C.

The addition of a small quantity of SO_2 to the di tallow amido amine ethoxylate, which also partially neutralises the amine, allows the use of less acetic acid and overcomes the acetic acid odour which might otherwise be apparent in the concentrate or the diluted fabric softener. The addition of SO_2 also yields a lighter colour product which is less prone to colour deterioration on storage.

Example 3

Domestic fabric softener formulations normally consist of concentrated fabric softener solutions as prepared in examples 1 and 2 dispersed into water to yeild translucent liquids containing normally 2% to 8% "active" softener. By "active" we mean the non solvent component in a fabric softener concentrate.

The ease with which these dispersions can be made is of considerable practical importance to the formulator as is the appearance and storage stability of the formulated dispersions.

Taking the classifications of prior art materials given by Egen, referred to above, all at 75% active in isopropanol.

	Temperature for handling	Water temperature for dispersion
I	melts 40°C to 50°C transport at 60°C	55 to 60°C
II, III	mobile at 20°C	40°C
IV	mobile at 20°C	20°C
V	mobile at 20°C	30°C
Example 2	mobile at 20°C	30°C

Example 1	Mobile at 20°C	30°C
Example 2 but not ethoxylated	Mobile at 40°C	70°C
Example 2 but 2 moles EO **	mobile at 20°C	20°C
Example 2 but 8 moles EO **	mobile at 20°C	20°C
Example 2 but methosulphated *	mobile at 20°C	20°C

* prepared by reacting monoethoxylated di amido amine as described in Example 1 with dimethyl sulphate in isopropanol solvent.

** prepared by adding a basic catalyst (KOH) to the mono ethoxylated di amido amine prepared as described in example 1 and continuing the addition of ethylene oxide until the calculated weight was absorbed.

Example 4

As stated in Example 3 the appearance and stability of the aqueous dispersion of the concentrates is important for consumer acceptability. Products which yield stable dispersions with viscosities in the range 100 to 500 centipoise as measured by a "Brookfield" viscometer, model LVT, find ready consumer acceptability. Products which give dispersions which change viscosity on storage are obviously undesirable.

In general compound type I gives very high viscosity 6% active dispersions which must be reduced by additives and special preparative techniques. (As described in J. Amer. Oil Chem. Soc. Vol 56, p 542, April 1979).

In general methosulphates, types II, III, IV and V give dispersions at 6% "active" with viscosities in the range 10 to 30 cp and are often formulated with other additives to increase their viscosity.

6% active, prepared as in Example 2 dispersed water	-	300 cp
6% active, prepared as in Example 2 but 2 moles E.O.	-	170 cp
6% active, prepared as in Example 2 but 8 moles E.O.	-	30 cp

Water hardness 300 ppm.

Dispersions prepared from products of examples 1 and 2 are stable to extended storage.

Fabric Softening Evaluation

The product of example 2 was evaluated against compounds of type I and III where n = 1 in a panel evaluation test as follows.

6% active dispersions of each material were prepared using soft water (20 ppm). These solutions were then further diluted with water. Napkins woven from 60% cotton and 40% polyester were washed in an automatic washing machine using a conventional low foam automatic washing powder. These napkins were then soaked for 10 minutes at 20 to 25°C in the dilute dispersion of softener.

The weight of active material used was in the range 0.1 to 0.3% of the napkin weight.

The napkins were then wrung out by hand and dried on a clothes line under the same conditions.

Each napkin was cut into 4 portions and each portion given to 5 people to rank in order of softness to the touch. The softest scoring 1, the second 2 and so on. The results were:-

	0.3%	Active Application	
	Example 2	Type I	Type II n=1
No. of 1sts	11	8	1
2nds	6	6	8
3rds	3	6	11
Weighted total	32	38	50

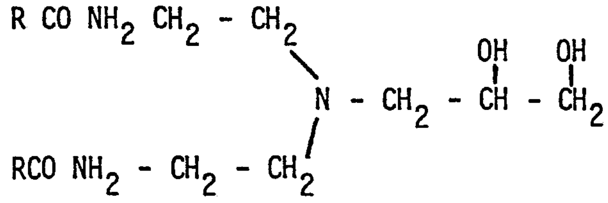
The significance of these results were assessed using the method devised by Kromer - Journal of Food Technology 1963 - 17/12/124.

The example 2 product is at least as good as the best commercial type as found by Egen and significantly better than type III, n=1.

A similar result was obtained at a 0.1% level of application.

	Example 2	type I	type III n=1
No. of 1sts	12	7	1
No. of 2nds	4	9	7
No. of 3rds	4	4	12
Weighted total	32	37	51

In a further panel test example 2 was compared to similar products, but with more moles of ethylene oxide added and with a di-hydroxy compound, employed as a partial acetate salt.



R = tallow

0.2% Application

	Example 2	type III n=1	2 moles E.O.	8 moles E.O.	di hydroxy	Water only
No. 1sts	7	6	0	1	6	0
No. 2nds	4	4	2	4	4	2
No. 3rds	5	3	4	4	2	2
No. 4ths	4	6	4	3	3	0
No. 5ths	0	0	5	4	3	8
No. 6ths	0	1	5	4	2	8
Weighed total	46	53	87	77	59	98

Using the Kromer method to evaluate these results:

For a panel of 20 and six samples, significance range is 52 to 88. Hence Example 2 is better and Water worse than all the others. Omitting results for Example 2 and water only from the scores above gives

	type III n=1	2 moles E.O.	8 moles E.O.	di hydroxy
Weighted total	38	62	57	43

For a set of 4 samples and a panel of 20 the significance range is 37 to 58, i.e. there is no significant difference between these 4 samples.

Rewettability Test

It is a well known fact that excessive or continual use of certain fabric conditioning materials can produce a waterproofing effect on fabrics. This effect is undesirable, particularly on fabrics designed for their moisture absorbancy e.g. towels and baby diapers.

Napkins treated by the same technique as that used to prepare the samples for the softening evaluation above were cut into strips and the test strips suspended in an aqueous solution of a dye, Kiton green (0.5 gm/litre, temperature = 20°C).

The rate at which the dye front travelled above the solution was measured.

Napkins treated with 0.2% weight of softener active were evaluated with the following results:-

Immersion Time (mm) Height of dye front above solution

Minutes	Example 2	type III n=1	2 moles E.O.	8 moles E.O.	di-hydroxy	type I	Water only
1	20	20	20	30	20	20	35
5	40	40	50	45	40	35	55
10	55	55	60	65	65	45	70
15	65	70	80	80	75	55	90
30	80	80	95	90	85	65	110

The product of Example 2 shows better rewettability properties than type I which has a similar softening ability.

WHAT WE CLAIM IS:-

1. A fluid, water-dispersible composition for use as a fabric softener, which comprises a water dispersible amido amine of the average formula:-

$$RNH\left[(CH_2)_n\ NR\right]_m R$$

wherein an average of from 20% to 80% of the R groups per molecule are acyl groups having an average of from 12 to 22 carbon atoms, at least 20% of the R groups are $-CH_2CH_2OH$ or $-CH_2CHOHCH_3$ or mixtures of these groups and any other R group is hydrogen, n is 2 or 3 and m is an integer from 2 to 5; or a water dispersible salt or partial salt thereof.

2. A composition according to Claim 1 wherein from 50 to 70% of the R groups are acyl groups and from 30 to 40% of the R groups are hydroxyethyl.

3. A composition according to either of Claims 1 and 2 wherein the acyl is derived from tallow or lard.

4. A composition according to any foregoing claim wherein the amido amine is present as its salt or partial salts with carboxylic or hydroxy carboxylic acid having from 1 to 3 carbon atoms.

5. A composition according to Claim 4 wherein the amido amine is from 10 to 80% neutralised with lactic or acetic acid.

6. A composition according to any foregoing Claim comprising up to 70% by weight of a fluid, water-miscible hydroxy aliphatic solvent.

7. A composition according to Claim 6 containing 10 to 50% by weight of the composition of the hydroxy aliphatic solvent.

8. A composition according to either of claims 6 and 7 wherein the hydroxy aliphatic solvent has a viscosity of less than 20 centipoises.

9. A composition according to any of Claims 6 to 8 wherein the hydroxy aliphatic solvent is a hydroxy- or polyhydroxyalkane or alkyl ether.

10. A composition according to Claim 9 wherein the hydroxy aliphatic solvent has less than four carbon atoms.

11. A composition according to any foregoing claim wherein n and m are each 2.

12. Ditallowyl mono(hydroxyethyl) diethylene triamine or a water dispersible salt thereof.

13. A composition according to any foregoing claim substantially as described herein with reference to any one of the examples.

14. A method of softening fabric which comprises applying thereto an aqueous solution or dispersion of composition according to any foregoing claim.

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EUROPEAN SEARCH REPORT

EP 79 301 558.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 933 871 (J.L. ARMSTRONG) * claims 1 to 3; column 5, lines 16 to 19 * --	1-14
D	JOURNAL OF THE AMERICAN OIL CHEMIST'S SOCIETY, Vol. 55, January 1978, Chicago R.R. EGAN "Cationic Surface Active Agents as Fabric Softeners" pages 118 to 121 * page 119, column 2, compound III * --	1,3, 11,12
	US - A - 3 844 959 (F.J. CRACCO et al.) * claims 1, 2, 5, 7 * --	1
D,A	GB - A - 1 483 984 (AZOTE ET PRODUITS CHIMIQUES) --	
A	DE - A1 - 2 539 310 (HOECHST) --	
A	US - A - 4 039 565 (P.E. THROCKMORTON et al.) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

D 06 M 13/40
C 07 C 103/44

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 07 C 103/44
D 06 M 13/40

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	18-01-1980	FROELICH

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