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**JOURNAL OF THE AMERICAN OIL CHEMIST'S
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EGAN "Cationic Surface Active Agents as Fabric
Softeners" pages 118 to 121**

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Compositions containing amido amine salts, and their use as fabric softeners

This invention relates to fabric softener compositions containing amido amino salts, 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 rewettability 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 dimethyl sulphate quaternised tertiary amine, (III) a dimethyl sulphate quaternised polyethoxylated di amido amine, (IV) a dimethyl sulphate quaternised polypropoxylated diamido amine and (V) a dimethyl sulphate quaternised alkyl amido alkyl imidazoline.

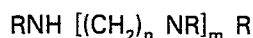
German Patent Application No. 2520150 (Brit. Pat. 1,483,984) for example describes the preparation of a quaternised mixture of a diamido diethylenetriamine and an imidazoline. The presence of the quaternised diamido diethylenetriamine is said to lower the softening effect of the mixture compared with 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. Surprisingly, 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 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 salts also perform well in rewettability tests, which is unusual for such effective softeners. We have not found that the softeners of this invention cause significantly more yellowing of fabric than quaternary softeners.

Our invention therefore provides a novel composition which comprises (A) a water dispersible salt or partial salt of an amido amine of the average formula:



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 $-\text{CH}_2\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ 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; which amido amine is at least 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 glycolic acid, and (B) a compatible amount, up to 70% preferably 10 to 50%, e.g. 25% by weight, of a fluid, water miscible hydroxyaliphatic solvent. Where R groups are acyl they can be saturated, e.g. stearyl, 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.

Typically, any water miscible hydroxy-, or polyhydroxy- alkane or alkylether having a viscosity of less than 0.03 N.S.M.^{-2} (30 centipoise) at 20°C may be used as the solvent. Preferred examples include isopropanol, hexylene glycol, propylene glycol, ethylene glycol monomethylether and mixtures thereof.

The product may additionally contain a minor proportion of salts of inorganic acids especially sulphites, which help to stabilise the product against oxidation.

The amido amines 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 amido amine salts, any glycerol remaining from the preparation of the diamide and the added solvent. The novel products of our invention may be 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

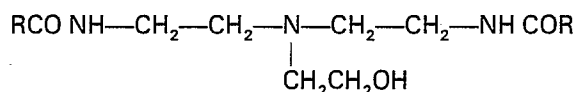
Example of a preparation of the subject of our patent

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



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%
	<hr/> 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 SO₂ 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 SO₂ also yields a lighter colour product which is less prone to colour deterioration on storage.

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Example 3

Domestic fabric softener formulations normally consist of concentrated fabric softener solutions as prepared in examples 1 and 2 dispersed into water to yield 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
15	I	melts 40°C to 50°C	55 to 60°C
		transport at 60°C	
20	II, III	mobile at 20°C	40°C
	IV	mobile at 20°C	20°C
	V	mobile at 20°C	30°C
25	Example 2	mobile at 20°C	30°C
	Example 1	mobile at 20°C	30°C
30	Example 2 but not ethoxylated	mobile at 40°C	70°C
35	Example 2 but 2 moles EO **	mobile at 20°C	20°C
40	Example 2 but 8 miles EO **	mobile at 20°C	20°C
	Example 2 but metho- sulphated *	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 0.1 to 0.5 N.S.M.⁻² (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 452, April 1979).

In general methosulphates, types II, III, IV and V give dispersions at 6% "active" with viscosities in the range 0.01 to 0.03 N.S.M.⁻² (10 to 30 cp) and are often formulated with other additives to increase their viscosity.

6% active, prepared as in Example 2 dispersed water — 0.30 N.S.M.⁻² (300 cp)

6% active, prepared as in Example 2 but 2 moles E.O. — 0.17 N.S.M.⁻² (170 cp)

5 Water hardness 300 ppm.
Dispersions prepared from products of examples 1 and 2 are stable to extend storage.

The product of example 2 was evaluated against compounds of type I and III where $n = 1$ in a 10 panel evaluation test as follows.

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

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:—

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

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

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



0.2% Application

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

Using the Kromer method to evaluate these results :

25 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
30 Weighted total	38	62	57	43

35 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

40 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).

45 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:

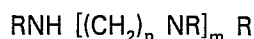
	Immersion Time		(mm) Height of dye front above solution					
50	Minutes	Example 2	Type III n =1	2 moles E.O.	8 moles E.O.	di- hydroxy	Type I	Water only
55	1	20	20	20	30	20	20	35
	5	40	40	50	45	40	35	55
60	10	55	55	60	65	65	45	70
	15	65	70	80	80	75	55	90
65	30	80	80	95	90	85	65	110

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

Claims

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1. A fluid, water-dispersible composition for use as a fabric softener, which comprises (A) a water dispersible salt or partial salt of an amido amine of the average formula:—



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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 $\text{—CH}_2\text{CH}_2\text{OH}$ or $\text{—CH}_2\text{CHOHCH}_3$ 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; which amido amine has been at least partially neutralised with a carboxylic or hydroxy carboxylic acid having from 1 to 3 carbon atoms, and (B) up to 70% by weight of a fluid, water-miscible hydroxy aliphatic solvent.

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2. A composition according to Claim 1 wherein the acyl is derived from tallow or lard.

3. A composition according to either of claims 1 and 2, wherein the amido amine is from 10 to 80% neutralised with lactic or acetic acid.

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4. A composition according to any foregoing claim containing 10 to 50% by weight of the composition of the hydroxy aliphatic solvent.

5. A composition according to any of the foregoing claims, wherein the hydroxy aliphatic solvent is a hydroxy- or polyhydroxyalkane or alkyl ether.

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6. A composition according to claim 5, wherein the hydroxy aliphatic solvent has less than four carbon atoms.

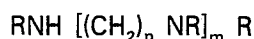
7. A composition according to any foregoing claim wherein n and m are each 2.

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

Patentansprüche

1. Flüssige, in Wasser dispergierbare Zubereitung zur Verwendung als Weichmacher für Textilien, enthaltend (A) ein in Wasser dispergierbares Salz oder partielles Salz eines Amidoamins der Durchschnittsformel

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in der durchschnittlich 20 bis 80% der Gruppen R je Molekül Acylgruppen mit durchschnittlich 12 bis 22 Kohlenstoffatomen und wenigstens 20% der Gruppen R $\text{—CH}_2\text{CH}_2\text{OH}$ oder $\text{—CH}_2\text{CHOHCH}_3$ oder Gemische dieser Gruppen sind und jedes andere R ein Wasserstoffatom bedeutet, n 2 oder 3 darstellt und m eine ganze Zahl von 2 bis 5 ist, wobei das Amidoamin wenigstens teilweise mit einer Karbonsäure oder Hydroxykarbonsäure mit 1 bis 3 Kohlenstoffatomen neutralisiert ist, sowie (B) bis 70-Gew.% eines flüssigen, mit Wasser mischbaren Hydroxygruppen enthaltenden aliphatischen Lösungsmittels.

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2. Zubereitung nach Anspruch 1, wobei die Acylgruppe von Talg oder Schweineschmalz abgeleitet ist.

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3. Zubereitung nach einem der Ansprüche 1 oder 2, wobei das Amidoamin von 10—80% mit Milchsäure oder Essigsäure neutralisiert ist.

4. Zubereitung nach den vorhergehenden Ansprüchen, enthaltend 10 bis 50% Gew.% des aliphatischen Hydroxygruppen enthaltenden Lösungsmittels, bezogen auf die Zubereitung.

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5. Zubereitung nach jedem der vorhergehenden Ansprüche, wobei das aliphatische Lösungsmittel mit Hydroxygruppen ein Hydroxy- oder Polyhydroxyalkan oder Alkyläther darstellt.

6. Zubereitung nach Anspruch 5, wobei das aliphatische Hydroxygruppen enthaltende Lösungsmittel weniger als 4 Kohlenstoffatome enthält.

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7. Zubereitung nach den vorhergehenden Ansprüchen, wobei in der Formel n und m jeweils 2 bedeuten.

8. Verfahren zum Weichmachen von Textilien, dadurch gekennzeichnet, daß auf die Textilien eine wässrige Lösung oder Dispersion einer Zubereitung nach jedem der vorhergehenden Ansprüche eingebracht wird.

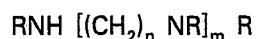
Revendications

1. Composition fluide, dispersable dans l'eau pour utilisation comme adoucissant pour matières textiles, caractérisée en ce qu'elle comprend:

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(A) un sel ou un sel partiel, dispersable dans l'eau, d'une amido-amine de formule moyenne:

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5 dans laquelle une moyenne de 20 à 80% des groupes R par molécule sont des groupes acyles ayant en moyenne de 12 à 22 atomes de carbone, au moins 20% des groupes R sont $\text{—CH}_2\text{CH}_2\text{OH}$ ou $\text{—CH}_2\text{CHOHCH}_3$ ou des mélanges de ces groupes et tout autre groupe R est l'hydrogène, n est 2 ou 3 et m est un nombre entier compris entre 2 et 5; cette amido-amine ayant été au moins partiellement neutralisée avec un acide carboxylique ou hydroxy-carboxylique ayant de 1 à 3 atomes de carbone, et (B) jusqu'à 70% en poids d'un solvant hydroxylé aliphatique, fluide, miscible à l'eau.

10 2. Composition selon la revendication 1, caractérisée en ce que le groupe acyle dérive du suif ou du lard.

3. Composition selon l'une des revendications 1 et 2, caractérisée en ce que l'amido-amine est neutralisée entre 10% et 80% avec l'acide lactique ou l'acide acétique.

4. Composition selon l'une quelconque des revendications précédentes, contenant de 10 à 50% en poids de la composition, en solvant hydroxylé aliphatique.

15 5. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le solvant hydroxylé aliphatique est un hydroxy- ou polyhydroxyalcane ou éther alkylique.

6. Composition selon la revendication 5, caractérisée en ce que le solvant hydroxylé aliphatique a moins de 4 atomes de carbone.

20 7. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que n et m sont chacun 2.

8. Procédé d'adoucissement des matières textiles, caractérisé en ce qu'il consiste à mettre sur les matières textiles une solution ou une dispersion aqueuse d'une composition selon l'une quelconque des revendications précédentes.

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