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(19)

(54) SOFTENING AGENT COMPOSITION

(71) We, KAO SOAP CO. LTD., a Japanese Company, of 1, 1-chome, Nihonbashi-Kayabacho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with a liquid softening agent composition for fabrics especially woven fabrics, the composition having excellent stability.

Owing to its excellent softening action on woven fabrics, a quaternary ammonium salt having two long-chain alkyl or β-hydroxyalkyl units per molecule, is now widely commercially available as a softening agent for household use.

Most of the softening agents marketed for household use are in the form of a liquid composition. The quaternary ammonium salt in the composition possesses two long-chain β-hydroxyalkyl groups showing affinity to water, but a low degree of solubility in water. Therefore, aqueous solutions having high concentrations of the quaternary ammonium salt readily convert to gels, making it difficult to obtain a stable composition having low viscosity.

A variety of methods have been attempted to obtain stable liquid compositions of low viscosity, for example by adding a non-ionic surface active agent, monoalkyl cationic surface active agent, or solvent.

For example, Japanese Patent Publication No. 3920/'70 discloses a liquid softening agent for woven fabrics composed of a quaternary ammonium salt, and non-ionic surface active agent consisting of an addition product of ethylene oxide and a higher alcohol, higher aliphatic acid or alkylphenol, and a solvent such as lower alcohol, glycerol, or glycol. Japanese Laid-open Patent Application No. 54300/'73 proposes blending of an alkyl polyoxyethylenated quaternary ammonium salt or alkylbetaine to the aforesaid composition to make a softening composition for the purpose of heightening the solution stability and imparting antistatic properties. However, we have found that the blend compositions recited in the above publication and application do not assist in obtaining a stable liquid composition, unless alkali metal salts such as sodium chloride are also present. If such alkali metal salts are absent, the liquid composition tends to gel, making it difficult to obtain a liquid composition. The incorporation of alkali metal salts may provide a composition having a low viscosity and improved recovery from freezing, but does not form stable dispersion systems. Therefore, it is necessary to incorporate large amounts of the aforementioned compounds such as non-ionic surface active agents or solvents for the purpose of giving satisfactory dispersion stability and recovery from freezing at any temperature.

However, the aforesaid stabilising effect, owing to its hydrotropy effects on the hydrophobic group, develops its effect during the treatment of the woven fabric; therefore, the quaternary salt is not absorbed sufficiently by the woven fabric, making it impossible to impart fully the softening effect to the woven fabric.

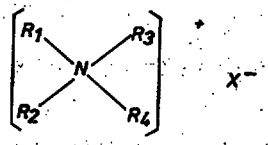
On the other hand, if the additives are incorporated in small amounts, although the resulting composition may have low viscosity initially, the dispersed particles become agglomerated upon heating or freezing and this gives rise to creaming or gellation.

Thus, there was no method until the advent of the present invention to incorporate the quaternary ammonium salt having two long-chain alkyl groups or

long-chain β-hydroxyalkyl groups in a stable aqueous liquid softening agent composition, while maintaining low viscosity.

Therefore, we have conducted extensive research in an effort to improve the aforementioned deficiencies of the earlier liquid softening agents, and have surprisingly found that the use of the quaternary ammonium salt in combination with a polyoxyethylene-oleyl ether, urea and water-soluble ammonium or amine salt, enable a composition to be obtained having improved dispersion stability and recovery from freezing without adversely affecting the softening properties.

According to the invention we provide a liquid softening agent composition for fabrics, comprising 3 to 20% by weight, based on the whole composition, of a quaternary ammonium salt (component A) represented by the general formula:



wherein R_1 and R_2 are each C_{12} to C_{20} alkyl group or C_{14} to C_{22} β-hydroxyalkyl group and can be the same or different, R_3 and R_4 are each a C_1 to C_3 alkyl group, a C_1 to C_3 hydroxyalkyl group, a benzyl group or a group $-(C_2H_4O)_nH$ in which n is an integer from 1 to 3, and can be the same or different, and X is a halogen atom or a C_1 to C_3 monoalkyl sulfuric acid group,
0.2 to 5% by weight of a polyoxyethyleneoleyl ether having an average mole number of added ethylene oxide groups of 8 to 200 (component B) 0.5 to 10% by weight of urea (Component C), and 0.08 to 2% by weight of a water-soluble ammonium or amine salt (component D) of ammonia, monoethanolamine, diethanolamine or triethanolamine and a mineral acid or a C_1 to C_3 carboxylic acid, wherein the ratios by weight of the components A, B, C and D present are within the following ranges:

B/A = 0.06 to 0.7,

C/A = 0.1 to 1.3, and

D/A = 0.025 to 0.17.

The mineral acid is preferably HCl, HNO_3 or H_2SO_4. The carboxylic acid is preferably acetic acid, hydroxyacetic acid, or formic acid.

The effects resulting from the combination of polyoxyethyleneoleyl ether, quaternary ammonium salt, urea and water-soluble ammonium or amine salt according to the present invention are illustrated by the following experiments.

Firstly, various compositions were made up as follows:

Distearyldimethylammonium chloride	(A) 6.0% by weight
Polyoxyethylene ($\bar{p}$=100) oleyl ether	(B) 0.24—5.40
Urea	(C) 0.48—9.00
Ammonium Chloride	(D) 0.12—1.20
Water	balance

Note: B/A = 0.04—0.9

C/A = 0.08—1.50

D/A = 0.020—0.200

Table 1 shows the relationship of the incorporation amount of polyoxyethylene ($\bar{p}$=100) oleyl ether, urea and ammonium chloride, to the viscosity, dispersion stability and recovery from freezing, based on the aforementioned incorporated composition.

The viscosity represents values (centipoise) measured at 25°C using a BM-

type viscometer, the recovery from freezing was found from the average of five tests in which freezing of a specimen was effected at −15°C and the composition then being left to stand at 30°C and melt and the dispersion stability was found from the presence or absence of the dispersed state after leaving a specimen in a vessel maintained at 50°C for 4 weeks.

TABLE 1

B/A	C/A	Viscosity (cp) D/A					Recovery from freezing					Dispersion stability				
		0.020	0.025	0.10	0.17	0.20	0.020	0.025	0.10	0.17	0.20	0.020	0.025	0.10	0.17	0.20
0.04	0.08	gel	gel	45	23	19	–	–	X	Δ	Δ	–	–	X	X	X
	0.10	gel	–	51	–	24	–	–	Δ	–	Δ	–	–	X	–	X
	0.60	gel	gel	112	42	40	–	–	X	Δ	Δ	–	–	Δ	X	Δ
	1.30	gel	–	2760	–	910	–	–	X	–	X	–	–	Δ	–	Δ
	1.50	gel	gel	gel	gel	gel	–	–	–	–	–	–	–	–	–	–
0.06	0.08	gel	1020	89	25	23	–	X	X	X	Δ	–	○	Δ	X	X
	0.10	gel	890	62	23	19	–	Δ	○	○	Δ	–	◎	○	○	X
	0.60	gel	763	73	57	31	–	○	◎	○	○	–	◎	◎	○	X
	1.30	gel	601	88	79	66	–	○	○	○	○	–	○	○	○	Δ
	1.50	gel	577	101	96	90	–	X	X	Δ	Δ	–	Δ	Δ	X	X
0.3	0.08	291	272	35	29	26	X	X	Δ	Δ	Δ	○	Δ	X	X	X
	0.10	235	201	30	26	20	X	○	○	○	Δ	○	○	○	○	X
	0.60	193	185	36	28	25	X	○	◎	○	○	○	◎	◎	○	Δ
	1.30	176	170	42	32	29	X	○	○	○	Δ	○	◎	◎	○	○
	1.50	170	163	51	39	33	X	Δ	Δ	Δ	X	○	○	○	Δ	Δ

TABLE 1 (Cont'd)

B/A	C/A	Viscosity (cp) D/A					Recovery from freezing					Dispersion stability				
		0.020	0.025	0.10	0.17	0.20	0.020	0.025	0.10	0.17	0.20	0.020	0.025	0.10	0.17	0.20
0.7	0.08	214	202	82	71	65	X	X	○	○	Δ	Δ	Δ	X	X	X
	0.10	207	181	73	54	44	X	◎	○	○	○	○	○	○	○	X
	0.60	190	173	76	55	47	Δ	○	◎	○	○	◎	◎	◎	○	Δ
	1.30	203	192	81	60	52	Δ	○	○	○	○	◎	◎	◎	○	○
	1.50	229	204	94	65	63	Δ	○	Δ	○	○	○	○	○	Δ	X
0.9	0.08	192	185	105	93	87	X	X	X	Δ	Δ	○	○	Δ	X	X
	0.10	201	–	99	–	89	X	–	Δ	–	Δ	○	–	Δ	–	X
	0.60	222	211	106	91	90	Δ	Δ	Δ	○	○	○	○	Δ	X	X
	1.30	235	–	111	–	88	Δ	–	Δ	–	○	○	–	○	–	X
	1.50	238	230	127	91	85	Δ	Δ	Δ	○	○	○	○	○	Δ	X
Control	a	27					X					○				
	b	93					○					X				
	c	gel					–					–				
	d	32					○					X				
	e	50					Δ					Δ				

Control

(a)	Distearyldimethylammonium chloride	6.0
	Polyoxyethylene ($\bar{p}$=100) lauryl ether	1.0
	Urea	2.0
	Ammonium chloride	0.5
	Water	balance
(b)	Distearyldimethylammonium chloride	6.0
	Polyoxyethylene ($\bar{p}$=100) oleyl ether	1.0
	Ethylene glycol	5.0
	Ammonium chloride	0.5
	Water	balance
(c)	Distearyldimethylammonium chloride	6.0
	Polyoxyethylene ($\bar{p}$=30) nonylphenyl ether	1.0
	Ethylene glycol	5.0
	Water	balance
(d)	Sodium chloride was incorporated in an amount of 0.07% to the Control (c).	
(e)	Distearyldimethylammonium chloride	6.0
	Stearylmethyldipolyoxyethylene ($\bar{p}$=50) ammonium chloride	2.0
	Propylene glycol	5.0
	Water	balance

Rating:

◎ : very good ○ : good Δ : poor X : very poor

As will be apparent from Table 1, it is possible to obtain a low-viscosity composition having excellent recovery from freezing and dispersion stability by appropriately incorporating the three components simultaneously, i.e., polyoxyethylene ($\bar{p}$=100) oleyl ether, urea and ammonium chloride into the distearyldimethylammonium chloride. A lack or an excess of even one of the aforesaid three components, causes one or both of the recovery from freezing and dispersion stability to deteriorate.

On the other hand, as shown by the Controls, the softening agent having excellent recovery from freezing and dispersion stability is not obtained if a polyoxyethylene ($\bar{p}$=100) lauryl ether is used as a non-ionic surface active agent (control (a)), if an ethylene glycol is used in place of urea (Control (b)), and if a non-ionic surface active agent, or monoalkyl ammonium, and solvent are used in combination (Controls (c) to (e)).

In this way, incorporation of the three components, i.e, polyoxyethyleneoleyl ether, urea and ammonium or amine salt into a quaternary ammonium salt, gives

marked effects such as excellent recovery from freezing and dispersion stability of the quaternary ammonium salt.

The quaternary ammonium salt (A) having two long-chain alkyl groups or β-hydroxyalkyl groups that provides softening effects, according to the present invention, should be incorporated in an amount of 3% or more from the standpoint of household uses, and not more than 20% from the standpoint of viscosity and preservation stability of the liquid composition.

Further, it is essential that the mixing ratios of the quaternary ammonium salt (A), polyoxyethyleneoleyl ether (B), urea (C) and ammonium or amine salt (D) lie within the ranges of B/A = 0.06—0.7, C/A = 0.1—1.3, and D/A = 0.025—0.17, from the viewpoint of viscosity, preservation stability and softness.

In practice, it is possible to incorporate an inorganic salt such as sodium chloride or polyoxyethylene saturated alkyl ether for the purpose of adjusting the viscosity, to add a pigment or a dyestuff to improve the appearance of the product, and to add perfumes to provide improved odour during and after use.

Some examples of the invention are given below, but it should be noted that the invention is not limited by them. Percentages are all on a weight basis in the Examples.

Example 1.

Distearyldimethylammonium chloride	7%
Polyoxyethylene ($\overline{p}$=130) oleyl ether	1.5
Urea	2
Ammonium chloride	0.5
Perfume, pigment	small amount
Water	balance

Example 2.

Di-β-hydroxystearyldiethylammonium chloride	20%
Polyoxyethylene ($\overline{p}$=20) oleyl ether	3
Urea	10
Triethanolamine hydrochloride	2
Perfume, pigment	small amount
Water	balance

Example 3.

Dilauryldipropylammonium bromide	15%
Polyoxyethylene ($\overline{p}$=180) oleyl ether	5
Urea	3
Ammonium acetate	0.5
Perfume, pigment	small amount
Water	balance

(13)

Example 4.

Dipalmitylmethylethylammonium ethyl sulfate	3%
Polyoxyethylene ($\overline{p}$=80) oleyl ether	0.2
Urea	0.5
Diethanolaminepropionic acid salt	0.1
Perfume, pigment	small amount
Water	balance

Example 5.

Diarachinyldihydroxyethylammonium chloride	10%
Polyoxyethylene ($\overline{p}$=100) oleyl ether	2
Urea	3
Ammonium chloride	1
Perfume, pigment	small amount
Water	balance

Example 6.

Di-hydrogenated tallowalkyl dimethyl ammonium chloride	6%
Polyoxyethylene ($\overline{p}$=100) oleyl ether	0.8
Polyoxyethylene ($\overline{p}$=100) lauryl ether	0.2
Urea	2
Ammonium chloride	0.5
Perfume, pigment	small amount
Water	balance

Table 2 shows the results of change of viscosity and stability when the compositions of the Examples 1—6 are preserved, in comparison with the four examples in which a polyoxyethyleneoleyl ether is removed from the composition of the Example 1 (Control A), in which urea is removed (Control B), in which ammonium chloride is removed (Control C), and in which said three components are removed (Control D). The dispersion stability was found from the observation of dispersed state after the specimen was left to stand in a constant-temperature vessel maintained at 50°C for 4 weeks, the recovery from freezing was determined from the testing repeated 5 times by freezing the specimen at −15°C and thawing the specimen by leaving it in an atmosphere of 30°C, and the viscosity was measured one day after the incorporation, after the freeze-thaw treatment, all measured at 25°C using a BM-type viscometer.

TABLE 2

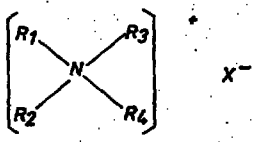
Example No.	Viscosity one day after the incorporation (cp)	Recovery from freezing		Dispersion stability	
		Viscosity (cp)		Viscosity (cp)	State
1	65	71	◎	63	◎
2	152	267	○	137	○
3	233	310	○	211	◎
4	32	39	◎	28	○
5	76	82	○	74	○
6	48	53	◎	47	◎
Control					
A	88	–	X	–	X
B	73	–	X	66	Δ
C	579	–	X	523	Δ
D	gel	–	–	–	–

Rating:
◎ : very good ○ : good Δ : poor X : very poor

The above results apparently indicate the superiority of the composition of the present invention.

WHAT WE CLAIM IS:—

1. A liquid softening agent composition for fabrics, comprising 3 to 20% by weight (based on the weight of the whole composition) of a quaternary ammonium salt (component A) represented by the general formula:



wherein R_1 and R_2 are each a C_{12} to C_{20} alkyl group or a C_{14} to C_{22} β-hydroxyalkyl group and can be the same or different, R_3 and R_4 are each a C_1 to C_3 alkyl group, a C_1 to C_3 hydroxyalkyl group, a benzyl group or a group $-(C_2H_4O)_nH$ in which n is an integer from 1 to 3, and can be the same or different, and X is a halogen atom or a C_1 to C_3 monoalkyl sulfuric acid group
0.2 to 5% by weight of a polyoxyethyleneoleyl ether having an average mole number of added ethylene oxide groups of 8 to 200 (component B), 0.5 to 10% by weight of urea (component C), and 0.08 to 2% by weight of a water-soluble ammonium or amine salt (component D) of ammonia, monoethanolamine, diethanolamine or triethanolamine and a mineral acid or a C_1 to C_3 carboxylic acid, wherein the ratios by weight of the components A, B, C and D present are within the following ranges:

B/A = 0.06 to 0.7,

TABLE 2

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2	152	267	○	137	○
3	233	310	○	211	◎
4	32	39	◎	28	○
5	76	82	○	74	○
6	48	53	◎	47	◎
Control					
A	88	–	X	–	X
B	73	–	X	66	Δ
C	579	–	X	523	Δ
D	gel	–	–	–	–

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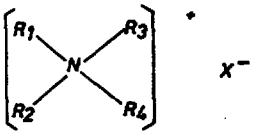
The above results apparently indicate the superiority of the composition of the present invention.

WHAT WE CLAIM IS:—

1. A liquid softening agent composition for fabrics, comprising 3 to 20% by weight (based on the weight of the whole composition) of a quaternary ammonium salt (component A) represented by the general formula:



wherein R_1 and R_2 are each a C_{12} to C_{20} alkyl group or a C_{14} to C_{22} β-hydroxyalkyl group and can be the same or different, R_3 and R_4 are each a C_1 to C_3 alkyl group, a C_1 to C_3 hydroxyalkyl group, a benzyl group or a group $-(C_2H_4O)_nH$ in which n is an integer from 1 to 3, and can be the same or different, and X is a halogen atom or a C_1 to C_3 monoalkyl sulfuric acid group

0.2 to 5% by weight of a polyoxyethyleneoleyl ether having an average mole number of added ethylene oxide groups of 8 to 200 (component B), 0.5 to 10% by weight of urea (component C), and 0.08 to 2% by weight of a water-soluble ammonium or amine salt (component D) of ammonia, monoethanolamine, diethanolamine or triethanolamine and a mineral acid or a C_1 to C_3 carboxylic acid, wherein the ratios by weight of the components A, B, C and D present are within the following ranges:

B/A = 0.06 to 0.7,

C/A = 0.1 to 1.3, and

D/A = 0.025 to 0.17.

2. A softening agent as claimed in Claim 1, in which the salt is a salt of hydrochloric acid, nitric acid or sulfuric acid.

3. A softening agent as claimed in Claim 1, in which the salt is a salt of acetic acid, hydroxyacetic acid or formic acid.

4. A softening agent as claimed in Claim 1, substantially as hereinbefore described with reference to any one of the Examples.

WITHERS & ROGERS,
Chartered Patent Agents,
148—150 Holborn,
London, EC1N 2NT.
Agents for the Applicants.

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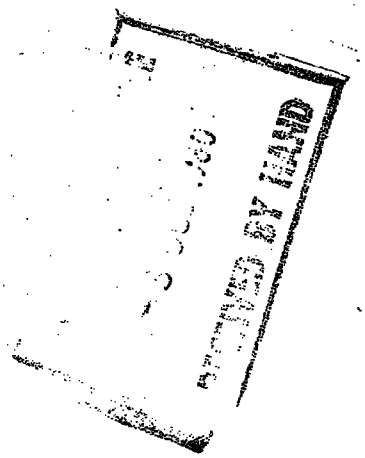
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