

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 1/835	A1	(11) International Publication Number: WO 97/08285 (43) International Publication Date: 6 March 1997 (06.03.97)
(21) International Application Number: PCT/US96/13427 (22) International Filing Date: 19 August 1996 (19.08.96) (30) Priority Data: 60/003,012 31 August 1995 (31.08.95) US (71) Applicant: COLGATE-PALMOLIVE COMPANY [US/US]; 300 Park Avenue, New York, NY 10022 (US). (72) Inventors: DEWEZ, Jacques; Thier Martin 15, B-4651 Battice (BE). THIBERT, Eric; Le Hac 22, B-4650 Herve (BE). (74) Agent: LIEBERMAN, Bernard; Colgate-Palmolive Company, 909 River Road, Piscataway, NJ 08855-1343 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STABLE FABRIC SOFTENER COMPOSITIONS		
(57) Abstract Fabric softening compositions which form and maintain stable aqueous dispersions in the absence of added oily perfume are disclosed. The stability of aqueous fabric softener compositions based on a mixture of an amido amine, such as bis(tallow amidoethyl)-2-hydroxyethyl amine and a quaternary diester fabric softener, such as N-methyl, N,N,N-triethanolamine ditallow ester quaternary ammonium salt is enhanced by inclusion in the composition of at least one fatty ester of a fatty acid or fatty alcohol, e.g., glycerol monostearate.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

STABLE FABRIC SOFTENER COMPOSITIONSBACKGROUND OF THE INVENTION

5

Field of the Invention

The present invention relates to fabric softener compositions and water-dilutable concentrates for addition to the rinse cycle in the fabric washing process.

10

Description of Related Art

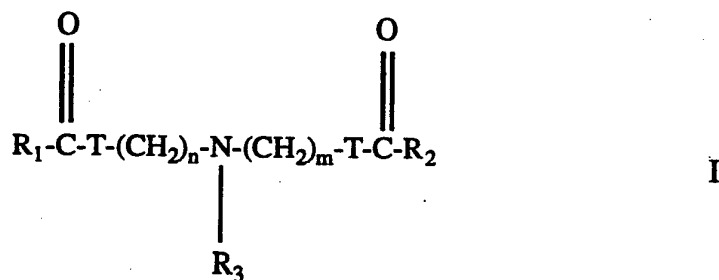
Aqueous compositions containing quaternary ammonium salts or imidazolinium compounds having at least one long chain hydrocarbyl group are commonly used to provide fabric softening benefits when used in a laundry rinse operation. Numerous patents have been issued for these types of compounds and compositions.

More recently, however, in view of concerns for the environmental safety (e.g. biodegradability) of the quaternary compound softeners, as well as limits in the amounts of these cationic compounds which can be stably incorporated in the more convenient to use liquid formulations, there have been many proposals for partial or total replacements of the conventional "quat" fabric softeners which are exemplified by dimethyl distearyl (or ditallow) ammonium chloride and various imidazolinium compounds.

30

Amido or ester amine compounds have been discovered which are more attractive as fabric softeners because they more readily biodegrade.

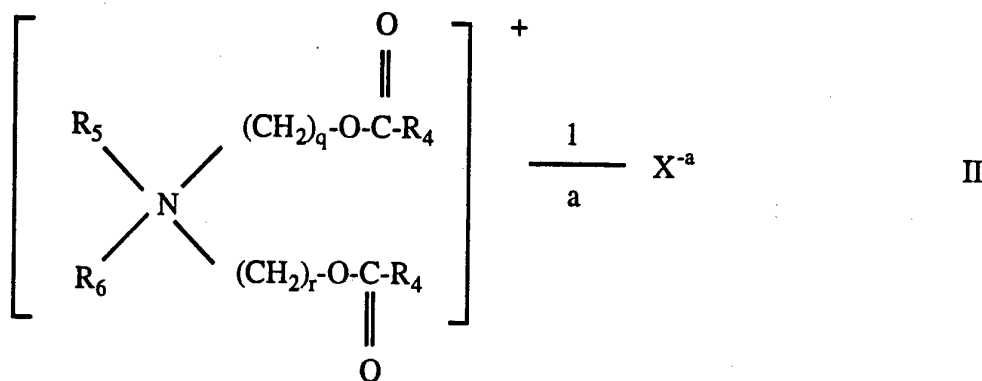
35 The compounds are organic or inorganic salts of compounds having the general formula I:



wherein R_1 and R_2 , independently, represent C_{12} to C_{20} alkyl or alkenyl; R_3 represents $(\text{CH}_2\text{CH}_2\text{O})_p\text{H}$, CH_3 or H ; T represents
 5 O or NH ; n and m are each, independently, a number of 1 to 5; and p is a number of from 1 to 10.

However, use of these compounds in combination with fatty emulsifiers in concentrated fabric softener aqueous
 10 dispersions or emulsions at levels in excess of about 10-11% by weight of the amine can cause a marked increase in the viscosity of the product (>2500 mPas), even in the presence of electrolytes (e.g. CaCl_2) or solvents, such that the product is not readily pourable from the container in which
 15 it is packaged.

Viscosity control and enhanced softening power in such aqueous compositions is achieved by combining the amido or ester amine of the formula I above with a biodegradable fatty
 20 ester quaternary ammonium compound (esterquat) of the formula II:



where each R_4 , independently, represents an aliphatic hydrocarbon group having from 8 to 22 carbon atoms; R_5 represents $(CH_2)_s-R_7$ (where R_7 represents an alkoxy carbonyl group containing from 8 to 22 carbon atoms, benzyl, phenyl, (C₁-C₄) alkyl substituted phenyl, OH or H); R_6 represents $(CH_2)_t-R_8$ (wherein R_8 represents benzyl, phenyl, (C₁-C₄) alkyl substituted phenyl, OH or H); q, r, s and t, each independently, represent a number of from 1 to 3; and x^{-a} is an anion of valence a.

Such compositions containing formula I and II components also contain an electrolyte salt as a gelation preventer to provide enhanced viscosity reduction. U.S. Patent 5,135,885 and copending U.S. application Serial No. 08/213,308, filed March 14, 1994, discloses aqueous based fabric softener concentrates containing species of the above described amido or ester amides and esterquat compounds.

The fabric softener (in concentrate or ready-to-use form) normally is formulated as an aqueous dispersion (macroemulsion) and also contains from about 0.25 to about 3% by weight of an added oil-based perfume to enhance consumer appeal. Concentrates formulated to be diluted by the consumer prior to use generally contain the perfume at high levels, e.g. from about 1-3% by weight. Typical perfumes are odoriferous materials based on floral extracts or woody-earthly bases containing exotic materials such as sandalwood oil, civet or patchouli oil. The perfume is normally added to a molten mixture of the softening agents just prior to emulsification in water.

However, in some cases it is desirable to formulate amido or ester amine/esterquat aqueous dispersions without addition of any perfume or with very little added perfume. This would allow the manufacturer to prepare large fabric masterbatches, portions of which could then be combined with different types of perfume to satisfy the different appeals of different consumers. Also, the provision of non-perfumed formulations

would allow the consumer to select one of a number of different perfume scents supplied with the product and mix the desired scent with the fabric softener composition prior to use.

5

10

Attempts to prepare emulsion masterbatches containing amido or ester amine/esterquat softening agents as described above without added perfume have demonstrated that the presence of the perfume is necessary in order to obtain emulsions having a stable viscosity. The perfume has been found to serve a physical/chemical role in the achievement of emulsions which maintain viscosity and which do not separate after periods of storage, since perfume-free emulsions of the type described herein are not viscosity stable after periods of ageing.

15

Accordingly, it is a primary object of this invention to provide stable fabric softener aqueous dispersion which remain stable in the absence of added oily perfume.

20

SUMMARY OF THE INVENTION

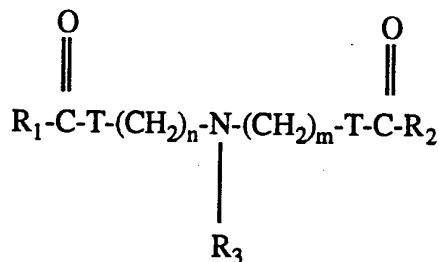
25

The present invention provides a stable fabric softener composition in the form of an aqueous dispersion (emulsion) which remains stable in the absence of added oily perfume, comprising a mixture of:

(i) from about 3 to about 40% by weight of a fabric softener combination comprising a mixture of A and B, wherein

30

(A) is an inorganic acid salt of a fabric softening compound of formula:



R_1 and R_2 represent C_{12} to C_{30} aliphatic hydrocarbon groups,

R_3 represents $(CH_2CH_2O)_pH$, CH_3 or H ;

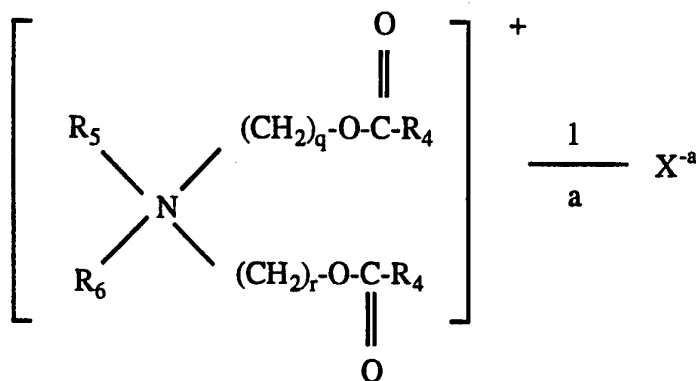
5 T represents O or NH ;

$n = 1$ to 5 ,

$m = 1$ to 5 , and

$p = 1$ to 10 ; and

10 (B) is biodegradable fatty ester quaternary ammonium compound of formula:



15 wherein each R_4 , independently, represents an aliphatic hydrocarbon group having from 8 to 22 carbon atoms, R_5 represents $(CH_2)_s-R_7$ (where R_7 represents an alkoxy carbonyl group containing from 8 to 22 carbon atoms, benzyl, phenyl, (C_1-C_4) -alkyl substituted phenyl, OH or H); R_6 represents
20 $(CH_2)_t-R_8$ (wherein R_8 represents benzyl, phenyl, (C_1-C_4) alkyl substituted phenyl, OH or H); q , r , s and t , each independently represent a number of from 1 to 3; and x is an anion of valence a ; said mixture further characterized that at least about 20% of the hydrocarbon substituent groups
25 present in components A and B are unsaturated;

(ii) a fatty ester of mono- or polyhydric alcohols having from 1 to about 24 carbon atoms in the hydrocarbon chain and mono- polycarboxylic acids having from 1 to
30 about 24 carbon atoms in the hydrocarbon chain, provided that the total number of carbon atoms in the ester is

equal to or greater than 16 and that at least one of the hydrocarbon radicals in the ester has 12 or more carbon atoms, said fatty ester being present in the composition such that the weight ratio of component (i) to component
5 (ii) is in the range of from about 40:1 to about 5:1; and

(iii) an aqueous carrier including an anti gelling amount of electrolyte.

10 The present invention also provide a method of imparting softness to fabrics by contacting the fabrics with a softening effective amount of the invention fabric softener composition, generally and preferably in the rinse cycle of an automatic laundry washing machine. The compositions may
15 be diluted with water prior to adding the composition to the washing machine (e.g., the rinse cycle dispenser), or may be added, at reduced amount, without dilution, i.e., ready to use.

20 Stable masterbatch compositions prepared herein may be perfumed prior to packaging or unperfumed packaged compositions may be supplied to the consumer and separately perfumed by the consumer prior to use.

25 DETAILED DESCRIPTION OF THE INVENTION

The fabric softening active ingredient A described above is an amido tertiary amine or an ester tertiary amine.

30 In the above formula for component A, R_1 and R_2 are each, independently, long chain aliphatic hydrocarbons, e.g., alkyl or alkenyl groups having from 12 to 30 carbon atoms, preferably from 16 to 22 carbon atoms. Linear hydrocarbon groups, such as, for example dodecyl, dodecenyl, octadecyl,
35 octadecenyl, behenyl, eicosyl, etc., are preferred. Typically, R_1 and R_2 , and more generally R_1 -CO- and R_2 -CO, will be derived from natural oils containing fatty acids or fatty acid mixtures, such as coconut oil, palm oil, tallow,

rape oil, and fish oil. Chemically synthesized fatty acids are also usable. Generally and preferably R_1 and R_2 are derived from the same fatty acid or fatty acid mixture. When R_1 and R_2 are derived from or contain up to about 80%, but preferably not more than 65% by weight of unsaturated (i.e., alkenyl) groups, the relatively poor softening performance of unsaturated moieties of the compound is overcome by the combination with the ester quat compound of formula B and an effective amount of a viscosity reducing electrolyte.

R_3 in formula A represents $(CH_2CH_2O)_pH$, CH_3 , or H, or mixtures thereof. When R_3 represents the preferred $(CH_2CH_2O)_pH$ group, p is a positive number representing the average degree of ethoxylation, and is preferably from 1 to 10, especially 1.4 to 6, and more preferably from about 1.5 to 4, and most preferably, from 1.5 to 3.0. n and m are integers of from 1 to 5, preferably 1 to 3, especially 2. The compounds of formula A in which R_3 represents the preferred $(CH_2CH_2O)_pH$ group are broadly referred to herein as ethoxylated amidoamines ($T=NH$) or ethoxylated ester amines ($T=O$), and the term hydroxyethyl is also used to describe the $(CH_2CH_2O)_pH$ group.

Suitable amidoamines for use herein include those sold under the tradename Varisoft™ 510, 511 and 512 by Shreex Chemical company or sold under the tradename Rewopal™ V3340 by Rewo of Germany.

The fabric softening active ingredient B described above is a quaternized ester compound. Each R_4 in formula B independently represents an aliphatic hydrocarbon group having from 8 to 22 carbon atoms, and preferably 14 to 18 carbon atoms. R_5 represents the group $(CH_2)_s-R_7$ which, depending on R_7 , may represent a long chain alkyl ester group ($R_7 = C_8-C_{22}$ alkoxy carbonyl), in which case the compounds of formula B are triester quaternary ammonium compounds.

Preferably, however, the fatty ester quaternary compounds are diester compounds, i.e. R_7 represents benzyl, phenyl, phenyl substituted by C_1 - C_4 alkyl, hydroxyl (OH) or hydrogen (H). Most preferably R_7 represent OH or H, especially preferably OH, e.g. R_5 is hydroxyethyl.

q, r and s, each, independently, represents a number of from 1 to 3.

X represents a counter ion of valence a.

X is preferably an anion selected from the group consisting of halo, sulfate, methosulfate, nitrate, acetate, phosphate, benzoate or oleate.

In a more preferred embodiment, each R_4 in formula B may be, for example, derived from hard or soft tallow, coco, stearyl, oleyl, and the like. Such compounds are commercially available, for example, Tetranyl AT-75, from Kao Corp. Japan, which is di-tallow ester triethanol amine quaternary ammonium methyl sulfate. Tetranyl AT-75 is based on a mixture of about 25% hard tallow and about 75% soft tallow. Accordingly, this product contains about 34% of unsaturated alkyl chains. A second example would be Hipochem X-89107, from High Point Chemical Corp.; which is an analogue of the Tetranyl AT-75 with about 100% saturation in the tallow moieties. However, in general, the quaternized ammonium ester compound of formula B may contain from about 5% to about 75% of unsaturated (long-chain) alkyl groups, preferably from about 20% to about 50% of unsaturated long-chain alkyl groups.

Best fabric softener performance is achieved where from at least about 20% up to about less than 70% of the combined hydrocarbon substituent group present in A and B are unsaturated.

The compounds of formula A and B are used in admixture, preferably in ratios of about 5:1 to about 1:5, more preferably from 2:1 to 1:2, especially 1.7:1 to 1:1.7, whereby both softening performance and stability and pourability are improved. That is, notwithstanding the poor softening performance of the unsaturated long-chain alkyl compounds when used individually, when used with the ester quat compound (which also preferably contains carbon to carbon double bonds), either alone or in combination with the hydrogenated amido amine compound, a surprisingly substantial improvement in softening performance is observed in pourable liquid formulations.

The total amounts of components A and B present in the composition is from about 3 to about 40 wt. percent, preferably from about 4 to about 30 wt.%, and the ratio, by weight of A:B is from about 2:1 to 1:2, and especially, from about 1.7:1 to 1:1.

These softener components are more particularly described in U.S. Patent 5,135,885 and copending U.S. Application Serial No. 08/213,308, the complete disclosures of which are incorporated herein by reference.

The emulsion or dispersion stabilizers used herein are fatty alkyl esters which may be derived from mono- or polyhydric alcohols having from 1 to about 24 carbon atoms in the hydrocarbon chain, and mono- or polycarboxylic acids having from 1 to about 24 carbon atoms in the hydrocarbon chain, with the provisos that the total number of carbon atoms in the ester is equal to or greater than 16 and at least one of the hydrocarbon radicals in the ester has 12 or more carbon atoms.

The acid portion of the fatty ester can be obtained from mono- or polycarboxylic acids having from 1 to about 24 carbon atoms in the hydrocarbon chain. Suitable examples of monocarboxylic acids include behenic acid, stearic acid,

oleic acid, palmitic acid, myristic acid, lauric acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, lactic acid, glycolic acid and dihydroxyisobutyric acid. Examples of suitable polycarboxylic acids include: n-butyl-malonic acid, isocitric acid, citric acid, maleic acid, malic acid and succinic acids.

The alcohol radical in the fatty ester can be represented by mono- or polyhydric alcohols having from 1 to 24 carbon atoms in the hydrocarbon chain. Examples of suitable alcohols include: behenyl, arachidyl, cocoyl, oleyl and lauryl alcohols, ethylene glycol, glycerol, polyglycerol, ethanol, isopropanol, vinyl alcohol, diglycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan.

Preferred fatty esters are ethylene glycol, glycerol, pentaerythritol and sorbitan esters wherein the fatty acid portion of the ester normally comprises a species selected from behenic acid, stearic acid, oleic acid, palmitic acid or myristic acid.

Specific examples of fatty alcohol esters for use herein include: stearyl acetate, palmityl di-lactate, cocoyl isobutyrate, oleyl maleate, oleyl dimaleate, and tallow propionate. Fatty acid esters useful in the present invention include: methyl oleate, xylitol monopalmitate, pentaerythritol monoleate or monostearate, sucrose monostearate, glycerol monostearate or monoleate, ethylene glycol monostearate and sorbitan esters. Suitable sorbitan ester include sorbitan monostearate, sorbitan palmitate, sorbitan monolaurate, sorbitan monomyristate, sorbitan monobehanate, sorbitan monoleate, sorbitan dilaurate, sorbitan distarate, sorbitan dibehenate, sorbitan di- or trioleate, and also mixed tallowalkyl sorbitan mono- and di-esters. Glycerol esters are equally highly preferred in the composition herein. These are the mono-, di-, or tri-esters of glycerol and the fatty acids of the class described above. Glycerol monostearate, glycerol mono-oleate, glycerol

monopalmitate, glycerol monobehenate, and glycerol distearate are specific examples of these preferred glycerol esters.

5 The most preferred esters for use herein are fatty esters of C₁₆-C₁₈ unsaturated fatty acids (e.g. oleic acids) with C₁ to C₈ mono- or polyhydric alcohols such as methanol, ethanol, sorbital, pentaerythritol, glycerol and polyglycerol. Preferred esters also have an HLB (Hydrophilic Balance) value in the range of about 0.5 to 5, more preferably from about 2
10 to 3. Glycerol monooleate is a particularly preferred fatty acid ester.

These fatty esters are incorporated into the composition at levels such that the weight ratio of the mixed fabric
15 softener components A and B to fatty ester is in the range of from about 40:1 to about 5:1, more particularly from about 28:1 to about 9:1. Generally speaking, the composition should contain from about 0.2 to about 2% by weight of the fatty ester component.

20 The fatty ester component functions as a dispersion or emulsion stabilizer in much the same way as the oily perfume component of perfumed dispersions. The fatty ester thus permits the preparation of stable unperfumed dispersions
25 having pourable viscosities which will not separate after periods of storage.

In the non-neutralized form, the fatty amide and fatty ester tertiary amine compounds of formula A are not readily
30 dispersible in water. Therefore, the amine function of amidoamine or ester amine compound is at least partially neutralized by a proton contributed by a dissociable acid, which may be inorganic, e.g., HCl, H₂SO₄, HNO₃, etc. or organic, e.g. acetic acid, propionic acid, lactic acid,
35 citric acid, glycolic acid, toluene sulfonic acid, maleic acid, fumaric acid, and the like. Mixtures of these acids may also be used, as may any other acid capable of neutralizing the amine function. The acid neutralized

compound is believed to form a reversible complex, that is, the bond between the amine function and proton will disappear under alkaline pH conditions. This is in contrast to quaternization, e.g., with a methyl group, wherein the quaternizing group is covalently bonded to the positively charged amine nitrogen and is essentially pH independent.

The amount of acid used will depend on the "strength" of the acid; strong acids such as HCl, and H₂SO₄ completely dissociate in water, and, therefore, provide a high amount of free protons (H⁺), while weaker acids, such as citric acid, glycolic acid, lactic acid, and other organic acids, do not dissociate completely and, therefore, require a higher concentration to achieve the same neutralizing effect. Generally, however, the amount of acid required to achieve complete protonation of the amine, will be achieved when the pH of the composition is rendered strongly acidic, namely between about 1.5 and 4. HCl and glycolic acid are preferred, and HCl is especially preferred.

The amount of acid used will normally range from about 0.20 to 1.5% by weight, depending on acid type and strength.

The compositions of this invention are provided as aqueous dispersion in which the fabric softener compounds of formula A and formula B are present in finely divided form stably dispersed in the aqueous phase. Generally, particle sizes of the dispersed particles of less than about 25 microns (μm), preferably less than 20 μm, especially preferably no more than 10 μm, on average are acceptable for both softening and stability insofar as the particle sizes can be maintained during actual use, typically in the rinse cycle of an automatic landry washing machine. The lower limit is not particularly critical but from a practical manufacturing standpoint will not generally be below about 0.01 μm, preferably at least about 0.05 μm. A preferred particle size range of the dispersed softener ingredients is from about 0.1 to about 8 μm.

The aqueous phase of the dispersion is primarily water, usually deionized or distilled water. Small amounts (e.g. up to about 5% by weight) of co-solvent may be present for adjustment of viscosity. Typically, lower mono- and poly-hydroxy alcohols will be used as the cosolvent, generally in amounts up to about 8% by weight of the composition. The preferred alcohols are those having from 2 to 4 carbon atoms, such as, for example, ethanol, propanol, isopropanol, an propylene glycol or ethylene glycol. Isopropyl alcohol (2-propanol) is especially preferred. However, co-solvents are not required and are generally avoided.

The compositions of this invention include an electrolyte to reduce dispersion viscosity. Generally, any of the alkali or alkaline earth metal salts of the mineral acids can be used as electrolyte. In view of availability, solubility and low toxicity, NaCl, CaCl₂, MgCl₂ and MgSO₄ and similar salts are preferred, and CaCl₂ is especially preferred. The amount of the electrolyte will be selected to assure that the composition does not form a gel. Generally, amounts of electrolyte salt of from about 0.0075 to 2.0 wt.%, preferably 0.05 to 1.5 wt.%, may be used.

An optional ingredient which may be present in the compositions is a rheology modifier to help reduce or eliminate variations in the aqueous dispersion viscosity over time. It should be understood, however, that so long as the viscosity does not increase to an unacceptably high level over the expected life of the product (including transportation from the manufacturing plant to the market place, shelf-life in the market place, and duration of consumption by the end user) a rheology modifier is not necessary. For example, the viscosity after, for instance, 8 to 10 weeks, should preferably not exceed about 1500 cps (at 25°C), especially preferably the viscosity should not exceed about 1000 cps (at 25°C) over the expected lifetime of the

product. In many cases, initial viscosities of up to about 200 cps can be achieved and maintained.

Therefore, if there is concern about increase in product viscosity, or if changes in viscosity over time are considered undesirable, a rheology modifier can be added to the composition. Examples of rheology modifiers are well known in the art and may be chosen from, for example, polymeric rheology modifiers and inorganic rheology modifiers. Examples of the former type include polyquaternium compounds, such as Polyquaternium-24 (a hydrophobically modified polymeric quaternary ammonium salt hydroxyethyl-cellulose, available from Amercho, Inc.); cationic polymers such as copolymers of acrylamide and quaternary ammonium acrylate; the Carbopols, and the like. Examples of inorganic rheology modifiers include, for example, alumina. Generally, only minor amounts, up to about 1.0%, preferably up to about 0.8%, such as, for example, 0.01 to 0.60 percent by weight, provide acceptable viscosity levels over time.

Other optional additive components commonly used in fabric softening compositions may be added in minor amounts to enhance either the appearance or performance properties of the liquid fabric softener compositions of this invention. Typical additives of this type include, but are not limited to colorants, e.g., dyes or pigments, bluing agents, preservatives, germicides, perfumes and thickeners.

The subject liquid fabric softener compositions may be prepared by adding the active ingredients, i.e., compounds A and B, and the fatty ester, usually as a melt, to the heated aqueous phase to which the acid component has been pre-mixed, under mixing conditions. Low-shear mixing is generally sufficient to adequately and uniformly disperse the active ingredients in and throughout the aqueous phase. Further particle size reduce can be obtained by subjecting the

composition to further treatment such as in a colloid mill or by high pressure homogenization.

5 The final product, whether in concentrate or diluted form must be easily pourable by the end user. Generally, therefore, final product viscosity (for a freshly prepared sample) should not exceed about 1500 centipoise (mPa), preferably not more than 1000 centipoise, but should not be too low, for example not less than about 20 centipoise. The
10 preferred viscosity for the invention concentrated product is in the range of 35 to 1000 centipoise. As used herein, unless otherwise specified, viscosity is measured at 25°C (22-26°C) using a Brookfield Viscometer Model RVTDV-II at 50 RPM using spindle n^o2 below 800 cps, n^o3 above 800 and below
15 2,000 cps, and spindle n^o4 above 2,000 and below 4,000 cps.

The dispersions of this invention may be provided in ready to use form or as concentrates containing a higher level of active ingredients. Concentrates will generally be
20 formulated for dilution with from about one to six volumes of water per volume of concentrate.

In addition, perfumes may be added directly to the fabric softener formulations prior to packaging without the
25 necessity to pre-emulsify the perfume component. Also, perfume may be added directly by the consumer prior to use of the fabric softener in the washing cycle. Thus the fabric softener may be differentiated to appeal to different consumer desires.

30 The following examples are illustrative of the invention.

Example 1

35 This example illustrates the preparation of a masterbatch (MB) composition containing about 14.3 wt.% active ingredients.

The following ingredients were combined to make a perfume-free masterbatch having an active ingredient (AI) content of about 14.3% (AI = amido amine and esterquat):

5	<u>RAW MATERIAL</u>	<u>NOMINAL %</u>
	Amidoamine partially hydrogenated (Rewopal™ V3340)	8.93
10	Esterquat partially hydrogenated (Tetranyl AT 750)	5.36
15	Glycerol monooleate (Radiasurf 7150)	1.02
	Hydrochloric acid	0.47
20	Preservative (Lactic/lactate)	0.26
	Calcium chloride dihydrate	0.09
25	Deionized water	balance

The mixing procedure employed was to charge a premix tank with molten amido amine, molten ester quat and molten fatty acid ester and heat to 65°C. The main tank was charged with deionized water and heated to 65°C. The HCl is then added under agitation and the content of the premix tank is next added under high agitation. The electrolyte (in solution) and preservative are then added. The product is mixed for about 10 minutes and then cooled down to 30°C.

35 Control A

A control perfume-free masterbatch was prepared as described in Example 1 above except that the glycerol monooleate was left out of the formulation.

40 Control B

A control perfume-containing masterbatch was prepared as described above except that the glycerol monooleate was left out of the formulation and 1.5 parts of perfume was included

in the formulation. The perfume was comprised of terpenes, natural extracts, a mixture of terpenic and aromatic alcohols, esters of terpenic and aromatic alcohols, lactone, polyglycols and musk.

5

A finished product (FP) containing about 14 wt.% AI was prepared by mixing 98 parts by weight of the Example 1 masterbatch with 1.5 parts perfume and 0.5 parts of a dye solution.

10

A 3.1 wt.% AI finished product (4:1 dilution) was prepared by combining 24.5 parts by weight of the Example 1 masterbatch with 0.32 parts perfume, 0.5 parts dye solution, 0.3 parts thickener and the balance water to 100 parts by weight total.

15

Viscosity measurements were taken on these formulations immediately after making (as made = AM), after 1 day storage and after 12 weeks storage, at 4°C, room temperature (RT), 35°C and 43°C.

20

Results are shown in Table 1.

TABLE 1

25

FORMULA	Brookfield Viscosity (cps)					
	AM 1 day		6 Weeks			
			4°C	RT	35°C	43°C
EX. 1	44	43	44	41	36	49
14% AI FP	48	43	45	38	38	38
3.5% AI FP	144	153	161	154	154	165
CONTROL A	1174	990	1780	856	1188	157
CONTROL B	45	39	38	40	32	32

35

The above results demonstrate that the viscosity of the products of the invention remained stable over an extended period of time. No separation of the product into separate layers was observed. Control A, which did not contain the fatty ester, exhibited a markedly higher viscosity as made

40

and after standing. The addition of perfume to Control A (Control B) resulted in a viscosity stable emulsion comparable to the products of the invention.

5

Example 2

10 A series of three different masterbatch products (perfumed products, unperfumed products and stabilized unperfumed products) containing about 28 wt.% amido amine and esterquat active ingredients were prepared by the procedure as in Example 1 and evaluated for viscosity stability. The perfume used was the same as described in Control B above. The composition of these formulations with reference to Tables 2-
15 4 was as follows:

Table 2 Perfumed Products

	<u>Ingredient</u>	<u>Nominal % (AI)</u>
	Water	balance
20	Hydrochloric acid	0.92
	Amidoamine	17.5
	Esterquat	10.5
	Perfume	2 or 2.4
	MgCl ₂ .6H ₂ O	0.64
25	Dye	0.01

Table 3 Unperfumed products

	Water	balance
	Hydrochloric acid	0.95
	Amidoamine	18.0
30	Esterquat	10.8
	MgCl ₂ .6H ₂ O	0.66

Table 4 Stabilized unperfumed products

	Water	balance
	Hydrochloric acid	0.92
35	Amidoamine	17.5
	Esterquat	10.5
	Stabilizing Ester	2
	MgCl ₂ .6H ₂ O	0.64

These formulations were evaluated for viscosity stability with the following results:

Table 2: Perfumed Product

Perfume Level %	Brookfield Viscosity (cps)					
	AM	1 day		6 Weeks		
		4°C	RT	35°C	43°C	
2.4	73	63	94	71	65	69
2	68	58	84	71	66	66

Table 3: Unperfumed Products

	Brookfield Viscosity (cps)					
	AM	1 day		6 Weeks		
		4°C	RT	35°C	43°C	
1	148	1470	1580	1380	1110	>4000
2	117	195	312	265	266	1350
3	86	650	810	625	486	3160
4	58	152	410	255	317	1300

Table 4: Stabilized Unperfumed Products

Ester 2%	Brookfield Viscosity (cps.)					
	AM	1 day		6 Weeks		
		4°C	RT	35°C	43°C	
a	88	91	144	104	94	80
b	84	94	161	105	101	141
c	78	87	149	105	80	69
d	78	87	110	81	63	59
e	83	109	174	114	98	110
f	73	70	140	80	65	65

Stabilizing Ester

- a = sorbitan monooleate
- b = sorbitan trioleate
- c = pentaerythritol monooleate
- d = glycerol monooleate
- e = polyglycerol monooleate
- f = methyl oleate

These results again demonstrate the relative viscosity stability of formulations containing the perfume (Table 2), poor viscosity stability of compositions free of both perfume and ester (Table 3) and good viscosity stability of unperfumed formulations containing various esters within the scope of the invention as stabilizers (Table 4).

The viscosity stable emulsions of the present invention may be supplied to the consumer as concentrates and free of added perfume, and the water and perfume separately added by the consumer. Concentrates may be diluted by the consumer with 0.5 to 6 parts water per part of concentrate. Post addition of perfume (and water) to the concentrate may be accomplished by simply mixing in the perfume (and water) at ambient temperatures. Such post addition of these ingredients does not effect or destroy the viscosity stability of the emulsion. This is illustrated by the following example.

Example 3

An unperfumed product containing about 21% amido amine/esterquat active ingredients was prepared by the procedure of Example 1. This PF-free (perfume free) product had the following composition:

Water	balance
Hydrochloric acid	0.69
Amidoamine	13.12
Esterquat	7.88
Glycerol monooleate	1.8
CaCl ₂ .2H ₂ O	0.2

A sample of this product at room temperature was then perfumed and dyed by gently mixing in 1.8% perfume and 0.01% dye and viscosity measurements were taken as made and at other times and temperatures as shown in Table 5. Three other samples were perfumed 1, 7 and 14 days after making as shown in Table 5.

Viscosity results were as follows:

Table 5

	Post add time (days)	Brookfield Viscosity (cps)					
		AM	1 day			4/6 Weeks	
				4°C	RT	35°C	43°C
	0	78	67	74	51	50	48
	1	85	78	81	59	55	55
	7	81	75	100	60	57	60
	14	78	78	84	62	58	58
	PF-Free	73	72	83	58	50	43

These results demonstrate the maintenance of relatively stable viscosities for the perfume-free and perfume-containing formulations whether perfumed immediately after formulation or after a period of days.

The product of this Example 3 was also diluted with both water, perfume and dye to provide a more dilute concentrate containing about 14% amido amine/esterquat and about 1.3% perfume. Dilution and post dilution viscosity data is shown in Table 6.

Table 6

	(days)	Brookfield Viscosity (cps.)					
		AM	1 day			4/6 Weeks	
				4°C	RT	35°C	43°C
	0	43	42	43	37	35	34
	1	45	45	47	42	40	38
	7	48	47	47	42	40	38
	14	42	46	45	41	39	39

The results demonstrate the maintenance of viscosity of the perfume-containing formulation after dilution with water.

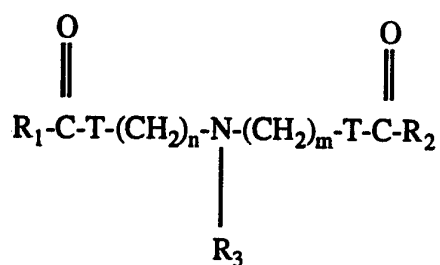
CLAIMS

What is claimed is:

1. A fabric softening composition in the form of an aqueous dispersion which is stable in the absence of oily perfume, comprising a mixture of:

(i) from about 3 to about 40% by weight of a fabric softener combination comprising a mixture of A and B, wherein

(A) is an inorganic acid salt of a fabric softening compound of formula:



R₁ and R₂ represent C₁₂ to C₃₀ aliphatic hydrocarbon groups,

R₃ represents (CH₂CH₂O)_pH, CH₃ or H;

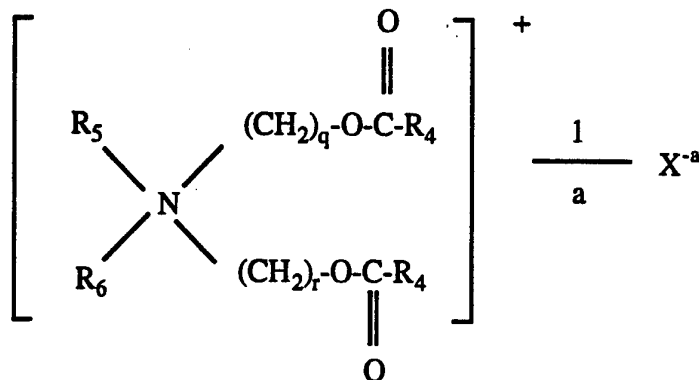
T represents O or NH;

n = 1 to 5,

m = 1 to 5, and

p = 1 to 10; and

(B) is biodegradable fatty ester quaternary ammonium compound of formula:



wherein each R_4 , independently, represent an aliphatic hydrocarbon group having from 8 to 22 carbon atoms, R_5 represents $(\text{CH}_2)_s - \text{R}_7$ (where R_7 represents an alkoxy carbonyl group containing from 8 to 22 carbon atoms, benzyl, phenyl, $(\text{C}_1 - \text{C}_4)$ -alkyl substituted phenyl, OH or H); R_6 represents $(\text{CH}_2)_t - \text{R}_8$ (wherein R_8 represents benzyl, phenyl, $(\text{C}_1 - \text{C}_4)$ alkyl substituted phenyl, OH or H); q , r , s and t , each independently represent a number of from 1 to 3; and x is an anion of valence a ;

said mixture further characterized that at least about 20% of the hydrocarbon substituent groups present in components A and B are unsaturated;

(ii) a fatty ester of mono- or polyhydric alcohols having from 1 to about 24 carbon atoms in the hydrocarbon chain and mono- polycarboxylic acids having from 1 to about 24 carbon atoms in the hydrocarbon chain, provided that the total number of carbon atoms in the ester is equal to or greater than 16 and that at least one of the hydrocarbon radicals in the ester has 12 or more carbon atoms, said fatty ester being present in the composition such that the weight ratio of component (i) to

component (ii) is in the range of from about 40:1 to about 5:1; and

(iii) an aqueous carrier including an anti gelling amount of electrolyte.

2. The composition of claim 1 wherein in the compound of formula A:

T = NH

R₁ and R₂ = C₁₆ to C₂₂ alkyl or alkenyl;

m = 1 to 3; n = 1 to 3;

R₃ = (CH₂CH₂O)_pH; and p = 1.5 to 3.5.

3. The composition of claim 1 wherein in the compound of formula B:

R₅ and R₆ are selected from C₁ to C₄ alkyl and CH₂CH₂OH, at least or both of R₅ or R₆ being CH₂CH₂OH;

R₄ is an aliphatic hydrocarbon having from 14 to 18 carbon atoms; and

X is an anion selected from the group consisting of halo, sulfate, methosulfate, nitrate, acetate, phosphate, benzoate or oleate.

4. The composition of claim 1 wherein the weight ratio of (A):(B) is in the range of from about 5:1 to about 1:5 and the total unsaturation being less than 70% of the hydrocarbon substituent groups present in A and B.

5. The composition of claim 1 wherein the total amount of (A) and (B) ranges from about 4 to about 30% by weight based on the total composition.

6. The composition of claim 5 wherein the weight ratio of component (i) to component (ii) ranges from about 28:1 to about 9:1.

5

7. The composition of claim 4 wherein the weight ratio of (A):(B) is in the range of from about 2:1 to 1:2.

10 8. The composition of claim 1 wherein said fatty ester component (ii) is selected from the group consisting of fatty esters of C₁₆ to C₁₈ unsaturated fatty acids and C₁ to C₈ mono-or polyhydric alcohols.

15 9. The composition of claim 8 wherein said fatty acid had an HLB value in the range of from about 0.5 to 5.

20 10. The composition of claim 8 wherein said fatty alcohol is selected from the group consisting of sorbitan monooleate, sorbitan trioleate, pentaerythritol monooleate, glycerol monooleate, polyglycerol monooleate methyl oleate and mixtures thereof.

25 11. The composition of claim 10 wherein said fatty alcohol is glycerol monooleate.

12. The composition of claim 1 wherein fatty ester component (ii) is present in the composition at a level of from about 0.2 to about 2% by weight.

30 13. The composition of claim 1 wherein said component A is selected from the group consisting of salts of bis(tallowamidoethyl)-2-hydroxyethylamine, bis(hydro-genated-tallowaminoethyl)-2-hydroxyethylamine and mixtures thereof.

35 14. The composition of claim 13 wherein said component B is N-methyl-N,N,N-triethanolamine-ditallow diester quaternary ammonium methosulfate.

15. The composition of claim 1 which additionally contains a protonic acid sufficient to at least partially neutralize component (A).

5 16. The composition of claim 15 wherein said acid is HCl.

10 17. The composition of claim 1 wherein said electrolyte is an alkali or alkaline earth metal salt present in said composition at a level of from about 0.0075 to about 2% by weight.

15 18. The composition of claim 17 wherein said electrolyte is CaCl_2 .

19. The composition of claim 1 in the form of a fabric softener concentrate having a content of active ingredients in the range of from about 10 to about 35% by weight.

20 20. The composition of claim 1 further containing from about 0.25 to about 3% by weight of added perfume.

25 21. The composition of claim 1 which is free of added perfume.

22. A method of imparting softness to fabrics comprising contacting the fabrics with a softening effective amount of the fabric softener composition of claim 1.

30 23. The method of claim 22 wherein said contacting is in the rinse cycle of an automatic washing machine.

35 24. The method of claim 22 wherein said fabric softener composition is diluted with from about 1 to about 6 volumes of water per volume of fabric softener composition prior to use.

25. The method of claim 22 wherein said fabric softener composition is free of added perfume and is mixed with perfume prior to use.

5 26. The method of claim 25 wherein from about 0.25 to about 3% by weight of perfume is mixed with said fabric softener composition prior to use.

INTERNATIONAL SEARCH REPORT

Internatio Application No
PCT/Us 96/13427

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/835

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 634 475 A (COLGATE PALMOLIVE CO) 18 January 1995 cited in the application see claims; example 1; tables 1,2 ---	1-5,7, 13-19, 21-23
A	EP 0 423 894 A (COLGATE PALMOLIVE CO) 24 April 1991 see the whole document ---	1-5,7, 13-19, 21-213
A	EP 0 443 313 A (KAO CORP) 28 August 1991 see claims ---	1-5, 17-19
A	EP 0 243 735 A (HENKEL KGAA) 4 November 1987 see claims 1-7 see examples -----	1,6-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 January 1997

Date of mailing of the international search report

14. 01. 97'

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/13427

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP-A-0634475	18-01-95	US-A-	5501806	26-03-96
		AU-B-	673079	24-10-96
		AU-A-	6730394	27-01-95
		BR-A-	9402813	04-07-95
		CA-A-	2128169	16-01-95
		ZA-A-	9405209	15-01-96

EP-A-0423894	24-04-91	AU-B-	638058	17-06-93
		AU-A-	6374190	18-04-91
		CA-A-	2027644	17-04-91
		GR-B-	1000962	16-03-93
		JP-A-	3185182	13-08-91
		JP-B-	6104956	21-12-94
		US-A-	5133885	28-07-92

EP-A-0443313	28-08-91	JP-A-	3269168	29-11-91
		JP-A-	4041775	12-02-92
		DE-D-	69101456	28-04-94
		DE-T-	69101456	14-07-94
		ES-T-	2062574	16-12-94
		HK-A-	152595	29-09-95

EP-A-0243735	04-11-87	DE-A-	3612479	15-10-87
		JP-A-	62243877	24-10-87
