ABSTRACT: Fabric softener compositions which are compatible with anionic and nonionic detergents, and methods of their preparation and use are disclosed. The softening agent of the compositions comprises certain combinations of three particular types of quaternary ammonium compounds as, for example, the combination of about 25 percent dimethyl diphenylstearylammonium chloride, 30-45 percent dimethyl hydrogenated tallow; C₁₇₋₂₆ sec-alkyl ammonium chloride and 45-30 percent dimethyl dihydrogenated tallow ammonium chloride.
This invention relates generally to laundry products and more particularly to compositions comprising particular proportions of certain quaternary ammonium compounds, which have utility as cationic fabric softeners in industrial and household applications. This invention is also concerned with methods of preparing such compositions and of softening fabrics wherein compositions of this invention are applied to the fabrics.

In the use of cationic fabric softeners, usually comprising the di-long chain alkyl quaternary ammonium compounds such as dimethyl dihydrogenated tallow ammonium chloride, care must be taken to avoid contact of the softener with anionic soaps and anionic detergents and builders generally used in washing fabric. Cationic softeners are generally not compatible with such materials and may be precipitated or rendered inactivated by contact with them. It has been estimated that over 50 percent of the potential consumer fabric softener market is thereby lost through the resulting necessity of adding the softener to the rinse cycle instead of to the wash cycle along with the cleansing agents; e.g. the soaps, detergents, builders, and the like. A second problem encountered in the use of known cationic fabric softeners is that the fabric may tend to resist the absorption of water after repeated applications (even though there are several intervening washings of the fabric), and the "rewet" property of the fabric can be drastically hindered. This problem is important where water absorption is desired, such as with diapers. Further, when a second material is added to an effective cationic softener, such as to the dimethyl dihydrogenated tallow ammonium chloride, it is generally found that the second material does not aid the quaternary in its function as a softening agent but in effect constitutes waste material so far as softening is concerned.

Therefore, it is an object of this invention to overcome the above disadvantages and to provide cationic softener compositions which provide highly desirable softening in the wash cycle during laundering of fabric. Another object is to provide softener compositions yielding such desirable side effects as reducing static or synthetic fabrics, reducing wrinkling of treated fabrics, and not adversely affecting rewet properties of the treated fabric or detergent and whiteness retention of fabric. Still another object is to provide methods of preparing and using such softener compositions. These and other objects and advantages of our invention will in part be obvious and will in part appear from a consideration of the following description.

The objects of the invention and others are achieved by a fabric softening composition comprising about 10 to 20 percent by weight of fabric-softening agents which comprise the combination, by weight based on the total weight of fabric-softening agents present in the composition, of: (A) about 25 percent diarylalkyl quaternary ammonium compounds; (B) from 1 to 75 percent mixed di-long chain alkyl quaternary ammonium compounds; and (C) from 74 to 1 percent dialkyl quaternary ammonium compounds. These combinations of quaternaries can be readily dispersed in warm water. They form stable dispersions, which show little or no tendency to precipitate, in aqueous solutions of anionic and/or nonionic detergents and the like materials. Furthermore, when fabrics are laundered with the compositions and a detergents amount of detergent, they are effectively not only washed by the detergent, but also softened by the composition.

A further illustrative, and even more specific, embodiment of the fabric-softening agents of our compositions is the combination comprising by weight about 25 percent dimethyl diphenylstearyl ammonium chloride; from 1 to 74 percent dimethyl mixed-dialkyl (hydrogenated tallow:secondary-alkyl \((C_n-C_m)\) ammonium chloride; and from 74 to 1 percent dimethyl dihydrogenated tallow ammonium chloride. The quaternaries may be combined by admixing the individually formed quaternaries, or by forming a blend of the quaternaries formed in situ by quaternizing the appropriate proportions of precursor chemicals.

A highly preferred specific imaginative embodiment of the fabric softening agent comprises, by weight, about 25 percent dimethyl diphenylestearyl ammonium chloride, 30-45 percent and particularly about 35 percent dimethyl mixed dialkyl \((\text{hydrogenated tallow:secondary-alkyl } (C_n-C_m))\) ammonium chloride, and 45-50 percent and particularly toward about 35 percent dimethyl dihydrogenated tallow ammonium chloride.

It can be seen from the foregoing that the softening compositions of this invention represent a refined balance of quaternaries combined in specific manners in order to produce a composition giving optimum results.

The quaternary compound types which are combined in specific ratios for use in this invention can be placed into three general classes as follows.

A. Diarylalkyl Quaternary Ammonium Compounds

This class of useful quaternaries has the following general formula:

\[
\begin{array}{c}
R_1-N-R_2 \\
R_1-\text{CH}-(\text{CH}_2)_m-\text{CH}-\text{CH}-(\text{CH}_2)_n-\text{CH}-
\end{array}
\]

wherein \(R_1\) is selected from the group consisting of phenyl, naphthyl, tolyl, anisyl, and xyllyl; \(R_2\) is selected from the group consisting of lower alkyl radicals containing from one to three carbon atoms and \(-(\text{CH}_2)_n\) where \(n\) is an integer from 0 to 10; A is an anion such as a halogen, a nitrate, a sulfate such as methyl sulfate or ethyl sulfate, a phosphate, an acetate, and the like; and \(x\) and \(y\) are each integers from 0 to 19 whose sum is an integer ranging from 5 to 19. Examples of such quaternaries are set forth in copending application Ser. No. 500,203 filed Oct. 21, 1965, now U.S. Pat. No. 3,444,200. Specific examples of quaternaries coming within the foregoing formula that are suitable for use in our compositions include dimethyl di(naphthylacetadetyl) ammonium chloride, dimethyl di(naphthylacetadetyl) ammonium chloride, dimethyl di(anisylacetadetyl) ammonium chloride, and dimethyl di(phenylacetadetyl) ammonium chloride is especially desirable.

B. Mixed-Dialkyl Quaternary Ammonium Compounds

These quaternaries are of the general formula:

\[
\begin{array}{c}
R_1-N-R_2 \\
R_1-\text{CH}-(\text{CH}_2)_m-\text{CH}-
\end{array}
\]

wherein \(R_1\) and \(R_2\) are each different or asymmetrical long chain alkyl radicals containing from eight to 24 carbon atoms; and \(R_1\) and \(R_2\) are as defined hereinabove. Suitable quaternaries of this class are described in copending application filed Feb. 29, 1968, Ser. No. 709,210 by Charles S. Wilhelmy et al., and titled QUATERNARY AMMONIUM SALTS OF MIXED AMINES, METHOD OF THEIR PREPARATION, AND THEIR USE (Case 4926/5042). The Canadian counterpart of the preceding application has issued in Canada as Canadian Patent 866,208. Desirable quaternaries of this class for use in the invention include those where \(R_1\) is selected from the group consisting of alkyl and \-(\text{CH}_2)_n\) where \(n\) is an integer from 1 to 5, and \(A\) is chloride. \(R_1\) and \(R_2\) may be straight or branched chain alkyl such as n-alkyl or secondary-alkyl, saturated or unsaturated alkyl and may be unsubstituted or substituted with relatively unreactive aryl groups such as phenyl, naphthyl, tolyl, anisyl, and the like. Examples of preferred quaternaries of this class include dimethyl hydrogenated tallow: \((C_{11}-C_{14})\)-secondary-alkyl ammonium
chloride, dimethyl hydrogenated tallow: coco ammonium chloride, methyl beta-hydroxyethoxyethyl hydrogenated tallow: \((C_{11}-C_{13})\)-secondary -alkyl ammonium chloride, bis(2-hydroxyethyl) hydrogenated tallow: \((C_{11}-C_{13})\)-secondary -alkyl ammonium chloride, dimethyl phenylethyl: hydrogenated tallow ammonium chloride.

C. Dialkyl Quaternary Ammonium Compounds

Quaternary ammonium compounds of this type that are useful in the present invention may be represented by the formula:

\[
\begin{array}{c}
R_1\setminus R_2 \\
\setminus R_3 \\
\setminus R_4
\end{array}
\]

wherein \(R_1\) and \(R_2\) are as defined hereinabove; and each \(R_3\) represents a long chain hydrocarbon derived from a fatty acid, usually having from eight to 24 carbon atoms and preferably 16 to 22 carbon atoms. Any known type of rinse added cationic softener such as quaternized imidazolines and/or amido-amine may be used to comprise component (C).

In using 75 percent active softening agents of this invention as fabric softeners in aqueous solutions, from 0.01 to 0.75 percent by weight, and preferably about 0.2 percent, is desirable for wash water addition. They may also be added to rinse water, and here 0.1 to 0.5 percent by weight may be used with about 0.1 percent being especially desirable. The percent by weight of softening agent is based on the weight of fabric to be treated, and thus a concentration of about 0.2 percent is about 5-7 grams per 6 to 7 pounds of fabric to be treated.

In selling softener formulations to the consumer, and aqueous concentration of about 1 to 20 percent by weight of the softener is generally utilized. Similar formulations for the composition of this invention may also be utilized for retail sale.

The composition of the invention may be combined with a wide range of detergent concentrations, depending generally upon the particular detergents used and the degree of cleansing effect desired. Conventionally used detergents and concentrations thereof, e.g., as recommended by detergent manufacturers, may be employed. From 0.1-0.5 percent in solution is preferred.

Our cationic softener composition is compatible with conventional soaps, synthetic detergents of the anionic and nonionic types, and mixtures thereof. Apparently the compatibility is due to the proportioning of the three different classes of quaternaries, particularly with regard to having about 25 percent dialkyl quaternary present. It appears that the aryIated constituents thereof provide detergent compatibility while the branch chain constituent gives linking compatibility between the two other quaternaries which provide the major softening and compatibility effects. About 25 percent proportion of dialkyl quaternary is desirable to achieve these effects.

The suitable conventional soaps may be described as the water-soluble, ammonium or alcali metal or organic base salts of various fatty acids having about from 12 to 18 carbon atoms. Suitable anionic synthetics may be described as those detergents having pronounced cleansing power and including in their molecular structure an alkyl radical containing from six to 18 carbon atoms and a sulfonic acid or sulfuric acid ester radical. Organic base, ammonium, sodium, or potassium salts of the anionic detergents may be used. The main types of detergents falling within this class are the alkylaryl sulfonates, such as sodium or potassium dodecylbenzene sulfonate, sodium or potassium octylphenyl sulfonate; the alkyl sulfates such as sodium or potassium salts of dodecyl, hexadecyl and octadecyl sulfates; the sulfonated fatty acid amines, such as sodium or potassium salts of the oleic acid amide of methyltaurine; and the sulfonated monoglycerides, such as the monococonut fatty acid ester of 1,2-hydroxypropylene-3-sodium sulfonate. Of this class, linear alkyl groups are especially desirable because of their biodegradable features; and preferably they contain 12 to 14 carbon atoms in their alkyl group, such as dodecylbenzene sulfonate or triethylene sulfonate. Useful nonionic detergents may be described as those detergents which do not ionize in solution, but owe their water solubility to nonionizing polar groups such as hydroxyl or ether linkages. The main types of detergents falling within this category are the polyoxyethylene ethers of the higher fatty alcohols and alkyl phenols; the polyethylene glycols of fatty acids; fatty alkanolamide condensation products; fatty acid ethylene oxide condensation products; condensation products of ethylene oxide and a fatty acid ether of a polyhydric alcohol or sugar; and the detergents prepared by heating together a higher fatty acid with an alkanolamine, e.g., mono-, di-, and triethanolamine; and the like.

The softener composition may contain, in addition, any of the usual optional ingredients such as dyes, perfumes, brighteners, and other optional additives. Any normally used laundry aids such as bleach, chlorine, oxygen, and water softeners may also be employed. No additional rewet agent is necessary, but may be employed.

A typical formulation of a softener of the invention, which may be added along with a heavy duty detergent to the wash cycle, is:

- **Softening agent**: (75% active)
  - 15.0% 25% dimethyl diphenylethyl ammonium chloride
  - 11.2% active
- **Sodium chloride**: about 0.1% Acetic acid or equivalent: 0.6% Water: qs Brighteners, color, and perfumes: qs

This formulation may preferably be added at a concentration of 0.2 percent by weight on the basis of the weight of the fabric, or about 5–7 grams of active material for an average 6–7 pound load of fabric. The formulation may be prepared by heating the softening agent to about 140°F. until it becomes a clear liquid, heating dilution water to about 140°F. and adding to the water first one-half of the salt and then the softening agent, then mixing to disperse while adding sufficient salt to thin to desired viscosity, add acid and color, and finally cool to the composition and add perfume.

This invention is further illustrated by the following specific examples, which are not to be construed in any way or manner as imposing limitations upon the scope of the present invention and the appended claims.

**EXAMPLE 1**

The effects of a 75 percent active combination of quaternary ammonium compounds of the invention when employed with four representative detergents was evaluated. The combination of quaternary ammonium compounds was:

1. about 25 percent dimethyl diphenylethyl ammonium chloride
2. 20–45 percent dimethyl hydrogenated tallow: \((C_{11}-C_{13})\)-sec-alkyl ammonium chloride, and
3. 45–30 percent dimethyl dihydrogenated tallow ammonium chloride.

The four detergents were:
1. built alkyl aryl sulfonate
2. built alkyl aryl sulfonate plus sodium soap
3. built alkyl sulfonate plus alkyl sulfate, and
4. built nonionic.

Concentrations of the softener combination of the invention were 0.1 percent by weight basis the fabric for rinse cycle addition, and 0.2 percent by weight basis the fabric for wash...
cycle addition. The concentration of the particular detergent used in the wash cycle was 0.2 percent. Each evaluation which was repeated 10 times, comprised a laundering procedure of introducing a standard 6-pound bundle into a top-loading automatic washer and washing for 12 minutes in water of 135 p.p.m. hardness at 140° F. Softening was determined by panel preference; rewet by wicking test procedure; detergency by reflectometer readings of soiled cloth; and whiteness retention and soil removal were determined by test cloths in the standard bundles.

Representative softening ratings as a percent of panel preference are set forth in Table I.

### TABLE I

<table>
<thead>
<tr>
<th>Detergent</th>
<th>Softener Preference</th>
<th>% Component of Softener of the invention as set forth in example I heretoforeabove</th>
<th>% Preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Control</td>
<td>-</td>
<td>-</td>
<td>0.0%</td>
</tr>
<tr>
<td><strong>Known Softener Rinse</strong>*</td>
<td><strong>Dimethyl dihydrogenated tallow ammonium chloride</strong>*</td>
<td>-</td>
<td>99.9%</td>
</tr>
<tr>
<td><strong>Untreated Control</strong></td>
<td><strong>Dimethyl dihydrogenated tallow ammonium chloride</strong>*</td>
<td>-</td>
<td>99.9%</td>
</tr>
</tbody>
</table>

*0.1% added on weight basis fabric
**0.2% added on weight basis fabric
***0.1% added on weight basis fabric

Table II sets forth the softening preferences of other combinations of the quaternary ammonium compounds of the invention.

### TABLE II

<table>
<thead>
<tr>
<th>Softener</th>
<th>% Preference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Control</td>
<td>-</td>
</tr>
<tr>
<td><strong>Softener of the invention</strong></td>
<td><strong>62.0%</strong></td>
</tr>
<tr>
<td>Dimethyl dihydrogenated tallow ammonium chloride</td>
<td><strong>99.9%</strong></td>
</tr>
</tbody>
</table>

An Ethoxylated Softener of the invention:

- 25% bis-(2-hydroxyethyl) phenylsinearyl ammonium chloride
- 50% bis-(2-hydroxyethyl) mixed hydroxyethyl tallow (C_{12-14}) succ-alkyl ammonium chloride
- 25% dimethyl dihydrogenated tallow ammonium chloride

untreated control

In the standard wicking test, capillary rise of a Kiton Red dye solution on a 1%-inch strip of Curity Diaper from the standard bundle is measured at 5-minute intervals over a 30-minute period. A softening agent is considered to have acceptable rewet properties if the rate of wetting is at least approximately 6.5-7.5 cm. after 30 minutes. In general, the combination of quaternaries of the invention was acceptable. The combination of the invention when wash-added to the built alkyl aryl sulfonate plus alkyl sulfate detergent exhibited clearly superior rewet in comparison to the same combination when rinse-added and also to dimethyl dihydrogenated tallow ammonium chloride when rinse cycle added.

In the detergency rating evaluations, it is generally accepted that all softeners, rinse-added or wash-added, lessen detergency. The rinse-added softener of the invention showed only a slight decrease from a control without softener, and the wash-added softener of the invention was only slightly lower. This reduction in detergency becomes less significant in light of the soil removal and whiteness retention evaluations.

Soil removal and whiteness retention were determined on standard soil test cloths included in family laundry bundles. These evaluations were augmented by observations and comments from consumer test panel evaluations as follows: the softener was added to the water containing detergent prior to adding the clothes or after the agitator had begun. The amount of detergent used was determined by manufacture's direction: suds level for high-sudsing detergents, and empirically for the low suders. In these evaluations, detergency was comparable whether the known softener dimethyl dihydrogenated tallow ammonium chloride was used in the rinse cycle or whether the softener combination of the invention was used in the wash cycle. Detergency reduction by the combination of the invention was within less than 10 percent of that by most rinse-added softeners. The whiteness retention was not affected by either rinse or wash-added softeners when the detergent was the built alkyl aryl sulfonate plus alkyl sulfate. No important differences were obtained with the other detergent systems.

In addition, the softener combination of the invention was evaluated for sanitizing properties. A quantitative evaluation for antibacterial properties of treated cloths was run according to AATCC Method 100–1961-T, using Staphylococcus aureus FDA Strain No. 209. Table III sets forth the percent reduction of incubated bacterial population by the sanitizing action of the softeners under this method and also in cold water washing with the built alkyl aryl sulfonate plus sodium soap detergent.

### TABLE III

<table>
<thead>
<tr>
<th>Bacterial Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Control</td>
</tr>
<tr>
<td>Dimethyl dihydrogenated tallow ammonium chloride</td>
</tr>
<tr>
<td>Softener of the invention</td>
</tr>
</tbody>
</table>

Cold water washing: reduction between wash cycle to rinse cycle

Untreated | 87.1% |
Softener of the invention | 99.9% |

While this invention has been described with respect to specific embodiments and preferred quaternary ammonium fabric softener compositions, it is not so limited; and it is to be understood that variations and modifications thereof, obvious to those skilled in the art, may be made without departing from the spirit or scope of this invention.

What is claimed is:

1. A fabric softener concentrate composition compatible with detergents in the wash waters of fabric during laundering, said composition consisting essentially of:
   - about 25 weight percent of a dialkyl quaternary ammonium compound having the formula...
wherein R is selected from the group consisting of phenyl, naphthyl, tolyl, anisyl and xylyl, R2 is selected from the group consisting of alkyl radicals having one to three carbon atoms and -(CH2CH2O)H wherein n is an integer of 1 to 10, x and y are integers having a sum of 5 to 19, and A is an anion; from 1 to about 74 weight percent of a mixed-dialkyl quaternary ammonium compound having the formula

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \quad \text{N}^- \quad \text{R}_1 \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

wherein R1 and R2 are different and each are mixtures of radicals selected from the group consisting of n-alkyl and secondary-alkyl radicals having eight to 24 carbon atoms, R3 and A are as defined above; and

from 1 to about 74 weight percent of a dialkyl quaternary ammonium compound having the formula

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \quad \text{N}^- \quad \text{R}_1 \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

wherein R1 is an alkyl group having eight to 24 carbon atoms, R3 and A are as defined above.

2. The composition of claim 1 wherein said mixed-dialkyl quaternary ammonium compound and said dialkyl quaternary ammonium compound are each present in about 30 to 45 weight percent.

3. The composition of claim 1 in which R3 is methyl.

4. The composition of claim 3 in which said dialkyl quaternary ammonium compound is dimethyl diphenyl stearyl ammonium chloride.

5. The composition of claim 3 in which R3 is hydrogenated tallow and R4 is secondary-alkyl (C12-C14).

6. The composition of claim 3 in which R4 is hydrogenated tallow.

7. A fabric softening composition compatible with detergents in the wash waters of fabrics during laundering consisting essentially of about 1 to 20 wt. percent of a fabric softener concentrate in aqueous solution, said fabric softener concentrate consisting essentially of:

- about 25 weight percent of a dialkyl quaternary ammonium compound having the formula

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \quad \text{N}^- \quad \text{R}_1 \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

wherein R is selected from the group consisting of phenyl, naphthyl, tolyl, anisyl and xylyl, R2 is selected from the group consisting of alkyl radicals having one to three carbon atoms and -(CH2CH2O)H wherein n is an integer of 1 to 10, x and y are integers having a sum of 5 to 19, and A is an anion; from 1 to about 74 weight percent of a mixed-dialkyl quaternary ammonium compound having the formula

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \quad \text{N}^- \quad \text{R}_1 \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

wherein R1 and R2 are different and each are mixtures of radicals selected from the group consisting of n-alkyl and secondary-alkyl radicals having eight to 24 carbon atoms, R3 and A are as defined above; and

9. A wash water for fabric consisting essentially of water an effective quantity of a detergent selected from the group consisting of organic anionic and nonionic detergent and about 0.01 to 0.5 wt. percent based upon the fabric being washed of a softener composition consisting essentially of:

- about 25 weight percent of a dialkyl quaternary ammonium compound having the formula

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \quad \text{N}^- \quad \text{R}_1 \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

wherein R is selected from the group consisting of phenyl, naphthyl, tolyl, anisyl and xylyl, R2 is selected from the group consisting of alkyl radicals having one to three carbon atoms and -(CH2CH2O)H wherein n is an integer of 1 to 10, x and y are integers having a sum of 5 to 19, and A is an anion; from 1 to about 74 weight percent of a mixed-dialkyl quaternary ammonium compound having the formula

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \quad \text{N}^- \quad \text{R}_1 \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_1 & \quad \text{R}_2 \\
\end{align*}
\]

wherein R1 is a alkyl group having eight to 24 carbon atoms, R3 and A are as defined above.
wherein \( R_1 \) and \( R_2 \) are different and each are mixtures of radicals selected from the group consisting of n-alkyl and secondary-alkyl radicals having eight to 24 carbon atoms, \( R_3 \) and \( A \) are as defined above; and from 1 to about 74 weight percent of a dialkyl quaternary ammonium compound having the formula

\[
\left[ \begin{array}{c}
R_4 \\
R_1-N-R_3 \\
R_2 \end{array} \right] [A^-]
\]

wherein \( R_4 \) is a alkyl group having eight to 24 carbon atoms, \( R_3 \) and \( A \) are as defined above.