(54) Title: RINSE ADDED FABRIC SOFTENING COMPOSITIONS AND METHOD OF USE FOR THE DELIVERY OF FRAGRANCE PRECURSORS

(57) Abstract

Rinse added fabric softening compositions containing pro-fragrant acetics or ketals which hydrolyze upon exposure of surfaces rinsed in solution of said compositions to a reduction in pH, thereby releasing a fragrance which is characteristic of one or more of the hydrolysis products.
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RINSE ADDED FABRIC SOFTENING COMPOSITIONS AND METHOD OF USE FOR THE DELIVERY OF FRAGRANCE PRECURSORS

FIELD OF THE INVENTION

The present invention relates to rinse added fabric softening compositions containing acetal and ketal pro-fragrance compounds and methods for accomplishing the delivery of such organic pro-fragrance compounds to textile articles and other surfaces rinsed with said compositions. More particularly, the invention relates to rinse added fabric softening compositions in which there is a delayed release of fragrances from surfaces rinsed in an aqueous bath in the presence of conventional fabric softening ingredients. The fragrance is released in fragrance-active form when the rinsed surface is subsequently contacted with a lower pH environment such as contact with water, carbon dioxide gas, humid air, or the like.

BACKGROUND OF THE INVENTION

Most consumers have come to expect scented laundry products and to expect that fabrics which have been laundered to also have a pleasing fragrance. It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carry-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Fragrance materials are often very costly and their inefficient use in rinse added fabric softener compositions and ineffective delivery to fabrics from the rinse results in a very high cost to both consumers and fabric softener manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in fabric softener products, especially for improvement in the provision of long-lasting fragrance to the rinsed fabrics.
Acetals and ketals have long been known in perfumery. See Steffen Arctander, "Perfume and Flavor Chemicals", Arctander, N.J., 1969. The majority of these are methyl and ethyl types, and molecular weights may range widely. See, for example, Arctander abstract numbers 6, 11, 210, 651, 689, 1697, 1702, 2480, 2478. For 2478, which is phenylacetaldehyde dicitronellyl acetal, molecular weight 414.7, Arctander reports "... and it is not exaggerated to say that this acetal is practically abandoned and obsolete in today's perfumery". For 2480, which is phenylacetaldehyde digeranyl acetal, Arctander reports "the title material does not offer substantial advantages or unique odor type and it may be considered of little more than academic interest today". This latter material was still commercially available in 1992 as ROSETAL A (Catalogue, IFF).

Carrier mechanisms for perfume delivery, such as by encapsulation, have been taught in the prior art. See for example, U.S. 5,188,753.

U.S. Patent 5,378,468, Suffis et al, issued Jan. 3, 1995 describes specific types of personal care compositions, such as deodorant sticks, comprising assertedly "body-activated" fragrances. The term apparently refers to the previously known tendency of materials such as acetals derived from fragrance alcohols to hydrolyze under acidic pH conditions thereby releasing fragrance. See, for example, U.S. 3,932,520, Hoffman, issued January 13, 1976.

Factors affecting substantivity of fragrance materials on fabrics are discussed in Estcher et al. JAOCS 71 p. 31-40 (1994).

The selected potential fragrance materials described by Suffis et al include particular acetals and ketals, exemplified by propylene glycol vanillin acetal. The materials exemplified apparently are rather hydrophilic short chain alcohol or diol derivatives of fragrance aldehydes and upon hydrolysis, deliver one mole of the aldehyde per mole of the potential fragrance material. The present inventors believe that short chain hydrophilic acetal materials are incompatible with acidic rinse added fabric softening compositions as described hereinafter. The Suffis et al development is designed to be incorporated with a personal care product vehicle, resulting in clear deodorant sticks and the like.

For rinse added fabric softening use, it is important that rather hydrophobic pro-fragrant compounds be used in order to enhance deposition onto surfaces in the wash solution and retention on the washed surface during rinsing. In Suffis et al, the compositions containing the potential fragrance materials are applied directly to the substrate (i.e. skin); therefore, the deposition problems resulting from dilution, rinsing, etc. are not at issue.
Acetals and ketals are conventionally known to be stable in basic, and unstable in acidic media. Indeed, acetals are frequently used in chemical synthesis as protecting groups for alcohols and aldehydes in basic pH systems. See, for example, March, Advanced Organic Chemistry, 3rd Ed., pp. 329-332 (Wiley, N.Y., 1985). When used as a protecting group, subsequent treatment of an acetal under acidic conditions liberates the parent alcohol and aldehyde.

It has now been discovered that pro-fragrance and pro-accord acetal and ketal compounds are surprisingly stable in the context of rinse added fabric softening compositions. While as not to be limited by theory, it is believed that this surprising enhancement in stability results from an interaction between the acetal pro-perfume and the fabric softening agents described herein. Specifically, it is believed that the hydrophobic pro-perfume associates with the vesicles contained in the product and is thereby protected from the acidic aqueous (continuous) phase of the product.

**SUMMARY OF THE INVENTION**

The present invention meets the aforementioned needs in that it has been surprisingly discovered that acetals and ketals are capable of imparting residual fragrances to surfaces rinsed with aqueous solutions of said compounds. In addition, it has been surprisingly discovered that more than one perfume or fragrance raw material (accord) can be released from one precursor pro-accord acetal or ketal molecule. The pro-fragrance acetal and ketal compounds described herein comprises fragrances in a stable, releasable "pro-fragrance" or "pro-accord" form. The compounds can be formulated into any product which is deliverable to fabric via the laundry rinse cycle, directly or indirectly, provided the product pH, carriers and adjunct materials are compatible with the pro-fragrance or pro-accord chemical form. Once in contact with fabric, the pro-accord is converted to the fragrance raw material mixture at a rate which provides extended fragrance benefits. The fragrance delivery systems of the present invention can be a mixture of any number of pro-fragrances or pro-accords and can cover any fragrance "characteristic" or desired fragrance volatility.

The first aspect of the present invention relates to compositions which are applied to fabric, said compositions having increased fragrance retention and fragrance longevity. The suitable compositions of the present invention are rinse added fabric softening compositions, comprising:

a) from about 0.01% to about 15% of pro-accord having the formula:
\[
\begin{align*}
R^1 & \\
R & -C-OR^2 \\
& OR^3
\end{align*}
\]
wherein \( R \) is \( C_3-C_{20} \) linear alkyl, \( C_4-C_{20} \) branched alkyl, \( C_6-C_{20} \) cyclic alkyl, \( C_6-C_{20} \) branched cyclic alkyl, \( C_6-C_{20} \) linear alkenyl, \( C_6-C_{20} \) branched alkenyl, \( C_6-C_{20} \) cyclic alkenyl, \( C_6-C_{20} \) substituted or unsubstituted aryl, and mixtures thereof; \( R^1 \) is hydrogen or \( R \); \( R^2 \) and \( R^3 \) are each independently selected from the group consisting of \( C_5-C_{20} \) linear alkyl, \( C_4-C_{20} \) branched alkyl, \( C_6-C_{20} \) cyclic alkyl, \( C_6-C_{20} \) branched cyclic alkyl, \( C_6-C_{20} \) linear alkenyl, \( C_6-C_{20} \) branched alkenyl, \( C_6-C_{20} \) cyclic alkenyl, \( C_6-C_{20} \) branched cyclic alkenyl, \( C_6-C_{20} \) aryl, \( C_7-C_{20} \) substituted aryl, and mixtures thereof; and

(b) from about 85% to about 99.99%, by weight of the composition, of ingredients useful for formulating fabric softening compositions; wherein said compositions have a neat pH of less than about 6, preferably from about 2.0 to about 4.5, and more preferably from about 2.0 to about 3.5 at 20 °C.

The compositions of the present invention preferably comprise from about 1% to about 80%, preferably from about 5 to about 50% of cationic fabric softening compound. Dilute liquid compositions of the present invention preferably contain from about 5% to about 15% of cationic fabric softening compound. Concentrated liquid compositions of the present invention preferably contain from about 15% to about 50%, more preferably from about 15% to about 35% of cationic fabric softening compound. Preferably, the cationic fabric softening compound is selected from biodegradable quaternary ammonium compounds as described hereinafter.

The present invention also relates to a method for contacting compositions comprising said pro-accord acetals and ketals described hereinbefore with a fabric. Preferred is a method for laundering soiled fabrics, comprising contacting said fabrics with an aqueous medium containing at least about 50 ppm, preferably from about 100 ppm to about 10,000 ppm of a rinse added fabric softening composition according to the above, preferably with agitation. Said method includes the process of treating textiles in a rinse cycle of a washing machine comprising the step of contacting textiles in a washing machine with a fabric softening effective amount of a rinse added fabric softening composition comprising:

(a) from about 0.01% to about 15% by weight, of a pro-accord described herein below; and
(b) from about 85% to about 99.99%, by weight of the composition, of ingredients useful for formulating fabric softening compositions; wherein said composition has a neat pH of less than about 6 at 20 °C.

These and other objects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The rinse added fabric softening compositions of the present invention comprise a fragrance delivery system which lays down one or more acetal or ketal pro-fragrances or pro-accords onto fabric during usage. Because the pro-accords of the present invention generally have a higher molecular weight than uncombined fragrance raw materials and other "pro-fragrance-type" compounds (i.e. pro-fragrances which only deliver a single equivalent of a fragrance raw material), they are a means for effectively delivering two or more fragrance raw materials in a manner which results in enhanced longevity of the fragrance raw materials on fabric.

Fragrances or scents are known by those skilled in the art of fragrances and perfumes as single fragrance raw material compounds while in mixtures of fragrance raw materials are known as "accords". The term "accord" as used herein is defined as "a mixture of two or more 'fragrance raw materials' which are artfully combined to impart a pleasurable scent, odor, essence, or fragrance characteristic". For the purposes of the present invention "fragrance raw materials" are herein defined as compounds having a molecular weight of at least 100 g/mol and which are useful in imparting an odor, fragrance, essence, or scent either alone or in combination with other "fragrance raw materials".

Typically "fragrance raw materials" comprise inter alia alcohols, ketones, aldehydes, esters, ethers, nitriles, and cyclic and acyclic alkenes such as terpenes. A listing of common "fragrance raw materials" can be found in various reference sources, for example, "Perfume and Flavor Chemicals", Vols. I and II; Steffen Arctander Allured Pub. Co. (1994) and "Perfumes: Art, Science and Technology"; Müller, P. M. and Lamparsky, D., Blackie Academic and Professional (1994) both incorporated herein by reference.
For example, but not by way of limitation, the fragrances or fragrance accords released by the acetals and ketals of the present invention have a "heart", "character", or "note" which is described as *inter alia* rose, jasmin, lilac, lily of the valley, violet, orange, peach, watermelon, and lemon. Accords may be further "modified" or "twisted" by the use of modifier top or middle notes which, as an additional benefit afforded by the present invention, can be incorporated into the pro-accord. For example, a "rose essence" may be combined with a "green" modifier to "shift the fragrance accord character".

**Pro-Fragrances and Pro-Accords**

The pro-fragrances of the present invention are acetal or ketal which deliver a single fragrance raw material. The pro-accords of the present invention deliver two or more fragrance raw materials. The fragrance raw materials selected to comprise the final released fragrance or accord are converted into a chemical species or reactive chemical form which releases the fragrance raw materials when the pro-fragrance or pro-accord is subjected to the proper conditions which trigger their release. The chemically modified forms of the fragrance raw materials in their releasable-form are the acetal and ketal "pro-fragrances" or "pro-accords" of the present invention.

**Molecular Weight**

The pro-fragrances and pro-accords of the present invention generally have a molecular weight of at least 300 g/mol, preferably greater than 325 g/mol, more preferably greater than 350 g/mol. It is also a condition of the present invention that the final molecular weight of the pro-accord is at least 2 times, preferably at least 2.25 times, more preferably 2.5 times, most preferably at least 2.75 times the molecular weight of the lowest fragrance material component.

For the purposes of the present invention, only fragrance raw materials having a molecular weight of at least 100 g/mol are considered "fragrance raw materials" according to the present invention. Therefore, low molecular weight materials *inter alia* methanol, ethanol, methyl acetate, ethyl acetate, and methyl formate which are common components of fragrance accords are excluded from the class of compounds defined herein as "fragrance raw materials". However, the formulator may wish to deliver these lower molecular weight materials (less than a molecular weight of 100 g/mol) as carriers, astringents, diluents, balancers, fixatives, or as other suitable adjunct materials.

By way of illustration and not limitation, the pro-accord di(9-decen-1-yl) 3-(4-tert-butylphenyl)-2-methylpropanal acetal is formed from two equivalents of the alcohol 9-decen-1-ol and one equivalent of the aldehyde 3-(4-tert-butylphenyl)-2-
methylpropanal (p-t-bucinal) which comprise the released binary accord. This pro-
accord has a molecular weight of approximately 499 g/mol. The lowest molecular
weight fragrance raw material which is a component of this pro-accord is 9-decen-1-
ol which has a molecular weight of approximately 156 g/mol. Therefore di(9-decen-
1-yl) 3-(4-tert-butylphenyl)-2-methylpropanal acetal has a molecular weight greater
than 3 times the molecular weight of the lowest molecular weight fragrance raw
material component (9-decen-1-ol) and hence is a most preferred pro-accord.

For the purposes of the present invention substituted or unsubstituted
alkyleneoxy units are defined as moieties having the formula:

\[ R^6 \]
\[ -(CH_2CHO)_x R^5 \]

wherein \( R^5 \) is hydrogen; \( R^6 \) is hydrogen, methyl, ethyl, and mixtures thereof; the
index \( x \) is from 1 to about 20.

For the purposes of the present invention substituted or unsubstituted
alkyleneoxyalkyl are defined as moieties having the formula:

\[ R^6 \]
\[ -(CH_2CHO)_x(CH_2)_y R^5 \]

wherein \( R^5 \) is hydrogen, C\(_1\)-C\(_{18}\) alkyl, C\(_1\)-C\(_4\) alkoxy, and mixtures thereof; \( R^6 \) is
hydrogen, methyl, ethyl, and mixtures thereof; the index \( x \) is from 1 to about 20 and
the index \( y \) is from 2 to about 30.

For the purposes of the present invention substituted or unsubstituted
alkylenearyl units are defined as moieties having the formula:

\[ -(CH_2)_p \]
\[ R^5 \]

wherein \( R^5 \) and \( R^6 \) are each independently hydrogen, hydroxy, C\(_1\)-C\(_4\) alkoxy,
nitrito, halogen, nitro, carboxyl (-\( \text{CHO} \); -\( \text{CO}_2\)H; -\( \text{CO}_2R' \); -CONH\(_2\); -CONHR';
-CONR'\(_2\); wherein \( R' \) is C\(_1\)-C\(_{12}\) linear or branched alkyl), amino, alkylamino, and
mixtures thereof, \( p \) is from 1 to about 34.

For the purposes of the present invention substituted or unsubstituted aryloxy
units are defined as moieties having the formula:
wherein $R^5$ and $R^6$ are each independently hydrogen, hydroxy, $C_1$-$C_4$ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO$_2$H; -CO$_2$R'; -CONH$_2$; -CONHR'; -CONR'$_2$; wherein $R'$ is $C_1$-$C_{12}$ linear or branched alkyl), amino, alkylamino, and mixtures thereof.

For the purposes of the present invention substituted or unsubstituted alkylenoxyaryl units are defined as moieties having the formula:

$$-(CH_2)_qO-\bigg]\quad (1)$$

wherein $R^5$ and $R^6$ are each independently hydrogen, hydroxy, $C_1$-$C_4$ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO$_2$H; -CO$_2$R'; -CONH$_2$; -CONHR'; -CONR'$_2$; wherein $R'$ is $C_1$-$C_{12}$ linear or branched alkyl), amino, alkylamino, and mixtures thereof, $q$ is from 1 to about 34.

For the purposes of the present invention substituted or unsubstituted oxyalkylenearyl units are defined as moieties having the formula:

$$-O(CH_2)_w\bigg]\quad (2)$$

wherein $R^5$ and $R^6$ are each independently hydrogen, hydroxy, $C_1$-$C_4$ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO$_2$H; -CO$_2$R'; -CONH$_2$; -CONHR'; -CONR'$_2$; wherein $R'$ is $C_1$-$C_{12}$ linear or branched alkyl), amino, alkylamino, and mixtures thereof, $w$ is from 1 to about 34.

The pro-fragrances and pro-accords according to the present invention are acetals and ketrals having the formula:

$$R^1$$

R\bigg]\quad (3)$$

OR$_3$
wherein hydrolysis of the acetal or ketal releases one equivalent of aldehyde or ketone and two equivalents of alcohol according to the following scheme:

\[
\begin{align*}
R^1 & \quad \text{R} - \text{C} - \text{OR}^2 \quad \rightarrow \quad \text{R} - \text{C} - \text{R}^1 + \text{R}^2\text{OH} + \text{R}^3\text{OH} \\
& \quad \text{R} - \text{C} - \text{OR}^3
\end{align*}
\]

wherein R is C₁₋C₂₀ linear alkyl, C₄₋C₂₀ branched alkyl, C₆₋C₂₀ cyclic alkyl, C₆₋C₂₀ branched cyclic alkyl, C₆₋C₂₀ linear alkenyl, C₆₋C₂₀ branched alkenyl, C₆₋C₂₀ cyclic alkenyl, C₆₋C₂₀ branched cyclic alkenyl, C₆₋C₂₀ substituted or unsubstituted aryl, preferably the moieties which substitute the aryl units are alkyl moieties, and mixtures thereof. R¹ is hydrogen, R, or in the case wherein the pro-fragrance or pro-accord is a ketal, R and R¹ can be taken together to form a ring. R² and R³ are independently selected from the group consisting of C₅₋C₂₀ linear, branched, or substituted alkyl; C₄₋C₂₀ linear, branched, or substituted alkenyl; C₅₋C₂₀ substituted or unsubstituted cyclic alkyl; C₆₋C₂₀ substituted or unsubstituted aryl, C₂₋C₄₀ substituted or unsubstituted alkyleneoxy; C₃₋C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆₋C₄₀ substituted or unsubstituted alkyleneary; C₆₋C₃₂ substituted or unsubstituted aryloxy; C₆₋C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆₋C₄₀ oxyalkylenearyl; and mixtures thereof. By the term "substituted" herein is meant "compatible moieties which replace a hydrogen atom". Non-limiting examples of substituents are hydroxy, nitro, halogen, nitro, carboxyl (-CHO; -CO₂H; -CO₂R'; -CONH₂; -CONHR'; -CONR'₂; wherein R' is C₁₋C₁₂ linear or branched alkyl), amino, C₁₋C₁₂ mono- and dialkylamino, and mixtures thereof.

Non-limiting examples of R² and R³ include methyl, 2,4-dimethyl-3-cyclohexene-1-methyl (Floralol), 2,4-dimethyl cyclohexane methyl (Dihydro floralol), 5,6-dimethyl-1-methylethenyl-bicyclo[2.2.1]hept-5-ene-2-methyl (Arbozo1), 2,4,6-trimethyl-3-cyclohexene-1-methyl (Isocyclo geranyl), 4-(1-methylethyl)cyclohexylmethyl (Mayol), α₃,3-trimethyl-2-norbormylmethyl, 1,1-dimethyl-1-(4-methycyclohex-3-enyl)methyl, ethyl, 2-phenylethyl, 2-cyclohexylethyl, 2-(o-methylphenyl)ethyl, 2-(m-methylphenyl)ethyl, 2-(p-methylphenyl)ethyl, 6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethyl (nopyl), 2-(4-methylphenoxy)ethyl, 3,3-dimethyl-Δ²-β-norbormanylethyl, 2-methyl-2-cyclohexylethyl, 1-(4-isopropylcyclohexyl)ethyl, 1-phenyl-1-hydroxyethyl, 1,1-dimethyl-2-phenylethyl, 1,1-dimethyl-2-(4-methylphenyl)ethyl, propyl, 1-phenylpropyl, 3-phenylpropyl, 2-phenylpropyl (Hydrotropic Alcohol), 2-(cyclododecyl)-propan-1-yl (Hydroxyambran), 2,2-dimethyl-3-(3-methylphenyl)propan-1-yl (Majantol), 2-methyl-3-phenylpropyl, 3-phenyl-2-propen-
1-yl (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-yl (methylcinnamyl alcohol), α-n-pentyl-3-phenyl-2-propen-1-yl (α-amylcinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propyl, butyl, 3-methylbutyl, 3-(4-methylcyclohex-3-ene)butyl, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butyl, 2-ethyl-4-(2,2,3-trimethylcyclopent-3-enyl)-2-buten-1-yl, 3-methyl-2-buten-1-yl, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-yl, 3-hydroxy-2-butane, ethyl 3-hydroxybutyrate, 4-phenyl-3-buten-2-yl, 2-methyl-4-phenylbutan-2-yl, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)butan-2-one, penty, cis-3-pentenyl, 3-methylpentyl, 3-methyl-3-penten-1-yl, 2-methyl-4-phenylpentyl (Pamplefleur), 3-methyl-5-phenylpentyl (Phenoxanyl), 2-methyl-5-phenylpentyl, 2-methyl-5-(2,3-dimethyltricyclo-2.2.1.0[2,6)]hept-3-yl)-2-penten-1-yl (santaly), 4-methyl-1-phenyl-2-pentyl, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-yl, 3-methyl-1-phenylpent-3-yl, 1,2-dimethyl-3-(1-methylene)cyclopent-1-yl, 2-isopropyl-4-methyl-2-hexenyl, cis-3-hexen-1-yl, trans-2-hexen-1-yl, 2-isopropenyl-5-methyl-4-hexen-1-yl (Lavandulyl), 2-ethyl-2-prenyl-3-hexenyl (silwanol), 2-ethylhexyl, 1-hydroxymethyl-4-isopropenyl-1-cyclohexenyl (Dihydrocuminy1), 1-methyl-4-isopropenylcyclohex-6-en-2-yl (carvenyl), 6-methyl-3-isopropenylcyclohex-1-yl, 1-methyl-4-isopropenylcyclohex-3-yl, 4-isopropyl-1-methylcyclohex-3-yl, 4-tert-butylcyclohexyl, 2-tert-butylcyclohexyl, 2-tert-butyl-4-methylcyclohexyl, 4-isopropylcyclohexyl, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-yl, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexyl, isobornylcyclohexyl, 3,3,5-trimethylcyclohexyl, 1-methyl-4-isopropylcyclohex-3-yl (menthol), 1,2-dimethyl-3-(1-methylethyl)-cyclohexan-1-yl, heptyl, 2,4-dimethylhept-1-yl, 2,4-dimethyl-2,6-heptadienyl, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-en-1-yl (myrtenyl), 4-methyl-2,4-heptadien-1-yl, 3,4,5,6,6-pentamethyl-2-heptyl, 3,6-dimethyl-3-vinyl-5-hepten-2-yl, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]heptyl, 1,7,7-trimethylbicyclo-[2.2.1]hept-2-yl, 2,6-dimethylhept-2-yl, 2,6,6-trimethylbicyclo[1.3.3]hept-2-yl, octyl, 2-octenyl, 2-methyloctan-2-yl, 2-methyl-6-methylene-7-octen-2-yl (myrcenyl), 7-methyloctan-1-yl, 3,7-dimethyl-6-octenyl, 3,7-dimethyl-7-octenyl, 3,7-dimethyl-6-octen-1-yl (citronellyl), 3,7-dimethyl-2,6-octadien-1-yl (geranyl), 3,7-dimethyl-2,6-octadien-1-yl (neryl), 3,7-dimethyl-1,6-octadien-3-yl (linally), 3,7-dimethyloctan-1-yl (pelagryl), 3,7-dimethyloctan-3-yl (tetrahydropinanyl), 2,4-octadien-1-yl, 3,7-dimethyl-6-octen-3-yl, 2,6-dimethyl-7-octen-2-yl, 2,6-dimethyl-5,7-octadien-2-yl, 4,7-dimethyl-4-vinyl-6-octen-3-yl, 3-methyloctan-3-yl, 2,6-dimethyloctan-2-yl, 2,6-dimethyloctan-3-yl, 3,6-dimethyloctan-3-yl, 2,6-dimethyl-7-octen-2-yl, 2,6-dimethyl-3,5-octadien-2-yl (mug; i), 3-methyl-1-octen-3-yl, 7-
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hydroxy-3,7-dimethyloctanal, 3-nonyl, 6,8-dimethylnonan-2-yl, 3-
(hydroxymethyl)-2-nonane, 2-nonen-1-yl, 2,4-nonadien-1-yl, 2,6-nonadien-1-yl,
cis-6-nonen-1-yl, 3,7-dimethyl-1,6-nonadien-3-yl, decyl, 9-deceny1, 2-benzyl-M-
dioxa-5-yl, 2-decen-1-yl, 2,4-decadien-1-yl, 4-methyl-3-decen-5-yl, 3,7,9-trimethyl-
1,6-decadien-3-yl (isobutyl linallyl), undecyl, 2-undecen-1-yl, 10-undecen-1-yl, 2-
dodecen-1-yl, 2,4-dodecadien-1-yl, 2,7,11-trimethyl-2,6,10-dodecatrien-1-yl
(farnesyl), 3,7,11-trimethyl-1,6,10-dodecatrien-3-yl, 3,7,11,15-tetramethylhexadec-
2-en-1-yl (phytyl), 3,7,11,15-tetramethylhexadec-1-en-3-yl (iso phytol), benzyl, p-
methoxybenzyl (anisy1), para-cymen-7-yl (cuminyl), 4-methylbenzyl, 3,4-
methylenedioxybenzyl, 2-(methyl)carboxy-1-hydroxyphenyl, 2-(benzyl)carboxy-1-
hydroxyphenyl, 2-(cis-3-hexenyl)-carboxy-1-hydroxyphenyl, 2-(n-pentyl)carboxy-1-
hydroxyphenyl, 2-(2-phenylethyl)carboxy-1-hydroxyphenyl, 2-(n-hexyl)carboxy-1-
hydroxyphenyl, 2-methyl-5-isopropyl-1-hydroxyphenyl, 4-ethyl-2-methoxyphenyl,
4-allyl-2-methoxy-1-hydroxyphenyl (eugenyl), 2-methoxy-4-(1-propenyl)-1-
hydroxyphenyl (isoeugenyl), 4-allyl-2,6-dimethoxy-1-hydroxyphenyl, 4-tert-butyl-1-
hydroxyphenyl, 2-ethoxy-4-methyl-1-hydroxyphenyl, 2-methyl-4-vinyl-1-
hydroxyphenyl, 2-isopropyl-5-methyl-1-hydroxyphenyl (thymyl), 2-(isopentyl)-
carboxy-1-hydroxyphenyl, 2-(ethyl)carboxy-1-hydroxyphenyl, 6-(methyl)carboxy-
2,5-dimethyl-1,3-dihydroxyphenyl, 5-methoxy-3-methyl-1-hydroxyphenyl, 2-tert-
butyl-4-methyl-1-hydroxyphenyl, 1-ethoxy-2-hydroxy-4-propenylphenyl, 4-methyl-
1-hydroxyphenyl, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-
hydroxybenzaldehyde, decahydro-2-naphthyl, 2,5,5-trimethyl-octahydro-2-naphthyl,
1,3,3-trimethyl-2-norbornyl (fenchyl), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-
methano-1H-inden-5-yl, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-
inden-5-yl, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuranyl, β-
caryophyllenyl, and mixtures thereof.

**Acetal Releasable Components:** The acetals of the present invention have
two types of releasable components, namely alcohols and aldehydes. Hydrolysis of
an acetal will yield two equivalents of releasable alcohol and one equivalent of
releasable aldehyde. In the case of pro-accords, the released aldehyde, when taken
together with the released fragrance raw material alcohol, forms a fragrance accord.
For example bis(cis-3-hexenyl) vanillin acetal releases the accord vanillin/cis-3-
hexenol.

When $R_1$ is hydrogen the pro-fragrances or pro-accords are capable of
releasing an aldehyde component. Preferred aldehydes which are releasable
components of the acetals of the present invention include but are not limited to
phenylacetaldehyde, p-methyl phenylacetaldehyde, p-isopropyl phenylacetaldehyde,
methylnonyl acetaldehyde, phenylpropanal, 3-(4-t-butylphenyl)-2-methyl propanal (Lilial), 3-(4-t-butylphenyl)-propanal (Bourgeonal), 3-(4-methoxyphenyl)-2-methylpropanal (Canthoxal), 3-(4-isopropylphenyl)-2-methylpropanal (Cymal), 3-(3,4-methylene dioxyphenyl)-2-methylpropanal (Helional), 3-(4-ethylphenyl)-2,2-dimethylpropanal (Floralzone), phenylbutanal, 3-methyl-5-phenylpentanal, hexanal, trans-2-hexenal, cis-hex-3-enal, heptanal, cis-4-heptenal, 2-ethyl-2-heptenal, 2,6-dimethyl-5-heptenal (Melonal), 2,4-heptadienal, octanal, 2-octanal, 3,7-dimethyloctanal, 3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-1,6-octadien-3-al, 3,7-dimethyl-6-octenal, 3,7-dimethyl-7-hydroxyoctan-1-al, nonanal, 6-nonenal, 2,4-nonadienal, 2,6-nonadienal, decanal, 2-methyl decanal, 4-decenal, 9-decenal, 2,4-decadienal, undecanal, 2-methyldecanal, 2-methylundecanal, 2,6,10-trimethyl-9-undecenal (Adoxal), undec-10-enyl aldehyde, undec-8-enanal, dodecanal, tridecanal, tetradecanal, anisaldehyde, bourgeonal, cinnamic aldehyde, α-amyl cinnamaldehyde, α-hexyl cinnamaldehyde, methoxy-cinnamaldehyde, citronellal, hydroxy-citronellal, isocyclocitrail, citronellyl oxyacet-aldehyde, cortexaldehyde, cumminic aldehyde, cyclamen aldehyde, florhydral, heliotropin, hydro tropic aldehyde, lilial, vanillin, ethyl vanillin, benzaldehyde, p-methyl benzaldehyde, 3,4-dimethoxy benzaldehyde, 3- and 4-(4-hydroxy-4-methyl-pentyl)-3-cyclohexene-1-carboxaldehyde (Lyral), 2,4-dimethyl-3-cyclohexene-1-carboxaldehyde (Triplal), 1-methyl-3-(4-methylpentyl)-3-cyclohexencarboxaldehyde (Vernaldehyde), p-methylphenoxyacetaldehyde (Xi aldehyde), and mixtures thereof.

More preferably the aldehydes released by the acetals of the present invention are 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde (Lyral), phenylacetaldehyde, methylnonyl acetaldehyde, 2-phenylpropan-1-al (hydrotropaldehyde), 3-phenylprop-2-en-1-al (cinnamaldehyde), 3-phenyl-2-penty1prop-2-en-1-al (α-amyl cinnamaldehyde), 3-phenyl-2-hexylprop-2-enal (α-hexyl cinnamaldehyde), 3-(4-isopropyl phenyl)-2-methyl propan-1-al (cyc lamaldehyde), 3-(4-ethylphenyl)-2,2-dimethylpropan-1-al (floralzone), 3-(4-tert-buty1phenyl)-2-methyl propanal, 3-(3,4-methylenedioxyphenyl)-2-methyl propan-1-al (helional), 3-(4-ethylphenyl)-2,2-dimethyl propanal, 3-(3-isopropyl phenyl)butan-1-al (flohydral), 2,6-dimethylhept-5-en-1-al (melonal), n-decanal, n-undecanal, n-dodecanal, 3,7-dimethyl-2,6-octadien-1-al (citral), 4-methoxy benzaldehyde (anisaldehyde), 3-methoxy-4-hydroxy benzaldehyde (vanillin), 3-ethoxy-4-hydroxy benzaldehyde (ethyl vanillin), 3,4-methylenedioxy benzaldehyde (heliotropin), 3,4-dimethoxy benzaldehyde

**Ketal Releasable Components**: The kets of the present invention have two types of releasable components, namely alcohols and ketones. Hydrolysis of a ketal
will yield two equivalents of releasable alcohol and one equivalent of releasable ketone. In the case of pro-accords, the released ketone, when taken together with the released fragrance raw material alcohol, forms a fragrance accord. For example bis(linalyl) β-ionone ketal releases the accord linalool/β-ionone.

When R¹ is a moiety as described herein above other than hydrogen, the pro-fragrances or pro-accords are capable of releasing an ketone component. Preferred ketones which are releasable components of the ketals of the present invention include but are not limited to α-damascone, β-damascone, δ-damascone, β-damascenone, muscone, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indenone (cashmeran), cis-jasmone, dihydrojasmone, α-ionone, β-ionone, dihydro-β-ionone, γ-methyl ionone, α-iso-methyl ionone, 4-(3,4-methylenedioxyphenyl)butan-2-one, 4-(4-hydroxyphenyl)butan-2-one, methyl β-naphthyl ketone, methyl cedryl ketone, 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (tonalid), l-carvone, 5-cyclohexadecen-1-one, acetophenone, decaitone, p-hydroxyphenylbutan-2-one, 2-(2-(4-methyl-3-cyclohexenyl-1-yl)propyl[cyclopentan-2-one, 2-sec-butylcyclohexanone, β-dihydro ionone, allyl ionone, α-irone, α-cetone, α-irisone, acetanisole, geranyl acetone, 1-(2-methyl-5-isopropyl-2-cyclohexenyl)-1-propanone, acetyl diisooamylene, methyl cyclocitrone, 4-t-pentyl cyclohexanone, p-t-butylocyclohexanone, α-t-butylcyclohexanone, ethyl amyl ketone, ethyl pentyl ketone, menthone, methyl-7,3-dihydro-2H-1,5-benzoxepine-3-one, fenchone, and mixtures thereof.

More preferably the ketones which are released by the ketals of the present invention are α-damascone, β-damascone, δ-damascone, β-damascenone, muscone, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indenone (cashmeran), cis-jasmone, dihydrojasmonone, α-ionone, β-ionone, dihydro-β-ionone, γ-methyl ionone, α-iso-methyl ionone, 4-(3,4-methylenedioxyphenyl)butan-2-one, 4-(4-hydroxyphenyl)butan-2-one, methyl β-naphthyl ketone, methyl cedryl ketone, 6-acetyl-1,1,2,4,4,7-hexamethyltetrautan (tonalid), l-carvone, 5-cyclohexadecen-1-one, and mixture thereof.

Non-limiting examples of alcohols suitably released by the hydrolysis of the acetals and ketals include methanol, 2,4-dimethyl-3-cyclohexene-1-methanol (Floralol), 2,4-dimethyl cyclohexane methanol (Dihydro floralol), 5,6-dimethyl-1-methylethylbenzylbicyclo[2.2.1]hept-5-ene-2-methanol (Arbozol), 2,4,6-trimethyl-3-cyclohexene-1-methanol (Isocyclo geraniol), 4-(1-methylcyclohexane) (Mayol), α-3,3-trimethyl-2-norborane methanol, 1,1-dimethyl-1-(4-methylcyclohex-3-enyl)methanol, ethanol, 2-phenylethanol, 2-cyclohexyl ethanol, 2-(o-methylphenyl)-ethanol, 2-(m-methylphenyl)ethanol, 2-(p-methylphenyl)ethanol, 6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-ethanol (nopol), 2-(4-methylphenoxy)ethanol,
3,3-dimethyl-\(\Delta^2\)-\(\beta\)-norbornane ethanol, 2-methyl-2-cyclohexylethanol, 1-(4-isopropylcyclohexyl)-ethanol, 1-phenylethanol, 1,1-dimethyl-2-phenylethanol, 1,1-dimethyl-2-(4-methyl-phenyl)ethanol, n-propanol, 2-propanol, 1-phenylpropanol, 3-phenylpropanol, 2-phenylpropanol (Hydrotropic Alcohol), 2-(cyclododecyl)propan-1-ol (Hydroxy-ambran), 2,2-dimethyl-3-(3-methylphenyl)propan-1-ol (Majantol), 2-methyl-3-phenylpropanol, 3-phenyl-2-propen-1-ol (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-ol (methylcinnamyl alcohol), \(\alpha\)-n-pentyl-3-phenyl-2-propen-1-ol (\(\alpha\)-amyl-cinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propanol, n-butanol, 2-butanol, 3-methylbutanol, 3-(4-methylcyclohex-3-ene)butanol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butanol, 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-2-buten-1-ol, 3-methyl-2-buten-1-ol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, 3-hydroxy-2-butanol, ethyl 3-hydroxybutyrate, 4-phenyl-3-buten-2-ol, 2-methyl-4-phenylbutan-2-ol, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)butan-2-one, pentanol, \(\text{cis}\)-3-pentenol, 3-methyl-pentanol, 3-methyl-3-penten-1-ol, 2-methyl-4-phenylpentanol (Pamplefleur), 3-methyl-5-phenylpentanol (Phenoxanol), 2-methyl-5-phenylpentanol, 2-methyl-5-(2,3-dimethyltricyclo[2.2.1.0(2,6)]hept-3-yl)-2-penten-1-ol (santalol), 4-methyl-1-phenyl-2-pentanol, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-ol, 3-methyl-1-phenylpentan-3-ol, 1,2-dimethyl-3-(1-methylethenyl)cyclopentan-1-ol, 2-isopropyl-5-methyl-2-hexenol, \(\text{cis}\)-3-hexen-1-ol, \text{trans}\)-2-hexen-1-ol, 2-isopropenyl-4-methyl-4-hexen-1-ol (Lavandol), 2-ethyl-2-prenyl-3-hexenol, 1-hydroxymethyl-4-isopropenyl-1-cyclohexene (Dihydrocuminal alcohol), 1-methyl-4-isopropenylcyclohex-6-en-2-ol (carvenol), 6-methyl-3-isopropenylcyclohexan-1-ol, 1-methyl-4-isopropenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol, 4-tert-butylcyclohexan-1-ol, 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol, 4-isopropyl-cyclohexan-1-ol, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexanol, isobornylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-4-isopropylcyclohexan-3-ol, 1,2-dimethyl-3-(1-methylethyl)cyclohexan-1-ol, heptanol, 2,4-dimethylheptan-1-ol, 2,4-dimethyl-2,6-heptadienol, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-ene (myrtenol), 4-methyl-2,4-heptadien-1-ol, 3,4,5,6,6-pentamethyl-2-heptanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]heptane, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 2,6-dimethylheptan-2-ol, 2,6,6-trimethylbicyclo[1.3.3]heptan-2-ol, octanol, 2-octenol, 2-methyloctan-2-ol, 2-methyl-6-methylene-7-octen-2-ol (myrtenol), 7-methyloctan-1-ol, 3,7-dimethyl-6-oxenol, 3,7-dimethyl-7-octenol, 3,7-dimethyl-6-
octen-1-ol (citronellol), 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctanal-1-ol (pelagrol), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-5,7-octadien-2-ol, 4,7-dimethyl-4-vinyl-6-octen-3-ol, 3-methyloctan-3-ol, 2,6-dimethyloctan-2-ol, 2,6-dimethyloctan-3-ol, 3,6-dimethyloctan-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-3,5-octadien-2-ol (muguel), 3-methyl-1-octen-3-ol, 7-hydroxy-3,7-dimethyloctanal, 3-nonenol, 2,6-nonenadien-1-ol, cis-6-nonen-1-ol, 6,8-dimethylnonan-2-ol, 3-(hydroxymethyl)-2-nonenone, 2-nonen-1-ol, 2,4-nonenadien-1-ol, 3,7-dimethyl-1,6-nonenadien-3-ol, decanol, 9-decenol, 2-benzyl-M-dioxoa-5-ol, 2-decen-1-ol, 2,4-decadien-1-ol, 4-methyl-3-decen-5-ol, 3,7,9-trimethyl-1,6-decadien-3-ol (isobutyl linalool), undecanol, 2-undecen-1-ol, 10-undecen-1-ol, 2-dodecen-1-ol, 2,4-dodecadien-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol), 3,7,11-trimethyl-1,6,10,-dodecatrien-3-ol, 3,7,11,15-tetramethyloctadec-2-en-1-ol (phytol), 3,7,11,15-tetramethyloctadec-3-en-3-ol (iso phytol), benzyl alcohol, p-methoxy benzyl alcohol (anisyl alcohol), para-cymen-7-ol (cuminy1 alcohol), 4-methyl benzyl alcohol, 3,4-methylenedioxy benzyl alcohol, methyl salicylate, benzyl salicylate, cis-3-hexenyl salicylate, n-pentyl salicylate, 2-phenylethyl salicylate, n-hexyl salicylate, 2-methyl-5-isopropylphenol, 4-ethyl-2-methoxyphenol, 4-allyl-2-methoxyphenol (eugenol), 2-methoxy-4-(1-propenyl)phenol (isoeugenol), 4-allyl-2,6-dimethoxy-phenol, 4-tert-buty1phenol, 2-ethoxy-4-methylphenol, 2-methyl-4-vinylphenol, 2-isopropyl-5-methylphenol (thymol), pentyl-ortho-hydroxy benzoate, ethyl 2-hydroxy-benzoate, methyl 2,4-dihydroxy-3,6-dimethylbenzoate, 3-hydroxy-5-methoxy-1-methylbenzene, 2-tert-butyl-4-methyl-1-hydroxybenzene, 1-ethoxy-2-hydroxy-4-propenylbenzene, 4-hydroxytoluene, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-hydroxybenzaldehyde, decahydro-2-naphthol, 2,5,5-trimethyl-octahydro-2-naphthol, 1,3,3-trimethyl-2-norbornanol (fenchol), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-ol, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-ol, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuran, β-caryophyllene alcohol, and mixtures thereof.

Preferred alcohols which are released by the acetals and ketals of the present invention are 4-(1-methylethyl)cyclohexanemethanol (mayol), 2,4-dimethyl-3-cyclohexen-1-ylmethanol (floralol), 2,4-dimethylcyclohex-1-ylmethanol (dihydrofloralol), 2,4,6-trimethyl-3-cyclohexen-1-ylmethanol (isocyclogeraniol), 2-phenylethanol, 1-(4-isopropylcyclohexyl)ethanol (mugetanol), 2-(o-methylphenyl)ethanol (ortho-hawthanol), 2-(m-methylphenyl)ethanol (meta-hawthanol), 2-(p-methylphenyl)ethanol (para-hawthanol), 2,2-dimethyl-3-(3-methylphenyl)propan-1-
ol (majantol), 3-phenyl-2-propen-1-ol (cinnamic alcohol), 2-methyl-4-(2,2,3-
trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol (santalaire), 3-methyl-5-phenylpentan-1-
ol (phenoxanol), 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol
(ebanol), 2-methyl-4-phenylpentan-1-ol (pamplefleur), cis-3-hexen-1-ol, 3,7-
dimethyl-6-octen-1-ol (citronellol), 3,7-dimethyl-2,6-octadien-1-ol (geraniol, nerol
or mixtures thereof), 7-methoxy-3,7-dimethyloctan-2-ol (osyrol), 6,8-
dimethylnonan-2-ol, cis-6-nonen-1-ol, 2,6-nonadien-1-ol, 4-methyl-3-decen-5-ol
(undecavertol), benzyl alcohol, 2-methoxy-4-(1-propenyl)phenol (isoeugenol), 2-
methoxy-4-(2-propenyl)phenol (eugenol), 4-hydroxy-3-methoxybenzaldehyde
(vanillin), and mixtures thereof.

Nonlimiting examples of acetals and ketals which are suitable for use in the
rinse added fabric softening compositions of the present invention are digeranyl
citral acetal; di(dodecyl) citral acetal; digeranyl vanillin acetal; didecyl hexyl
cinnamaldehyde acetal; didecyl ethyl citral acetal; di(dodecyl) ethyl citral; didecyl
anisaldehyde acetal; di(phenylethyl) ethyl vanillin acetal; digeranyl p-t-bucinal
acetal; didecyl tripal acetal; di(dodecyl) tripal acetal; digeranyl decanal acetal;
di(dodecyl) decanal acetal; dicitronellyl lauryl acetal; di(tetradecyl) lauryl acetal;
di(octadecccyl) helional acetal; di(phenylethyl) citronellal acetal; di(3-methyl-5-phenyl
pentanol) citronellal acetal; di(phenylethyl) isocitral acetal; di(phenylethyl)
floralzone acetal; didodecyl floralzone acetal; di(2-ethylhexyl) octanal acetal; di
(9-decen-1-yl) p-t-bucinal acetal; di(cis-3-hexenyl) methyl nonyl acetaldehyde
acetal and di(phenylethyl) p-t bucal acetal.

The compositions of the present invention comprise two essential elements,
pro-fragrance or pro-accord acetal or ketal ingredients, and ingredients useful for
formulating fabric softening compositions.

Fabric Softening Ingredients

The preferred fabric softening agents which comprise the rinse added fabric
softening compositions of the present invention have the formula:

\[
\left(\frac{R}{4-m}\right)^{+} N_{m} - \left(\frac{CH_{2}}{n} Q - R\right)^{m} X^{+}
\]

or the formula:
wherein Q is a carbonyl unit having the formula:

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{C} \quad \text{C} \\
\text{O} \quad \text{O} \\
\text{C} \quad \text{O} \\
\text{N} \quad \text{C} \\
\text{C} \quad \text{N}
\end{array}
\]

each R unit is independently hydrogen, C₁₋C₆ alkyl, C₁₋C₆ hydroxyalkyl, and mixtures thereof; each R¹ unit is independently linear or branched C₁₁₋C₂₂ alkyl, linear or branched C₁₁₋C₂₂ alkenyl, and mixtures thereof, R² is hydrogen, C₁₋C₄ alkyl, C₁₋C₄ hydroxyalkyl, and mixtures thereof; X is a cation which is compatible with fabric softener actives and adjunct ingredients; the index m is from 1 to 4; the index n is from 1 to 4.

An example of a preferred fabric softener active is a mixture of quaternized amines having the formula:

\[
R₂\text{--N}^+\left[\text{(CH}_2\text{n--O--C--R)}\right]_2^{-}X^-
\]

wherein R is preferably methyl; R¹ is a linear or branched alkyl or alkenyl chain comprising at least 11 atoms, preferably at least 16 atoms. In the above fabric softener example, the unit -O₂CR¹ represents a fatty acyl unit which is typically derived from a triglyceride source. The triglyceride source is preferably derived from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

The preferred fabric softening actives of the present invention are the Diester and/or Diamide Quaternary Ammonium (DEQA) compounds, the diesters and diamides having the formula:

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{O} \\
\text{C} \\
\text{N} \\
\text{C}
\end{array}
\]
wherein R, R\textsuperscript{1}, X, and n are the same as defined herein above and Q has the formula:

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\hline
\text{C} \\
\hline
\text{C} \\
\hline
\end{array}
\quad \text{or} \quad
\begin{array}{c}
\text{H} \\
\text{N} \\
\hline
\text{O} \\
\hline
\text{C} \\
\hline
\end{array}
\]

These preferred fabric softening actives are formed from the reaction of an amine with a fatty acyl unit to form an amine intermediate having the formula:

\[
R - N \left[ \left( \begin{array}{c} \text{(CH}_2\text{)}_n \end{array} \right) - Z \right]
\]

wherein R is preferably methyl, Z is -OH, -NH\textsubscript{2}, or mixtures thereof; followed by quaternization to the final softener active.

Non-limiting examples of preferred amines which are used to form the DEQA fabric softening actives according to the present invention include methyl bis(2-hydroxyethyl)amine having the formula:

![Methyl Bis(2-Hydroxyethyl)amine Structure]

methyl bis(2-hydroxypropyl)amine having the formula:

![Methyl Bis(2-Hydroxypropyl)amine Structure]

methyl (3-aminopropyl) (2-hydroxyethyl)amine having the formula:

![Methyl (3-Aminopropyl) (2-Hydroxyethyl)amine Structure]

and methyl bis(2-aminoethyl)amine having the formula:

![Methyl Bis(2-Aminoethyl)amine Structure]
The counterion, $X^(-)$ above, can be any softener-compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and the like, more preferably chloride. The anion can also, but less preferably, carry a double charge in which case $X^{(-)}$ represents half a group.

Tallow and canola are convenient and inexpensive sources of fatty acyl units which are suitable for use in the present invention as $R^1$ units. The following are non-limiting examples of quaternary ammonium compounds suitable for use in the compositions of the present invention. The term "tallowyl" as used herein below indicates the $R^1$ unit is derived from a tallow triglyceride source and is a mixture of fatty acyl units. Likewise, the use of the term canolyl refers to a mixture of fatty acyl units derived from canola oil.

Table II

**Fabric Softener Actives**

N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
N,N-di(canolyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride
N,N-di(2-tallowyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyloxy-2-ethyl)-N-(2-canolyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
N,N,N-tricanoyl-oxy-ethyl)-N-methyl ammonium chloride;
N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyloxy-2-oxoethyl)-N-(canoly)-N,N-dimethyl ammonium chloride;
1,2-ditallowyloxy-3-N,N,N-trimethylammoniopropane chloride; and
1,2-dicanolyloxy-3-N,N,N-trimethylammoniopropane chloride;
and mixtures of the above actives.
Particularly preferred is N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl
ammonium chloride, where the tallow chains are at least partially unsaturated.
The level of unsaturation contained within the tallow, canola, or other fatty
acyl unit chain can be measured by the Iodine Value (IV) of the corresponding fatty
acid, which in the present case should preferably be in the range of from 5 to 100
with two categories of compounds being distinguished, having a IV below or above
25.

Indeed, for compounds having the formula:

\[
\left[ (R)_{4-m}^+ \left( (CH_2)_n - Q - R \right)_m \right] X^-
\]
derived from tallow fatty acids, when the Iodine Value is from 5 to 25, preferably 15
to 20, it has been found that a \textit{cis/trans} isomer weight ratio greater than about 30/70,
preferably greater than about 50/50 and more preferably greater than about 70/30
provides optimal concentrability.

For compounds of this type made from tallow fatty acids having a Iodine
Value of above 25, the ratio of \textit{cis} to \textit{trans} isomers has been found to be less critical
unless very high concentrations are needed.

Other suitable examples of fabric softener actives are derived from fatty acyl
groups wherein the terms "tallowyl" and canolyl" in the above examples are replaced
by the terms "cocoyl, palmyl, lauryl, oleyl, ricinoleyl, stearyl, palmityl," which
correspond to the triglyceride source from which the fatty acyl units are derived.
These alternative fatty acyl sources can comprise either fully saturated, or preferably
at least partly unsaturated chains.

As described herein before, R units are preferably methyl, however, suitable
fabric softener actives are described by replacing the term "methyl" in the above
examples in Table II with the units "ethyl, ethoxy, propyl, propoxy, isopropyl, butyl,
isobutyl and t-butyl.

The counter ion, X, in the examples of Table II can be suitably replaced by
bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the
anion, X, is merely present as a counterion of the positively charged quaternary
ammonium compounds. The nature of the counterion is not critical at all to the
practice of the present invention. The scope of this invention is not considered limited to any particular anion.

The quaternary ammonium or their non-quaternized amine precursor compounds are present at levels of from about 1% to about 80% of compositions herein, depending on the composition execution which can be dilute with a preferred level of active from about 5% to about 15%, or concentrated, with a preferred level of active from about 15% to about 50%, most preferably about 15% to about 35%.

For the preceding fabric softening agents, the pH of the compositions herein is an important parameter of the present invention. Indeed, it influences the stability of the quaternary ammonium or amine precursors compounds, especially in prolonged storage conditions.

The pH, as defined in the present context, is measured in the neat compositions at 20 °C. While these compositions are operable at pH of less than about 6.0, for optimum hydrolytic stability of these compositions, the neat pH, measured in the above-mentioned conditions, must be in the range of from about 2.0 to about 4.5, preferably about 2.0 to about 3.5. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

Examples of suitable acids include the inorganic mineral acids, carboxylic acids, in particular the low molecular weight (C1-C5) carboxylic acids, and alkylsulfonic acids. Suitable inorganic acids include HCl, H2SO4, HNO3 and H3PO4. Suitable organic acids include formic, acetic, citric, methylsulfonic and ethylsulfonic acid. Preferred acids are citric, hydrochloric, phosphoric, formic, methylsulfonic acid, and benzoic acids.

Additional Softening Agents

Softening agents which are also useful in the compositions of the present invention are nonionic fabric softener materials, preferably in combination with cationic softening agents. Typically, such nonionic fabric softener materials have a HLB of from about 2 to about 9, more typically from about 3 to about 7. Such nonionic fabric softener materials tend to be readily dispersed either by themselves, or when combined with other materials such as single-long-chain alkyl cationic surfactant described in detail hereinafter. Dispersibility can be improved by using more single-long-chain alkyl cationic surfactant, mixture with other materials as set forth hereinafter, use of hotter water, and/or more agitation. In general, the materials selected should be relatively crystalline, higher melting, (e.g. >40 °C) and relatively water-insoluble.

The level of optional nonionic softener in the compositions herein is typically from about 0.1% to about 10%, preferably from about 1% to about 5%.
Preferred nonionic softeners are fatty acid partial esters of polyhydric alcohols, or anhydrides thereof, wherein the alcohol, or anhydride, contains from 2 to 18, preferably from 2 to 8, carbon atoms, and each fatty acid moiety contains from 12 to 30, preferably from 16 to 20, carbon atoms. Typically, such softeners contain from one to 3, preferably 2 fatty acid groups per molecule.

The polyhydric alcohol portion of the ester can be ethylene glycol, glycerol, poly (e.g., di-, tri-, tetra, penta-, and/or hexa-) glycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan. Sorbitan esters and polyglycerol monostearate are particularly preferred.

The fatty acid portion of the ester is normally derived from fatty acids having from 12 to 30, preferably from 16 to 20, carbon atoms, typical examples of said fatty acids being lauric acid, myristic acid, palmitic acid, stearic acid, oleic and behenic acid.

Highly preferred optional nonionic softening agents for use in the present invention are the sorbitan esters, which are esterified dehydration products of sorbitol, and the glycerol esters.

Commercial sorbitan monostearate is a suitable material. Mixtures of sorbitan stearate and sorbitan palmitate having stearate/palmitate weight ratios varying between about 10:1 and about 1:10, and 1,5-sorbitan esters are also useful.

Glycerol and polyglycerol esters, especially glycerol, diglycerol, triglycerol, and polyglycerol mono- and/or di-esters, preferably mono-, are preferred herein (e.g. polyglycerol monostearate with a trade name of Radiasurf 7248).

Useful glycerol and polyglycerol esters include mono-esters with stearic, oleic, palmitic, lauric, isostearic, myristic, and/or behenic acids and the diesters of stearic, oleic, palmitic, lauric, isostearic, behenic, and/or myristic acids. It is understood that the typical mono-ester contains some di- and tri-ester, etc.

The "glycerol esters" also include the polyglycerol, e.g., diglycerol through octaglycerol esters. The polyglycerol polyols are formed by condensing glycerin or epichlorohydrin together to link the glycerol moieties via ether linkages. The mono- and/or diesters of the polyglycerol polyols are preferred, the fatty acyl groups typically being those described hereinbefore for the sorbitan and glycerol esters.

Additional fabric softening agents useful herein are described in U.S. Pat. No. 4,661,269, issued April 28, 1987, in the names of Toan Trinh, Errol H. Wahl, Donald M. Swartley, and Ronald L. Hemingway; U.S. Pat. No. 4,439,335, Burns, issued March 27, 1984; and in U.S. Pat. Nos.: 3,861,870, Edwards and Diehl; 4,308,151, Cambre; 3,886,075, Bernardino; 4,233,164, Davis; 4,401,578, Verbruggen; 3,974,076, Wiersema and Rieke; 4,237,016, Rudkin, Clint, and Young;
and European Patent Application publication No. 472,178, by Yamamura et al., all of said documents being incorporated herein by reference.

For the purposes of the present invention, the further suitable softening agents which are useful for inclusion in the rinse added fabric softening compositions of the present invention can be broadly classified into one of three general categories:

(a) the reaction product of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof (preferably from about 10% to about 80%); and/or

(b) cationic nitrogenous salts containing only one long chain acyclic aliphatic $C_{15-22}$ hydrocarbon group (preferably from about 3% to about 40%); and/or

(c) cationic nitrogenous salts having two or more long chain acyclic aliphatic $C_{15-22}$ hydrocarbon groups or one said group and an arylalkyl group (preferably from about 10% to about 80%);

with said (a), (b) and (c) preferred percentages being by weight of the fabric softening agent component of the present invention compositions.

Following are the general descriptions of the preceding (a), (b), and (c) softener ingredients (including certain specific examples which illustrate, but do not limit the present invention).

**Component (a)**

Softening agents (actives) of the present invention may be the reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof. These reaction products are mixtures of several compounds in view of the multi-functional structure of the polyamines.

The preferred Component (a) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures. More specifically, the preferred Component (a) is a compound selected from the group consisting of substituted imidazoline compounds having the formula:
wherein $R^7$ is an acyclic aliphatic $C_{15}$-$C_{21}$ hydrocarbon group and $R^8$ is a divalent $C_1$-$C_3$ alkylene group.

Component (a) materials are commercially available as: Mazamide® 6, sold by Mazer Chemicals, or Ceranine® HC, sold by Sandoz Colors & Chemicals; stearic hydroxyethyl imidazoline sold under the trade names of Alkazine® ST by Alkaril Chemicals, Inc., or Schercozoline® S by Scher Chemicals, Inc.; $N,N''$-ditallowalkyldiethylenetriamine; 1-tallowamidoethyl-2-tallowimidazoline (wherein in the preceding structure $R^1$ is an aliphatic $C_{15}$-$C_{17}$ hydrocarbon group and $R^8$ is a divalent ethylene group).

Certain of the Components (a) can also be first dispersed in a Bronsted acid dispersing aid having a pKa value of not greater than about 4; provided that the pH of the final composition is not greater than about 6. Some preferred dispersing aids are hydrochloric acid, phosphoric acid, or methylsulfonic acid.

Both $N,N''$-ditallowalkyldiethylenetriamine and 1-tallow(amideethyl)-2-tallowimidazoline are reaction products of tallow fatty acids and diethylenetriamine, and are precursors of the cationic fabric softening agent methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate (see "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemicals' Society, January 1978, pages 118-121). $N,N''$-ditallow alkoyldiethylenetriamine and 1-tallowamidoethyl-2-tallowimidazoline can be obtained from Witco Chemical Company as experimental chemicals. Methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is sold by Witco Chemical Company under the tradename Varisoft® 475.

Component (b)

The preferred Component (b) is a cationic nitrogenous salt containing one long chain acyclic aliphatic $C_{15}$-$C_{22}$ hydrocarbon group, preferably selected from acyclic quaternary ammonium salts having the formula:
wherein R^9 is an acyclic aliphatic C_{15}-C_{22} hydrocarbon group, R^{10} and R^{11} are C_{1}-C_{4} saturated alkyl or hydroxy alkyl groups, and A^- is an anion.

Examples of Component (b) are the monoalkyltrimethylammonium salts such as monotallowtrimethylammonium chloride, mono(hydrogenated tallow)trimethylammonium chloride, palmityltrimethyl ammonium chloride and soyatrimethylammonium chloride, sold by Witco Chemical Company under the trade name Adogen® 471, Adogen® 441, Adogen® 444, and Adogen® 415, respectively. In these salts, R^9 is an acyclic aliphatic C_{16}-C_{18} hydrocarbon group, and R^{10} and R^{11} are methyl groups. Mono(hydrogenated tallow)trimethylammonium chloride and monotallowtrimethylammonium chloride are preferred.

Other examples of Component (b) are behenyltrimethylammonium chloride wherein R^9 is a C_{22} hydrocarbon group and sold under the trade name Kemamine® Q2803-C by Humko Chemical Division of Witco Chemical Corporation; soyadimethylethlammonium ethylsulfate wherein R^9 is a C_{16}-C_{18} hydrocarbon group, R^{10} is a methyl group, R^{11} is an ethyl group, and A^- is an ethylsulfate anion, sold under the trade name Jordaquat® 1033 by Jordan Chemical Company; and methyl-bis(2-hydroxyethyl)-octadecylammonium chloride wherein R^9 is a C_{18} hydrocarbon group, R^{10} is a 2-hydroxyethyl group and R^{11} is a methyl group and available under the trade name Ethoquad® 18/12 from Armak Company.

Other examples of Component (b) are 1-ethyl-1-(2-hydroxy ethyl)-2-isoheptadecyldimadazolinium ethylsulfate, available from Mona Industries, Inc. under the trade name Monaquat® ISIES; mono(tallowoyloxyethyl) hydroxyethyl(dimethylammonium chloride, i.e., monoester of tallow fatty acid with di(hydroxyethyl)dimethylammonium chloride, a by-product in the process of making diester of tallow fatty acid with di(hydroxyethyl)dimethylammonium chloride, i.e., di(tallowoyloxyethyl) dimethylammonium chloride.

Component (c)

Preferred cationic nitrogenous salts having two or more long chain acyclic aliphatic C_{15}-C_{22} hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture are selected from the group consisting of:
acyclic quaternary ammonium salts having the formula:

\[
\begin{array}{c}
\text{R}^{12} \\
\text{R}^{14} - \text{N} - \text{R}^{12} \\
\text{R}^{13}
\end{array}
\] A^-

wherein \( R^{12} \) is an acyclic aliphatic \( C_{15}-C_{22} \) hydrocarbon group, \( R^{13} \) is a \( C_{1}-C_{4} \) saturated alkyl or hydroxyalkyl group, \( R^{14} \) is selected from the group consisting of \( R^{12} \) and \( R^{13} \) groups, and \( A^- \) is an anion defined as above.

Examples of Component (c) are the well-known dialkylidimethylammonium salts such as ditalloewdimethylammonium chloride, ditalloewdimethylammonium methylsulfate, di(hydrogenatedtallow)dimethylammonium chloride, distearyldimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenatedtallow)di methylammonium chloride and ditalloewdimethylammonium chloride are preferred. Examples of commercially available dialkylidimethyl ammonium salts usable in the present invention are di(hydrogenatedtallow)dimethylammonium chloride (trade name Adogen® 442), ditalloewdimethylammonium chloride (trade name Adogen® 470), distearyldimethylammonium chloride (trade name Arosurf® TA-100), all available from Witco Chemical Company. Dibehenyldimethylammonium chloride is sold under the trade name Kemamine Q-2802C by Humko Chemical Division of Witco Chemical Corporation.

Other examples of Component (c) are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively: dimethylstearylbenzyl ammonium chloride sold under the trade names Varisoft® SDC by Witco Chemical Company and Ammonyx® 490 by Onyx Chemical Company.

An even more preferred composition contains Component (a): the reaction product of about 2 moles of hydrogenated tallow fatty acids with about 1 mole of N-2-hydroxyethylenelediamine and is present at a level of from about 20% to about 70% by weight of the fabric softening component of the present invention compositions; Component (b): mono(hydrogenated tallow)trimethyl ammonium chloride present at a level of from about 3% to about 30% by weight of the fabric softening component of the present invention compositions; Component (c): selected
from the group consisting of di(hydrogenated tallow)dimethylammonium chloride, ditallowdimethylammonium chloride, methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate, diethanol ester dimethylammonium chloride, and mixtures thereof; wherein Component (c) is present at a level of from about 20% to about 60% by weight of the fabric softening component of the present invention compositions; and wherein the weight ratio of said di(hydrogenated tallow)dimethylammonium chloride to said methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is from about 2:1 to about 6:1.

In the cationic nitrogenous salts described hereinafter, the anion A- provides charge neutrality. Most often, the anion used to provide charge neutrality in these salts is a halide, such as chloride or bromide. However, other anions can be used, such as methylsulfate, ethylsulfate, hydroxide, acetate, formate, citrate, sulfate, carbonate, and the like. Chloride and methylsulfate are preferred herein as anion A-.

As used herein, when the diester is specified, it will include the monoester that is normally present in manufacture. For softening, under no/low detergent carry-over laundry conditions the percentage of monoester should be as low as possible, preferably no more than about 2.5%. However, under high detergent carry-over conditions, some monoester is preferred. The overall ratios of diester to monoester are from about 100:1 to about 2:1, preferably from about 50:1 to about 5:1, more preferably from about 13:1 to about 8:1. Under high detergent carry-over conditions, the di/monoester ratio is preferably about 11:1. The level of monoester present can be controlled in the manufacturing of the softener compound.

**Liquid carrier**

Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohols such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

**Concentration aids**

Concentrated compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. Surfactant
concentration aids are typically selected from the group consisting of single long chain alkyl cationic surfactants; nonionic surfactants; amine oxides; fatty acids; or mixtures thereof, typically used at a level of from 0 to about 15% of the composition.

Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition.

Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader range of temperature, especially at low temperatures, compared to the inorganic electrolytes.

Specific examples of alkylene polyammonium salts include 1-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

4. Other ingredients

Still other optional ingredients include, but are not limited to Soil Release Agents, perfumes, preservatives/stabilizers, chelants, bacteriocides, colorants, optical brighteners, antifoam agents, and the like.

Soil Release Agents

Soil Release agents are desirably used in fabric softening compositions of the instant invention. Suitable soil release agents include those of U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselin: such ester oligomers can be prepared by (a) ethoxylating allyl alcohol, (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure and (c) reacting the product of (b) with
sodium metabisulfite in water; the nonionic end-capped 1,2-
propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8,
1987 to Gosselink et al, for example those produced by
transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG
and poly(ethyleneglycol) ("PEG"); the partly- and fully- anionic-end-capped
oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as
oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxoa-8-
hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric
compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example
produced from DMT, Me-capped PEG and EG and/or PG, or a combination of
DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the
anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896,
October 31, 1989 to Maldonado, Gosselink et al, the latter being typical of SRA's
useful in both laundry and fabric conditioning products, an example being an ester
composition made from m-sulfobenzoic acid monosodium salt, PG and DMT
optionally but preferably further comprising added PEG, e.g., PEG 3400. Another
preferred soil release agent is a sulfonated end-capped type described in US
5,415,807.

Perfumes
While the pro-fragrances of the present invention can be used alone and
simply mixed with essential fabric softening ingredient, most notably surfactant,
you can also be desirably combined into three-part formulations which combine (a)
a non-fragranced fabric softening base comprising one or more synthetic fabric
softeners, (b) one or more pro-fragrant β-keto-esters in accordance with the
invention and (c) a fully-formulated fragrance. The latter provides desirable in-
package and in-use (wash-time) fragrance, while the pro-fragrance provides a long-
term fragrance to the laundered textile fabrics.

In formulating the present fabric softening compositions, the fully-
formulated fragrance can be prepared using numerous known odorant ingredients of
natural or synthetic origin. The range of the natural raw substances can embrace not
only readily-volatile, but also moderately-volatile and slightly-volatile components
and that of the synthetics can include representatives from practically all classes of
fragrant substances, as will be evident from the following illustrative compilation:
natural products, such as tree moss absolute, basil oil, citrus fruit oils (such as
bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil,
patchouli oil, petitgrain oil Paraguay, wormwood oil, alcohols, such as farnesol,
geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol, aldehydes,
such as citral, Helional™, alpha-hexyl-cinnamaldehyde, hydroxycitronelal, Lilial™ (p-tert-butyl-alpha-methylhydrocinnamaldehyde), methylionylacetaldehyde, ketones, such as allylionone, alpha-ionone, beta-ionone, isoraldein (isomethylalpha-ionone), methylionone, esters, such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, citronellyl ethoxolate, decyl acetate, dimethylbenzylcarbinyl acetate, dimethylbenzylcarbinyl butyrate, ethyl acetoacetate, ethyl acetylated, hexenyl isobutyrate, linalyl acetate, methyl dihydrojasmonate, styrallyl acetate, vetiveryl acetate, etc., lactones, such as gamma-undecalactone, various components often used in perfumery, such as musk ketone, indole, p-menthan-8-thiol-3-one, and methyl-eugenol. Likewise, any conventional fragrant acetal or ketal known in the art can be added to the present composition as an optional component of the conventionally formulated perfume (c). Such conventional fragrant acetals and ketals include the well-known methyl and ethyl acetals and ketals, as well as acetals or ketals based on benzaldehyde, those comprising phenylethyl moieties, or more recently developed specialties such as those described in a United States Patent entitled "Acetals and Ketals of Oxo Tetralins and Oxo-Indanes, see U.S. Pat. No. 5,084,440," issued January 28, 1992, assigned to Givaudan Corp. Of course, other recent synthetic specialties can be included in the perfume compositions for fully-formulated fabric softening compositions. These include the enol ethers of alkyl-substituted oxo-tetralins and oxo-indanes as described in U.S. Pat. 5,332,725, July 26, 1994, assigned to Givaudan; or Schiff Bases as described in U.S. Pat. 5,264,615, December 9, 1991, assigned to Givaudan. It is preferred that the pro-fragrant material be added separately from the conventional fragrances to the fabric softening compositions of the invention.

**Stabilizers**

Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG
and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C8-C22) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone or mixed with citric acid and/or other chelators such as isopropyl citrate, Dequest® 2010, available from Monsanto with a chemical name of 1-hydroxyethylidene-1, 1-diphosphonic acid (etidronic acid), and Tiron®, available from Kodak with a chemical name of 4,5-dihydroxy-m-benzene-sulfonic acid/sodium salt, EDDS, and DTPA®, available from Aldrich with a chemical name of diethyleneetriaminepentaacetic acid. The chemical names and CAS numbers for some of the above stabilizers are listed in Table II below.

**TABLE II**

<table>
<thead>
<tr>
<th>Antioxidant</th>
<th>CAS No.</th>
<th>Chemical Name used in Code of Federal Regulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irganox® 1010</td>
<td>6683-19-8</td>
<td>Tetrakis (methylene(3,5-di-tert-buty1-4-hydroxyhydrocinnamate)) methane</td>
</tr>
<tr>
<td>Irganox® 1035</td>
<td>41484-35-9</td>
<td>Thiodiethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamate]</td>
</tr>
<tr>
<td>Irganox® 1098</td>
<td>23128-74-7</td>
<td>N,N'-Hexamethylene bis[3,5-di-tert-butyl-4-hydroxyhydrocinnamamide]</td>
</tr>
<tr>
<td>Irganox® B 1171</td>
<td>31570-04-4</td>
<td>1:1 Blend of Irganox® 1098 and Irgafos® 168</td>
</tr>
<tr>
<td>Irganox® 1425</td>
<td>65140-91-2</td>
<td>Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)</td>
</tr>
<tr>
<td>Irganox® 3114</td>
<td>65140-91-2</td>
<td>Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)</td>
</tr>
<tr>
<td>Irganox® 3125</td>
<td>34137-09-2</td>
<td>3,5-Di-tert-butyl-4-hydroxy-hydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)triazine-2,4,6-(1H, 3H, 5H)-trione</td>
</tr>
<tr>
<td>Irgafos® 168</td>
<td>31570-04-4</td>
<td>Tris(2,4-di-tert-butyl-phenyl)phosphate</td>
</tr>
</tbody>
</table>
Examples of reductive agents include sodium borohydride, hypophosphorous acid, Irgafos® 168, and mixtures thereof.

The following examples illustrate the β-keto-esters and compositions of this invention, but are not intended to be limiting thereof.

**Synthesis of pro-fragrances**

Acetals and ketals can be prepared by the acid catalyzed reaction of an aldehyde or ketone with an alcohol (or diol), using conventional acid catalysis such as HCl or p-toluenesulfonic acid, or supported sulfonic acid catalysts e.g., AMBERLYST 15™. See Meskens, F., *Synthesis*, (7) 501 (1981) and Meskens, F., *Janssen Chim Acta* (1) 10 (1983). Many aldehyde, ketone and alcohols useful in the synthesis of acetal and ketal pro-fragrances of the present invention are sensitive to strong acid conditions and can undergo undesirable side reactions. See Bunton, C.A. et al, *J. Org. Chem.* (44), 3238, (1978), and Cort, O., et al, *J. Org. Chem.* (51), 1310 (1986). It is also known that acetals of *alpha, beta* unsaturated aldehydes can undergo migration of the double bond under the inappropriate selection of the acid catalyst. See Meskens, F., *Synthesis*, (7), 501, (1981) and Lu, T.-J., et al. *J. Org. Chem.* (60), 2931, (1995), Miyashita, M., et al. *J. Org. Chem.* (44), 3772 (1977). For acid sensitive materials, acid catalysts with pKa's between 3 and 4 are the most desirable to minimize double bond migration while maintaining the reactivity necessary to produce the acetal (or ketal). For example, in the synthesis of digeranyl decanal, p-toluenesulfonic acid (pKa =1) causes undesirable side reactions with geranion. Citric acid (pKa1=3.1, pKa2=4.8, pKa3=6.4) or pyridinium p-toluenesulphonate can be used to form the acetal without side reactions.

Another technique of avoiding side reactions in preparing acetals of acid sensitive materials, such as geranion, is by transacetalization of a dimethyl acetal with a higher molecular weight alcohol, using a mild Lewis acid such as titanium.

When prepared according to the before mentioned synthetic routes, the acetals of the present invention may also contain minor levels of the corresponding vinyl ether.

**EXAMPLE 1**

**Preparation of di(9-decen-1-y1) *p*-t-bucinal acetal**

9-Decen-1-ol in the amount of 48.55 g (0.311 mol), *p*-t-Bucinal in the amount of 21.25 g (0.104 mol), pyridinium *p*-toluenesulfonate in the amount of 1.31 g (5.20 mmol) and benzene in the amount of 200 mL are combined in a 500 mL single-necked round-bottomed flask fitted with a Dean-Stark trap, condenser, argon inlet, and heating mantel. The mixture is brought to reflux. After 18 h, the
theoretical amount of water is collected in the Dean-Stark trap. After cooling, the reaction mixture is treated with 5 g of solid sodium carbonate for 2 h and filtered. The solvent is removed under reduced pressure followed by removal of unreacted starting materials via bulb-to-bulb distillation at 65-85 °C (0.2 mm Hg) yielding a yellow oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether) to give a near colorless oil. Purity of the product is determined by thin layer chromatography and the structure confirmed by mass spectrometry, 1H and 13C NMR.

EXAMPLE 2

Preparation of a p-t-Bucinal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxanol

p-t-Bucinal in the amount of 161.18 g (0.789 mol), β-γ-hexenol in the amount of 37.95 g (0.379 mol), 9-decen-1-ol in the amount of 187.88 g (1.202 mol), phenoxanol in the amount of 187.88 g (1.05 mol), pyridinium p-toluenesulphonate in the amount of 1.35 g (5.37 mmol) and benzene in the amount of 200 mL are combined in a flask fitted with a condenser, argon inlet and Dean-Stark trap. The mixture is heated to reflux for 48 h at which time the theoretical amount of water is collected. After cooling, the reaction mixture is treated with 2 g of solid sodium methoxide and 5 g solid sodium carbonate. The solvent is removed by rotary evaporation followed by removal of unreacted starting materials via bulb-to-bulb distillation at 80-90 °C, 0.05 mm Hg to give an orange/brown mixture. The resulting mixture is taken up in an equal amount of dichloromethane and the resulting solution filtered through a celite plug. The filtrate is concentrated by rotary evaporation to yield a yellow oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether) to give a near colorless oil. Purity of the product is determined by thin layer chromatography and GC analysis and the structure confirmed by mass spectrometry, 1H and 13C NMR.

EXAMPLE 3

Preparation of a tripal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxanol

Tripal in the amount of 100.00 g (0.724 mol), β-γ-hexenol in the amount of 34.84 g (0.348 mol), 9-decen-1-ol in the amount of 172.43 g (1.103 mol), phenoxanol in the amount of 172.43 g (0.967 mol), pyridinium p-toluenesulphonate in the amount of 1.30 g (5.17 mmol) and benzene in the amount of 200 mL are combined in a flask fitted with a condenser, argon inlet and Dean-Stark trap. The mixture is heated to reflux for 48 h at which time the theoretical amount of water is collected. After cooling, the reaction mixture is treated with 2 g of solid sodium
methoxide and 5 g of solid sodium carbonate. The solvent is removed by rotary evaporation followed by removal of unreacted starting materials via bulb-to-bulb distillation at 80-90 °C, 0.05 mm Hg to give a red/brown mixture. The resulting mixture is taken up in an equal amount of dichloromethane and the resulting solution filtered through a celite plug. The filtrate is concentrated by rotary evaporation to yield a yellow oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether) to give a near colorless oil. Purity of the product is determined by thin layer chromatography and GC analysis and the structure confirmed by mass spectrometry, $^1$H and $^{13}$C NMR.

**EXAMPLE 4**

**Preparation of di(β-γ-hexenyl) p-t-bucinal acetal**

$p$-$t$-Bucinal in the amount of 44.97 g (0.220 mol), β-γ-hexenol in the amount of 48.48 g (0.484 mol), pyridinium p-toluenesulfonate in the amount of 0.65 g (2.59 mmol) and toluene in the amount of 200 mL are combined in a flask fitted with a condenser, argon inlet and Dean-Stark trap. The mixture is heated to reflux for 24 h at which time the theoretical amount of water is collected. After cooling, the reaction mixture is treated with 1 g of solid sodium methoxide and 3 g of solid sodium carbonate for 2 h and then filtered. The solvent is removed by rotary evaporation followed by removal of unreacted starting materials via bulb-to-bulb distillation at 80-90 °C (0.05 mm Hg) to give an orange/red oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether) to give a near colorless oil. Purity of the product is determined by thin layer chromatography and GC analysis and the structure confirmed by mass spectrometry, $^1$H and $^{13}$C NMR.

**EXAMPLE 5**

**Preparation of a di(β-citronellyl) acetal blend of $p$-$t$-bucinal, triplal, citral, a-hexylcinnamic aldehyde and decanal**

$p$-$t$-Bucinal in the amount of 4.5 g (0.0220 mol), triplal in the amount of 0.30 g (0.0022 mol), citral in the amount of 0.20 g (0.013 mol), a-hexylcinnamic aldehyde in the amount of 4.5 g (0.0208 mol), decanal in the amount of 0.50 g (0.0032 mol), β-citronellol in the amount of 28.50 g (0.173 mol), p-toluenesulfonic acid in the amount of 0.10 g (5.0 mmol) and toluene in the amount of 70 mL are combined in a flask fitted with a condenser, argon inlet and Dean-Stark trap. The mixture is heated to reflux for 6 h at which time the theoretical amount of water is collected. After cooling, the reaction mixture is treated with 2 g of solid sodium carbonate for 30 minutes and filtered. The solvent is removed by rotary evaporation followed by removal of unreacted starting materials via bulb-to-bulb distillation at
80-90 °C, 0.05 mm Hg to give a yellow/red liquid. The liquid is purified by column chromatography (elution with 1% ethyl acetate dissolved in petroleum ether) to give oil. Purity of the product is determined by thin layer chromatography and GC analysis and the structure confirmed by $^1$H and $^{13}$C NMR.

**EXAMPLE 6**

*Preparation of didodecyl floralzone acetal*

Floralzone in the amount of 10.00 g (0.053 mol), dodecanol in the amount of 21.32 g (0.116 mol), $p$-toluenesulfonic acid in the amount of 0.50 g (2.63 mmol) and toluene in the amount of 75 mL are combined in a flask fitted with a condenser, argon inlet and Dean-Stark trap. The mixture is heated to reflux for 24 h. After cooling, the reaction mixture is treated with 1 g of solid sodium methoxide and 1 g of solid sodium carbonate for 2 h and then filtered. The solvent is removed by rotary evaporation followed by removal of unreacted starting materials via bulb-to-bulb distillation at 80-90 °C (0.05 mm Hg) to give an orange/red oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether). Purity of the product is determined by thin layer chromatography and GC analysis and the structure confirmed by $^1$H and $^{13}$C NMR.

Examples of Liquid Fabric Softener Compositions Containing Acetal Pro-perfumes

**Formulation Example:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEQA (1)</td>
<td>25.0</td>
<td>23.3</td>
<td>23.3</td>
<td>25.0</td>
<td>23.3</td>
<td>25.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.0</td>
<td>3.65</td>
<td>3.65</td>
<td>4.0</td>
<td>3.65</td>
<td>4.0</td>
</tr>
<tr>
<td>HCl</td>
<td>0.01</td>
<td>0.74</td>
<td>0.74</td>
<td>0.01</td>
<td>0.74</td>
<td>0.01</td>
</tr>
<tr>
<td>Chelant (2)</td>
<td>-</td>
<td>2.50</td>
<td>2.50</td>
<td>-</td>
<td>2.50</td>
<td>-</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>-</td>
<td>0.10</td>
<td>0.10</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
</tr>
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<tr>
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<td>0.42</td>
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<td>Product of Example 6 (11)</td>
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<tr>
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<td>66.54</td>
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(1) Di-(soft-tallowyloxyethyl) dimethyl ammonium chloride
(2) Diethylenetriamine Pentaacetic acid
(3) DC-2310, sold by Dow-Corning
(4) Kathon CG, sold by Rohm & Haas
(5) Copolymer of propylene terephthalate and ethyleneoxide
(6) Di(9-decen-1-yl) p-t-bucinal acetal
(7) p-t-bucinal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxyanol
(8) Triplal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxyanol
(9) Di(β-γ-hexenyl) p-t-bucinal acetal
(10) Di(β-citronellyl) acetal blend of p-t-bucinal, citral, α-hexycinnamic aldehyde and decanal
(11) Didodecyl floralozone acetal

Process: Example A is made in the following manner: A blend of 250g DEQA(1) and 40g ethanol are melted at about 70°C. A 25% aqueous solution of HCl in the amount of 40g is added to about 675g of deionized water also at 70°C containing the antifoam. The DEQA/alcohol blend is added to the water/HCl over a period of about five minutes with very vigorous agitation (IKA Paddle Mixer, model RW 20 DZM at 1500 rpm). A 25% aqueous solution of CaCl₂ in the amount of 13.8g is added to the dispersion dropwise over 1 minute, followed by milling with an IKA Ultra Turrax T-50 high shear mill for 5 minutes. The dispersion is then cooled to room temperature by passing it through a plate and frame heat exchanger. Following cool-down, the soil release polymer is added into the dispersion in the
form of a 40% solution and stirred for 10 minutes. The product of Example 1 (6) in the amount of 5.0g is blended into the dispersion with moderate agitation. Finally, another 4.6g of 25% CaCl₂ is mixed into the dispersion and stirred for several hours.

Examples D and F are made in a like manner, excepting that the pro-perfume material is blended with the perfume component and the resulting mixture is added to the cooled product.

Example B is made in the following manner: A blend of 233g DEQA(1) and 36.5g ethanol are melted at about 75°C. A 25% aqueous solution of HCl in the amount of 0.3g is added to about 670g of deionized water also at 75°C containing the antifoam. The DEQA/alcohol blend is added to the water/HCl over a period of about two minutes with very vigorous agitation (IKA Padel Mixer, model RW 20 DZM at 1500 rpm). A 2.5% aqueous solution of CaCl₂ in the amount of 2.5g is added to the dispersion dropwise over 5 minutes. Meanwhile, 61g of a 41% aqueous solution of the chelant is acidified by the addition of a 25% solution of HCl to a measured pH of 3. A small amount, about 8g, of the acidified chelant solution is stirred into the dispersion, followed by milling with an IKA Ultra Turrax T-50 high shear mill for 5 minutes. The dispersion is then cooled to room temperature. Following cool-down, the soil release polymer is added into the dispersion in the form of a 40% solution and stirred for 10 minutes. The remaining acidified chelant solution is added over 3 minutes. The product of Example 2 (7) in the amount of 4.2g is added, followed by the addition of ammonium chloride in the form of a 20% aqueous solution. Finally, the remaining CaCl₂ is added in the form of a 25% solution.

Examples C and E are made in a like manner, excepting that the pro-perfume material is blended with the perfume component and the resulting mixture is added to the cooled product.

Additional Formulation Examples:

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<th>Ingredient</th>
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<td>18.2</td>
<td>19.2</td>
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<td>Isopropyl alcohol</td>
<td>3.1</td>
<td>2.9</td>
<td>3.1</td>
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<tr>
<td>Tallow Alcohol Ethoxylate-25</td>
<td>-</td>
<td>1.20</td>
<td>-</td>
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Poly(glycerol monostearate) & - & 2.40 & -  \\
HCl & 0.02 & 0.08 & 0.02  \\
CaCl₂ & 0.12 & 0.18 & 0.12  \\
Silicone Antifoam & 0.02 & 0.02 & 0.02  \\
Soil Release Polymer (5) & 0.19 & 0.19 & 0.19  \\
Poly(ethyleneglycol) 4000MW & 0.60 & 0.60 & 0.60  \\
Perfume & 0.70 & 0.70 & 0.40  \\
Product of Example 2 (7) & 0.42 & - & -  \\
Product of Example 3 (8) & - & 0.42 & -  \\
Product of Example 5 (10) & - & - & 0.86  \\
Water & 75.63 & 73.11 & 75.49  \\

(1) Di-(hardtallowoxyethyl) dimethyl ammonium chloride  
(5) Copolymer of propylene terephthalate and ethyleneoxide  
(7) p-t-Bucinal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxanol  
(8) Triplal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxanol  
(10) Di(β-citronellyl) acetal blend of p-t-bucinal, citral, α-hexycinnamic aldehyde and decanal

Additional Examples of Liquid Fabric Softener Compositions Containing Pro-perfumes

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<th>L Wt.%</th>
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<td>Low Salt Kathon (3)</td>
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<td>CaCl₂</td>
<td>*</td>
<td>*</td>
<td>*</td>
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<tr>
<td>Product of Example 1 (6)</td>
<td>0.42</td>
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<td>-</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------</td>
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</tr>
<tr>
<td>Product of Example 2 (7)</td>
<td>-</td>
<td>0.42</td>
<td>-</td>
</tr>
<tr>
<td>Product of Example 4 (9)</td>
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<tr>
<td>Water</td>
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</table>

*Added as needed to adjust viscosity

1. Di-(hardtallowoxyethyl) dimethyl ammonium chloride
2. Silicone DC-2310, sold by Dow-Corning
3. Kathon CG, sold by Rohm & Haas
4. Di(9-decen-1-yl) p-t-bucinal acetal
5. p-t-Bucinal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxyanol
6. Di(β-γ-hexenyl) p-t-bucinal acetal
M. Experimental Procedure:

A batch process is used. The procedure is divided in two parts: the preparation of the base product (prepared in the lab. without perfume and technology) and the addition of the perfume and the technology(ies).

Base product (to prepare a batch of 17 kg of base)

A. The main tank is loaded with the water needed (15.1 kg) and is heated to 43°C. Start agitation at 800 rpm and mix blue dye. The mixer used is a Lightnin model LIU08.
B. Add HCl (3.8 g) by hand (31% activity).
C. Preheat DEQA (1)/ethanol at 75°C (1760 g at 85% actives level) and inject into tank with water at a rate of 22 ml/min.
D. Manually add low salt Kathon (3.4 g) and silicone antifoam (25.7 g).
E. Mix about 5 minutes

Finished product preparation (to prepare 0.250 kg of finished product composition)

F. The product of example 1 (1.050 g) is added to a 249g aliquot of the above product by mixing with an IKA Ultra Turrax T-50 at 6000 rpm for 15 minutes.

Examples K and L are made in a like manner, except that the perfume material is added at the required amount.

Stability of pro-fragrant acetal compositions in acidic media

Acetals are generally considered to be unstable with respect to hydrolysis under acidic conditions. For example, when the acetal prepared according to Example 2 was dissolved in a 90:10 dioxane:water mixture (the hydrophobic acetal is not soluble in water alone) at a nominal pH of 3, only 50% of the material remained intact (i.e. not hydrolyzed) after 7 days at room temperature.

When the same acetal was formulated into a Liquid Fabric Conditioner (see Formulation Example G) which had a nominal pH 3, the following recovery data were obtained:

95% of acetal recovered (i.e. not hydrolyzed) after 4 weeks at room temp.
91% of acetal recovered (i.e. not hydrolyzed) after 4 weeks at 100°F (38°C).

These data clearly show that the acetal is markedly and surprisingly more stable in the Liquid Fabric Conditioner matrix than it is in solution.
WHAT IS CLAIMED IS:

1. A rinse added fabric softening composition comprising:
   (a) from 0.01% to 15% of an acetal or ketal having the formula:

   \[ R^1 \]
   \[ R - C - OR^2 \]
   \[ OR^3 \]

   wherein \( R \) is C₃-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; \( R^1 \) is hydrogen or \( R \); \( R^2 \) and \( R^3 \) are each independently selected from the group consisting of C₅-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ substituted aryl, and mixtures thereof; and

   (b) from 85% to 99.99%, by weight of the composition, of ingredients useful for formulating fabric softening compositions; wherein said compositions have a neat pH of less than 6 at 20 °C.

2. A composition according to Claim 1 wherein the acetal or ketal releases an alcohol having the formula:

   \[ R^2OH \] or \[ R^3OH \]

   wherein said alcohols comprise at least one fragrance raw material alcohol.

3. A composition according to either Claim 1 or 2 wherein the fragrance raw material alcohol which is capable of being released is selected from the group consisting of amyl alcohol; undecylenic alcohol; osyrol; sandalore; dihydro carveol; dihydro linalool; dihydromyrcenol; dihydro terpineol; dimetol; mycenol; alpha-terpineol; tetrahydro linalool; tetrahydro mugol;
tetrahydro myrcenol; amyI cinnamic alcohol; decenol; trans-2-hexenol; patchoumiIt; prenoI; cuminIy alcohol; para-t0ly alcohol; phenylethyl carbinol; ethyl vaniIIIn; isoamyI salicylate; para-hydroxyphenyl butanone; phenethyl salicylate; ethyl linalool; linalool; dihydromyrcenol; nerolidol; beta gamma hexenol; decyl alcohol; dihydoro floralol; hawthanol; heptyl alcohol; isoamyI alcohol; isocyco geraniol; isonyoII geraniol; mayol; methyl lavendar ketone; octyl alcohol; phenyl propyI alcohol; rhodinol 70; rosIIva; camellol dh; cyclohexyl propyl alcohol; isobutyl benzyl alcohol; lavIInol; phenyl ethyl methyl carbinol; propyl benzyl carbinol; iso pulegal; menthol; patchone; rootanol; roselea; trans decahydro beta naphthol; verdol; cinnamic alcohol; farnesol; geraniol; nerol; anIsic alcohol; benzyl alcohol; undecavertol; eugenol; isoeugenol; and vaniIIIn.

4. The composition of any of Claims 1-3 wherein the acetal is fromed from a fragrance raw material aldehyde selected from the group consisting of adosal; chrysanIIIal; cyclamal; cymal; trans-4-decanal; ethyl vaniIIIn; helionol; hydrotrope aldehyde; hydroxycitronellal; isocyclol citral; melonal; methyl nonyl aldehyde; methyl octyl aldehyde; octyl aldehyde; phenyl propanal; citronellal; dodecyl aldehyde; hexylcinnamic aldehyde; myracle aldehyde; vaniIIIn; anIsic aldehyde; citral; decyl aldehyde; floralozone; p.t.-bucinal; and triplal.

5. A composition according to any of Claims 1-4 wherein the acetal or ketal releases a mixture of fragrance raw material alcohols.

6. A composition according to any of Claims 1-5 wherein said pro-fragrant acetal comprises one or more acetals selected from the group consisting of: di(9-decen-1-yl) p-t-bucinal acetal; p-t-bucinal acetal blend made from a mixture of beta-g-hexenol, 9-decen-1-ol and phenoIIanol; triplal acetal blend made from a mixture of beta-g-hexenol, 9-decen-1-ol and phenoIIanol; di(beta-g-hexenyl) p-t-bucinal acetal; di(beta-citronellyl) acetal blend of p-t-bucinal, citral, alpha-hexycinnamic aldehyde and decanal; and didodecyl floralozone acetal.

7. A composItIon according to any of Claims 1-6 wherein component (b) comprises one or more ingredients selected from the group consisting of: cationic fabric softening agents; nonionic fabric softening agents; liquid
carrier; concentration aid; soil release agent; perfume; and
preservatives/stabilizers.

8. A composition according to any of Claims 1-7 wherein component (b) comprises from 1% to 80% of cationic fabric softening agent.

9. A composition according to any of Claims 1-8 wherein component (b) comprises:
   i) from 5% to 50% of a cationic fabric softening agent;
   ii) at least 50% of a liquid carrier; and
   iii) optionally, from 0 to 15% of concentration aids.

10. The composition according to any of Claims 1-9 wherein said cationic fabric softening agent is a biodegradable quaternary ammonium compound having the formula:

\[
\left[ (R)_{4-m}^{+} \right] N^{+} \left[ (CH_2)_n^- O \right]^{-m} \left( CH_2 \right)_n^- Q - R^1 \]

wherein Q has the formula:

\[
\begin{align*}
\text{O} & \quad \text{or} \quad \text{O} \\
\text{O} & \quad \text{C} & \quad \text{O}
\end{align*}
\]

R is C1-C6 alkyl, C1-C6 hydroxyalkyl, benzyl, and mixtures thereof; each
R^1 is independently linear or branched C11-C22 alkyl, linear or branched
C11-C22 alkenyl, and mixtures thereof; X is any softener compatible anion;
m is 2 or 3; n is 1 to 4.

11. Rinse added fabric softening compositions comprising:
   (a) from 0.01% to 15% of an acetal or ketal having the formula:

\[
R^1 \quad \begin{array}{c}
\text{R} \\
\text{C} \\
\text{OR}^2 \\
\text{OR}^3
\end{array}
\]
wherein R is C₃-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₁₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹ is hydrogen or R; R² and R³ are each independently selected from the group consisting of C₅-C₂₀ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ aryl, C₇-C₂₀ substituted aryl, and mixtures thereof; and

b) from 85% to 99.99%, by weight of the composition, of ingredients useful for formulating fabric softening compositions comprising:

i) from 5% to 50% of a cationic fabric softening agent;

ii) at least 50% of a liquid carrier;

iii) optionally, from 0 to 15% of concentration aids;

provided said compositions have a neat pH of from 2 to 4.5 at 20 °C.

A composition according to Claim 11 wherein said acetal is selected from the group consisting of: di(9-decen-1-yl) p-t-bucinal acetal; p-t-bucinal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxyanol; tripal acetal blend made from a mixture of β-γ-hexenol, 9-decen-1-ol and phenoxyanol; di(β-γ-hexenyl) p-t-bucinal acetal; di(β-citronellyl) acetal blend of p-t-bucinal, citral, α-hexycinnamic aldehyde and decanal; and didodecyl floralozone acetal; and wherein said cationic fabric softening agent is a biodegradable quaternary ammonium compound having the formula:

\[
\begin{align*}
&\left[ (R)_{4-m}^+ N \left[ \left( CH_2 \right)_n Q \right]_m \right]^- \\
&\text{wherein Q has the formula:}
\end{align*}
\]

\[
\begin{align*}
&\text{or}
\end{align*}
\]

R is C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, benzyl, and mixtures thereof; each R¹ is independently linear or branched C₁₁-C₂₂ alkyl, linear or branched C₁₁-C₂₂ alkenyl, and mixtures thereof; X is any softener compatible anion; m is 2 or 3; n is 1 to 4.
13. A process of treating textiles in a rinse cycle of a washing machine comprising the step of contacting textiles in a washing machine with a fabric softening effective amount of a rinse added fabric softening composition comprising:

(a) from 0.01% to 15% of an acetal or ketal having the formula:

\[
\begin{align*}
  &R^1 \\
  &R \quad \text{--}\quad \text{OR}^2 \\
  &\quad \text{--} \quad \text{OR}^3
\end{align*}
\]

wherein \( R \) is \( \text{C}_3-\text{C}_{20} \) linear alkyl, \( \text{C}_4-\text{C}_{20} \) branched alkyl, \( \text{C}_6-\text{C}_{20} \) cyclic alkyl, \( \text{C}_6-\text{C}_{20} \) branched cyclic alkyl, \( \text{C}_6-\text{C}_{20} \) linear alkenyl, \( \text{C}_6-\text{C}_{20} \) branched alkenyl, \( \text{C}_6-\text{C}_{20} \) cyclic alkenyl, \( \text{C}_6-\text{C}_{20} \) branched cyclic alkenyl, \( \text{C}_6-\text{C}_{20} \) substituted or unsubstituted aryl, and mixtures thereof; \( R^1 \) is hydrogen or \( R \); \( R^2 \) and \( R^3 \) are each independently selected from the group consisting of \( \text{C}_5-\text{C}_{20} \) linear alkyl, \( \text{C}_4-\text{C}_{20} \) branched alkyl, \( \text{C}_6-\text{C}_{20} \) cyclic alkyl, \( \text{C}_6-\text{C}_{20} \) branched cyclic alkyl, \( \text{C}_6-\text{C}_{20} \) linear alkenyl, \( \text{C}_6-\text{C}_{20} \) branched alkenyl, \( \text{C}_6-\text{C}_{20} \) cyclic alkenyl, \( \text{C}_6-\text{C}_{20} \) branched cyclic alkenyl, \( \text{C}_6-\text{C}_{20} \) aryl, \( \text{C}_7-\text{C}_{20} \) substituted aryl; and

(b) from 85% to 99.99%, by weight of the composition, of ingredients useful for formulating fabric softening compositions; provided said compositions have a neat pH of less than 6 at 20 °C.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6  C11D3/20  C11D3/50

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 database consulted during the international search (name of database and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 94 06441 A (THE MENNEN COMPANY) 31 March 1994</td>
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3

Date of the actual completion of the international search
4 December 1997

Date of mailing of the international search report
17/12/1997

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Ketterer, M
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<td>US 5 531 910 A (J. C. SEVERNS ET. AL.) 2 July 1996 see column 1, line 49 - line 63</td>
<td>1</td>
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<td>P,A</td>
<td>US 5 562 847 A (S. W. WAIT ET. AL.) 8 October 1996 see column 1, line 45 - line 57</td>
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<tr>
<td>A</td>
<td>DATABASE WPI Week 9340 Derwent Publications Ltd., London, GB; AN 93-317784'40! XP002048918 &quot;perfum formulation&quot; &amp; JP 05 230 496 (NIPPON SEIKA KK) , 7 September 1993 see abstract &amp; JP 05 230 496 A</td>
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### INTERNATIONAL SEARCH REPORT

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<th>Publication date</th>
<th>Patent family member(s)</th>
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<tr>
<td>US 5500138 A</td>
<td>19-03-96</td>
<td>AU 3832195 A</td>
<td>15-05-96</td>
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<td></td>
<td>EP 0787176 A</td>
<td>06-08-97</td>
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<td></td>
<td>WO 9612785 A</td>
<td>02-05-96</td>
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<tr>
<td>WO 9406441 A</td>
<td>31-03-94</td>
<td>US 5378468 A</td>
<td>03-01-95</td>
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<td></td>
<td>AU 679464 B</td>
<td>03-07-97</td>
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<td>AU 5138693 A</td>
<td>12-04-94</td>
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<td>BR 9305641 A</td>
<td>09-01-96</td>
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<td>EP 0625905 A</td>
<td>30-11-94</td>
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<td>MX 9305826 A</td>
<td>31-03-94</td>
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<td>US 5626852 A</td>
<td>06-05-97</td>
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<td>US 4614611 A</td>
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<tr>
<td>EP 278020 A</td>
<td>17-08-88</td>
<td>DE 3603661 A</td>
<td>13-08-87</td>
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<tr>
<td>US 5531910 A</td>
<td>02-07-96</td>
<td>WO 9703174 A</td>
<td>30-01-97</td>
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<td>US 5668102 A</td>
<td>16-09-97</td>
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<td>08-10-96</td>
<td>WO 9716522 A</td>
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Form PCT/ISA/210 (patent family annex) (July 1992)