**Title:** AUTOMATIC DISHWASHING DETERGENTS COMPRISING β-KETOESTER PRO-FRAGRANCES

**Abstract**

The present invention relates to Automatic Dishwasher Detergent (ADD) compositions having a fragrance delivery system which comprises β-ketoester pro-fragrances which are capable of releasing fragrance raw materials which provide an aesthetically pleasurable benefit to tableware as well as the automatic diswashing appliance. The present invention also relates to methods for providing lasting fragrance to dishware and to automatic diswashing appliances.
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AUTOMATIC DISHWASHING DETERGENTS
COMPRISING β-KETOESTER PRO-FRAGRANCES

CROSS REFERENCE
This application claims priority under Title 35, United States Code 119(e)
from Provisional Application Serial No. 60/024,117, filed August 19, 1996.

FIELD OF THE INVENTION
The present invention relates to automatic dishwashing detergent (ADD)
compositions comprising β-ketoester pro-fragrance compounds which release
fragrance raw material alcohols thereby providing a "freshness" or "clean" scent to
tableware and flatware. The present invention also relates to a method for providing
a fragrance benefit to tableware by contacting soiled tableware with an automatic
dishwashing detergent composition described herein.

BACKGROUND OF THE INVENTION
Automatic dishwashing, particularly in domestic appliances, is an art very
different from fabric laundering. Domestic fabric laundering is normally done in
purpose-built machines having a tumbling action. These are very different from
spray-action domestic automatic dishwashing appliances. The spray action in the
latter tends to cause foam. Foam can easily overflow the low sills of domestic
dishwashers and slow down the spray action, which in turn reduces the cleaning
action. Thus, in the distinct field of domestic machine dishwashing, the use of
common foam-producing laundry detergent surfactants is normally restricted. These
aspects are but a brief illustration of the unique formulation constraints in the
domestic dishwashing field.

Automatic dishwashing with bleaching chemicals is different from fabric
bleaching. In automatic dishwashing, use of bleaching chemicals involves
promotion of soil removal from dishes, though soil bleaching may also occur.
Additionally, soil antiredeposition and anti-spotting effects from bleaching
chemicals are desirable. Some bleaching chemicals (such as a hydrogen peroxide
source, alone or together with tetraacetylethylenediamine, a.k.a. "TAED") can, in
certain circumstances, be helpful for cleaning dishware.

On account of the foregoing technical constraints as well as consumer needs
and demands, automatic dishwashing detergent (ADD) compositions are undergoing
continual change and improvement. Moreover environmental factors such as the restriction of phosphate, the desirability of providing ever-better cleaning results with less product, providing less thermal energy, and less water to assist the washing process, have all driven the need for improved ADD compositions.

However, one area of ADD technology which has not received sufficient focus is in the area of perfumes and fragrances which deliver a pleasurable scent to the cleaned dishware and flatware and also serve to signal that the dishes are clean. Surprisingly the β-ketoester pro-fragrances of the present invention are stable to the ingredients which comprise ADD compositions and are readily released both during the wash and rinse cycles as well as during the drying cycle. When ADD compositions which comprise the β-ketoesters of the present invention are used the consumer experiences a "fresh" and "cleaned" smell once the dishwasher is opened. The β-ketoester pro-fragrances are adaptable to the needs of the formulator, for example, the pro-fragrances can be designed to be releasable upon extended contact with water, or they can be heat labile. In addition, the formulator may wish to provide a fragrance admixture or "accord" wherein some fragrances are released by contact with water while others are activated by heat. This allows for the delivery of fragrance raw material alcohols via pro-fragrances even when "energy-minders", for example, nil or low heat dryers, are used by the consumer.

Accordingly, there remains a need in the art for a fragrance delivery system wherein fragrance raw material alcohols are delivered to flatware and tableware by way of an ADD composition which provides the tableware and flatware with a "fresh" or "clean" scent after washing.

BACKGROUND ART

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that fragrance raw material alcohols can be delivered onto tableware and flatware "through the wash" from a single precursor pro-fragrance molecule having high surface substantivity and that these pro-fragrances thereby impart a "fresh" or "clean" aesthetic fragrance to the cleaned dishware. In addition, pro-fragrance material is typically deposited upon the walls and within the interstices of the automatic dishwasher appliance itself and is slowly released over time thereby providing a fresher scent to the environment when the appliance is idle or when partially loaded. This continued release of one or more fragrance raw material alcohols after the cleaned dishware has been removed provides the consumer with a more pleasurable kitchen environment and assists in overcoming and masking the "undesirable food odors" which can form when soiled dishes or flatware accumulate in the automatic dishwasher prior to there being a sufficient number of soil articles present to constitute a "full load".

The first aspect of the present invention relates to an automatic dishwashing detergent composition comprising:

a) at least about 0.01%, preferably from about 0.01% to about 15%, more preferably from about 1% to about 5%, most preferably from about 0.1% to about 1% by weight, of a β-ketoester having the formula:

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

wherein R is alkoxy derived from a fragrance raw material alcohol; R\(^1\), R\(^2\), and R\(^3\) are each independently hydrogen, C\(_1\)-C\(_{30}\) substituted or unsubstituted linear alkyl, C\(_3\)-C\(_{30}\) substituted or unsubstituted branched alkyl, C\(_3\)-C\(_{30}\) substituted or unsubstituted cyclic alkyl, C\(_2\)-C\(_{30}\) substituted or unsubstituted linear alkenyl, C\(_3\)-C\(_{30}\) substituted or unsubstituted branched alkenyl, C\(_3\)-C\(_{30}\) substituted or unsubstituted cyclic alkenyl, C\(_2\)-C\(_{30}\) substituted or unsubstituted linear alkynyl, C\(_3\)-C\(_{30}\) substituted or unsubstituted branched alkynyl, C\(_6\)-C\(_{30}\) substituted or unsubstituted aryl, C\(_2\)-C\(_{20}\) substituted or unsubstituted alkyleneoxy, C\(_3\)-C\(_{20}\) substituted or unsubstituted alkyleneoxyalkyl, C\(_7\)-C\(_{20}\) substituted or unsubstituted alkyleneary,
C₆₋C₂₀ substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at least one R¹, R², or R³ is a unit having the formula:

\[
\begin{align*}
\text{O} & \quad \text{R}^4 \\
\text{R}^5 & \quad \text{R}^6
\end{align*}
\]

wherein R⁴, R⁵, and R⁶ are each independently hydrogen, C₁₋C₃₀ substituted or unsubstituted linear alkyl, C₃₋C₃₀ substituted or unsubstituted branched alkyl, C₃₋C₃₀ substituted or unsubstituted cyclic alkyl, C₁₋C₃₀ substituted or unsubstituted linear alkoxy, C₃₋C₃₀ substituted or unsubstituted branched alkoxy, C₃₋C₃₀ substituted or unsubstituted cyclic alkoxy, C₂₋C₃₀ substituted or unsubstituted linear alkenyl, C₃₋C₃₀ substituted or unsubstituted branched alkenyl, C₃₋C₃₀ substituted or unsubstituted cyclic alkenyl, C₂₋C₃₀ substituted or unsubstituted linear alkynyl, C₃₋C₃₀ substituted or unsubstituted branched alkynyl, C₆₋C₃₀ substituted or unsubstituted alkylenearyl, C₆₋C₃₀ substituted or unsubstituted aryl; or R⁴, R⁵, and R⁶ can be taken together to form C₆₋C₃₀ substituted or unsubstituted aryl; and mixtures thereof;

b) at least about 0.1% by weight, preferably from about 0.1% to about 15%, of a detressive surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant said surfactant is a nonionic surfactant having the formula:

\[
\text{R}^2\text{O}\{\text{CH}_2\text{CH}((\text{CH}_3)\text{O})_x\{\text{CH}_2\text{CH}_2\text{O}\}_y\text{CH}_2\text{CH}((\text{OH})\text{R}^3
\]

wherein R² is C₄₋C₁₈ linear or branched alkyl; R³ is C₂₋C₂₆ linear or branched alkyl; x is an integer having an average value of from 0.5 to about 1.5, preferably about 1; and y is an integer having a value of least about 15, preferably at least about 20;

c) from about 5% to about 90% by weight, of a builder;

d) optionally from about 0.1% to about 6% by weight, of a detersive enzyme;

e) optionally, from about 0.1% to about 40% by weight, of a bleaching agent; and
f) the balance carriers and adjunct ingredients.

The present invention also relates to methods for providing a fragrance benefit to dishware which compress the step of contacting in an automatic dishwashing appliance a solution of the ADD compositions of the present invention with soiled dishware.

The present invention relates to ADD compositions in all product and composition forms *inter alia* liquid, gel, and solid granular form.

The present invention further relates to providing an aesthetically pleasing fragrance or scent to automatic dishwashers after use of the compositions of the present invention, especially when the appliance is idle and accumulating sufficient soiled dishware prior to the next wash cycle. 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.

**DETAILED DESCRIPTION OF THE INVENTION**

The automatic dishwashing detergent compositions of the present invention comprise a fragrance delivery system which lays down one or more "pro-fragrance" compounds onto dishware (i.e. ceramic, plastic) or flatware (i.e. stainless steel knives, forks, and spoons) surfaces during the automatic dishwasher wash cycle wherein said compounds are capable of releasing a fragrance raw material alcohol or ketone. For the purposes of the present invention the term "dishware" is defined herein as "items which are typically cleaned in an automatic dishwasher including, dishes, bowls, pots, pans, knives, forks, spoons and the like which are used to prepare, serve, and eat food therewith". However, any item which can be suitably cleaned in an automatic dishwasher is not excluded from the added benefit of the pleasurable scent or fragrance. The terms "dishware", "flatware" and "tableware" are used interchangeably throughout the present specification and are taken to mean, in general, utensils or items used for cooking, serving and eating of food, for example, plates, dishes, cups, glasses, knives, forks, spoons, etc. all of which may comprise any suitable material *inter alia* stainless steel, copper, glass, porcelain.

The key advantages provided by the β-ketoester pro-fragrances of the present invention include chemical stability in the final product matrix, ease of formulation into the product matrix, and a highly desirable rate of fragrance raw material alcohol and ketone release.
The β-ketoester "pro-fragrances" of the present invention begin delivering the fragrance raw materials to the dishware surface once the dishware is exposed to the ADD composition aqueous liquor. These "pro-fragrance" compounds are rapidly deposited onto the dishware surface due to the high substantivity of the compounds and once deposited, begin to release the fragrance raw materials during the wash, rinse, and drying cycles. Because the β-ketoester pro-fragrances of the present invention generally have a higher molecular weight than uncombined fragrance raw material alcohols and ketones, they are therefore less volatile, thereby making the pro-fragrances of the present invention an effective means for delivering fragrance raw materials to dishware even upon exposure to the prolonged heating which occurs during automatic dishwasher drying cycles. Once the automatic dishwashing cycle is complete, that is the dishware is dry and ready for use, the "pro-fragrance" compounds continue to release the fragrance raw materials both on the dishware and within the automatic appliance itself and because this release of material is protracted, the dishware as well as the appliance remains "fresh" and "clean" smelling longer.

For the purposes of the present invention "fragrance raw materials" are herein defined as alcohols and ketones having a molecular weight of at least about 100 g/mol and which are useful in imparting an odor, fragrance, essence, or scent either alone or in combination with other "fragrance raw material alcohols and ketones".

Most of the fragrance raw materials which comprise the β-ketoester pro-fragrances of the present invention are not deliverable as individual compounds to dishware or flatware via the automatic dishwasher either due to solubility factors (lost or rinsed away during the cleaning cycles), substantivity factors (do not sufficiently adhere to dishware or flatware surface), or volatility factors (evaporation during the drying cycle). Therefore, the pro-fragrances described herein are a means for delivering certain fragrance raw materials to dishware or flatware which could not have previously been effectively or efficiently delivered.

For the purposes of the present invention the term "pro-fragrance" is defined as "a β-ketoester which releases a fragrance raw material alcohol" whereas a "pro-accord" is defined as "β-ketoester which release two or more fragrance raw materials". For the purposes of the present invention, however, since a material that is a "pro-fragrance" in one embodiment can serve as a "pro-accord" in a different embodiment, the term "pro-fragrance" is used interchangeably with the term "pro-accord" and either term may be used to stand equally well for either β-ketoester pro-fragrance molecules, β-ketoester pro-accord molecules, or both collectively.
**β-Ketoester Pro-fragrances**

The compositions according to the present invention comprise one or more β-ketoesters having the formula:

\[
\text{R}^1 - \text{O} - \text{R}^2 \text{R}_3
\]

wherein R is alkoxy derived from a fragrance raw material alcohol. Non-limiting examples of preferred fragrance raw material alcohols include 2,4-dimethyl-3-cyclohexene-1-methanol (Floralol), 2,4-dimethyl cyclohexane methanol (Dihydro floralol), 5,6-dimethyl-1-methylethenylbicyclo[2.2.1]hept-5-ene-2-methanol (Arbozol), α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,α,ɑ
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, cis-3-hexen-1-ol, trans-2-hexen-1-ol, 2-isoproenyl-4-methyl-4-hexen-1-ol (Lavandulol), 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 (dihydrocarveol), 1-methyl-4-isopropenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol, 4-tert-butylcyclo-hexanol, 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol (rootanol), 4-isopropyl-cyclohexanol, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexanol, isbornylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-4-isopropylcyclohexan-3-ol, 1-methyl-4-isopropylcyclohexan-8-ol (dihydroterpineol), 1,2-dimethyl-3-(1-methylethyl)cyclohexan-1-ol, heptanol, 2,4-dimethylheptan-1-ol, 6-heptyl-5-hepten-2-ol (isolinalool), 2,4-dimethyl-2,6-heptadienol, 6,6-dimethyl-2-oxymethyl-bicyclo[3.1.1]hept-2-ene (myrtanol), 4-methyl-2,4-heptadien-1-ol, 3,4,5,6-pentamethyl-2-heptanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, 6,6-dimethyl-3-hydroxy-2-methylenecyclo[3.1.1]heptane, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 2,6-dimethylheptan-2-ol (dimetol), 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 (myrcenol), 7-methyloctan-1-ol, 3,7-dimethyl-6-octenol, 3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octen-1-ol (citronellyl), 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-7-methoxyoctan-2-ol (osyrol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctan-1-ol (pelargol), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol (dihydrolinalool), 2,6-dimethyl-7-octen-2-ol (dihydromyrcenol), 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 (muguol), 3-methyl-1-octen-3-ol, 7-hydroxy-3,7-dimethyloctanal, 3-nonanol, 2,6-nonadien-1-ol, cis-6-nonien-1-ol, 6,8-dimethylnonan-2-ol, 3-(hydroxymethyl)-2-nonanone, 2-nonien-1-ol, 2,4-nonadien-1-ol, 3,7-dimethyl-1,6-nonadien-3-ol, decanol, 9-decenol, 2-benzyl-M-dioxa-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-1,6,10,12-dodecatrien-3-ol (nerolidol), 3,7,11,15-tetramethylhexadec-2-en-1-ol (phytol), 3,7,11,15-tetramethylhexadec-1-en-3-ol (iso phytol), benzyl alcohol, p-methoxy benzyl alcohol (anisyl alcohol), para-cymen-7-ol (cuminal 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-butylphenol, 2-ethoxy-4-methylphenol, 2-methyl-4-vinylphenol, 2-isopropyl-5-methylphenol (thymol), pentoxy-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, decahydronaphthal, 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, vanillin, ethyl vanillin, and mixtures thereof.

More preferably, the fragrance raw material alcohol is selected from the group consisting of cis-3-hexen-1-ol, hawthanol [admixture of 2-(o-methylphenyl)-ethanol, 2-(m-methylphenyl)ethanol, and 2-(p-methylphenyl)ethanol], heptan-1-ol, decan-1-ol, 2,4-dimethyl cyclohexane methanol, 4-methylbutan-1-ol, 2,4,6-trimethyl-3-cyclohexene-1-methanol, 4-(1-methylethyl)cyclohexane methanol, 3-(hydroxy-methyl)-2-nonanone, octan-1-ol, 3-phenylpropanol, Rhodinol 70 [3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octenol admixture], 9-decen-1-ol, α-3,3-trimethyl-2-norboranethanol, 3-cyclohexylpropan-1-ol, 4-methyl-1-phenyl-2-pentanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, phenyl ethyl methanol; propyl benzyl methanol, 1-methyl-4-isopropenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol (menthol), 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol, 4-isopropylycyclo-hexanol, trans-decahydro-β-naphthol, 2-tert-butylcyclohexanol, 3-phenyl-2-propen-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol, 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 4-methoxybenzyl alcohol, benzyl alcohol, 4-allyl-2-methoxyphenol, 2-methoxy-4-(1-propenyl)phenol, vanillin, and mixtures thereof.

R₁, R₂, and R₃ are each independently hydrogen, C₁-C₃₀ substituted or unsubstituted linear alkyl, C₃-C₃₀ substituted or unsubstituted branched alkyl, C₃-C₃₀ substituted or unsubstituted cyclic alkyl, C₂-C₃₀ substituted or unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀
substituted or unsubstituted aryl, C₂⁻C₂₀ substituted or unsubstituted alkyleneoxy, C₃⁻C₂₀ substituted or unsubstituted alkyleneoxyalkyl, C₇⁻C₂₀ substituted or unsubstituted alkylenearyl, C₆⁻C₂₀ substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at least one R¹, R², or R³ is a unit having the formula:

\[
\begin{array}{c}
\text{R}^4 \\
\text{R}^5 \\
\text{R}^6
\end{array}
\]

wherein R⁴, R⁵, and R⁶ are each independently hydrogen, C₁⁻C₃₀ substituted or unsubstituted linear alkyl, C₃⁻C₃₀ substituted or unsubstituted branched alkyl, C₃⁻C₃₀ substituted or unsubstituted cyclic alkyl, C₁⁻C₃₀ substituted or unsubstituted linear alkoxy, C₃⁻C₃₀ substituted or unsubstituted branched alkoxy, C₃⁻C₃₀ substituted or unsubstituted cyclic alkoxy, C₂⁻C₃₀ substituted or unsubstituted linear alkenyl, C₃⁻C₃₀ substituted or unsubstituted branched alkenyl, C₃⁻C₃₀ substituted or unsubstituted cyclic alkenyl, C₂⁻C₃₀ substituted or unsubstituted linear alkynyl, C₃⁻C₃₀ substituted or unsubstituted branched alkynyl, C₅⁻C₃₀ substituted or unsubstituted alkylenearyl, C₆⁻C₃₀ substituted or unsubstituted aryl; or R⁴, R⁵, and R⁶ can be taken together to form C₆⁻C₃₀ substituted or unsubstituted aryl; and mixtures thereof.

Preferably at least two R¹, R², or R³ units are hydrogen. In one embodiment of the present invention preferably R⁴, R⁵, and R⁶ units are each hydrogen. In addition, preferably when two R⁴, R⁵, and R⁶ units are hydrogen, the remaining unit is C₁⁻C₂₀ substituted or unsubstituted linear alkyl, C₃⁻C₂₀ substituted or unsubstituted branched alkyl, C₃⁻C₂₀ substituted or unsubstituted cyclic alkyl; more preferably methyl. Also preferably R⁴, R⁵, and R⁶ are taken together to form a C₆⁻C₃₀ substituted or unsubstituted aryl unit, preferably substituted or unsubstituted phenyl and naphthyl.

For the purposes of the present invention the term "substituted" as it applies to linear alkyl, branched alkyl, cyclic alkyl, linear alkenyl, branched alkenyl, cyclic alkenyl, branched alkoxy, cyclic alkoxy, alkynyl, and branched alkynyl units are defined as "carbon chains which comprise substitutents other than branching of the carbon atom chain", for example, other than the branching of alkyl units (e.g. isopropyl, isobutyl). Non-limiting examples of "substituents" include hydroxy, C₁⁻C₁₂ alkoxy, preferably methoxy; C₃⁻C₁₂ branched alkoxy, preferably isopropoxy; C₃⁻C₁₂ cyclic alkoxy; nitrilo; halogen, preferably chloro and bromo, more preferably chloro; nitro; morpholino; cyano; carboxyl, non-limiting examples of
which are -CHO; -CO₂⁻M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR²⁹; wherein R⁹ is C₁-C₁₂ linear or branched alkyl); -SO₃⁻M⁺; -OSO₃⁻M⁺; -N(R¹⁰)₂; and -N⁺(R¹⁰)₃X⁻ wherein each R¹⁰ is independently hydrogen or C₁-C₄ alkyl; and mixtures thereof; wherein M is hydrogen or a water soluble cation; and X is chlorine, bromine, iodine, or other water soluble anion.

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

\[
R^8 \quad -(CH₂CHO)_x R^7
\]

wherein R⁷ is hydrogen; R⁸ is hydrogen, methyl, ethyl, and mixtures thereof; the index x is from 1 to about 10.

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

\[
R^8 \quad -(CH₂CHO)_x(CH₂)y R^7
\]

wherein R⁷ is hydrogen, C₁-C₁₈ alkyl, C₁-C₄ alkoxy, and mixtures thereof; R⁸ is hydrogen, methyl, ethyl, and mixtures thereof; the index x is from 1 to about 10 and the index y is from 2 to about 18.

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

or α and β-naphthyl moieties having the formula:

\[
\text{or } \quad \text{or}
\]

wherein R⁷ and R⁸ can be substituted on either ring, alone or in combination, and R⁷ and R⁸ are each independently hydrogen, hydroxy, C₁-C₆ alkyl, C₂-C₆ alkenyl, C₁-C₄ alkoxy, C₃-C₆ branched alkoxy, nitrilo, halogen, nitro, morpholino, cyano,
carboxyl (-CHO; -CO₂⁻M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl), -SO₃⁻ M⁺, -OSO₃⁻ M⁺, -N(R¹⁰)₂, and N⁺(R¹⁰)₃X⁻ wherein each R¹⁰ is independently hydrogen, C₁-C₄ alkyl, or mixtures thereof; and mixtures thereof, R⁷ and R⁸ are preferably hydrogen, C₁-C₆ alkyl, -CO₂⁺M⁺, -SO₃⁻ M⁺, -OSO₃⁻ M⁺, and mixtures thereof; more preferably R⁷ or R⁸ is hydrogen and the other moiety is C₁-C₆; wherein M is hydrogen or a water soluble cation and X is chlorine, bromine, iodine, or other water soluble anion.

Examples of other water soluble anions include organic species such as fumarate, succinate, tartrate, oxalate and the like, inorganic species include sulfate, hydrogen sulfate, phosphate and the like.

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

\[ -(CH₂)ₚ- \]

wherein R⁷ and R⁸ are each independently hydrogen, hydroxy, C₁-C₄ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂⁺M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl), amino, alkylamino, and mixtures thereof, p is from 1 to about 14; M is hydrogen or a water soluble cation.

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

\[ -(CH₂)ₚO- \]

wherein R⁷ and R⁸ are each independently hydrogen, hydroxy, C₁-C₄ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂⁺M⁺; -CO₂R⁹; -CONH₂; -CONHR⁹; -CONR⁹₂; wherein R⁹ is C₁-C₁₂ linear or branched alkyl), amino, alkylamino, and mixtures thereof, q is from 1 to about 14; M is hydrogen or a water soluble cation.

Surprisingly, the pro-fragrances which comprise the fragrance delivery systems of the present invention are capable of releasing at least one fragrance raw material, preferably the β-ketoester pro-fragrances release two or more fragrance raw materials. For example, the pro-fragrance 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate having the formula:
releases, depending upon usage conditions, at least two fragrance raw materials *inter alia* linalool, β-naphthyl methyl ketone, myrcene, α-terpinolene, and Δ-3-carene.

The β-ketoester pro-fragrances which comprise the fragrance delivery systems of the present invention are capable of releasing their fragrance compounds by more than a single chemical mechanism, a point which is key to the variety of fragrance raw materials which are released from a single pro-accord compound. Therefore, depending upon the desires of the formulator, the pro-fragrances of the present invention are capable of releasing a different mixture of fragrance raw materials depending upon the releasing milieu. For example, the pro-fragrance 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate produces a different fragrance when undergoing fragrance raw material release in water than when said pro-fragrance is subjected to the high temperature typical of an automatic clothes dryer. Typically the pro-fragrances of the present invention release a mixture of alcohols, esters, ketones, hydrocarbyl materials, especially terpenes, having aesthetically pleasing qualities, and mixtures thereof. For the purposes of the present invention the term "hydrocarbyl material" is defined as a compound which essentially comprises only carbon and hydrogen *inter alia* alkanes, alkenes, and alkynes whether linear, cyclic, branched, or combinations thereof. An example, of a hydrocarbyl material which is capable of being released by a pro-fragrance of the present invention is myrcene. For the purposes of the present invention the term "terpene" is used to designate hydrocarbons *inter alia* myrcene, limonene, and α-terpinene. However, those skilled in the art of perfumes as well as organic chemistry recognize that geraniol and nerol which are listed under "fragrance raw material alcohols" herein above are also terpenes. Throughout the present specification the term "terpene" is used interchangeably with "hydrocarbyl" and when "terpene" is used broadly, it refers to all alcohols, ketones, alkenes, etc. that are generally regarded as terpenes, and when the term "terpene" is used narrowly it refers primarily to alkanes, alkenes, etc. having typically 10 carbon atoms (terpenes) or 15 carbon atoms (sesquiterpenes).

Examples of alcohols releasable by the pro-fragrances are described herein above and are typically the fragrance raw material alcohols which are used to form
the parent compounds. However, during the process of fragrance raw material release, these fragrance raw material alcohols are capable of undergoing further modification, including isomerization and/or rearrangement. Therefore, in addition to the original alcohol used to form the parent β-ketoester pro-fragrance, additional alcohols may be formed by transformations which occur during the release process. Depending upon the choices the formulator makes when designing the pro-accord molecules in formulating a fragrance delivery system according to the present invention, these transformations can take place to a greater or lesser degree.

Non-limiting examples of terpenes releasable by the pro-fragrances of the present invention include the hydrocarbyl materials myrcene, ocimene, β-farnesene, cis-achillene, trans-achillene, carvomenthene, limonene, α-terpinene, γ-terpinene, terpinolene, α-phellandrene, β-phellandrene, 2-carene, 3-carene, α-pinene, β-pinene, camphene, and other terpenes, for example, (-)-(2S,4R)-2-(2-methyl-1-propenyl)-4-methyltetrahydropyran (cis rose oxide), (--)-(2S,4S)-2-(2-methyl-1-propenyl)-4-methyltetrahydropyran (trans rose oxide), 2-methyl-2-vinyl-5-(α-hydroxyisopropyl)tetrahydrofuran (linalool oxide), and mixtures thereof.

Non-limiting examples of ketones which are releasable by the pro-accords of the fragrance delivery systems of the present invention are α-damascone, β-damascone, δ-damascone, β-damascenone, muscone, 3,3-dimethylbutanone, methyl phenyl ketone (acetone), 4-phenylbutan-2-one (benzyl acetone), 2-acetyl-3,3-dimethyl norbornane (camek dh), 6,7-dihydro-1,2,3,3-pentamethyl-4(3H) indanone (cashmeran), 4-(1,3)-benzodioxol-5-yl 3-buten-2-one (cassione), 4-(3,4-methylenedioxyphenyl)-2-butane (dulcyl), 3-octanone, 6-acetyl-1,2,3,4-tetrahydronaphthalene ketone (florantone t), ethyl-2-n-hexyl acetocacetate (gelsone), 2,6-dimethylundeca-2,6-dien-10-one, 6,10-dimethyl-5,9-undecadien-2-one, 3,3-dimethylcyclohexyl methyl ketone (herbac), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (α-ionone), 3-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (δ-methyl ionone), 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-methyl-3-buten-2-one (y-methyl ionone), 3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (irisanthemone), 4-(2,3,5-trimethyl-4-cyclohexen-1-yl)-3-buten-2-one (iriton), 4-methyl-(2,5,6,6-tetramethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone), 1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-acetonaphthone (iso cyclomone e), 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene (Iso E Super®), acetyl diisoamylene (Koavone®), methyl amyl ketone, 2-acetonaphthone cedr-8-enyl methyl ketone (methyl cedrylone), 2,3,6-trimethyl-cyclohexen-4-yl-1-methyl ketone (methyl cyclo citrone), hexahydroacetophenone (methyl cyclohexyl ketone), 6-
methyl-3,5-heptadien-2-one, 6-methyl-5-hepten-2-one, 2-octanone, 3-
(hydroxymethyl)-2-nonanone, 4-acetyl-1,1-dimethyl-6-tert-butyl indane (musk
indanone), 2,6-dinitro-3,5-dimethyl-4-acetyl-tert-butyl benzene (musk ketone), 1-
para-menthlen-6-yl propanone (nerone), para-methoxy acetophenone (acetanisole), 6-
acetyl-1,1,2,3,3,5-hexamethyl indan (Phantolid®), 7-acetyl-1,1,3,4,4,6-hexamethyl
tetralin (Tonalid®, Musk Plus®), 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane
(Traseolid 70®, methyl-2,6,10-trimethyl-2,5,9-cyclododecatriene-1-yl ketone
(Trimofix O®), methyl cedrylone (Vertofix Coeur®), 4-(4-hydroxy-3-
methoxyphenyl)-2-butanone, cis-jasmone, dihydrojasmine, α-ionone, β-ionone,
dihydro-β-ionone, 4-(4-hydroxyphenyl)butan-2-one, l-carvone, 5-cyclohexadecen-1-
one, decatone, 2-[2-(4-methyl-3-cyclohexenyl-1-yl)propyl]cyclopentan-2-one, 2-sec-
butyl[cyclohexanone, allyl ionone, α-cetone, geranyl acetone, 1-(2-methyl-5-
isopropyl-2-cyclohexenyl)-1-propanone, acetyl diisoamylyene, methyl cyclocitrone,
4-ter-pentyl cyclohexanone, p-ter-butylcyclohexanone, o-ter-butylcyclohexanone,
menthone, methyl-7,3-dihydrop-2H-1,5-benzodioxepine-3-one, fenchone, methyl
hydroxynaphthyl ketone, and mixtures thereof.

According to the present invention all isomers of a fragrance raw material
whether in the form of the β-ketoester pro-fragrance or the released fragrance raw
material, are suitable for use in the present invention. When optical isomers are
possible, fragrance raw materials may be included as either the separate chemical
isomer or as the combined racemic mixture. For example, 3,7-dimethyl-6-octen-1-
ol, commonly known by those of ordinary skill in the art as β-citronellol or cephrol,
comprises a pair of optical isomers, R-(+)β-citronellol and S-(−)β-citronellol. Each
of these materials separately or as a racemic pair are suitable for use as fragrance
raw materials in the present invention. However, those skilled in the art of
fragrances, by utilization of the present invention, should not disregard the olfactory
differences that individual optical isomers, admixtures of optical isomers or
admixtures of positional isomers impart. By way of example, carvone, 2-methyl-5-
(1-methylethenyl)-2-cyclohexene-1-one exists as two isomers; d-carvone and l-
carvone. d-Carvone is found in oil of caraway and renders a completely different
fragrance from l-carvone which is found in spearmint oil. According to the present
invention a pro-fragrance which releases d-carvone will result in a different scent or
fragrance than one which releases l-carvone. The same applies to l-carvone. In
addition, isomers such as cis/trans isomers, for example, nerol (3,7-dimethyl-cis-
2,6-octadien-1-ol) and geraniol (3,7-dimethyl-trans-2,6-octadien-1-ol), are well
known to those skilled in the art of perfumery and these two terpene alcohols, which
commonly occur as an admixture, have different fragrance characteristics.
Therefore, when formulating fragrance raw materials which comprise mixtures of isomers such as nerol/geraniol, the formulator must also take into account whether different sources of raw material have different ratios of isomers.

An example of a preferred pro-fragrance is 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate having the formula:

![Chemical structure](image)

which releases at least the fragrance raw material alcohol, linalool, having the formula:

![Chemical structure](image)

and the fragrance raw material ketone, methyl naphthyl ketone, having the formula:

![Chemical structure](image)

A further example of a preferred pro-fragrance includes 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate having the formula:

![Chemical structure](image)
which releases at least the fragrance raw material alcohol, dihydromyrcenol, having the formula:

![Chemical structure]

and the fragrance raw material ketone, methyl 4-methoxyphenyl ketone, having the formula:

![Chemical structure]

Further non-limiting examples of preferred pro-fragrances include 3,7-dimethyl-1,6-octadien-3-yl 3-(α-naphthyl)-3-oxo-propionate, [linalyl (1-naphthoyl)acetate], having the formula:

![Chemical structure]

2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, [3-(4-methoxyphenyl)-3-oxo-propionic acid dihydromyrcenyl ester], having the formula:

![Chemical structure]
2,6-dimethyl-7-octen-2-yl 3-(4-nitrophenyl)-3-oxo-propionate, [3-(4-nitrophenyl)-3-oxo-propionic acid dihydromyrcenyl ester], having the formula:

2,6-dimethyl-7-octen-2-yl 3-(β-naphthyl)-3-oxo-propionate, [dihydromyrcenyl (2-naphthoyl)acetate], having the formula:

3,7-dimethyl-1,6-octadien-3-yl 3-(4-methoxyphenyl)-3-oxo-propionate, [3-(4-methoxyphenyl)-3-oxo-propionic acid linalyl ester], having the formula:

(α,α-4-trimethyl-3-cyclohexenyl)methyl 3-(β-naphthyl)-3-oxo-propionate, [α-terpinyl (2-naphthoyl)acetate], having the formula:
9-decen-1-yl 3-(β-naphthyl)-3-oxo-propionate, [9-decen-1-yl (2-naphthyl)acetate], known alternatively as, *roslava* 2'-acetonaphthone, having the formula:

![Chemical Structure](image)

3,7-dimethyl-1,6-octadien-3-yl 3-(nonanyl)-3-oxo-propionate, [linalyl (nonanoyl)acetate], known alternatively as, octyl [(linalyl) α-acetyl] ketone, having the formula:

![Chemical Structure](image)

Additional non-limiting examples of preferred pro-fragnances which comprise the fragrance delivery systems of the present invention include cis 3-hexen-1-yl 3-(β-naphthyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate, 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, 2,6-dimethyl-7-octen-2-yl 3-(β-naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-2,2-dimethylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-2,6-octadienyl 3-(β-naphthyl)-3-oxo-propionate, 3,7-dimethyl-2,6-octadienyl 3-heptyl-3-oxo-propionate, and mixtures thereof.

**Automatic Dishwashing Detergent Compositions**

The present invention relates to automatic dishwashing detergent (ADD) compositions which can be high density or low density granular, gels, or pastes.

The ADD compositions which provide enhanced fragrance longevity to fabric, comprise:

a) at least about 0.01%, preferably from about 0.01% to about 15%, more preferably from about 1% to about 5%, most preferably from about 0.1% to about 1% by weight, of a β-ketoester described herein above;

b) at least about 0.1% by weight, preferably from about 0.1% to about 15%, of a detergents surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and
mixtures thereof, preferably said surfactant said surfactant is a nonionic surfactant having the formula:

$$R^2O(CH_2CH(CH_3)O)_{x}[CH_2CH_2O]_yCH_2CH(OH)R^3$$

wherein $R^2$ is C$_4$-C$_{18}$ linear or branched alkyl; $R^3$ is C$_2$-C$_{26}$ linear or branched alkyl; $x$ is an integer having an average value of from 0.5 to about 1.5; and $y$ is an integer having a value of least about 15;

c) from about 5% to about 90% by weight, of a builder;
d) optionally from about 0.1% to about 6%, preferably from about 0.01% to about 1% by weight, of a detergitive enzyme;
e) optionally, from about 0.1% to about 40% by weight, of a bleaching agent; and
f) the balance carriers and adjunct ingredients.

More preferred compositions of the present invention comprise:
a) at least about 0.01%, preferably from about 0.01% to about 15%, more preferably from about 1% to about 5%, most preferably from about 0.1% to about 1% by weight, of a $\beta$-ketoester described herein above;
b) at least about 0.1% by weight, preferably from about 0.1% to about 15%, of a detergitive surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant said surfactant is a nonionic surfactant having the formula:

$$R^2O(CH_2CH(CH_3)O)_{x}[CH_2CH_2O]_yCH_2CH(OH)R^3$$

wherein $R^2$ is C$_4$-C$_{18}$ linear or branched alkyl; $R^3$ is C$_2$-C$_{26}$ linear or branched alkyl; $x$ is an integer having an average value of from 0.5 to about 1.5; and $y$ is an integer having a value of least about 15;

c) from about 5% to about 90% by weight, of a builder;
d) optionally from about 0.1% to about 6% by weight, of a detergitive enzyme;
e) from about 0.1% to about 40% by weight, of a bleaching agent;
f) from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 0.5% to about 8% by weight, of a bleach activator; and
f) the balance carriers and adjunct ingredients.

**Surfactants**

The surfactant useful in the present invention Automatic Dishwashing compositions is desirably included in the present detergent compositions at levels of from about 0.1% to about 15% of the composition.

The surfactant employed in the compositions of the present invention includes a nonionic surfactant or mixtures of various nonionic surfactants. While a wide range of nonionic surfactants may be selected from for purposes of the mixed nonionic surfactants useful in the present invention ADD compositions, it is necessary that the nonionic surfactant at a minimum comprise a surfactant selected from the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

\[
R^2O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_yCH_2CH(OH)R^3
\]

wherein \( R^2 \) is C\(_4\)-C\(_{18}\) linear or branched alkyl; \( R^3 \) is C\(_2\)-C\(_{26}\) linear or branched alkyl; \( x \) is an integer having an average value of from 0.5 to about 1.5, preferably about 1; and \( y \) is an integer having a value of least about 15 more preferably at least about 20.

Preferably, the surfactant of the formula above comprises at least about 10 carbon atoms in the terminal epoxide unit [CH\(_2\)CH(OH)R\(^3\)]. Suitable surfactants of this formula, according to the present invention, are Olin Corporation's POLYTERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

Of course, one of ordinary skill in the art will recognize that the surfactant of formula I may be employed in combination with other commercially available nonionic surfactants, particularly low foaming nonionic surfactants (LFNIs) to comprise the surfactant of the present invention.

**Low-Foaming Nonionic Surfactant**

LFNI may be present in amounts from 0 to about 10% by weight, preferably from about 0.1% to about 10%, and most preferably from about 0.25% to about 4%. LFNIs are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, non-phosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxylated surfactants, especially ethoxy-lates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene
(PO/EO/PO) reverse block polymers. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 95°F (35°C), more preferably solid at about 77°F (25°C). For ease of manufacture, a preferred LFNI has a melting point between about 77°F (25°C) and about 140°F (60°C), more preferably between about 80°F (26.6°C) and 110°F (43.3°C).

In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C₁₆-C₂₀ alcohol), preferably a C₁₈ alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Highly preferred ADDs herein wherein the LFNI is present make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 100%, preferably from about 30% to about 70%, of the total LFNI.

Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements described hereinbefore include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C₁₂-₁₈ aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant compounds designated PLURONIC® and TETRONIC® by the BASF-
Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

Suitable for use as LFNI in the ADD compositions are those LFNI having relatively low cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below about 32°C and preferably lower, e.g., 0°C, for optimum control of sudsing throughout a full range of water temperatures.

LFNIs which may also be used include those POLY-TERGENT® SLF-18 nonionic surfactants from Olin Corp., and any biodegradable LFNI having the melting point properties discussed hereinabove.

These and other nonionic surfactants are well known in the art, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detersive Systems", incorporated by reference herein.

Preferred are ADD compositions comprising mixed surfactants wherein the sudsing (absent any silicone suds controlling agent) is less than 2 inches, preferably less than 1 inch, as determined by the disclosure below.

(b) Anionic Co-surfactant

The present invention may also include an anionic co-surfactant. However, the automatic dishwashing detergent compositions herein are preferably substantially free from anionic co-surfactants. It has been discovered that certain anionic co-surfactants, particularly fatty carboxylic acids, can cause unsightly films on dishware. Moreover, many anionic surfactants are high foaming. When included, the anionic co-surfactant is typically of a type having good solubility in the presence of calcium. Such anionic co-surfactants are further illustrated by sulfobetaines, alkyl(polyethoxy)sulfates (AES), alkyl (polyethoxy)carboxylates, and short chained C₆-C₁₀ alkyl sulfates.
Builders

Detergent builders other than silicates can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are used in automatic dishwashing to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. The compositions will typically comprise at least about 1% builder. High performance compositions typically comprise from about 5% to about 90%, more typically from about 5% to about 75% by weight, of the detergent builder. Lower or higher levels of builder, however, are not excluded.

Inorganic or non-phosphate-containing detergent builders include, but are not limited to, phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulfates, citrate, zeolite or layered silicate, and aluminosilicates.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Various grades and types of sodium carbonate and sodium sesquicarbonate may be used, certain of which are particularly useful as carriers for other ingredients, especially detergents surfactants.

Aluminosilicate builders may be used in the present compositions though are not preferred for automatic dishwashing detergents. (See U.S. Pat. 4,605,509 for examples of preferred aluminosilicates.) Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula: Na₂O·Al₂O₃·xSiO₂·yH₂O wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In another embodiment, the crystalline aluminosilicate ion exchange material has the formula:
Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]·xH₂O wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. Individual particles can desirably be even smaller than 0.1 micron to further assist kinetics of exchange through maximization of surface area. High surface area also increases utility of aluminosilicates as adsorbents for surfactants, especially in granular compositions. Aggregates of silicate or aluminosilicate particles may be useful, a single aggregate having dimensions tailored to minimize segregation in granular compositions, while the aggregate particle remains dispersible to submicron individual particles during the wash. As with other builders such as carbonates, it may be desirable to use zeolites in any physical or morphological form adapted to promote surfactant carrier function, and appropriate particle sizes may be freely selected by the formulator.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt or "overbased". When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergent builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethylxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polycarboxylic acids such as ethylenediaminetetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxsuccinic acid, and soluble salts thereof.
Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty laundry detergent and automatic dishwashing formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in combination with zeolite, the aforementioned BRITESIL types, and/or layered silicate builders. Oxydisuccinates are also useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedionates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurysuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like.

Laurysuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.


Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, may also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity but are generally not desired. Such use of fatty acids will generally result in a diminution of sudsing in laundry compositions, which may need to be taken into account by the formulator. Fatty acids or their salts are undesirable in Automatic Dishwashing (ADD) embodiments in situations wherein soap scums can form and be deposited on dishware.

Where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used though such materials are more commonly used in a low-level mode as chelants or stabilizers.

Phosphate detergent builders for use in ADD compositions are well known. They include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates,

Preferred levels of phosphate builders herein are from about 10% to about 75%, preferably from about 15% to about 50%, of phosphate builder.

**Enzymes**

The compositions of the present invention also include the presence of at least one deterasive enzyme. "Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in an ADD composition. Preferred deterasive enzymes are hydrolases such as proteases, amylases and lipases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more bleach compatible, have a remaining degree of bleach deactivation susceptibility.

In general, as noted, preferred ADD compositions herein comprise one or more deterasive enzymes. If only one enzyme is used, it is preferably an amyolytic enzyme when the composition is for automatic dishwashing use. Highly preferred for automatic dishwashing is a mixture of proteolytic enzymes and amyolytic enzymes. More generally, the enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders, etc. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated in the instant detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal or soil removal effect on substrates such as fabrics, dishware and the like. Since enzymes are catalytic materials, such amounts may be very small. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 6%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial
preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For automatic dishwashing purposes, it may be desirable to increase the active enzyme content of the commercial preparations, in order to minimize the total amount of non-catalytically active materials delivered and thereby improve spotting/filming results.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S as ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al., published January 9, 1985).

An especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Amylases suitable herein include, for example, α-amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL® Novo Industries.

Engineering of enzymes (e.g., stability-enhanced amylase) for improved stability, e.g., oxidative stability is known. See, for example J. Biological Chem.,
Vol. 260, No. 11, June 1985, pp 6518-6521. "Reference amylase" refers to a conventional amylase inside the scope of the amylase component of this invention. Further, stability-enhanced amylases, also within the invention, are typically compared to these "reference amylases".

The present invention, in certain preferred embodiments, can make use of amylases having improved stability in detergents, especially improved oxidative stability. A convenient absolute stability reference-point against which amylases used in these preferred embodiments of the instant invention represent a measurable improvement is the stability of TERMAMYL® in commercial use in 1993 and available from Novo Nordisk A/S. This TERMAMYL® amylase is a "reference amylase", and is itself well-suited for use in the ADD (Automatic Dishwashing Detergent) compositions of the invention. Even more preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylthylendiamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, all measured versus the above-identified reference-amylase. Preferred amylases herein can demonstrate further improvement versus more challenging reference amylases, the latter reference amylases being illustrated by any of the precursor amylases of which preferred amylases within the invention are variants. Such precursor amylases may themselves be natural or be the product of genetic engineering. Stability can be measured using any of the art-disclosed technical tests. See references disclosed in WO 94/02597, itself and documents therein referred to being incorporated by reference.

In general, stability-enhanced amylases respecting the preferred embodiments of the invention can be obtained from Novo Nordisk A/S, or from Genencor International.

Preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the Baccillus amylases, especially the Bacillus alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

As noted, "oxidative stability-enhanced" amylases are preferred for use herein despite the fact that the invention makes them "optional but preferred" materials rather than essential. Such amylases are non-limitingly illustrated by the following:
(a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the B. licheniformis alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as B. amyloliquefaciens, B. subtilis, or B. stearothermophilus;

(b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from B. licheniformis NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8,15,197,256,304,366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®;

(c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S. These amylases do not yet have a tradename but are those referred to by the supplier as QL37+M197T.

Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases.

Cellulases usable in, but not preferred, for the present invention include both bacterial or fungal cellulases. Typically, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and H. cibum strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful.

Suitable lipase enzymes for detergent use include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This
lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLE® enzyme derived from *Humincola lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein. Another preferred lipase enzyme is the D96L variant of the native *Humincola lanuginosa* lipase, as described in WO 92/05249 and Research Disclosure No. 35944, March 10, 1994, both published by Novo. In general, lipolytic enzymes are less preferred than amylases and/or proteases for automatic dishwashing embodiments of the present invention.

Peroxidase enzymes can be used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. The present invention encompasses peroxidase-free automatic dishwashing composition embodiments.


The preferred detergent compositions herein include those where the detergent enzyme is a protease and/or amylase enzyme. Whereas, conventional amylases such as TERMAMYL® may be used with excellent results, preferred ADD compositions can use oxidative stability-enhanced amylases. Such an amylase
is available from Novo Nordisk (described more fully in WO 94/02597, published February 3, 1994) and from Genencor International (described more fully in WO 94/18314, published August 18, 1994). Oxidative stability is enhanced by substitution of the methionine residue located in position 197 of *B. Licheniformis* or the homologous position variation of a similar parent amylase. Typical proteases include Esperase, Savinase, and other proteases as described hereinafter.

**Bleaches**

Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms. An "effective amount" of a source of hydrogen peroxide is any amount capable of measurably improving stain removal (especially of tea stains) from soiled dishware compared to a hydrogen peroxide source-free composition when the soiled dishware is washed by the consumer in a domestic automatic dishwasher in the presence of alkali.

More generally a source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen peroxide. Levels may vary widely and are usually in the range from about 0.1% to about 70%, more typically from about 0.5% to about 30%, by weight of the ADD compositions herein.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.
While not preferred for ADD compositions of the present invention which comprise detersive enzymes, the present invention compositions may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC").

While effective ADD compositions herein may comprise only the nonionic surfactant and builder, fully-formulated ADD compositions typically will also comprise other automatic dishwashing detergent adjunct materials to improve or modify performance. These materials are selected as appropriate for the properties required of an automatic dishwashing composition. For example, low spotting and filming is desired -- preferred compositions have spotting and filming grades of 3 or less, preferably less than 2, and most preferably less than 1, as measured by the standard test of The American Society for Testing and Materials ("ASTM") D3556-85 (Reapproved 1989) "Standard Test Method for Deposition on Glassware During Mechanical Dishwashing".

The preferred compositions herein comprise a bleaching system which is a source of hydrogen peroxide, preferably perborate and/or percarbonate, and preferably also comprise a cobalt-containing bleach catalyst or a manganese-containing bleach catalyst. Preferred cobalt-containing bleach catalysts have the formula:

$$[\text{Co(NH}_3\text{)}_n\text{(M)}_m\text{(B)}_b\text{]}_{\text{T}_y}$$

wherein cobalt is in the +3 oxidation state; $n$ is 4 or 5 (preferably 5); $M$ is one or more ligands coordinated to the cobalt by one site; $m$ is 0, 1 or 2 (preferably 1); $B$ is a ligand coordinated to the cobalt by two sites; $b$ is 0 or 1 (preferably 0), and when $b=0$, then $m+n=6$, and when $b=1$, then $m=0$ and $n=4$; and $T$ is one or more counteranions present in a number $y$, where $y$ is an integer to obtain a charge-balanced salt (preferably $y$ is 1 to 3; most preferably 2 when $T$ is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 $M^{-1}$ s$^{-1}$ (25°C). Also, in another mode, the compositions of the present invention are those wherein the bleach catalyst is a member selected from the group consisting of manganese bleach catalysts, especially manganese "TACN", as described more fully hereinafter.

Additional bleach-improving materials can be present such as bleach activator materials, including tetraacetylthlyenediamine ("TAED") and cationic bleach activators, e.g., 6-trimethylammoniocaproyl caprolactam, tosylate salt.
Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms. An "effective amount" of a source of hydrogen peroxide is any amount capable of measurably improving stain removal (especially of tea stains) from soiled dishware compared to a hydrogen peroxide source-free composition when the soiled dishware is washed by the consumer in a domestic automatic dishwasher in the presence of alkali.

More generally a source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen peroxide. Levels may vary widely and are usually in the range from about 0.1% to about 70%, more typically from about 0.5% to about 30%, by weight of the ADD compositions herein.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

While not preferred for ADD compositions of the present invention which comprise detergents enzymes, the present invention compositions may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC").

While effective ADD compositions herein may comprise only the nonionic surfactant and builder, fully-formulated ADD compositions typically will also comprise other automatic dishwashing detergent adjunct materials to improve or
modify performance. These materials are selected as appropriate for the properties required of an automatic dishwashing composition. For example, low spotting and filming is desired -- preferred compositions have spotting and filming grades of 3 or less, preferably less than 2, and most preferably less than 1, as measured by the standard test of The American Society for Testing and Materials ("ASTM") D3556-85 (Reapproved 1989) "Standard Test Method for Deposition on Glassware During Mechanical Dishwashing".

The present invention encompasses (but is not limited to) granular-form, fully-formulated ADD's in which additional ingredients, including other enzymes (especially proteases and/or amylases) are formulated. However, fully formulated liquid compositions such as gels are also included in the scope of the invention.

The instant invention also encompasses cleaning methods; more particularly, a method of washing tableware in a domestic automatic dishwashing appliance, comprising treating the soiled tableware in an automatic dishwasher with an aqueous alkaline bath comprising an ADD composition as provided hereinbefore.

As already noted, the invention has advantages, including the excellent greasy soil removal, good dishcare, and good overall cleaning.

Accordingly, it is an object of the present invention to provide an automatic dishwashing composition having excellent greasy soil removal, good dishcare and good overall cleaning. It a further object of the present invention to provide a composition employing an epoxy-capped poly(oxyalkylated) alcohol surfactant in combination with a detersive enzyme to provide this superior cleaning. These and other objects, features and advantages will be apparent from the following description and the appended claims.

ADJUNCT INGREDIENTS

Automatic dishwashing compositions of the present invention comprise detressive enzymes (to assist with tough food cleaning, especially of starchy and proteinaceous soils), builder and a nonionic surfactant, and preferably also include a bleaching agent (such as a chlorine bleach or a source of hydrogen peroxide) and/or detressive enzymes. Bleaching agents useful herein include chlorine oxygen bleaches (e.g., hypochlorite; no NaDCC) and sources of hydrogen peroxide, including any common hydrogen-peroxide releasing salt, such as sodium perborate, sodium percarbonate, and mixtures thereof. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). In the preferred embodiments, additional ingredients such as water-soluble silicates (useful to provide alkalinity and assist in controlling corrosion), dispersant polymers (which modify and inhibit crystal growth of calcium and/or magnesium salts), chelants
(which control transition metals), and alkalis (to adjust pH) are present. Additional bleach-modifying materials such as conventional bleach activators, e.g. TAED and/or bleach catalysts, may be added, provided that any such bleach-modifying materials are delivered in such a manner as to be compatible with the purposes of the present invention. The present detergent compositions may, moreover, comprise one or more processing aids, fillers, perfumes, conventional enzyme particle-making materials including enzyme cores or "nonpareils", as well as pigments, and the like.

In general, materials used for the production of ADD compositions herein are preferably checked for compatibility with spotting/filming on glassware. Test methods for spotting/filming are generally described in the automatic dishwashing detergent literature, including DIN and ASTM test methods. Certain oily materials, especially at longer chain lengths, and insoluble materials such as clays, as well as long-chain fatty acids or soaps which form soap scum are therefore preferably limited or excluded from the instant compositions.

Amounts of the essential ingredients can vary within wide ranges, however preferred automatic dishwashing detergent compositions herein (which typically have a 1% aqueous solution pH of above about 8, more preferably from about 9.5 to about 12, most preferably from about 9.5 to about 10.5) are those wherein there is present: from about 5% to about 90%, preferably from about 5% to about 75%, of builder; from about 0.1% to about 40%, preferably from about 0.5% to about 30%, of bleaching agent; from about 0.1% to about 15%, preferably from about 0.2% to about 10%, of the nonionic surfactant; from about 0.0001% to about 1%, preferably from about 0.001% to about 0.05%, of a metal-containing bleach catalyst (most preferred cobalt catalysts useful herein are present at from about 0.001% to about 0.01%); and from about 0.1% to about 40%, preferably from about 0.1% to about 20% of a water-soluble (two ratio) silicate. Such fully-formulated embodiments typically further comprise from about 0.1% to about 15% of a polymeric dispersant, from about 0.01% to about 10% of a chelant, and from about 0.0001% to about 10% of a detertive enzyme, though further additional or adjunct ingredients may be present. Detergent compositions herein in granular form typically limit water content, for example to less than about 7% free water, for best storage stability. Of course, the compositions may also be in liquid or gel form as well.

While the present invention compositions may be formulated using chlorine-containing bleach additive, preferred ADD compositions of this invention (especially those comprising detergine enzymes) are substantially free of chlorine bleach. By "substantially free" of chlorine bleach is meant that the formulator does not deliberately add a chlorine-containing bleach additive, such as a
dichloroisocyanurate, to the preferred ADD composition. However, it is recognized that because of factors outside the control of the formulator, such as chlorination of the water supply, some non-zero amount of chlorine bleach may be present in the wash liquor. The term "substantially free" can be similarly constructed with reference to preferred limitation of other ingredients.

By "effective amount" herein is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance cleaning of a soiled surface. Likewise, the term "catalytically effective amount" refers to an amount of metal-containing bleach catalyst which is sufficient under whatever comparative test conditions are employed, to enhance cleaning of the soiled surface. In automatic dishwashing, the soiled surface may be, for example, a porcelain cup with tea stain, a porcelain cup with lipstick stain, dishes soiled with simple starches or more complex food soils, or a plastic spatula stained with tomato soup. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some machines have considerably longer wash cycles than others. Some users elect to use warm water without a great deal of heating inside the appliance; others use warm or even cold water fill, followed by a warm-up through a built-in electrical coil. Of course, the performance of bleaches and enzymes will be affected by such considerations, and the levels used in fully-formulated detergent and cleaning compositions can be appropriately adjusted.

Detertive ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. They are further selected based on the form of the composition, i.e., whether the composition is to be sold as a liquid, paste (semi-solid), or solid form. Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total, from about 30% to about 99.9%, preferably from about 70% to about 95%, by weight of the compositions), include other active ingredients such as non-phosphate builders, chelants, enzymes, suds suppressors, dispersant polymers (e.g., from BASF Corp. or Rohm & Haas), color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, dyes, fillers, germicides, alkalinity sources, hydrotrpobs, anti-oxidants, enzyme stabilizing agents, perfumes, solubilizing agents, carriers, processing aids, pigments, pH control agents, and, for liquid formulations, solvents, as described in detail hereinafter.
Enzyme Stabilizing System

The enzyme-containing compositions, especially liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergents enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, and mixtures thereof.

The stabilizing system of the ADDs herein may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is relatively large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely known and readily available, and are illustrated by salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetraacetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by several of the ingredients separately listed under better recognized functions, (e.g., other components of the invention such as sodium perborate), there is no requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any scavenger which is majorly incompatible with other ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are
desirably protected in a particle such as that described in U.S. Patent 4,652,392, Baginski et al.

Optional Bleach Adjuncts

(a) Bleach Activators

Preferably, the peroxoxygen bleach component in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzylocaprolactam (BzCL), 4-nitrobenzoxycaprolactam, 3-chlorobenzoylcaprolactam, benzyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C10-OBS), benzyloxyvalerolactam (BZVL), octanoyloxybenzenesulphonate (C8-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzylocaprolactam and benzyloxyvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and 4,412,934, Chung et al, and copending patent applications U. S. Serial Nos. 08/064,624, 08/064,623, 08/064,621, 08/064,562, 08/064,564, 08/082,270 and copending application to M. Burns, A. D. Willey, R. T. Hartshorn, C. K. Ghosh, entitled "Bleaching Compounds Comprising Peroxyacid Activators Used With Enzymes" and having U.S. Serial No. 08/133,691 (P&G Case 4890R), all of which are incorporated herein by reference.

The mole ratio of peroxoxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 3:1.

Quaternary substituted bleach activators may also be included. The present detergent compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in copending U.S. Serial No. 08/298,903, 08/298,650, 08/298,906 and 08/298,904 filed August 31, 1994, incorporated herein by reference.

(b) Organic Peroxides, especially Diacyl Peroxides

These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.
(c) **Metal-containing Bleach Catalysts**

The present invention compositions and methods utilize metal-containing bleach catalysts that are effective for use in ADD compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of theses catalysts include MnIV2(u-O)3(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(PF6)2 ("MnTACN"), MnIII2(u-O)1(u-OAc)2(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(ClO4)2, MnIV4(u-O)6(1,4,7-triazacyclononane)4-(ClO4)2, MnIII3MnIV4(u-O)1(u-OAc)2(1,4,7-trimethyl-1,4,7-triazacyclononane)2-(ClO4)3, and mixtures thereof. See also European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononone, and mixtures thereof.

The bleach catalysts useful in automatic dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084.

See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH3)3.(PF6).

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulsitol, mannotol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:
wherein R¹, R², R³, and R⁴ can each be selected from H, substituted alkyl and aryl groups such that each R¹-N=C-R² and R³-C=N-R⁴ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR⁵R⁶, NR⁷ and C=O, wherein R⁵, R⁶, and R⁷ can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe-,bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl₂, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, Co(2,2'-bispyridylamine)₂O₂ClO₄, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Other examples include Mn gluconate, Mn(CF₃SO₃)₂, Co(NH₃)₅Cl, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N₄MnIII(u-O)₂MnIVN₄⁺ and [Bipy₂MnIII(u-O)₂MnIVbipy₂]-(ClO₄)₃.

The bleach catalysts may also be prepared by combining a water-soluble ligand with a water-soluble manganese salt in aqueous media and concentrating the resulting mixture by evaporation. Any convenient water-soluble salt of manganese can be used herein. Manganese (II), (III), (IV) and/or (V) is readily available on a commercial scale. In some instances, sufficient manganese may be present in the wash liquor, but, in general, it is preferred to detergent composition Mn cations in the compositions to ensure its presence in catalytically-effective amounts. Thus, the sodium salt of the ligand and a member selected from the group consisting of MnSO₄, Mn(ClO₄)₂ or MnCl₂ (least preferred) are dissolved in water at molar ratios of ligand:Mn salt in the range of about 1:4 to 4:1 at neutral or slightly alkaline pH. The water may first be de-oxygenated by boiling and cooled by spraying with nitrogen. The resulting solution is evaporated (under N₂, if desired) and the resulting solids are used in the bleaching and detergent compositions herein without further purification.

In an alternate mode, the water-soluble manganese source, such as MnSO₄, is added to the bleach/cleaning composition or to the aqueous bleaching/cleaning bath which comprises the ligand. Some type of complex is apparently formed in
situ, and improved bleach performance is secured. In such an in situ process, it is convenient to use a considerable molar excess of the ligand over the manganese, and mole ratios of ligand:Mn typically are 3:1 to 15:1. The additional ligand also serves to scavenge vagrant metal ions such as iron and copper, thereby protecting the bleach from decomposition. One possible such system is described in European patent application, publication no. 549,271.

While the structures of the bleach-catalyzing manganese complexes useful in the present invention have not been elucidated, it may be speculated that they comprise chelates or other hydrated coordination complexes which result from the interaction of the carboxyl and nitrogen atoms of the ligand with the manganese cation. Likewise, the oxidation state of the manganese cation during the catalytic process is not known with certainty, and may be the (+II), (+III), (+IV) or (+V) valence state. Due to the ligands' possible six points of attachment to the manganese cation, it may be reasonably speculated that multi-nuclear species and/or "cage" structures may exist in the aqueous bleaching media. Whatever the form of the active Mn-ligand species which actually exists, it functions in an apparently catalytic manner to provide improved bleaching performances on stubborn stains such as tea, ketchup, coffee, wine, juice, and the like.

Other bleach catalysts are described, for example, in European patent applications, publication no. 408,131 (cobalt complex catalysts), European patent application, publication nos. 384,503, and 306,089 (metalloporphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Preferred are cobalt (III) catalysts having the formula:

$$\text{Co}[(\text{NH}_3)_n\text{M}^\text{III}_m\text{B}^\text{b}_t\text{T}^\text{q}_q\text{P}^\text{p}_p]_y$$

wherein cobalt is in the +3 oxidation state; \(n\) is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); \(M^\text{III}\) represents a monodentate ligand; \(m\) is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); \(B^\text{b}\) represents a bidentate ligand; \(b\) is an integer from 0 to 2; \(T^\text{q}\) represents a tridentate ligand; \(t\) is 0 or 1; \(Q\) is a tetradentate ligand; \(q\) is 0 or 1; \(P\) is a pentadentate ligand; \(p\) is 0 or 1; and \(n + m + 2b + 3t + 4q + 5p = 6; Y\) is one or more appropriately selected counteranions present in a number \(y\).
where \( y \) is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when \( Y \) is a \(-1\) charged anion), to obtain a charge-balanced salt, preferred \( Y \) are selected from the group consisting of chloride, iodide, \( \text{I}_3^- \), formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, \( \text{PF}_6^- \), \( \text{BF}_4^- \), \( \text{B(Ph)}_4^- \), phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof [optionally, \( Y \) can be protonated if more than one anionic group exists in \( Y \), e.g., \( \text{HPO}_4^{2-} \), \( \text{HCO}_3^- \), \( \text{H}_2\text{PO}_4^- \), etc., and further, \( Y \) may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants, e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc., and/or anionic polymers, e.g., polyacrylates, polymethacrylates, etc.]; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts (preferably less than about 0.2 volts) versus a normal hydrogen electrode.

Preferred cobalt catalysts of this type have the formula:

\[
[\text{Co(NH}_3\text{)}_n\text{(M}_1\text{)}_m\text{]}\text{Y}_y
\]

wherein \( n \) is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); \( M^1 \) is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when \( m \) is greater than 1) combinations thereof; \( m \) is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); \( m+n = 6 \); and \( Y \) is an appropriately selected counteranion present in a number \( y \), which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when \( Y \) is a \(-1\) charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentamine chloride salts having the formula \([\text{Co(NH}_3\text{)}_5\text{Cl}\text{]}\text{Y}_y\), and especially \([\text{Co(NH}_3\text{)}_5\text{Cl}\text{]}\text{Cl}_2\).

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:

\[
[\text{Co(NH}_3\text{)}_n\text{(M}_b\text{)}_m\text{(B)}_b\text{]}\text{Y}_y
\]

wherein cobalt is in the +3 oxidation state; \( n \) is 4 or 5 (preferably 5); \( M \) is one or more ligands coordinated to the cobalt by one site; \( m \) is 0, 1 or 2 (preferably 1); \( B \) is a ligand coordinated to the cobalt by two sites; \( b \) is 0 or 1 (preferably 0), and when \( b=0 \), then \( m+n = 6 \), and when \( b=1 \), then \( m=0 \) and \( n=4 \); and \( T \) is one or more appropriately selected counteranions present in a number \( y \), where \( y \) is an integer to obtain a charge-balanced salt (preferably \( y \) is 1 to 3; most preferably 2 when \( T \) is a -
I charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 M⁻¹ s⁻¹ (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I₃⁻, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF₆⁻, BF₄⁻, B(Ph)₄⁻, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO₄²⁻, HCO₃⁻, H₂PO₄⁻, etc. Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F⁻, SO₄²⁻, NCS⁻, SCN⁻, S₂O₃⁻², NH₃, PO₄³⁻, and carboxylates (which preferably are monocarboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO₄²⁻, HCO₃⁻, H₂PO₄⁻, HOC(O)CH₂C(O)O⁻, etc.) Preferred M moieties are substituted and unsubstituted C₁-C₃₀ carboxylic acids having the formulas:

R-C(O)O⁻

wherein R is preferably selected from the group consisting of hydrogen and C₁-C₃₀ (preferably C₁-C₈) unsubstituted and substituted alkyl, C₆-C₃₀ (preferably C₆-C₁₈) unsubstituted and substituted aryl, and C₃-C₃₀ (preferably C₅-C₁₈) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of -NR'₃, -NR'₄⁺, -C(O)OR', -OR', -C(O)NR'R₂, wherein R' is selected from the group consisting of hydrogen and C₁-C₆ moieties. Such substituted R therefore include the moieties -(CH₂)ₙOH and -(CH₂)ₙNR'₄⁺, wherein n is an integer from 1 to about 16, preferably from about 2 to about 10, and most preferably from about 2 to about 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched C₄-C₁₂ alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.
The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as $k_{OH}$) for cobalt pentaamine catalysts complexed with oxalate ($k_{OH}=2.5 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} (25^\circ C)$), NCS$^-$ ($k_{OH}=5.0 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} (25^\circ C)$), formate ($k_{OH}=5.8 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} (25^\circ C)$), and acetate ($k_{OH}=9.6 \times 10^{-4} \text{ M}^{-1} \text{s}^{-1} (25^\circ C)$). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[\text{Co(NH}_3)_5\text{OAc}]_2$ $\text{Ty}$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[\text{Co(NH}_3)_5\text{OAc}]\text{Cl}_2$; as well as $[\text{Co(NH}_3)_5\text{OAc(OAc)}]_2$; $[\text{Co(NH}_3)_5\text{OAc}(\text{PF}_6)]_2$; $[\text{Co(NH}_3)_5\text{OAc}(\text{SO}_4)]_2$; $[\text{Co(NH}_3)_5\text{OAc}]_2(\text{BF}_4)$; and $[\text{Co(NH}_3)_5\text{OAc}(\text{NO}_3)]_2$.


These catalysts may be coprocessed with adjunct materials so as to reduce the color impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

As a practical matter, and not by way of limitation, the cleaning compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst by weight of the cleaning compositions.
**pH and Buffering Variation**

Many detergent compositions herein will be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art.

The preferred ADD compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. The pH-adjusting components are selected so that when the ADD is dissolved in water at a concentration of 1,000 - 10,000 ppm, the pH remains in the range of above about 8, preferably from about 9.5 to about 11. The preferred nonphosphate pH-adjusting component of the invention is selected from the group consisting of:

(i) sodium carbonate or sesquicarbonate;
(ii) sodium silicate, preferably hydrous sodium silicate having SiO₂:Na₂O ratio of from about 1:1 to about 2:1, and mixtures thereof with limited quantities of sodium metasilicate;
(iii) sodium citrate;
(iv) citric acid;
(v) sodium bicarbonate;
(vi) sodium borate, preferably borax;
(vii) sodium hydroxide; and
(viii) mixtures of (i)-(vii).

Preferred embodiments contain low levels of silicate (i.e. from about 3% to about 10% SiO₂).

Illustrative of highly preferred pH-adjusting component systems are binary mixtures of granular sodium citrate with anhydrous sodium carbonate, and three-component mixtures of granular sodium citrate trihydrate, citric acid monohydrate and anhydrous sodium carbonate.

The amount of the pH adjusting component in the instant ADD compositions is preferably from about 1% to about 50%, by weight of the composition. In a preferred embodiment, the pH-adjusting component is present in the ADD composition in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.
For compositions herein having a pH between about 9.5 and about 11 of the initial wash solution, particularly preferred ADD embodiments comprise, by weight of ADD, from about 5% to about 40%, preferably from about 10% to about 30%, most preferably from about 15% to about 20%, of sodium citrate with from about 5% to about 30%, preferably from about 7% to 25%, most preferably from about 8% to about 20% sodium carbonate.

The essential pH-adjusting system can be complemented (i.e. for improved sequestration in hard water) by other optional detergency builder salts selected from nonphosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, nonphosphorus organic builders can be used for their sequestering properties. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid; nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethoxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts.

**Water-Soluble Silicates**

The present automatic dishwashing detergent compositions may further comprise water-soluble silicates. Water-soluble silicates herein are any silicates which are soluble to the extent that they do not adversely affect spotting/filming characteristics of the ADD composition.

Examples of silicates are sodium metasilicate and, more generally, the alkali metal silicates, particularly those having a SiO$_2$:Na$_2$O ratio in the range 1.6:1 to 3.2:1; and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6® is a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, Na SKS-6 and other water-soluble silicates useful herein do not contain aluminum. NaSKS-6 is the 8-Na$_2$SiO$_5$ form of layered silicate and can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi$_x$O$_{2x+1}$yH$_2$O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the α-, β- and γ-forms. Other silicates may also be useful, such as for example magnesium silicate,
which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Silicates particularly useful in automatic dishwashing (ADD) applications include granular hydrous 2-ratio silicates such as BRITESIL® H20 from PQ Corp., and the commonly sourced BRITESIL® H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

**Chelating Agents**

The compositions herein may also optionally contain one or more transition-metal selective sequestrants, "chelants" or "chelating agents", e.g., iron and/or copper and/or manganese chelating agents. Chelating agents suitable for use herein can be selected from the group consisting of aminocarboxylates, phosphonates (especially the aminophosphonates), polyfunctionally-substituted aromatic chelating agents, and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to control iron, copper and manganese in washing solutions which are known to decompose hydrogen peroxide and/or bleach activators; other benefits include inorganic film prevention or scale inhibition. Commercial chelating agents for use herein include the DEQUEST® series, and chelants from Monsanto, DuPont, and Nalco, Inc.

Aminocarboxylates useful as optional chelating agents are further illustrated by ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetetraacetates, nitriolo-triacetates, ethylenediamine tetraacetonates, triethylenetetraminehexacacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof. In general, chelant mixtures may be used for a combination of functions, such as multiple transition-metal control, long-term product stabilization, and/or control of precipitated transition metal oxides and/or hydroxides.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A highly preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially (but not limited to) the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The
trisodium salt is preferred though other forms, such as magnesium salts, may also be useful.

Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are acceptable in detergent compositions, and include the ethylenediaminetetraakis (methylene phosphonates) and the diethylenetriaminepentakis (methylene phosphonates). Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

If utilized, chelating agents or transition-metal-selective sequestrants will preferably comprise from about 0.001% to about 10%, more preferably from about 0.05% to about 1% by weight of the compositions herein.

Dispersant Polymer

Preferred ADD compositions herein may additionally contain a dispersant polymer. When present, a dispersant polymer in the instant ADD compositions is typically at levels in the range from 0 to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 8% by weight of the ADD composition. Dispersant polymers are useful for improved filming performance of the present ADD compositions, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.5. Particularly preferred are polymers which inhibit the deposition of calcium carbonate or magnesium silicate on dishware.

Dispersant polymers suitable for use herein are further illustrated by the film-forming polymers described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983.

Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1,000 to about 500,000, more preferably is from about 1,000 to about 250,000, and most preferably, especially if the ADD is for use in North American automatic dishwashing appliances, is from about 1,000 to about 5,000.

Other suitable dispersant polymers include those disclosed in U.S. Patent No. 3,308,067 issued March 7, 1967, to Diehl. Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence of monomeric segments containing no carboxylate radicals such as methyl vinyl ether, styrene, ethylene, etc.
is suitable provided that such segments do not constitute more than about 50% by weight of the dispersant polymer.

Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50%, preferably less than about 20%, by weight of the dispersant polymer can also be used. Most preferably, such dispersant polymer has a molecular weight of from about 4,000 to about 20,000 and an acrylamide content of from about 0% to about 15%, by weight of the polymer.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 20% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% by weight of a substituted acrylic monomer or its salt and have the general formula: \[-(\text{C}(\text{R}^2)\text{C}(\text{R}^1)(\text{C}(\text{O})\text{OR}^3))\] wherein the apparently unfilled valencies are in fact occupied by hydrogen and at least one of the substituents \(\text{R}^1\), \(\text{R}^2\), or \(\text{R}^3\), preferably \(\text{R}^1\) or \(\text{R}^2\), is a 1 to 4 carbon alkyl or hydroxyalkyl group; \(\text{R}^1\) or \(\text{R}^2\) can be a hydrogen and \(\text{R}^3\) can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein \(\text{R}^1\) is methyl, \(\text{R}^2\) is hydrogen, and \(\text{R}^3\) is sodium.

Suitable low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of about 3,500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766, and 5,084,535.

Agglomerated forms of the present ADD compositions may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan. Such compounds for example, having a melting point within the range of from about 30°C to about 100°C, can be obtained at molecular weights of 1,450, 3,400, 4,500, 6,000, 7,400, 9,500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula: \( HO(CH_2CH_2O)_m(CH_2CH(CH_3)O)_n(CH(CH_3)CH_2O)_oOH \) wherein \( m, n, \) and \( o \) are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrins and starch hydrolysates described in U.S. Pat No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDonald, issued Feb. 27, 1979. Preferred cellulose-derived dispersant polymers are the carboxymethyl celluloses.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polyaspartate.

Material Care Agents

The present ADD compositions may contain one or more material care agents which are effective as corrosion inhibitors and/or anti-tarnish aids. Such materials are preferred components of machine dishwashing compositions especially in certain European countries where the use of electroplated nickel silver and sterling silver is still comparatively common in domestic flatware, or when aluminum protection is a concern and the composition is low in silicate. Generally, such material care agents
include metasilicate, silicate, bismuth salts, manganese salts, paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminum fatty acid salts, and mixtures thereof.

When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the ADD composition. Suitable corrosion inhibitors include paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from about 20 to about 50; preferred paraffin oil is selected from predominantly branched C25-45 species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68. A paraffin oil meeting those characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70. Additionally, the addition of low levels of bismuth nitrate (i.e., Bi(NO₃)₃) is also preferred.

Other corrosion inhibitor compounds include benzotriazole and comparable compounds; mercaptans or thiols including thionaphtol and thioanthanol; and finely divided Aluminum fatty acid salts, such as aluminum tristearate. The formulator will recognize that such materials will generally be used judiciously and in limited quantities so as to avoid any tendency to produce spots or films on glassware or to compromise the bleaching action of the compositions. For this reason, mercaptan anti-tarnishes which are quite strongly bleach-reactive and common fatty carboxylic acids which precipitate with calcium in particular are preferably avoided.

Silicone and Phosphate Ester Suds Suppressors

The ADD's of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%. However, generally (for cost considerations and/or deposition) preferred compositions herein do not comprise suds suppressors or comprise suds suppressors only at low levels, e.g., less than about 0.1% of active suds suppressing agent.

Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxyanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica and/or with surface-active nonsilicon
components, as illustrated by a suds suppressor comprising 12% silicone/silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

If it is desired to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891, issued April 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the instant compositions.

Other Optional Adjuncts

Depending on whether a greater or lesser degree of compactness is required, filler materials can also be present in the instant ADDs. These include sucrose, succrose esters, sodium sulfate, potassium sulfate, etc., in amounts up to about 70%, preferably from 0% to about 40% of the ADD composition. Preferred filler is sodium sulfate, especially in good grades having at most low levels of trace impurities.

Sodium sulfate used herein preferably has a purity sufficient to ensure it is non-reactive with bleach; it may also be treated with low levels of sequestrants, such as phosphonates or EDDS in magnesium-salt form. Note that preferences, in terms of purity sufficient to avoid decomposing bleach, applies also to pH-adjusting component ingredients, specifically including any silicates used herein.

Although optionally present in the instant compositions, the present invention encompasses embodiments which are substantially free from sodium chloride or potassium chloride.

Hydrotrope materials such as sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, etc., can be present, e.g., for better dispersing surfactant.

Bleach-stable perfumes (stable as to odor); and bleach-stable dyes such as those disclosed in U.S. Patent 4,714,562, Roselle et al, issued December 22, 1987 can also be added to the present compositions in appropriate amounts. Other common detergent ingredients consistent with the spirit and scope of the present invention are not excluded.
Since ADD compositions herein can contain water-sensitive ingredients or ingredients which can co-react when brought together in an aqueous environment, it is desirable to keep the free moisture content of the ADDs at a minimum, e.g., 7% or less, preferably 4% or less of the ADD; and to provide packaging which is substantially impermeable to water and carbon dioxide. Coating measures have been described herein to illustrate a way to protect the ingredients from each other and from air and moisture. Plastic bottles, including refillable or recyclable types, as well as conventional barrier cartons or boxes are another helpful means of assuring maximum shelf-storage stability. As noted, when ingredients are not highly compatible, it may further be desirable to coat at least one such ingredient with a low-foaming nonionic surfactant for protection. There are numerous waxy materials which can readily be used to form suitable coated particles of any such otherwise incompatible components; however, the formulator prefers those materials which do not have a marked tendency to deposit or form films on dishes including those of plastic construction.

Some preferred substantially chlorine bleach-free granular automatic dishwashing compositions of the invention are as follows: a substantially chlorine-bleach free automatic dishwashing composition comprising amylase (e.g., TERMAMYL®) and/or a bleach stable amylase and a bleach system comprising a source of hydrogen peroxide selected from sodium perborate and sodium percarbonate and a cobalt catalyst as defined herein.

There is also contemplated a substantially chlorine-bleach free automatic dishwashing composition comprising an oxidative stability-enhanced amylase and a bleach system comprising a source of hydrogen peroxide selected from sodium perborate and sodium percarbonate, a cobalt catalyst, and TAED or NOBS.

Method for Cleaning:

The present invention also encompasses a method for cleaning soiled tableware comprising contacting said tableware with an aqueous medium comprising a β-ketoester of the present invention. Preferred aqueous medium have an initial pH in a wash solution of above about 8, more preferably from about 9.5 to about 12, most preferably from about 9.5 to about 10.5.

This invention also encompasses a method of washing tableware in a domestic automatic dishwashing appliance, comprising treating the soiled tableware in an automatic dishwasher with an aqueous alkaline bath comprising amylase, a cobalt catalyst, and one or more β-ketoester "pro-fragrances" of the present invention.
The following examples illustrate the β-keto-esters and compositions of this invention, but are not intended to be limiting thereof.

**EXAMPLE 1**

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate**

Lithium diisopropylamide (101.0 mL of a 2.0 M solution, 0.202 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is placed in a dry ice-acetone bath. 3,7-Dimethyl-1,6-octadien-3-yl acetate (linalyl acetate) in the amount of (18.66 g, 0.095 mol) is dissolved in THF (5 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min before being treated with a solution of 2-naphthoyl chloride in the amount of (17.43 g, 0.090 mol) dissolved in THF (25 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (53 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether) to give an 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 2**

**Preparation of 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate**

N-Isopropylcyclohexylamine (25.00 g, 0.177 mol) and THF in the amount of 200 mL is placed into a 1000 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is placed in an ice-methanol bath cooled to -5 °C and its contents treated with n-butyllithium in the amount of (70.8 mL of a 2.50 M solution, 0.177 mol). The mixture is stirred for 20 min and then cooled to -78 °C. 2,6-Dimethyl-7-octen-2-yl acetate (dihydromyrcenyl acetate) in the amount of (17.55 g, 0.089 mol) is dissolved in THF (10 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min before being treated with a solution of p-methoxybenzoyl chloride in the amount of (15.10 g, 0.090 mol) dissolved in THF (25 mL) over 30 min and then stirred for 1 h. The mixture is warmed to 0 °C and then treated with 90 mL of 20% HCl an hour later.
The mixture is poured into a separatory funnel containing ether (100 ml) and water (200 ml). The aqueous layer is extracted with ether (100 ml). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 ml), water (2 x 100 ml) and brine (100 ml), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 5% ethyl acetate dissolved in petroleum ether) to give an oil. Purity of the product is determined by thin layer chromatography and the structure confirmed by ¹H and ¹³C NMR.

EXAMPLE 3

**Preparation of 2,6-dimethyl-7-octen-2-yl 3-(4-nitrophenyl)-3-oxo-propionate**

Lithium diisopropylamide (121.0 mL of a 2.0 M solution, 0.243 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is placed in a dry ice-acetone bath. 2,6-Dimethyl-7-octen-2-yl acetate (22.66 g, 0.114 mol) is dissolved in THF (5 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min before being treated with a solution of 4-nitrobenzoyl chloride (20.00 g, 0.108 mol) dissolved in THF (25 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (70 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.

EXAMPLE 4

**Preparation of 2,6-dimethyl-7-octen-2-yl 3-(β-naphthyl)-3-oxo-propionate**

Lithium diisopropylamide in the amount of (100.0 mL of a 2.0 M solution, 0.201 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. 2,6-Dimethyl-7-octen-2-yl acetate in the amount of (18.75 g, 0.095 mol) is dissolved in THF (5 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min before being treated with a solution of 2-naphthoyl chloride in the amount of (17.00 g, 0.089 mol) dissolved in THF (25 mL) over 30 min. The mixture is
warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (55 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 2% ethyl acetate dissolved in petroleum ether) to give an oil. Purity of the product is determined by thin layer chromatography and the structure confirmed by ¹H and ¹³C NMR.

EXAMPLE 5

Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(4-methoxyphenyl)-3-oxo-propionate

Lithium diisopropylamide (119.0 mL of a 2.0 M solution, 0.238 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. 3,7-dimethyl-1,6-octadien-3-yl acetate (22.04 g, 0.112 mol) is dissolved in THF (5 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min before being treated with a solution of p-anisoyl chloride (35.00 g, 0.106 mol) dissolved in THF (30 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (80 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.

EXAMPLE 6

Preparation of (α,β-4-trimethyl-3-cyclohexenyl)methyl 3-(β-naphthyl)-3-oxo-propionate

Lithium diisopropylamide (171.0 mL of a 2.0 M solution, 0.342 mol) is placed into a 1000 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to
-78 °C. (α,α-4-Trimethyl-3-cyclohexenyl)methyl acetate (30.00 g, 0.153 mol) is dissolved in THF (10 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min. before being treated with a solution of 2-naphthoyl chloride (29.00 g, 0.152 mol) dissolved in THF (50 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (105 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a semi-white solid which is triturated in cold n-pentane to yield a white powder having ¹H and ¹³C NMR spectra consistent with the desired product.

EXAMPLE 7

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(α-naphthyl)-3-oxo-propionate**

Lithium diisopropylamide (96.3 mL of a 2.0 M solution, 0.193 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. 3,7-dimethyl-1,6-octadien-3-yl acetate (17.81 g, 0.091 mol) is dissolved in THF (5 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min. before being treated with a solution of 1-naphthoyl chloride (16.82 g, 0.086 mol) dissolved in THF (25 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (53 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.
EXAMPLE 8

**Preparation of cis 3-hexen-1-yl 3-(β-naphthyl)-3-oxo-propionate**

Lithium diisopropylamide (133.0 mL of a 2.0 M solution, 0.266 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. *cis* 3-Hexenyl acetate (17.80 g, 0.125 mol) is dissolved in THF (10 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min. before being treated with a solution of 2-naphthoyl chloride (22.51 g, 0.118 mol) dissolved in THF (30 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (70 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ andfiltered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.

EXAMPLE 9

**Preparation of 9-decen-1-yl 3-(β-naphthyl)-3-oxo-propionate**

Lithium diisopropylamide (79.8 mL of a 2.0 M solution, 0.160 mol) is placed into a 250 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. 9-Decen-1-yl acetate (14.91 g, 0.075 mol) is dissolved in THF (5 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min. before being treated with a solution of 2-naphthoyl chloride (13.80 g, 0.071 mol) dissolved in THF (25 mL) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (47 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.
EXAMPLE 10

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(nonanyl)-3-oxo-propionate**

Lithium diisopropylamide (133.7 mL of a 2.0 M solution, 0.267 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. 3,7-dimethyl-1,6-octadien-3-yl acetate (24.73 g, 0.126 mol) is dissolved in THF (40 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min. before being treated with a solution of nonanoyl chloride (21.88 g, 0.119 mol) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (60 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.

EXAMPLE 11

**Preparation of 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate**

Lithium diisopropylamide (75.7 mL of a 2.0 M solution, 0.151 mol) is placed into a 500 mL three-necked round-bottomed flask fitted with a magnetic stirrer, internal thermometer, argon inlet, and addition funnel. The flask is cooled to -78 °C. 2,6-Dimethyl-7-octen-2-yl acetate (14.14 g, 0.071 mol) is dissolved in THF (20 mL) and the resulting solution added to the flask over 45 min. Once addition is complete, the mixture is stirred for an additional 15 min. before being treated with a solution of nonanoyl chloride (12.38 g, 0.067 mol) over 30 min. The mixture is warmed to -20 °C and stirred at that temperature for 18 h. After warming to 0 °C, the mixture is quenched with 20% HCl (55 mL). The mixture is poured into a separatory funnel containing ether (150 mL) and water (250 mL). The aqueous layer is extracted with ether (150 mL). The combined organic layers are washed with saturated NaHCO₃ solution (2 x 100 mL), water (2 x 150 mL) and brine (150 mL), dried over MgSO₄ and filtered. The solvent is removed by rotary evaporation to give an orange/red oil. The oil is purified by column chromatography (elution with 2% ethyl acetate/petroleum ether) to yield a colorless oil having ¹H and ¹³C NMR spectra consistent with the desired product.
EXAMPLE 12

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate**

A mixture of linalool (100 g, 0.648 mol) and 4-dimethylaminopyridine (0.40 g, 3.20 mmol) in a 500 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal thermometer is heated to 55 °C. Diketene (54.50 g, 0.648 mol) is added dropwise in the course of 30 min. The mixture has a slight exotherm and turns from yellow to red during this time. After stirring an additional hour at 50 °C, the mixture is cooled to room temperature. At this point, NMR analysis indicates the reaction is complete. The material from this lot is carried onto the next step. Purification of an earlier sample from this route by flash chromatography (elution with dichloromethane) yields the desired product in 92% yield and nearly colorless.

EXAMPLE 13

**Preparation of 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate**

A mixture of dihydromyrcenol (37.88 g, 0.240 mol) and 4-dimethylaminopyridine (0.16 g, 1.30 mmol) in a 100 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal thermometer is heated to 50-60 °C. Diketene (20.16 g, 0.240 mol) is added dropwise in the course of 15 min. The mixture has a slight exotherm and turned from yellow to red during this time. After stirring an additional hour at 50 °C, the mixture is cooled to room temperature. At this point, NMR analysis indicates the reaction is complete. Purification of the product mixture by flash chromatography (elution with dichloromethane) yields the desired product in 95% yield as a nearly colorless oil.

EXAMPLE 14

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate**

Crude 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate (154.51, 0.648 mol) from above is placed in a 3000 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal thermometer. The contents are dissolved in 350 mL of dichloromethane and treated with powdered calcium hydroxide (50.44 g, 0.681 mol). The mixture is stirred at 30 °C for 30 min and then heated to 40 °C. 2-Naphthoyl chloride (142.12 g, 0.746 mol) dissolved in 20 mL of dichloromethane is added dropwise over 15 min. The mixture continues to be heated at this temperature for 1 h. Ammonium chloride (36.41 g, 0.681 mol) dissolved in 250 mL of water is added to the reaction mixture and the pH adjusted to ~9 with 28% ammonium hydroxide. After stirring 30 min at 35 °C the pH is adjusted to ~1 with 20% HCl. The mixture is transferred to a separatory funnel
containing diethyl ether (500 mL) and water (500 mL). The layers are separated and
the organic phase is washed with saturated NaHCO₃ solution (2 x 500 mL), dried
over MgSO₄, filtered and concentrated by rotary evaporation to give a yellow red
oil. At this point a light yellow solid precipitates from the mixture. An equal
volume of hexane is added and the solids is collected by filtration and dried. NMR
analysis indicates the solid is 2-naphthoic acid. The eluent is concentrated again by
rotary evaporation to give a red oil. The oil is taken up in an equal volume of
dichloromethane, passed through a plug of silica gel (400 g) and eluted with
dichloromethane. The mixture is concentrated by rotary evaporation and stripped by
Kugelrohr distillation (40 °C, 0.10 mm Hg, 30 min) to yield 173.26 g (76.3%) of the
product as a red oil; this product is a mixture of a 1:10 molar ratio of linalyl
acetoacetate to linalyl (2-naphthoyl)acetate. A portion of this material is purified by
column chromatography (elution with 2.5% ethyl acetate in hexanes) to give the
desired product as a light yellow oil.

EXAMPLE 15

Preparation of 3,7-dimethyl-1,6-octadien-3-yl
3-(β-naphthyl)-3-oxo-2,2-dimethylpropionate

Sodium hydride (2.30 g, 0.057 mol, 60%) and tetrahydrofuran (50 mL) are
placed into a 250 mL three-necked round-bottomed flask fitted with a magnetic
stirrer, ice bath, addition funnel, internal thermometer and argon inlet. The contents
of the flask are cooled to 0 °C. 3,7-Dimethyl-1,6-octadien-3-yl
3-(β-naphthyl)-3-oxo-propionate (8.94 g, 0.025 mol) dissolved in 50 mL of
tetrahydrofuran is added dropwise to the flask over 30 min. During addition, the
mixture evolves gas. After stirring for 1 h, methyl iodide (7.24 g, 0.051 mol) is
added to the reaction mixture. Stirring continues for 2 h at 0 °C and then at room
temperature for 18 h. The mixture is neutralized with 20% HCl and extracted with
diethyl ether. The organic layers are washed with saturated NaHCO₃ solution,
water, dried over MgSO₄, filtered, concentrated by rotary evaporation and purified
by flash chromatography to yield the desired compound. Structure is confirmed by
¹H and ¹³C NMR.

EXAMPLE 16

Preparation of 3,7-dimethyl-1,6-octadien-3-yl
3-(β-naphthyl)-3-oxo-2-methylpropionate

Sodium hydride (3.92 g, 0.098 mol, 60%) and tetrahydrofuran (100 mL) are
placed into a 250 mL three-necked round-bottomed flask fitted with a magnetic
stirrer, ice bath, addition funnel, internal thermometer and argon inlet. The contents
of the flask are cooled to 0 °C. 3,7-Dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-
oxo-propionate (15.28 g, 0.044 mol) dissolved in 50 mL of tetrahydrofuran is added dropwise to the flask over 30 min. During addition, the mixture evolves gas. After stirring for 1 h, methyl iodide (10.65 g, 0.075 mol) is added to the reaction mixture. Stirring continues for 2 h at 0 °C and then at room temperature for 18 h. The mixture is neutralized with 20% HCl and extracted with diethyl ether. The organic layers are washed with saturated NaHCO₃ solution, water, dried over MgSO₄, filtered, concentrated by rotary evaporation and purified by flash chromatography to yield the desired compound. Structure is confirmed by ¹H and ¹³C NMR.

EXAMPLE 17

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-(hexyl)-3-oxo-propionate**

3,7-Dimethyl-1,6-octadien-3-yl 3-oxo-butyrate (30.00 g, 0.126 mol), dichloromethane (50 mL) and methyl ethyl ketone (10 mL) are combined in a 500 mL three-necked round-bottomed flask fitted with an internal thermometer, addition funnel, condenser and argon inlet. Calcium hydroxide (9.80 g, 0.132 mol, powdered) is added to the flask and the slurry stirs for 1 h. Heptanoyl chloride (17.84 g, 0.120 mol) in 10 mL of dichloromethane is added over 15 min so as to keep the reaction temperature between 35-40 °C. The reaction continues to stir at 35-40 °C for 2 h. Ammonium chloride (7.06 g, 0.132 mol) dissolved in 20 mL of water is added to the flask. After 20 min, concentrated ammonium hydroxide is added to the mixture to adjust the pH to ~9.0. After 1 h, 20% HCl solution is added to drop the pH to ~1.0. After 1 h, the mixture is poured into 300 mL of dichloromethane. The layers are separated and the aqueous phase extracted with 100 mL of dichloromethane. The combine organic layers are washed with saturated NaHCO₃ solution, water, dried over MgSO₄, filtered, concentrated by rotary evaporation and purified by flash chromatography to yield the desired compound. Structure is confirmed by ¹H and ¹³C NMR.

EXAMPLE 18

**Preparation of 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-2-benzylbutyrate**

Potassium carbonate (3.92 g, 0.028 mol), 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate (4.80 g, 0.030 mol), benzyl chloride (4.80 g, 0.038 mol) and acetone (15 mL) are placed in a 50 mL round-bottomed flask fitted with a magnetic stirrer, condenser and argon inlet. The mixture is heated to reflux for 18 h. The cooled mixture is filtered and concentrated by rotary evaporation. The resulting oil is purified on silica gel to yield the desired compound. Structure is confirmed by thin layer chromatography and ¹H and ¹³C NMR.
The following nonlimiting examples further illustrate ADD compositions of the present invention.

**TABLE I**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>weight %</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tripolyphosphate (STPP)</td>
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<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Sodium carbonate</td>
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<td>24.0</td>
<td>45.0</td>
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<tr>
<td>Hydrated 2.0 r silicate</td>
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<td>20.0</td>
<td>13.5</td>
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<tr>
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<td>13.5</td>
</tr>
<tr>
<td>Tergitol 1559 2</td>
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<td>2.0</td>
</tr>
<tr>
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<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Protease 4</td>
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</tr>
<tr>
<td>Amylase 5</td>
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<td>0.83</td>
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<tr>
<td>Sodium perborate monohydrate 6</td>
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<td>0.5</td>
</tr>
<tr>
<td>Bleach catalyst 7</td>
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</tr>
<tr>
<td>Bleach catalyst 8</td>
<td></td>
<td>0.008</td>
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</tr>
<tr>
<td>Dibenzoyl peroxide 9</td>
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<td>4.4</td>
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<tr>
<td>Pro-fragrance 10</td>
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<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Minors, sodium sulfate, misc.</td>
<td></td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>

1. POLY-TERGENT® SLF-18B; epoxy-capped poly(oxyalkylated) alcohol according to Example III of WO 94/22800 wherein 1,2 epoxydodecane is substituted for 1,2-epoxydecane.
2. Ethoxylated secondary alcohol supplied by Union Carbide (cloud point = 60°C).
3. Terpolymer selected from either 60% acrylic acid/20% maleic acid/20% ethyl acrylate, or 70% acrylic acid/10% maleic acid/20% ethyl acrylate.
4. *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.
5. Available from Novo Nordisk A/S as QL37+M197T.
6. 15.5% active AvO.
7. Pentaammineacetatocobalt(III) nitrate.
8. Manganese TACN.
9. 18% Active.
10. Pro-fragrance according to Example 1.

The ADD's of the above dishwashing detergent composition examples are used to wash lipstick-stained plastic and ceramic, tea-stained cups, starch-soiled and
spaghetti-soiled dishes, milk-soiled glasses, starch, cheese, egg or babyfood-soiled flatware, and tomato-stained plastic spatulas by loading the soiled dishes in a domestic automatic dishwashing appliance and washing using either cold fill, 60°C peak, or uniformly 45-50°C wash cycles with a product concentration of the exemplary compositions of from about 1,000 to about 8,000 ppm, with excellent results.

The following examples further illustrate phosphate built ADD compositions which contain a bleach/ enzyme particle, but are not intended to be limiting thereof. All percentages noted are by weight of the finished compositions, other than the perborate (monohydrate) component, which is listed as AvO.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>weight %</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium tripolyphosphate (STPP)</td>
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<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>20.0</td>
<td>30.5</td>
<td></td>
</tr>
<tr>
<td>Hydrated 2.0 r silicate</td>
<td>8.0</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Nonionic surfactants 1</td>
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<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Benzotriazole</td>
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<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Polymer 2</td>
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<td></td>
</tr>
<tr>
<td>Protease 3</td>
<td>0.83</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>Amylase 4</td>
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<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Protease 5</td>
<td>--</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Sodium perborate monohydrate 6</td>
<td>2.2</td>
<td>0.7</td>
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</tr>
<tr>
<td>Bleach catalyst 7</td>
<td>0.008</td>
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</tr>
<tr>
<td>Bleach catalyst 8</td>
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<td>0.004</td>
<td></td>
</tr>
<tr>
<td>Dibenzoyl peroxide 9</td>
<td>0.2</td>
<td>0.15</td>
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</tr>
<tr>
<td>Paraffin</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Pro-fraction 10</td>
<td>1.5</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Minors, sodium sulfate, misc.</td>
<td>balance</td>
<td>balance</td>
<td></td>
</tr>
</tbody>
</table>

1. POLY-TERGENT® SLF-18B; epoxy-capped poly(oxyalkylated) alcohol according to Example III of WO 94/22800 wherein 1,2 epoxydodecane is substituted for 1,2-epoxydecane.

2. Polyacrylate or Acusol 480N or polyacrylate/poly(methacrylate) copolymers.

3. Bacillus amyloliquefaciens subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.
4. As described in WO 9510603 A and available from Novo as DURAMYL®.
5. SAVINASE® 12T available from Novo Industries A/S.
6. Per cent available oxygen.
7. Pentaammineacetatocobalt(III) nitrate.
8. Manganese TACN.
9. 18% Active.
10. Pro-fragrance according to Example 1.
WHAT IS CLAIMED IS:

1. An automatic dishwashing detergent composition comprising:
   a) at least about 0.01%, preferably from about 0.01% to about 15%,
   more preferably from about 1% to about 5%, most preferably from
   about 0.1% to about 1% by weight, of a β-ketoester having the
   formula:

   \[
   \begin{array}{c}
   \text{R}^1 \\
   \text{R}^2 \\
   \text{R}^3 \\
   \text{O}
   \end{array}
   \]

   wherein \( R \) is alkoxy derived from a fragrance raw material alcohol;
   \( R^1, R^2, \) and \( R^3 \) are each independently hydrogen, \( C_1-C_{30} \) substituted
   or unsubstituted linear alkyl, \( C_3-C_{30} \) substituted or unsubstituted
   branched alkyl, \( C_3-C_{30} \) substituted or unsubstituted cyclic alkyl, \( C_2-
   C_{30} \) substituted or unsubstituted linear alkenyl, \( C_3-C_{30} \) substituted
   or unsubstituted branched alkenyl, \( C_3-C_{30} \) substituted or
   unsubstituted cyclic alkenyl, \( C_2-C_{30} \) substituted or unsubstituted
   linear alkynyl, \( C_3-C_{30} \) substituted or unsubstituted branched alkynyl,
   \( C_6-C_{30} \) substituted or unsubstituted alkylenearyl, \( C_6-C_{30} \) substituted
   or unsubstituted aryl, \( C_2-C_{20} \) substituted or unsubstituted
   alkyleneoxy, \( C_3-C_{20} \) substituted or unsubstituted alkyleneoxyalkyl,
   \( C_7-C_{20} \) substituted or unsubstituted alkylenearyl, \( C_6-C_{20} \) substituted
   or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at
   least one \( R^1, R^2, \) or \( R^3 \) is a unit having the formula:

   \[
   \begin{array}{c}
   \text{R}^4 \\
   \text{R}^5 \\
   \text{R}^6 \\
   \text{O}
   \end{array}
   \]

   wherein \( R^4, R^5, \) and \( R^6 \) are each independently hydrogen, \( C_1-C_{30} \)
   substituted or unsubstituted linear alkyl, \( C_3-C_{30} \) substituted or
   unsubstituted branched alkyl, \( C_3-C_{30} \) substituted or unsubstituted
   cyclic alkyl, \( C_1-C_{30} \) substituted or unsubstituted linear alkoxy, \( C_3-
   C_{30} \) substituted or unsubstituted branched alkoxy, \( C_3-C_{30} \)
   substituted or unsubstituted cyclic alkoxy, \( C_2-C_{30} \) substituted or
unsubstituted linear alkenyl, C₃-C₃₀ substituted or unsubstituted branched alkenyl, C₃-C₃₀ substituted or unsubstituted cyclic alkenyl, C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted alkynylearyl; or R⁴, R⁵, and R⁶ can be taken together to form C₆-C₃₀ substituted or unsubstituted aryl; and mixtures thereof;

b) at least about 0.1% by weight, preferably from about 0.1% to about 15%, of a detergentsurfactant; and

c) the balance carriers and adjunct ingredients.

2. A composition according to Claim 1 wherein R¹ has the formula:

\[ \text{R}^4 \text{R}^5 \text{R}^6 \text{O} \]

R², R³, R⁴ and R⁵ are each hydrogen; and R⁶ is hydrogen, C₁-C₁₆ substituted or unsubstituted linear alkyl, C₃-C₁₆ substituted or unsubstituted branched alkyl, and mixtures thereof.

3. A composition according to Claim 1 wherein R¹ has the formula:

\[ \text{R}^4 \text{R}^5 \text{R}^6 \text{O} \]

R² and R³ are each hydrogen, R⁴, R⁵ and R⁶ are taken together to form C₆-C₃₀ substituted or unsubstituted phenyl, naphthyl, and mixtures thereof.

4. A composition according to Claim 1 wherein said β-ketoester is selected from the group consisting of 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(4-nitrophenyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(β-naphthyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(4-methoxyphenyl)-3-oxo-propionate, (α,α-4-trimethyl-3-cyclohexenyl)methyl 3-(β-naphthyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(α-naphthyl)-3-oxo-propionate, cis 3-hexen-1-yl 3-(β-
naphthyl)-3-oxo-propionate, 9-decen-1-yl 3-(β-naphthyl)-3-oxo-propionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate, 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate, 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate, 2,6-dimethyl-7-octen-2-yl 3-(β-naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-2,2-dimethylpropionate, 3,7-dimethyl-1,6-octadien-3-yl 3-(β-naphthyl)-3-oxo-2-methylpropionate, 3,7-dimethyl-2,6-octadienyl 3-(β-naphthyl)-3-oxo-propionate, 3,7-dimethyl-2,6-octadienyl 3-heptyl-3-oxo-propionate, and mixtures thereof.

5. A composition according to Claim 1 further comprising at least about 0.1% by weight, preferably from about 0.1% to about 15%, of a detergentsurfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant having the formula:

$$R^2O[CH_2CH(CH_3)O]_x[CH_2CH_2O]_yCH_2CH(OH)R^3$$

wherein $R^2$ is C4-C18 linear or branched alkyl; $R^3$ is C2-C26 linear or branched alkyl; $x$ is an integer having an average value of from 0.5 to about 1.5; and $y$ is an integer having a value of least about 15.

6. A composition according to Claim 1 further comprising from about 5% to about 90% by weight, of a builder.

7. A composition according to Claim 1 further comprising from about 0.1% to about 6% by weight, of a detergents enzyme.

8. A composition according to Claim 7 comprising an enzyme wherein said detergents enzyme is an amylase.

9. A composition according to Claim 1 further comprising from about 0.1% to about 40% by weight, of a bleaching agent.

10. A composition according to Claim 1 further comprising a metal-containing bleach catalyst selected from the group consisting of manganese-containing bleach catalysts, cobalt-containing bleach catalysts, and mixtures thereof.
11. A composition according to Claim 1 further comprising a metal-containing bleach catalyst selected from the group consisting of manganese-containing bleach catalysts, cobalt-containing bleach catalysts, and mixtures thereof.

12. A composition according to Claim 11 wherein the cobalt-containing bleach catalyst has the formula:

$$\text{Co}[(\text{NH}_3)_n\text{M}^m\text{B}^b\text{T}^t\text{Q}^q\text{P}^p] \ Y_y$$

wherein cobalt is in the +3 oxidation state; \( n \) is an integer from 0 to 5; \( M^m \) represents a monodentate ligand; \( m \) is an integer from 0 to 5; \( B^b \) represents a bidentate ligand; \( b \) is an integer from 0 to 2; \( T^t \) represents a tridentate ligand; \( t \) is 0 or 1; \( Q \) is a tetradentate ligand; \( q \) is 0 or 1; \( P \) is a pentadentate ligand; \( p \) is 0 or 1; and \( n + m + 2b + 3t + 4q + 5p = 6 \); \( Y \) is one or more appropriately selected counteranions present in a number \( y \), where \( y \) is an integer from 1 to 3, to obtain a charge-balanced salt; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts versus a normal hydrogen electrode.

13. A composition according to Claim 12 wherein the bleach catalyst is selected from the group consisting of pentaamineacetatocobalt (III) nitrate, 
MnTACN, and mixtures thereof.

14. A composition according to Claim 1 wherein the adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotrropes, enzymes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides, anti corrosion agents, and mixtures thereof.
15. An automatic dishwashing detergent composition comprising:
   a) at least about 0.01%, preferably from about 0.01% to about 15%,
   more preferably from about 1% to about 5%, most preferably from
   about 0.1% to about 1% by weight, of a β-ketoester having the
   formula:

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

   wherein \( R \) is alkoxy derived from a fragrance raw material alcohol;
   \( R^1, R^2, \) and \( R^3 \) are each independently hydrogen, \( C_1-C_{30} \) substituted
   or unsubstituted linear alkyl, \( C_3-C_{30} \) substituted or unsubstituted
   branched alkyl, \( C_3-C_{30} \) substituted or unsubstituted cyclic alkyl, \( C_2-
   C_{30} \) substituted or unsubstituted linear alkenyl, \( C_3-C_{30} \) substituted
   or unsubstituted branched alkenyl, \( C_3-C_{30} \) substituted or
   unsubstituted cyclic alkenyl, \( C_2-C_{30} \) substituted or unsubstituted
   linear alkynyl, \( C_3-C_{30} \) substituted or unsubstituted branched alkynyl,
   \( C_6-C_{30} \) substituted or unsubstituted alkylenearyl, \( C_6-C_{30} \) substituted
   or unsubstituted aryl, \( C_2-C_{20} \) substituted or unsubstituted
   alkyleneoxy, \( C_3-C_{20} \) substituted or unsubstituted alkyleneoxyalkyl,
   \( C_7-C_{20} \) substituted or unsubstituted alkylenearyloxy, \( C_6-C_{20} \) substituted
   or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at
   least one \( R^1, R^2, \) or \( R^3 \) is a unit having the formula:

   \[
   \begin{align*}
   &R^4 \quad \text{R}^5 \\
   \text{O} \\
   \text{R}^6 \\
   \end{align*}
   \]

   wherein \( R^4, R^5, \) and \( R^6 \) are each independently hydrogen, \( C_1-C_{30} \)
   substituted or unsubstituted linear alkyl, \( C_3-C_{30} \) substituted or
   unsubstituted branched alkyl, \( C_3-C_{30} \) substituted or unsubstituted
   cyclic alkyl, \( C_1-C_{30} \) substituted or unsubstituted linear alkoxy, \( C_3-
   C_{30} \) substituted or unsubstituted branched alkoxy, \( C_3-C_{30} \)
   substituted or unsubstituted cyclic alkoxy, \( C_2-C_{30} \) substituted or
   unsubstituted linear alkenyl, \( C_3-C_{30} \) substituted or unsubstituted
   branched alkenyl, \( C_3-C_{30} \) substituted or unsubstituted cyclic alkenyl,
C₂-C₃₀ substituted or unsubstituted linear alkynyl, C₃-C₃₀ substituted or unsubstituted branched alkynyl, C₆-C₃₀ substituted or unsubstituted alkylenearylyl; or R⁴, R⁵, and R⁶ can be taken together to form C₆-C₃₀ substituted or unsubstituted aryl; and mixtures thereof;

b) at least about 0.1% by weight, preferably from about 0.1% to about 15%, of a detergent surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant said surfactant is a nonionic surfactant having the formula:

\[ R^2O[CH₂CH(CH₃)O]ₓ[CH₂CH₂O]₁yCH₂CH(OH)R³ \]

wherein R² is C₄-C₁₈ linear or branched alkyl; R³ is C₂-C₂₆ linear or branched alkyl; x is an integer having an average value of from 0.5 to about 1.5; and y is an integer having a value of least about 15;

c) from about 5% to about 90% by weight, of a builder;

d) optionally from about 0.1% to about 6% by weight, of a detergent enzyme;

e) optionally, from about 0.1% to about 40% by weight, of a bleaching agent; and

f) the balance carriers and adjunct ingredients.

16. A composition according to Claim 15 wherein the cobalt-containing bleach catalyst has the formula:

\[ \text{Co}[(\text{NH}_₃)ₙM'_mB'_bT'_tQ_qP_p] Y_y \]

wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5; M' represents a monodentate ligand; m is an integer from 0 to 5; B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and \( n + m + 2b + 3t + 4q + 5p = 6 \); Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3, to obtain a charge-balanced salt; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the
cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts versus a normal hydrogen electrode.

17. A composition according to Claim 16 wherein the bleach catalyst is selected from the group consisting of pentaamineacetatocobalt (III) nitrate, MnTACN, and mixtures thereof.

18. A composition according to Claim 1 further comprising a chlorine bleaching agent.

19. A method of washing tableware in a domestic automatic dishwashing appliance, said method comprising treating the soiled tableware in an automatic dishwasher with an aqueous alkaline bath comprising an automatic dishwashing detergent comprising one or more β-ketoesters having the formula:

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

wherein R is alkoxy derived from a fragrance raw material alcohol; R^1, R^2, and R^3 are each independently hydrogen, C_1-C_{30} substituted or unsubstituted linear alkyl, C_3-C_{30} substituted or unsubstituted branched alkyl, C_3-C_{30} substituted or unsubstituted cyclic alkyl, C_2-C_{30} substituted or unsubstituted linear alkenyl, C_3-C_{30} substituted or unsubstituted branched alkenyl, C_3-C_{30} substituted or unsubstituted cyclic alkenyl, C_2-C_{30} substituted or unsubstituted linear alkynyl, C_3-C_{30} substituted or unsubstituted branched alkynyl, C_6-C_{30} substituted or unsubstituted alkylenearyl, C_6-C_{30} substituted or unsubstituted aryl, C_2-C_{20} substituted or unsubstituted alkyleneoxy, C_3-C_{20} substituted or unsubstituted alkyleneoxyalkyl, C_7-C_{20} substituted or unsubstituted alkylenearyl, C_6-C_{20} substituted or unsubstituted alkyleneoxyaryl, and mixtures thereof; provided at least one R^1, R^2, or R^3 is a unit having the formula:
wherein $R^4$, $R^5$, and $R^6$ are each independently hydrogen, C$_{1-C30}$ substituted or unsubstituted linear alkyl, C$_{3-C30}$ substituted or unsubstituted branched alkyl, C$_{3-C30}$ substituted or unsubstituted cyclic alkyl, C$_{1-C30}$ substituted or unsubstituted linear alkoxy, C$_{3-C30}$ substituted or unsubstituted branched alkoxy, C$_{3-C30}$ substituted or unsubstituted cyclic alkoxy, C$_{2-C30}$ substituted or unsubstituted linear alkenyl, C$_{3-C30}$ substituted or unsubstituted branched alkenyl, C$_{3-C30}$ substituted or unsubstituted cyclic alkenyl, C$_{2-C30}$ substituted or unsubstituted linear alkynyl, C$_{3-C30}$ substituted or unsubstituted branched alkynyl, C$_{6-C30}$ substituted or unsubstituted alkylenearyl; or $R^4$, $R^5$, and $R^6$ can be taken together to form C$_{6-C30}$ substituted or unsubstituted aryl; and mixtures thereof.