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(21) International Application Number: PCT/US98/07935 (22) International Filing Date: 23 April 1998 (23.04.98) (30) Priority Data: 60/044,802 24 April 1997 (24.04.97) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): MORELLI, Joseph, Paul [US/US]; 541 Howell Street, Cincinnati, OH 45220 (US). WAITE, Scott, William [US/US]; 12175 Elkwood Drive, Cincinnati, OH 45240 (US). GOSSELINK, Eugene, Paul [US/US]; 3754 Susanna Drive, Cincinnati, OH 45251 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: BR, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: LAUNDRY DETERGENT COMPOSITIONS COMPRISING FRAGRANCE PRO-ACCORDS (57) Abstract The present invention relates to a fragrance delivery system for use in laundry detergent compositions which provides a long lasting "freshness" or "clean" scent to fabric. The compositions described herein deliver highly fabric substantive pro-accords to the fabric surface during laundering wherein the pro-accords release their fragrance raw materials over a period of up to two weeks. The present invention also relates a method for delivering a pleasurable scent to fabric which has a lasting freshness quality by contacting the fabric with a laundry detergent composition which comprises the fragrance-releasable pro-accords.		

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LAUNDRY DETERGENT COMPOSITIONS COMPRISING FRAGRANCE PRO-ACCORDS

FIELD OF THE INVENTION

The present invention relates to laundry detergent compositions which provide a "freshness" or "clean" scent to fabric. The compositions described herein deliver pro-accords to the fabric during laundering. The pro-accords then release fragrance raw materials which provide the fabric with a pleasing, fresh-like odor. The present invention also relates a method for delivering a pleasurable scent to fabric which has a lasting freshness quality.

BACKGROUND OF THE INVENTION

In addition to the removal of stains, dirt, soil, grime, and grease from fabric, laundry detergent formulators have attempted to deliver a "fresh" or "clean" odor to washed clothing to provide an olfactory aesthetic benefit and to serve as a signal that the product is effective. Laundry detergent compositions, including rinse-added fabric softeners and dryer-added substrates, are currently formulated with perfume and fragrance ingredients which are aesthetically pleasing to the consumer but which fail to deliver a prolonged "fragrance" or "pleasurable smell" to the finished, cleaned fabric.

Among the most readily perceived fragrance materials are the perfume "top" and "middle" notes which are highly volatile compounds and which are usually detectable at low levels. However, these highly volatile materials are typically lost either during the prolonged heating which takes place in an automatic dryer or they lack the substantivity necessary to deposit onto the fabric surface and are therefore lost during the laundry rinsing process.

Attempts have been made to deliver perfume ingredients onto fabric which can survive the laundry rinsing and drying cycles and therefore provide a residual "fresh" or "clean" odor to the washed material. However, none of these attempts have suitably provided fabric with a protracted release of fragrance raw materials which provide a "fresh" or "clean" smell for a period up to two weeks after washing.

Accordingly, there remains a need in the art for a fragrance delivery system wherein perfume raw materials are delivered to fabric by way of a laundry detergent composition which provides the cleaned clothing or fabric with a "fresh" or "clean" smell for a period up to two weeks after washing. Also, there is a need for a method for determining the parameters which allow the formation of compounds which comprise the fragrance delivery systems.

BACKGROUND ART

In addition to the above-cited references, the following relate to the subject matter of fragrance ingredients. U.S. 5,232,612 Trinh *et al.*, issued August 3, 1996; U.S. 5,506,201 McDermott *et al.*, issued April 9, 1996; U.S. 5,378,468 Suffis *et al.*, issued January 3, 1995; U. S. 5,266,592 Grub *et al.*, issued November 30, 1993; U. S. 5,081,111 Akimoto *et al.*, issued January 14, 1992; U. S. 4,994,266 Wells, issued February 19, 1991; U.S. 4,524,018 Yemoto *et al.*, issued June 18, 1985; U. S. 3,849,326 Jagers *et al.*, issued November 19, 1974; U. S. 3,779,932 Jagers *et al.*, issued December 18, 1973; JP 07-179,328 published July 18, 1995; JP 05-230496 published September 7, 1993; WO 96/14827 published May 23, 1996; WO 95/04,809 published February 16, 1995; and WO 95/16660 published June 22, 1995. In addition, P.M. Muller, D. Lamparsky Perfumes Art, Science, & Technology Blackie Academic & Professional, (New York, 1994) is included herein by reference.

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs in that it has been surprisingly discovered that perfume or fragrance accords can be delivered onto fabric "through the wash" from a single precursor pro-accord molecule having high fabric substantivity and that these pro-accords impart a "fresh" or "clean" aesthetic odor benefit to the fabric. In addition to the short-term pleasurable odor benefits, the pro-accords according to the present invention continue to release their fragrance raw materials for as long as several weeks depending upon the structure of the pro-accord.

The pro-accords described herein comprise fragrance raw materials in a stable, releasable form. The pro-accord containing laundry detergent compositions of the present invention can comprise any number of pro-accords which when taken together are capable of releasing complex perfume fragrances. In addition, the pro-accords of the present invention are suitable for delivery of any type of fragrance "characteristic" desired by the formulator.

The first aspect of the present invention relates to laundry detergent compositions which provide fabric with enhanced fragrance longevity, comprising:

- a) at least about 0.01%, preferably from about 0.01% to about 10%, more preferably from about 0.1% to about 1% by weight, of a fragrance delivery system comprising one or more pro-accords, said pro-accords formed from at least one fragrance raw material and capable of releasing two or more fragrance raw materials wherein provided said pro-accord:

- i) comprises fragrance raw materials having a molecular weight greater than or equal to about 100 g/mol;
 - ii) has a molecular weight greater than or equal to about 300 g/mol;
 - iii) has a molecular weight at least two times greater than the lowest molecular weight fragrance raw material which comprises said pro-accord; and
 - iv) has a fragrance release half-life of less than about 1 hour when measured in a 90:10 dioxane/1 N HCl mixture at pH 0, preferably a fragrance release half-life of less than about 12 hours when measured in NaH_2PO_4 buffer at pH 2.5;
- b) at least about 0.01% by weight, preferably from about 0.1% to about 60%, more preferably from about 0.1% to about 30% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant; and
- c) the balance carriers and adjunct ingredients said 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, dispersants, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, 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.

A further aspect of the present invention relates to methods for selecting a suitable pro-accord for use in providing a fragrance benefit to fabric wherein the fragrance has enhanced odor longevity.

A yet further aspect of the present invention relates to methods for providing an extended "fresh" and "clean" odor benefit to fabric comprising the step of laundering fabric in an aqueous solution of a laundry detergent composition comprising one or more pro-accords described herein. 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 ($^{\circ}\text{C}$) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The laundry detergent compositions of the present invention comprise a fragrance delivery system which lays down one or more fragrance "pro-accord" compounds onto the fabric surface during the laundry wash cycle. Because the pro-accords of the present invention generally have a higher molecular weight than uncombined fragrance raw materials and other "pro-fragrance-type" compounds (i.e. those pro-fragrances which only deliver a single equivalent of a fragrance raw material), the pro-accords of the present invention are a means for effectively delivering two or more fragrance raw materials to the fabric surface even upon exposure to prolonged heating which occurs during automatic dryer usage.

Once the laundry cycle is complete, the "pro-accord" begins to release the fragrance or perfume accord and because this release of material is protracted, the fabric remains "fresh" and "clean" smelling longer. However, pro-accords according to the present invention can also be designed to be "heat activated" so as to release a "freshening scent" to the fabric during drying. Therefore, heat-activated pro-accords can be delivered to the fabric surface. This results in a fabric having high "initial scent" as well as the lower "clean" and "fresh" scent obtained by the protracted release of non-activated accords. What is meant herein by "heat activated" pro-accords are compounds which have a higher release rate of their fragrance materials after exposure to elevated temperatures. Therefore the formulator may achieve an initial high fragrance delivery coupled with the longer term sustained release.

The pro-accords of the present invention are therefore a means for delivering two or more fragrance raw materials onto fabric and thereby providing the fabric with a longer and more sustained "fresh" or "clean" smell. These mixtures of two or more released fragrance raw materials are known by those skilled in the art of fragrances and perfumes as "accords", thus the term "pro-accord" is used to describe the compounds which comprise the fragrance delivery system of the present invention. The term "accord" as used herein is defined as "mixtures of two or more 'fragrance raw materials' which are combined to impart a pleasurable scent, odor, or fragrance characteristic". The term "binary accord" as used herein is defined as "a mixture of two complimentary fragrance raw materials which together deliver a fragrance note". For the purposes of the present invention "fragrance raw materials" are herein defined as compounds having a molecular weight of at least 100 g/mol and which are useful in imparting an odor, fragrance, essence, or scent either alone or in combination with other "fragrance raw materials".

Most of the fragrance raw materials which comprise the pro-accords of the present invention are not deliverable as individual compounds to fabric via the

laundry cycle either due to solubility factors (lost or rinsed away during the laundry cycles), substantivity factors (do not sufficiently adhere to fabric surface), or volatility factors (evaporation during the drying cycle). Therefore, the pro-accords described herein are a means for delivering certain fragrance raw materials to fabric which could not have previously been effectively or efficiently delivered.

The preferred pro-accords of the present invention are orthoesters and orthocarbonates. The "fragrance raw materials" which comprise the preferred embodiments are fragrance raw material alcohols. A listing of common fragrance raw material alcohols can be found in various reference sources, for example, "Perfume and Flavor Chemicals", Vols. I and II; Steffen Arctander Allured Pub. Co. (1994) and "Perfumes: Art, Science and Technology"; Müller, P. M. and Lamparsky, D., Blackie Academic and Professional (1994) all of which are incorporated herein by reference.

For example, but not by way of limitation, the fragrance accords released by the pro-accords of the present invention have a "heart", "character", or "note" which is described as *inter alia* rose, jasmin, lilac, lily of the valley, violet, orange, peach, watermelon, and lemon. The accord may be further "modified" or "twisted" by the use of modifier top or middle notes which, as an additional benefit afforded by the present invention, can be incorporated into the pro-accord. For example, a "rose essence" may be combined with a "green" modifier to "shift the fragrance accord character".

For the purposes of the present invention the terms "fresh", "fresh-like", "fresh smelling", "clean", "clean-like" and "clean smelling" are terms used to describe the sensory effect produced by the release of the fragrance raw materials which comprise the pro-accords of the present invention. The presence of perfume components and fragrance raw materials upon a fabric up to two weeks after washing are regarded as imparting the aforementioned sensory effects.

Pro-Accords

The pro-accords of the present invention are comprised of one or more fragrance raw materials. These fragrance raw materials are then converted into a different chemical form which incorporates the fragrance raw materials in a manner which allows the release of the original fragrance raw material as well as other "newly formed" materials. These chemically modified forms of the fragrance raw materials are the "pro-accords" of the present invention. One principle aspect of the present invention is the ability of pro-accords described herein to deliver more than one fragrance raw material when the "pro-accord" has been formed from only one fragrance raw material. All of the pro-accords of the present invention are capable

of releasing at least two fragrance raw materials (hereinafter "binary accord") upon deposition onto fabric. There are two types of pro-accords; "symmetrical" pro-accords and "unsymmetrical" pro-accords each described herein further below.

Molecular Weight

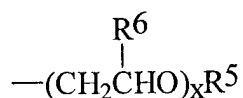
The pro-accords of the present invention generally have a molecular weight of at least 300 g/mol, preferably greater than 325 g/mol, more preferably greater than 350 g/mol. It is also a condition of the present invention that the final molecular weight of the pro-accord is at least 2 times, preferably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

For the purposes of the present invention, only fragrance raw materials having a molecular weight of at least 100 g/mol are considered "fragrance raw materials" according to the present invention. Therefore, low molecular weight materials *inter alia* methanol, ethanol, methyl acetate, ethyl acetate, and methyl formate which are common components of fragrance accords are excluded from the class of compounds defined herein as "fragrance raw materials". However, the formulator may wish to deliver these lower molecular weight materials (less than a molecular weight of 100 g/mol) as carriers, astringents, diluents, balancers, or as other suitable adjunct materials and is therefore not precluded from forming a pro-accord material which delivers, in addition to a fragrance raw material accord, a suitable astringent, carrier, diluent, extender, balancer, etc. Preferably a pro-accord which does not comprise a low molecular weight adjunct is present in addition to any pro-accord which releases an adjunct material.

By way of illustration and not limitation, the pro-accord tris-geranyl orthoformate is considered, for the purposes of the present invention to be formed from three equivalents of geraniol. This pro-accord releases the binary accord geraniol/geranyl formate. This pro-accord has a molecular weight of approximately 472 g/mol. The lowest molecular weight fragrance raw material which is a component of tris-geranyl orthoformate is geraniol which has a molecular weight of approximately 154 g/mol. Therefore tris-geranyl orthoformate has a molecular weight greater than 3 times the molecular weight of the lowest molecular weight fragrance raw material component (geraniol) and hence is a most preferred pro-accord.

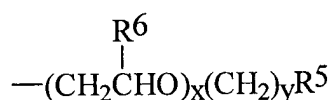
For the purposes of the present invention substituted or unsubstituted alkyleneoxy units are defined as moieties having the formula:

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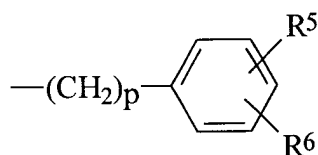
wherein R⁵ is hydrogen; R⁶ is hydrogen, methyl, ethyl, and mixtures thereof; the index x is from 1 to about 20.

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



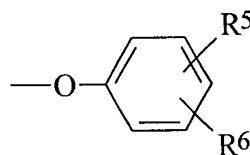
wherein R⁵ is hydrogen, C₁-C₁₈ alkyl, C₁-C₄ alkoxy, and mixtures thereof; R⁶ is hydrogen, methyl, ethyl, and mixtures thereof; the index x is from 1 to about 20 and the index y is from 2 to about 30.

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



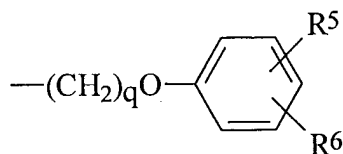
wherein R⁵ and R⁶ are each independently hydrogen, hydroxy, C₁-C₄ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂H; -CO₂R'; -CONH₂; -CONHR'; -CONR'₂); wherein R' is C₁-C₁₂ linear or branched alkyl), amino, alkylamino, and mixtures thereof, p is from 1 to about 34.

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



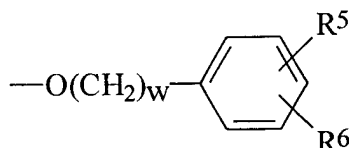
wherein R⁵ and R⁶ are each independently hydrogen, hydroxy, C₁-C₄ alkoxy, nitrilo, halogen, nitro, carboxyl (-CHO; -CO₂H; -CO₂R'; -CONH₂; -CONHR'; -CONR'₂); wherein R' is C₁-C₁₂ linear or branched alkyl), amino, alkylamino, and mixtures thereof.

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



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

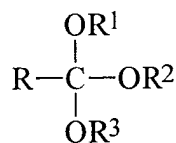
For the purposes of the present invention substituted or unsubstituted oxyalkylenearyl units are defined as moieties having the formula:



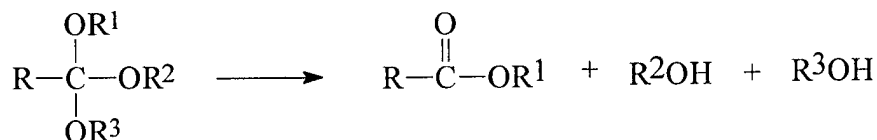
wherein R^5 and R^6 are each independently hydrogen, hydroxy, C_1 - C_4 alkoxy, nitrilo, halogen, nitro, carboxyl ($-\text{CHO}$; $-\text{CO}_2\text{H}$; $-\text{CO}_2\text{R}'$; $-\text{CONH}_2$; $-\text{CONHR}'$; $-\text{CONR}'_2$; wherein R' is C_1 - C_{12} linear or branched alkyl), amino, alkylamino,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

Orthoesters

One class compounds useful as pro-accords according to the present invention are orthoesters having the formula:



wherein hydrolysis of the orthoester releases fragrance raw material components according to the following scheme:



wherein R is hydrogen, C_1 - C_8 linear alkyl, C_4 - C_{20} branched alkyl, C_6 - C_{20} cyclic alkyl, C_6 - C_{20} branched cyclic alkyl, C_6 - C_{20} linear alkenyl, C_6 - C_{20} branched alkenyl, C_6 - C_{20} cyclic alkenyl, C_6 - C_{20} branched cyclic alkenyl, C_6 - C_{20} substituted or unsubstituted aryl, preferably the moieties which substitute the aryl

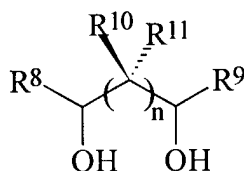
units are alkyl moieties, and mixtures thereof, preferably R is hydrogen, methyl, ethyl, and phenyl. R^1 , R^2 and R^3 are independently C_1 - C_{20} linear, branched, or substituted alkyl; C_2 - C_{20} linear, branched, or substituted alkenyl; C_5 - C_{20} substituted or unsubstituted cyclic alkyl; C_6 - C_{20} substituted or unsubstituted aryl, C_2 - C_{40} substituted or unsubstituted alkyleneoxy; C_3 - C_{40} substituted or unsubstituted alkyleneoxyalkyl; C_6 - C_{40} substituted or unsubstituted alkylenearyl; C_6 - C_{32} substituted or unsubstituted aryloxy; C_6 - C_{40} substituted or unsubstituted alkyleneoxyaryl; C_6 - C_{40} oxyalkylenearyl; and mixtures thereof. By the term "substituted" herein is meant "compatible moieties which replace a hydrogen atom". Non-limiting examples of substituents are hydroxy, nitrilo, halogen, nitro, carboxyl ($-\text{CHO}$; $-\text{CO}_2\text{H}$; $-\text{CO}_2\text{R}'$; $-\text{CONH}_2$; $-\text{CONHR}'$; $-\text{CONR}'_2$; wherein R' is C_1 - C_{12} linear or branched alkyl), amino, C_1 - C_{12} mono- and dialkylamino, and mixtures thereof.

Non-limiting examples of R^1 , R^2 and R^3 are methyl, 2,4-dimethyl-3-cyclohexene-1-methyl (Floralol), 2,4-dimethyl cyclohexane methyl (Dihydro floralol), 5,6-dimethyl-1-methylethenyl-bicyclo[2.2.1]hept-5-ene-2-methyl (Arbozol), 2,4,6-trimethyl-3-cyclohexene-1-methyl (Isocyclo geranyl), 4-(1-methylethyl)cyclohexylmethyl (Mayol), α -3,3-trimethyl-2-norboranylmethyl, 1,1-dimethyl-1-(4-methylcyclohex-3-enyl)methyl, ethyl, 2-phenylethyl, 2-cyclohexylethyl, 2-(o-methylphenyl)ethyl, 2-(m-methylphenyl)ethyl, 2-(p-methylphenyl)ethyl, 6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethyl (nopyl), 2-(4-methylphenoxy)ethyl, 3,3-dimethyl- Δ^2 - β -norbornanylethyl, 2-methyl-2-cyclohexylethyl, 1-(4-isopropylcyclohexyl)ethyl, 1-phenyl-1-hydroxyethyl, 1,1-dimethyl-2-phenylethyl, 1,1-dimethyl-2-(4-methylphenyl)ethyl, propyl, 1-phenylpropyl, 3-phenylpropyl, 2-phenylpropyl (Hydrotropic Alcohol), 2-(cyclododecyl)-propan-1-yl (Hydroxyambran), 2,2-dimethyl-3-(3-methylphenyl)propan-1-yl (Majantol), 2-methyl-3-phenylpropyl, 3-phenyl-2-propen-1-yl (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-yl (methylcinnamyl alcohol), α -n-pentyl-3-phenyl-2-propen-1-yl (α -amylcinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propyl, butyl, 3-methylbutyl, 3-(4-methylcyclohex-3-ene)butyl, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butyl, 2-ethyl-4-(2,2,3-trimethylcyclopent-3-enyl)-2-buten-1-yl, 3-methyl-2-buten-1-yl, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-yl, 3-hydroxy-2-butanone, ethyl 3-hydroxybutyrate, 4-phenyl-3-buten-2-yl, 2-methyl-4-phenylbutan-2-yl, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)butan-2-one, pentyl, *cis*-3-pentenyl, 3-methylpentyl, 3-methyl-3-penten-1-yl, 2-methyl-4-phenylpentyl (Pamplefleur), 3-methyl-5-phenylpentyl

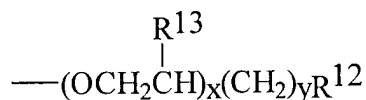
(Phenoxany), 2-methyl-5-phenylpentyl, 2-methyl-5-(2,3-dimethyltricyclo-[2.2.1.0(2,6)]hept-3-yl)-2-penten-1-yl (santalyl), 4-methyl-1-phenyl-2-pentyl, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-yl, 3-methyl-1-phenylpent-3-yl, 1,2-dimethyl-3-(1-methylethenyl)cyclopent-1-yl, 2-isopropyl-4-methyl-2-hexenyl, *cis*-3-hexen-1-yl, *trans*-2-hexen-1-yl, 2-isopropenyl-5-methyl-4-hexen-1-yl (Lavandulyl), 2-ethyl-2-prenyl-3-hexenyl (silwanol), 2-ethylhexyl, 1-hydroxymethyl-4-isopropenyl-1-cyclohexenyl (Dihydrocuminy), 1-methyl-4-isopropenylcyclohex-6-en-2-yl (carvenyl), 6-methyl-3-isopropenylcyclohex-1-yl, 1-methyl-4-isopropenylcyclohex-3-yl, 4-iso-propyl-1-methylcyclohex-3-yl, 4-tert-butylcyclohexyl, 2-tert-butylcyclohexyl, 2-tert-butyl-4-methylcyclohexyl, 4-isopropylcyclohexyl, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-yl, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexyl, isobornylcyclohexyl, 3,3,5-trimethylcyclohexyl, 1-methyl-4-isopropylcyclohex-3-yl (menthol), 1,2-dimethyl-3-(1-methylethyl)-cyclohexan-1-yl, heptyl, 2,4-dimethylhept-1-yl, 2,4-dimethyl-2,6-heptandienyl, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-en-1-yl (myrtenyl), 4-methyl-2,4-heptadien-1-yl, 3,4,5,6,6-pentamethyl-2-heptyl, 3,6-dimethyl-3-vinyl-5-hepten-2-yl, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]-heptyl, 1,7,7-trimethylbicyclo-[2.2.1]hept-2-yl, 2,6-dimethylhept-2-yl, 2,6,6-trimethylbicyclo[1.3.3]hept-2-yl, octyl, 2-octenyl, 2-methyloctan-2-yl, 2-methyl-6-methylene-7-octen-2-yl (myrcenyl), 7-methyloctan-1-yl, 3,7-dimethyl-6-octenyl, 3,7-dimethyl-7-octenyl, 3,7-dimethyl-6-octen-1-yl (citronellyl), 3,7-dimethyl-2,6-octadien-1-yl (geranyl), 3,7-dimethyl-2,6-octadien-1-yl (neryl), 3,7-dimethyl-1,6-octadien-3-yl (linalyl), 3,7-dimethyloctan-1-yl (pelagryl), 3,7-dimethyloctan-3-yl (tetrahydrolinalyl), 2,4-octadien-1-yl, 3,7-dimethyl-6-octen-3-yl, 2,6-dimethyl-7-octen-2-yl, 2,6-dimethyl-5,7-octadien-2-yl, 4,7-dimethyl-4-vinyl-6-octen-3-yl, 3-methyloctan-3-yl, 2,6-dimethyloctan-2-yl, 2,6-dimethyloctan-3-yl, 3,6-dimethyloctan-3-yl, 2,6-dimethyl-7-octen-2-yl, 2,6-dimethyl-3,5-octadien-2-yl (mugyl), 3-methyl-1-octen-3-yl, 7-hydroxy-3,7-dimethyloctanalyl, 3-nonyl, 6,8-dimethylnonan-2-yl, 3-(hydroxymethyl)-2-nonanone, 2-nonen-1-yl, 2,4-nonadien-1-yl, 2,6-nonadien-1-yl, *cis*-6-nonen-1-yl, 3,7-dimethyl-1,6-nonadien-3-yl, decyl, 9-decenyl, 2-benzyl-M-dioxa-5-yl, 2-decen-1-yl, 2,4-decadien-1-yl, 4-methyl-3-decen-5-yl, 3,7,9-trimethyl-1,6-decadien-3-yl (isobutyl linalyl), undecyl, 2-undecen-1-yl, 10-undecen-1-yl, 2-dodecen-1-yl, 2,4-dodecadien-1-yl, 2,7,11-trimethyl-2,6,10-dodecatrien-1-yl (farnesyl), 3,7,11-trimethyl-1,6,10,-dodecatrien-3-yl, 3,7,11,15-tetramethylhexadec-2-en-1-yl (phytyl), 3,7,11,15-tetramethylhexadec-1-en-3-yl (iso phytol), benzyl, p-methoxybenzyl (anisyl), *para*-cymen-7-yl (cuminy), 4-methylbenzyl, 3,4-methylenedioxybenzyl, 2-(methyl)carboxy-1-hydroxyphenyl, 2-(benzyl)carboxy-1-

hydroxyphenyl, 2-(*cis*-3-hexenyl)-carboxy-1-hydroxyphenyl, 2-(*n*-pentyl)carboxy-1-hydroxyphenyl, 2-(2-phenylethyl)carboxy-1-hydroxyphenyl, 2-(*n*-hexyl)carboxy-1-hydroxyphenyl, 2-methyl-5-isopropyl-1-hydroxyphenyl, 4-ethyl-2-methoxyphenyl, 4-allyl-2-methoxy-1-hydroxyphenyl (eugenyl), 2-methoxy-4-(1-propenyl)-1-hydroxyphenyl (isoeugenyl), 4-allyl-2,6-dimethoxy-1-hydroxyphenyl, 4-*tert*-butyl-1-hydroxyphenyl, 2-ethoxy-4-methyl-1-hydroxyphenyl, 2-methyl-4-vinyl-1-hydroxyphenyl, 2-isopropyl-5-methyl-1-hydroxyphenyl (thymyl), 2-(isopentyl)-carboxy-1-hydroxyphenyl, 2-(ethyl)carboxy-1-hydroxyphenyl, 6-(methyl)carboxy-2,5-dimethyl-1,3-dihydroxyphenyl, 5-methoxy-3-methyl-1-hydroxyphenyl, 2-*tert*-butyl-4-methyl-1-hydroxyphenyl, 1-ethoxy-2-hydroxy-4-propenylphenyl, 4-methyl-1-hydroxyphenyl, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-hydroxybenzaldehyde, decahydro-2-naphthyl, 2,5,5-trimethyl-octahydro-2-naphthyl, 1,3,3-trimethyl-2-norbornyl (fenchyl), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-yl, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-yl, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuranlyl, β -caryophyllenyl, and mixtures thereof.

A further example of orthoesters according to the present invention are cyclic orthoesters derived from at least one diol having the formula:

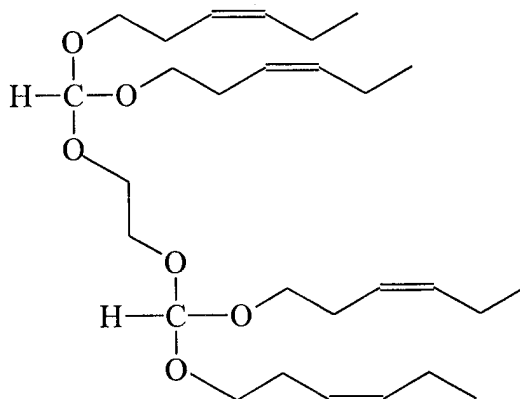


wherein R^8 , R^9 , R^{10} , and R^{11} are each independently hydrogen, C_1 - C_{20} linear or branched alkyl, C_1 - C_{20} linear or branched alkenyl, C_1 - C_{20} linear, branched or cyclic alkylencarboxy, C_1 - C_{20} linear, branched, or cyclic carboxyalkyl, C_1 - C_{20} linear or branched alkyleneamino, C_1 - C_{20} linear or branched aminoalkyl, C_1 - C_{20} linear, branched, or cyclic alkylencarboxamido, C_1 - C_{20} linear or branched carboxamidoalkyl, alkyleneoxy having the formula:



wherein R^{12} is hydrogen or methyl; R^{13} is hydrogen or C_1 - C_2 alkyl; n is from 0 to 4, x is from 1 to about 20, y is from 0 to about 20.

Also R¹, R², or R³ units may serve to link two pro-accords for the purpose of providing greater substantivity. An example of "pro-accord linking" by a diol has the following formula:



Orthoester Releasable Components: Hydrolysis of the orthoesters of the present invention result in the delivery of two types of releasable component, namely alcohols and esters. More specifically, hydrolysis of an orthoester yields two equivalents of releasable alcohol, preferably a primary or secondary alcohol and one equivalent of releasable ester. The released ester, when taken together with the released alcohol, forms a binary fragrance accord. For example tris-geranyl orthoformate releases the binary accord geraniol/geranyl formate.

Examples of preferred esters which are releasable components of the orthoesters of the present invention include, but are not limited to, geranyl formate, citronellyl formate, phenylethyl formate, phenoxyethyl formate, *trans*-2-hexenyl formate, *cis*-3-hexenyl formate, *cis*-6-nonenyl formate, 9-decenyl formate, 3,5,5-trimethylhexyl formate, 3-methyl-5-phenylpentanyl formate, 6-methylheptan-2-yl formate, 4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl formate, 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl formate, 4-isopropylcyclohexyleth-2-yl formate, 6,8-dimethylnonan-2-yl formate, decahydro- β -naphthyl formate, 4-isopropylcyclohexylmethyl formate, linalyl formate, lavandulyl formate, citronellyl formate, α -terpinyl formate, nopyl formate, isobornyl formate, bornyl formate, isobornyl formate, guaiayl formate, 2-*tert*-butylcyclohexyl formate, 4-*tert*-butylcyclohexyl formate, decahydro- β -naphthyl formate, menthyl formate, p-menthanyl formate, neryl formate, cinnamyl formate, ethyl acetate, butyl acetate, isoamyl acetate, hexyl acetate, 3,5,5-trimethylhexyl acetate, geranyl acetate, citronellyl acetate, phenylethyl acetate, phenoxyethyl acetate, *trans*-2-hexenyl acetate, *cis*-3-hexenyl acetate, *cis*-6-nonenyl acetate, 9-decenyl acetate, 3-methyl-5-phenylpentanyl acetate, 6-methyl-heptan-2-yl acetate, 4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl acetate, 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-

yl)-4-penten-2-yl acetate, decahydro- β -naphthyl acetate, menthyl acetate, benzyl acetate, 4-isopropylcyclohexyleth-2-yl acetate, 6,8-dimethylnonan-2-yl acetate, 1-phenylethyl acetate, 4-isopropylcyclohexylmethyl acetate, linalyl acetate, lavandulyl acetate, citronellyl acetate, α -terpinyl acetate, nopyl acetate, isobornyl acetate, bornyl acetate, isobornyl acetate, guaiyl acetate, 2-*tert*-butylcyclohexyl acetate, 4-*tert*-butylcyclohexyl acetate, decahydro- β -naphthyl acetate, menthyl acetate, p-menthanyl acetate, neryl acetate, cinnamyl acetate, ethyl propionate, ethyl butyrate, butyl butyrate, isoamyl butyrate, hexyl butyrate, *cis*-3-hexenyl butyrate, *cis*-3-hexenyl isobutyrate, ethyl isovalerate, 2-methylbutyrate, ethyl hexanoate, 2-propenyl hexanoate, ethyl heptanoate, 2-propenyl heptanoate, ethyl octanoate, ethyl 2-*trans*-4-*cis*-decadienoate, methyl 2-nonynoate, benzyl propionate, benzyl isovalerate, phenylethyl isobutyrate, phenylethyl isovalerate, α,α -dimethyl phenylethyl butyrate, methyl benzoate, hexyl benzoate, benzyl benzoate, ethyl phenylacetate, geranyl phenylacetate, 1-phenylethyl phenylacetate, methyl cinnamate, benzyl cinnamate, phenylethyl cinnamate, geranyl propionate, geranyl isobutyrate, geranyl isovalerate, linalyl propionate, linalyl butyrate, linalyl isobutyrate, citronellyl propionate, citronellyl isobutyrate, citronellyl isovalerate, citronellyl tiglate, allyl 3-cyclohexylpropionate, methyl dihydrojasmonate, methyl 2-hexyl-3-oxocyclopentane-carboxylate, and mixtures thereof.

Non-limiting examples of alcohols suitably released by the hydrolysis of the orthoester pro-accords include methanol, 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), 2,4,6-trimethyl-3-cyclohexene-1-methanol (Isocyclo geraniol), 4-(1-methylethyl)cyclohexanemethanol (Mayol), α -3,3-trimethyl-2-norborane methanol, 1,1-dimethyl-1-(4-methylcyclohex-3-enyl)methanol, ethanol, 2-phenylethanol, 2-cyclohexyl ethanol, 2-(*o*-methylphenyl)-ethanol, 2-(*m*-methylphenyl)ethanol, 2-(*p*-methylphenyl)ethanol, 6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-ethanol (nopol), 2-(4-methylphenoxy)ethanol, 3,3-dimethyl- Δ^2 - β -norbornane ethanol, 2-methyl-2-cyclohexylethanol, 1-(4-isopropylcyclohexyl)-ethanol, 1-phenylethanol, 1,1-dimethyl-2-phenylethanol, 1,1-dimethyl-2-(4-methyl-phenyl)ethanol, *n*-propanol, 2-propanol, 1-phenylpropanol, 3-phenylpropanol, 2-phenylpropanol (Hydrotropic Alcohol), 2-(cyclododecyl)propan-1-ol (Hydroxy-ambran), 2,2-dimethyl-3-(3-methylphenyl)propan-1-ol (Majantol), 2-methyl-3-phenylpropanol, 3-phenyl-2-propen-1-ol (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-ol (methylcinnamyl alcohol), α -*n*-pentyl-3-phenyl-2-propen-1-ol (α -amyl-cinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propanol, *n*-butanol, 2-butanol, 3-methylbutanol, 3-(4-

methylocyclohex-3-ene)butanol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butanol, 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-2-buten-1-ol, 3-methyl-2-buten-1-ol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, 3-hydroxy-2-butanone, ethyl 3-hydroxybutyrate, 4-phenyl-3-buten-2-ol, 2-methyl-4-phenylbutan-2-ol, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)butan-2-one, pentanol, *cis*-3-pentenol, 3-methyl-pentanol, 3-methyl-3-penten-1-ol, 2-methyl-4-phenylpentanol (Pamplefleur), 3-methyl-5-phenylpentanol (Phenoxanol), 2-methyl-5-phenylpentanol, 2-methyl-5-(2,3-dimethyltricyclo[2.2.1.0(2,6)]hept-3-yl)-2-penten-1-ol (santalol), 4-methyl-1-phenyl-2-pentanol, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-ol, 3-methyl-1-phenylpentan-3-ol, 1,2-dimethyl-3-(1-methylethenyl)cyclopentan-1-ol, 2-isopropyl-5-methyl-2-hexenol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, 2-isopropenyl-4-methyl-4-hexen-1-ol (Lavandulol), 2-ethyl-2-prenyl-3-hexenol, 1-hydroxymethyl-4-iso-propenyl-1-cyclohexene (Dihydrocuminy alcohol), 1-methyl-4-isopropenylcyclohex-6-en-2-ol (carvenol), 6-methyl-3-isopropenylcyclohexan-1-ol, 1-methyl-4-iso-propenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol, 4-tert-butylcyclo-hexanol, 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol, 4-isopropyl-cyclohexanol, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexanol, isobornylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-4-isopropylcyclohexan-3-ol, 1,2-dimethyl-3-(1-methylethyl)cyclohexan-1-ol, heptanol, 2,4-dimethylheptan-1-ol, 2,4-dimethyl-2,6-heptandienol, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-ene (myrtenol), 4-methyl-2,4-heptadien-1-ol, 3,4,5,6,6-pentamethyl-2-heptanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]heptane, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 2,6-dimethylheptan-2-ol, 2,6,6-trimethylbicyclo[1.3.3]heptan-2-ol, octanol, 2-octenol, 2-methyloctan-2-ol, 2-methyl-6-methylene-7-octen-2-ol (myrcenol), 7-methyloctan-1-ol, 3,7-dimethyl-6-octenol, 3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octen-1-ol (citronellol), 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctan-1-ol (pelagrol), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-5,7-octadien-2-ol, 4,7-dimethyl-4-vinyl-6-octen-3-ol, 3-methyloctan-3-ol, 2,6-dimethyloctan-2-ol, 2,6-dimethyloctan-3-ol, 3,6-dimethyloctan-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-3,5-octadien-2-ol (muguol), 3-methyl-1-octen-3-ol, 7-hydroxy-3,7-dimethyloctanal, 3-nonanol, 2,6-nonadien-1-ol, *cis*-6-nonen-1-ol, 6,8-dimethylnonan-2-ol, 3-(hydroxymethyl)-2-nonanone, 2-nonen-1-ol, 2,4-nonadien-1-

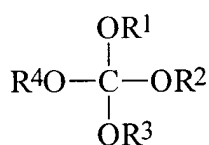
ol, 3,7-dimethyl-1,6-nonadien-3-ol, decanol, 9-decenol, 2-benzyl-M-dioxa-5-ol, 2-decen-1-ol, 2,4-decadien-1-ol, 4-methyl-3-decen-5-ol, 3,7,9-trimethyl-1,6-decadien-3-ol (isobutyl linallol), undecanol, 2-undecen-1-ol, 10-undecen-1-ol, 2-dodecen-1-ol, 2,4-dodecadien-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol), 3,7,11-trimethyl-1,6,10,-dodecatrien-3-ol, 3,7,11,15-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 (cuminy 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), pentyl-*ortho*-hydroxy benzoate, ethyl 2-hydroxy-benzoate, methyl 2,4-dihydroxy-3,6-dimethylbenzoate, 3-hydroxy-5-methoxy-1-methylbenzene, 2-tert-butyl-4-methyl-1-hydroxybenzene, 1-ethoxy-2-hydroxy-4-propenylbenzene, 4-hydroxytoluene, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-hydroxybenzaldehyde, decahydro-2-naphthol, 2,5,5-trimethyl-octahydro-2-naphthol, 1,3,3-trimethyl-2-norbornanol (fenchol), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-ol, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-ol, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuran, β -caryophyllene alcohol, and mixtures thereof.

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

methoxy-4-(2-propenyl)phenol (eugenol), 4-hydroxy-3-methoxybenzaldehyde (vanillin), and mixtures thereof.

Non-limiting examples of orthoester pro-accords according to the present invention are tris(geranyl orthoformate, tris(*cis*-3-hexen-1-yl) orthoformate, tris(phenylethyl) orthoformate, bis(citronellyl) ethyl orthoacetate, tris(citronellyl) orthoformate, tris(*cis*-6-nonenyl) orthoformate, tris(phenoxyethyl) orthoformate, tris(geranyl, neryl) orthoformate (70:30 geranyl:neryl), tris(9-decenyl) orthoformate, tris(3-methyl-5-phenylpentanyl) orthoformate, tris(6-methylheptan-2-yl) orthoformate, tris([4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl] orthoformate, tris[3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl] orthoformate, tris(menthyl orthoformate, tris(4-isopropylcyclohexylethyl-2-yl) orthoformate, tris(6,8-dimethylnonan-2-yl) orthoformate, tris(phenylethyl) orthoacetate, tris(*cis*-3-hexen-1-yl) orthoacetate, tris(*cis*-6-nonenyl) orthoacetate, tris(citronellyl) orthoacetate, bis(geranyl) benzyl orthoacetate, tris(geranyl) orthoacetate, tris(4-isopropylcyclohexylmethyl) orthoacetate, tris(benzyl) orthoacetate, tris(2,6-dimethyl-5-heptenyl) orthoacetate, bis(*cis*-3-hexen-1-yl) amyl orthoacetate, and neryl citronellyl ethyl orthobutyrate. Orthoester pro-accords can be used to deliver *inter alia* binary fragrance accords, fragrance accords having a "binary characteristic" accord component in combination with a modifier accord, and fragrance accords comprising astringents, fixatives, or diluents.

The orthocarbonate pro-accords of the present invention have the general formula:



wherein R¹, R², R³, and R⁴ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₄₀ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; any two R¹, R², R³, and R⁴ are taken together to form a ring having from 5 to 7 atoms wherein said ring is substituted or unsubstituted; and mixtures thereof; preferably at least two of the moieties R¹, R², R³, and R⁴ are derived from a fragrance raw material alcohol, more preferably at least three of the

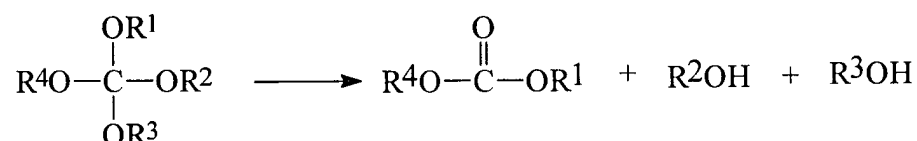
moieties R¹, R², R³, and R⁴ are derived from a fragrance raw material alcohol, most preferably each R¹, R², R³, and R⁴ is derived from a fragrance raw material alcohol.

Non-limiting examples of R¹, R², R³, and R⁴ are methyl, 2,4-dimethyl-3-cyclo-hexene-1-methyl (Floralol), 2,4-dimethyl cyclohexane methyl (Dihydro floralol), 5,6-dimethyl-1-methylethenyl-bicyclo[2.2.1]hept-5-ene-2-methyl (Arbozol), 2,4,6-trimethyl-3-cyclohexene-1-methyl (Isocyclo geranyl), 4-(1-methylethyl)cyclohexylmethyl (Mayol), α -3,3-trimethyl-2-norboranylethyl, 1,1-dimethyl-1-(4-methylcyclohex-3-enyl)methyl, ethyl, 2-phenylethyl, 2-cyclohexylethyl, 2-(o-methylphenyl)ethyl, 2-(m-methylphenyl)ethyl, 2-(p-methylphenyl)ethyl, 6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-ethyl (nopyl), 2-(4-methylphenoxy)ethyl, 3,3-dimethyl- Δ^2 - β -norbornanylethyl, 2-methyl-2-cyclohexylethyl, 1-(4-isopropylcyclohexyl)ethyl, 1-phenyl-1-hydroxyethyl, 1,1-dimethyl-2-phenylethyl, 1,1-dimethyl-2-(4-methylphenyl)ethyl, propyl, 1-phenylpropyl, 3-phenylpropyl, 2-phenylpropyl (Hydrotropic Alcohol), 2-(cyclododecyl)-propan-1-yl (Hydroxyambran), 2,2-dimethyl-3-(3-methylphenyl)propan-1-yl (Majantol), 2-methyl-3-phenylpropyl, 3-phenyl-2-propen-1-yl (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-yl (methylcinnamyl alcohol), α -n-pentyl-3-phenyl-2-propen-1-yl (α -amylcinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propyl, butyl, 3-methylbutyl, 3-(4-methylcyclohex-3-ene)butyl, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butyl, 2-ethyl-4-(2,2,3-trimethylcyclopent-3-enyl)-2-buten-1-yl, 3-methyl-2-buten-1-yl, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-yl, 3-hydroxy-2-butanone, ethyl 3-hydroxybutyrate, 4-phenyl-3-buten-2-yl, 2-methyl-4-phenylbutan-2-yl, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)butan-2-one, pentyl, *cis*-3-pentenyl, 3-methylpentyl, 3-methyl-3-penten-1-yl, 2-methyl-4-phenylpentyl (Pamplefleur), 3-methyl-5-phenylpentyl (Phenoxanyl), 2-methyl-5-phenylpentyl, 2-methyl-5-(2,3-dimethyltricyclo[2.2.1.0(2,6)]hept-3-yl)-2-penten-1-yl (santalyl), 4-methyl-1-phenyl-2-pentyl, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-yl, 3-methyl-1-phenylpent-3-yl, 1,2-dimethyl-3-(1-methylethenyl)cyclopent-1-yl, 2-isopropyl-4-methyl-2-hexenyl, *cis*-3-hexen-1-yl, *trans*-2-hexen-1-yl, 2-isopropenyl-5-methyl-4-hexen-1-yl (Lavandulyl), 2-ethyl-2-prenyl-3-hexenyl (silwanol), 2-ethylhexyl, 1-hydroxymethyl-4-isopropenyl-1-cyclohexenyl (Dihydrocuminy), 1-methyl-4-isopropenylcyclohex-6-en-2-yl (carvenyl), 6-methyl-3-isopropenylcyclohex-1-yl, 1-methyl-4-isopropenylcyclohex-3-yl, 4-iso-propyl-1-methylcyclohex-3-yl, 4-tert-butylcyclohexyl, 2-tert-butylcyclohexyl, 2-tert-butyl-4-methylcyclohexyl, 4-isopropylcyclohexyl, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-yl, 2-(5,6,6-

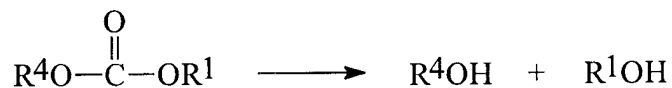
trimethyl-2-norbornyl)cyclohexyl, isobornylcyclohexyl, 3,3,5-trimethylcyclohexyl, 1-methyl-4-isopropylcyclohex-3-yl (menthol), 1,2-dimethyl-3-(1-methylethyl)-cyclohexan-1-yl, heptyl, 2,4-dimethylhept-1-yl, 2,4-dimethyl-2,6-heptandienyl, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-en-1-yl (myrtenyl), 4-methyl-2,4-heptadien-1-yl, 3,4,5,6,6-pentamethyl-2-heptyl, 3,6-dimethyl-3-vinyl-5-hepten-2-yl, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]-heptyl, 1,7,7-trimethylbicyclo[2.2.1]hept-2-yl, 2,6-dimethylhept-2-yl, 2,6,6-trimethylbicyclo[1.3.3]hept-2-yl, octyl, 2-octenyl, 2-methyloctan-2-yl, 2-methyl-6-methylene-7-octen-2-yl (myrcenyl), 7-methyloctan-1-yl, 3,7-dimethyl-6-octenyl, 3,7-dimethyl-7-octenyl, 3,7-dimethyl-6-octen-1-yl (citronellyl), 3,7-dimethyl-2,6-octadien-1-yl (geranyl), 3,7-dimethyl-2,6-octadien-1-yl (neryl), 3,7-dimethyl-1,6-octadien-3-yl (linalyl), 3,7-dimethyloctan-1-yl (pelagryl), 3,7-dimethyloctan-3-yl (tetrahydrolinalyl), 2,4-octadien-1-yl, 3,7-dimethyl-6-octen-3-yl, 2,6-dimethyl-7-octen-2-yl, 2,6-dimethyl-5,7-octadien-2-yl, 4,7-dimethyl-4-vinyl-6-octen-3-yl, 3-methyloctan-3-yl, 2,6-dimethyloctan-2-yl, 2,6-dimethyloctan-3-yl, 3,6-dimethyloctan-3-yl, 2,6-dimethyl-7-octen-2-yl, 2,6-dimethyl-3,5-octadien-2-yl (mugyl), 3-methyl-1-octen-3-yl, 7-hydroxy-3,7-dimethyloctan-1-yl, 3-nonyl, 6,8-dimethylnonan-2-yl, 3-(hydroxymethyl)-2-nonanone, 2-nonen-1-yl, 2,4-nonadien-1-yl, 2,6-nonadien-1-yl, cis-6-nonen-1-yl, 3,7-dimethyl-1,6-nonadien-3-yl, decyl, 9-decenyl, 2-benzyl-M-dioxa-5-yl, 2-decen-1-yl, 2,4-decadien-1-yl, 4-methyl-3-decen-5-yl, 3,7,9-trimethyl-1,6-decadien-3-yl (isobutyl linalyl), undecyl, 2-undecen-1-yl, 10-undecen-1-yl, 2-dodecen-1-yl, 2,4-dodecadien-1-yl, 2,7,11-trimethyl-2,6,10-dodecatrien-1-yl (farnesyl), 3,7,11-trimethyl-1,6,10-dodecatrien-3-yl, 3,7,11,15-tetramethylhexadec-2-en-1-yl (phytyl), 3,7,11,15-tetramethylhexadec-1-en-3-yl (iso phytol), benzyl, p-methoxybenzyl (anisyl), *para*-cymen-7-yl (cuminy), 4-methylbenzyl, 3,4-methylenedioxybenzyl, 2-(methyl)carboxy-1-hydroxyphenyl, 2-(benzyl)carboxy-1-hydroxyphenyl, 2-(*cis*-3-hexenyl)-carboxy-1-hydroxyphenyl, 2-(*n*-pentyl)carboxy-1-hydroxyphenyl, 2-(2-phenylethyl)carboxy-1-hydroxyphenyl, 2-(*n*-hexyl)carboxy-1-hydroxyphenyl, 2-methyl-5-isopropyl-1-hydroxyphenyl, 4-ethyl-2-methoxyphenyl, 4-allyl-2-methoxy-1-hydroxyphenyl (eugenyl), 2-methoxy-4-(1-propenyl)-1-hydroxyphenyl (isoeugenyl), 4-allyl-2,6-dimethoxy-1-hydroxyphenyl, 4-*tert*-butyl-1-hydroxyphenyl, 2-ethoxy-4-methyl-1-hydroxyphenyl, 2-methyl-4-vinyl-1-hydroxyphenyl, 2-isopropyl-5-methyl-1-hydroxyphenyl (thymyl), 2-(isopentyl)-carboxy-1-hydroxyphenyl, 2-(ethyl)carboxy-1-hydroxyphenyl, 6-(methyl)carboxy-2,5-dimethyl-1,3-dihydroxyphenyl, 5-methoxy-3-methyl-1-hydroxyphenyl, 2-*tert*-butyl-4-methyl-1-hydroxyphenyl, 1-ethoxy-2-hydroxy-4-propenylphenyl, 4-methyl-1-hydroxyphenyl, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-

hydroxybenzaldehyde, decahydro-2-naphthyl, 2,5,5-trimethyl-octahydro-2-naphthyl, 1,3,3-trimethyl-2-norbornyl (fenchyl), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-yl, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-yl, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuranyl, β -caryophyllenyl, and mixtures thereof.

The orthocarbonate pro-accords of the present invention undergo an initial hydrolysis according to the following scheme:



and therein release one equivalent of a carbonate fragrance raw material and two equivalents of one or more fragrance raw materials. In addition to the initial release of two equivalents of alcohol by the scheme depicted herein above, the carbonate fragrance raw materials which are released by the orthocarbonates can continue to hydrolyze and further release two equivalents of one or more fragrance raw material alcohol according to the following scheme:



thereby providing up to four equivalents of fragrance raw material alcohol per equivalent of delivered orthocarbonate. The carbonate which is released by the orthocarbonate may be a fragrance raw material precursor or itself a pro-accord (capable of releasing two different fragrance raw materials), preferably the carbonate which is released serves as a fragrance raw material, fixative, etc. An orthocarbonate which comprises four different fragrance raw materials will always release a carbonate that is a pro-accord (hydrolyzes to release a binary accord) in addition to any further fragrance properties attributable to the carbonate.

The alcohols which are released by the orthocarbonate pro-accords of the present invention may be "fragrance raw material alcohols", astringent alcohols, disinfectant alcohols, or carrier alcohols. For the purposes of the present invention "fragrance raw material alcohols" are defined herein as "alcohols having a molecular weight greater than 100 g/mol and which when used alone or in combination with other fragrance raw material alcohols have a generally pleasurable odor".

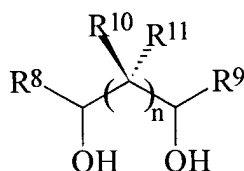
Non limiting examples of alcohols which can be suitably released by the orthocarbonate pro-accords of the present invention are methanol, 2,4-dimethyl-3-

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), 2,4,6-trimethyl-3-cyclohexene-1-methanol (Isocyclo geraniol), 4-(1-methylethyl)cyclohexanemethanol (Mayol), α -3,3-trimethyl-2-norborane methanol, 1,1-dimethyl-1-(4-methylcyclohex-3-enyl)methanol, ethanol, 2-phenylethanol, 2-cyclohexyl ethanol, 2-(o-methylphenyl)-ethanol, 2-(m-methylphenyl)ethanol, 2-(p-methylphenyl)ethanol, 6,6-dimethylbicyclo-[3.1.1]hept-2-ene-2-ethanol (nopol), 2-(4-methylphenoxy)ethanol, 3,3-dimethyl- Δ^2 - β -norbornane ethanol, 2-methyl-2-cyclohexylethanol, 1-(4-isopropylcyclohexyl)-ethanol, 1-phenylethanol, 1,1-dimethyl-2-phenylethanol, 1,1-dimethyl-2-(4-methyl-phenyl)ethanol, n-propanol, 2-propanol, 1-phenylpropanol, 3-phenylpropanol, 2-phenylpropanol (Hydrotropic Alcohol), 2-(cyclododecyl)propan-1-ol (Hydroxy-ambran), 2,2-dimethyl-3-(3-methylphenyl)propan-1-ol (Majantol), 2-methyl-3-phenylpropanol, 3-phenyl-2-propen-1-ol (cinnamyl alcohol), 2-methyl-3-phenyl-2-propen-1-ol (methylcinnamyl alcohol), α -n-pentyl-3-phenyl-2-propen-1-ol (α -amyl-cinnamyl alcohol), ethyl-3-hydroxy-3-phenyl propionate, 2-(4-methylphenyl)-2-propanol, n-butanol, 2-butanol, 3-methylbutanol, 3-(4-methylcyclohex-3-ene)butanol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)butanol, 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-2-buten-1-ol, 3-methyl-2-buten-1-ol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, 3-hydroxy-2-butanone, ethyl 3-hydroxybutyrate, 4-phenyl-3-buten-2-ol, 2-methyl-4-phenylbutan-2-ol, 4-(4-hydroxyphenyl)butan-2-one, 4-(4-hydroxy-3-methoxyphenyl)butan-2-one, pentanol, *cis*-3-pentenol, 3-methyl-pentanol, 3-methyl-3-penten-1-ol, 2-methyl-4-phenylpentanol (Pamplefleur), 3-methyl-5-phenylpentanol (Phenoxanol), 2-methyl-5-phenylpentanol, 2-methyl-5-(2,3-dimethyltricyclo[2.2.1.0(2,6)]hept-3-yl)-2-penten-1-ol (santalol), 4-methyl-1-phenyl-2-pentanol, (1-methyl-bicyclo[2.1.1]hepten-2-yl)-2-methylpent-1-en-3-ol, 3-methyl-1-phenylpentan-3-ol, 1,2-dimethyl-3-(1-methylethenyl)cyclopentan-1-ol, 2-isopropyl-5-methyl-2-hexenol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1-ol, 2-isopropenyl-4-methyl-4-hexen-1-ol (Lavandulol), 2-ethyl-2-prenyl-3-hexenol, 1-hydroxymethyl-4-iso-propenyl-1-cyclohexene (Dihydrocuminy alcohol), 1-methyl-4-isopropenylcyclohex-6-en-2-ol (carvenol), 6-methyl-3-isopropenylcyclohexan-1-ol, 1-methyl-4-iso-propenylcyclohexan-3-ol, 4-isopropyl-1-methylcyclohexan-3-ol, 4-tert-butylcyclo-hexanol, 2-tert-butylcyclohexanol, 2-tert-butyl-4-methylcyclohexanol, 4-isopropyl-cyclohexanol, 4-methyl-1-(1-methylethyl)-3-cyclohexen-1-ol, 2-(5,6,6-trimethyl-2-norbornyl)cyclohexanol, isobornylcyclohexanol, 3,3,5-trimethylcyclohexanol, 1-methyl-4-isopropylcyclohexan-3-ol, 1,2-dimethyl-3-(1-methylethyl)cyclohexan-1-ol, heptanol,

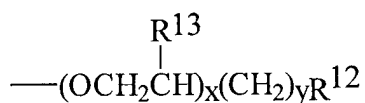
2,4-dimethylheptan-1-ol, 2,4-dimethyl-2,6-heptandienol, 6,6-dimethyl-2-oxymethylbicyclo[3.1.1]hept-2-ene (myrtenol), 4-methyl-2,4-heptadien-1-ol, 3,4,5,6,6-pentamethyl-2-heptanol, 3,6-dimethyl-3-vinyl-5-hepten-2-ol, 6,6-dimethyl-3-hydroxy-2-methylenebicyclo[3.1.1]heptane, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 2,6-dimethylheptan-2-ol, 2,6,6-trimethylbicyclo[1.3.3]heptan-2-ol, octanol, 2-octenol, 2-methyloctan-2-ol, 2-methyl-6-methylene-7-octen-2-ol (myrcenol), 7-methyloctan-1-ol, 3,7-dimethyl-6-octenol, 3,7-dimethyl-7-octenol, 3,7-dimethyl-6-octen-1-ol (citronellol), 3,7-dimethyl-2,6-octadien-1-ol (geraniol), 3,7-dimethyl-2,6-octadien-1-ol (nerol), 3,7-dimethyl-1,6-octadien-3-ol (linalool), 3,7-dimethyloctan-1-ol (pelagrol), 3,7-dimethyloctan-3-ol (tetrahydrolinalool), 2,4-octadien-1-ol, 3,7-dimethyl-6-octen-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-5,7-octadien-2-ol, 4,7-dimethyl-4-vinyl-6-octen-3-ol, 3-methyloctan-3-ol, 2,6-dimethyloctan-2-ol, 2,6-dimethyloctan-3-ol, 3,6-dimethyloctan-3-ol, 2,6-dimethyl-7-octen-2-ol, 2,6-dimethyl-3,5-octadien-2-ol (mugulol), 3-methyl-1-octen-3-ol, 7-hydroxy-3,7-dimethyloctanal, 3-nonanol, 2,6-nonadien-1-ol, *cis*-6-nonen-1-ol, 6,8-dimethylnonan-2-ol, 3-(hydroxymethyl)-2-nonanone, 2-nonen-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 linallol), undecanol, 2-undecen-1-ol, 10-undecen-1-ol, 2-dodecen-1-ol, 2,4-dodecadien-1-ol, 2,7,11-trimethyl-2,6,10-dodecatrien-1-ol (farnesol), 3,7,11-trimethyl-1,6,10,-dodecatrien-3-ol, 3,7,11,15-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 (cuminy 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), pentyl-*ortho*-hydroxy benzoate, ethyl 2-hydroxy-benzoate, methyl 2,4-dihydroxy-3,6-dimethylbenzoate, 3-hydroxy-5-methoxy-1-methylbenzene, 2-*tert*-butyl-4-methyl-1-hydroxybenzene, 1-ethoxy-2-hydroxy-4-propenylbenzene, 4-hydroxytoluene, 4-hydroxy-3-methoxybenzaldehyde, 2-ethoxy-4-hydroxybenzaldehyde, decahydro-2-naphthol, 2,5,5-trimethyl-octahydro-2-naphthol, 1,3,3-trimethyl-2-norbornanol (fenchol), 3a,4,5,6,7,7a-hexahydro-2,4-dimethyl-4,7-methano-1H-inden-5-ol, 3a,4,5,6,7,7a-hexahydro-3,4-dimethyl-4,7-methano-1H-inden-5-ol, 2-methyl-2-vinyl-5-(1-hydroxy-1-methylethyl)tetrahydrofuran, β -caryophyllene alcohol, and mixtures thereof.

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

In addition to the above mentioned releasable fragrance material alcohols, the orthocarbonates according to the present invention can be formed from at least one diol having the formula:

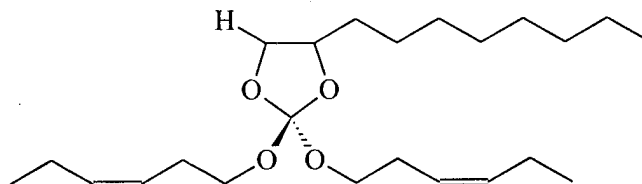


wherein R⁸, R⁹, R¹⁰, and R¹¹ are each independently hydrogen, C₁-C₂₀ linear or branched alkyl, C₁-C₂₀ linear or branched alkenyl, C₁-C₂₀ linear, branched or cyclic alkylencarboxy, C₁-C₂₀ linear, branched, or cyclic carboxyalkyl, C₁-C₂₀ linear or branched alkyleneamino, C₁-C₂₀ linear or branched aminoalkyl, C₁-C₂₀ linear, branched, or cyclic alkylencarboxamido, C₁-C₂₀ linear or branched carboxamidoalkyl, alkyleneoxy having the formula:



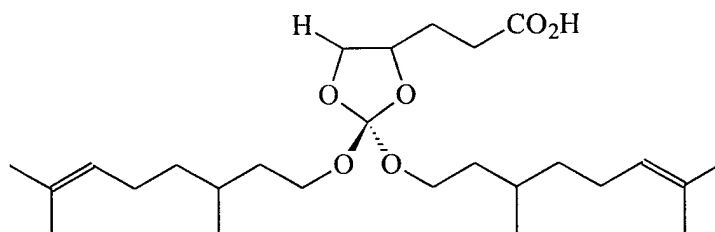
wherein R¹² is hydrogen or methyl; R¹³ is hydrogen or C₁-C₂ alkyl; n is from 0 to 4, x is from 1 to about 20, y is from 0 to about 20.

An example of a cyclic orthocarbonate having one R⁸ or R⁹ unit which is a C₁-C₂₀ linear, branched, or cyclic alkyl has the formula:



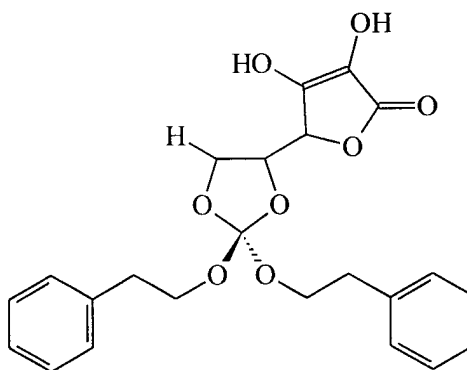
wherein R² and R³ are each *cis*-3-hexenyl.

An example of a cyclic orthocarbonate having one R⁸ or R⁹ unit which is a C₁-C₂₀ linear, branched, or cyclic alkylencarboxy has the formula:



wherein R² and R³ are each citronellyl.

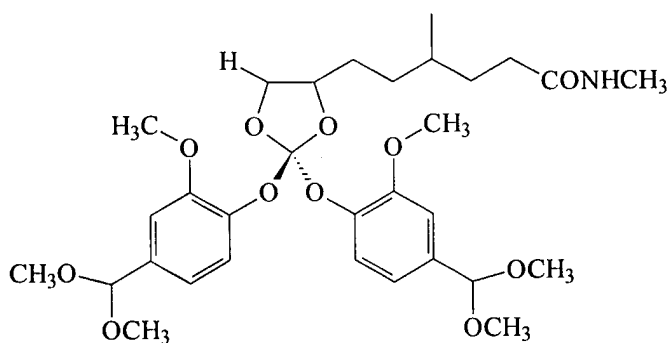
An example of a cyclic orthocarbonate having one R⁸ or R⁹ unit which is a C₁-C₂₀ linear, branched, or cyclic alkylencarboxy has the formula:



wherein R² and R³ are each 2-phenylethyl.

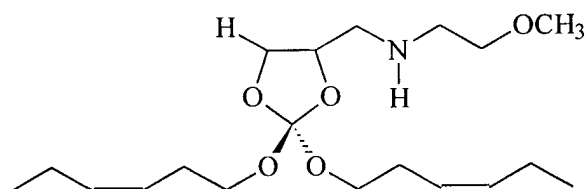
An example of a cyclic orthocarbonate having one R⁸ or R⁹ unit which is a C₁-C₂₀ linear, branched, or cyclic alkylencarboxy has the formula:

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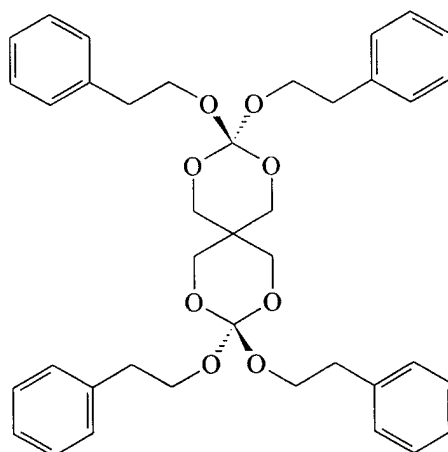
wherein R^2 and R^3 are each vanillyl bis(methoxy) acetal.

An example of a cyclic orthocarbonate having one R^8 or R^9 unit which is a C_1 - C_{20} linear, branched, or cyclic alkyleneamino has the formula:



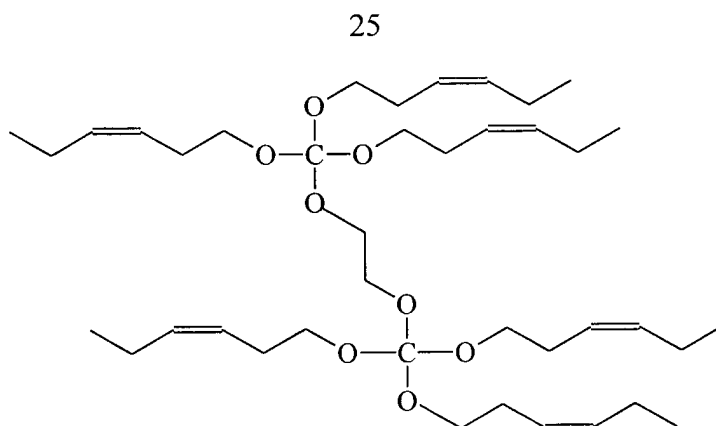
wherein R^2 and R^3 are each *cis*-3-hexenyl.

A further preferred orthocarbonate has the R^8 or R^9 unit taken together to form a spiro bis(orthocarbonate) an example of which has the formula:



wherein the R^2 and R^3 units of each orthoester is a 2-phenylethyl moiety.

In addition, an R^1 , R^2 , R^3 , or R^4 unit may serve to link two pro-accords for the purpose of providing greater substantivity. An example of pro-accords linking by a diol has the following formula:



The more preferred orthocarbonate pro-accords of the present invention comprise at least three of the R^1 , R^2 , R^3 , and R^4 moieties which are derived from a fragrance raw material alcohol, thereby the preferred pro-fragrances have a molecular weight which is at least 3 times the molecular weight of the lowest "fragrance raw material alcohol" which comprises the orthocarbonate pro-fragrance. Further, the more preferred orthocarbonate pro-fragrances have a molecular weight which is greater than or equal to 325 g/mol.

Non-limiting examples of more preferred orthocarbonate pro-accords according to the present invention include: methyl tris(geranyl) orthocarbonate, ethyl tris(geranyl) orthocarbonate, methyl tris(phenylethyl) orthocarbonate, ethyl tris(phenylethyl) orthocarbonate, methyl tris(*cis*-3-hexenyl) orthocarbonate, ethyl tris(*cis*-3-hexenyl) orthocarbonate, methyl tris(citronellyl) orthocarbonate, ethyl tris(citronellyl) orthocarbonate, methyl tris(linalyl) orthocarbonate, ethyl tris(linalyl) orthocarbonate, methyl tris(menthyl) orthocarbonate, ethyl tris(menthyl) orthocarbonate, dodecyl tris(geranyl) orthocarbonate, and dodecyl tris(phenylethyl) orthocarbonate.

The most preferred orthocarbonate pro-accords of the present invention have each of the R^1 , R^2 , R^3 , and R^4 moieties derived from a fragrance raw material alcohol, thereby the preferred pro-fragrances have a molecular weight which is at least 4 times the molecular weight of the lowest "fragrance raw material alcohol" which comprises the orthocarbonate pro-accord. Further, the preferred orthocarbonate pro-accords have a molecular weight which is greater than or equal to 350 g/mol.

Non-limiting examples of most preferred orthocarbonate pro-accords according to the present invention include: tetra-geranyl orthocarbonate, tetra-phenylethyl orthocarbonate, tetrakis(3-methyl-5-phenylpentyl) orthocarbonate, tetrakis(*cis*-3-hexenyl) orthocarbonate, bis(geranyl) bis(*cis*-3-hexenyl) orthocarbonate, bis(phenylethyl) bis(*cis*-3-hexenyl) orthocarbonate,

tetrakis(citronellyl) orthocarbonate, tetrakis(linalyl) orthocarbonate, bis(linalyl) bis(geranyl) orthocarbonate, tetrakis(myrcenyl) orthocarbonate, tetrakis(cinnamyl) orthocarbonate.

Fragrance Release Half-life

The pro-accords useful in the laundry detergent compositions of the present invention generally have high substantivity. This high substantivity is a pre-requisite in that the pro-accord must be suitably deposited upon the target fabric in order for the pro-accords of the present invention to be in a position to provide the increased fragrance longevity benefits described herein. However, the pro-accords of the present invention can be formulated to deliver the fragrance accords over any time period useful to the formulator, for example, within a time period desirable to the consumer.

For the purposes of the present invention the pro-accords generally have a "Fragrance Release Half-life" of less than or equal to about 1 hour when measured in 1 N HCl buffer at pH 0, more preferably a "fragrance release half-life" of less than or equal to about 12 hours when measured in NaH₂PO₄ buffer at pH 2.5. The "Fragrance Release Half-life" is defined herein as follows.

Pro-accords deliver their corresponding mixture of fragrance raw materials or fragrance accords according to the equation:



wherein the accord which is released may be a binary accord or a multiple fragrance raw material accord.

The rate at which the accord is released is defined by the formula:

$$\text{Rate} = k[\text{Pro-accord}]$$

and can be further expressed by the formula:

$$-\frac{d[\text{Pro-accord}]}{dt} = k[\text{Pro-accord}]$$

wherein k is the release rate constant and [Pro-accord] is the concentration of pro-accord. For the purposes of the present invention the "Fragrance Release Half-life", $t_{1/2}$, is related to the release rate constant by the formula:

$$t_{1/2} = \frac{0.693}{k}$$

and this relationship is used for the purposes of the present invention to determine the "fragrance Release Half-life" (FRHL).

Due to the hydrophobic nature of some pro-accords, it is necessary to conduct the determination of $t_{1/2}$ and k in a mixture of 90/10 dioxane/acid buffered water. The HCl buffered water is obtained by using a 1 N HCl volumetric standard solution (available from J. T. Baker). The phosphate buffered water is prepared by admixing 5.6 gm of phosphoric acid (H_3PO_4) and 26.3 gm of sodium dihydrogen phosphate (NaH_2PO_4) with one liter of de-ionized water. The pH values of the aqueous solutions are confirmed using a pH meter. Next 10 mL of the aqueous buffer is admixed with 90 mL of dioxane (99.9% HPLC grade, available from Sigma Aldrich) and is preheated to 30° C. The preheated 90/10 dioxane/acid buffered water is then added to the pro-accord and the hydrolysis kinetics are then monitored by conventional HPLC techniques at 30° C. The amount of pro-accord used is less than one-tenth the amount of water on a molar basis to insure pseudo first-order kinetic conditions.

Pro-accords having $t_{1/2}$ less than 1 hour in pH 0 HCl buffer show fragrance release benefits on surfaces such as fabric articles over weeks, and exhibit a delayed onset to these benefits after laundering. More preferably, the pro-accords have a $t_{1/2}$ less than 12 hours in pH 2.5 phosphate buffer which show fragrance release benefits which are noticeable immediately after conclusion of the wash and which extend for several days up to two weeks.

Table I lists several pro-accords according to the present invention with their corresponding $t_{1/2}$ (at pH 2.5) values.

Table I

Pro-accord	$t_{1/2}$ *
tri-(phenylethyl) orthoformate	5.9
tetra-(phenylethyl) orthocarbonate	4.8

* $t_{1/2}$ for the purposes of the present invention is measured in hours.

As indicated in the table above tris(phenylethyl) orthoformate is suitable for use as a pro-fragrance for delivering a "rose-floral" character note to an accord having enhance longevity. In some instances, it is desirable to formulate pro-accords having one or more pro-fragrances which deliver a rapid release of fragrance raw material in addition to the delayed onset of a fragrance. In such cases the hydrolysis rate, and therefore the determination of $t_{1/2}$ must be measured in a buffer system which can accommodate this more rapid hydrolysis rate. For example, the pro-fragrance tris(phenylethyl) orthoacetate is used to deliver a rapid onset of a

"rose-floral" middle note by releasing the fragrance raw material phenylethyl alcohol. The relative release rate of this pro-accord can be suitably determined by substituting a phosphate buffer comprising 4.6 gm of sodium dihydrogen phosphate (NaH_2PO_4) and 7.9 gm of disodium hydrogen phosphate (Na_2HPO_4) admixed with 1 liter of water for the phosphate buffer described herein above.

Therefore, by admixing sufficient quantities of tris(phenylethyl) orthoformate and tris(phenylethyl) orthoacetate into a pro-accord the formulator can achieve a rapid as well as delayed onset of the "rose-floral" character note provided by the perfume raw material phenylethyl alcohol.

The pro-accords of the present invention are stable under pH conditions encountered in the formulation and storage of detergent products which have a pH of from about 7.1 to 13, and during solution-use of such products. Due to their high molecular weight and hydrophobicity, these pro-accord compounds give reasonably good deposition from a laundering solution onto fabrics. Because the pro-accords are subject to hydrolysis when the pH is reduced, they hydrolyze to release their component fragrance compounds when the fabrics upon which they have been deposited are exposed even to reduced pH such as present in rinse water, air and humidity. The reduction in pH should be at least 0.1, preferably at least about 0.5 units. Preferably the pH is reduced by at least 0.5 units to a pH of 7.5 or less, more preferably 6.9 or less. Preferably, the solution in which the fabric (or other surface) is washed is alkaline.

The pro-accords of the present invention in addition have a ClogP value of at least greater than or equal to 3, preferably greater than or equal to 4, more preferably greater than or equal to 5, most preferably greater than or equal to 6.

Calculation of CLogP

The pro-accords of the invention are characterized by their octanol/water partition coefficient P. The octanol/water partition coefficient of a pro-accord is the ratio between its equilibrium concentration in octanol and in water. Since the partition coefficients of the pro-accord compounds are large, they are more conveniently given in the form of their logarithm to the base 10, logP.

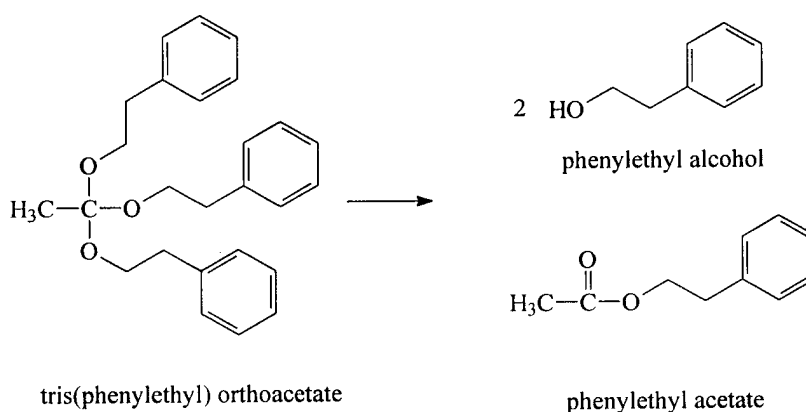
The logP of many compounds have been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), contains many, along with citations to the original literature.

However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (CLogP) is determined by the fragment approach of Hansch and Leo (cf., A.

Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P.G. Sammens, J.B. Taylor and C.A. Ramsden, Eds., p. 295, Pergamon Press, 1990). The fragment approach is based on the chemical structure of a compound and takes into account the numbers and type of atoms, the atom connectivity, and chemical bonding. The CLogP values, which are the most reliable and widely used estimates for this physicochemical property, can be used instead of the experimental logP values in the selection of pro-accords.

Symmetrical Pro-accords

Symmetrical pro-accords are pro-accords which release the same fragrance raw materials regardless of hydrolysis pathway. An example of a symmetrical pro-accord is tris(phenylethyl) orthoacetate which releases a binary accord having a "rose" characteristic comprising 2 parts phenylethyl alcohol and 1 part phenylethyl acetate according to the following scheme:



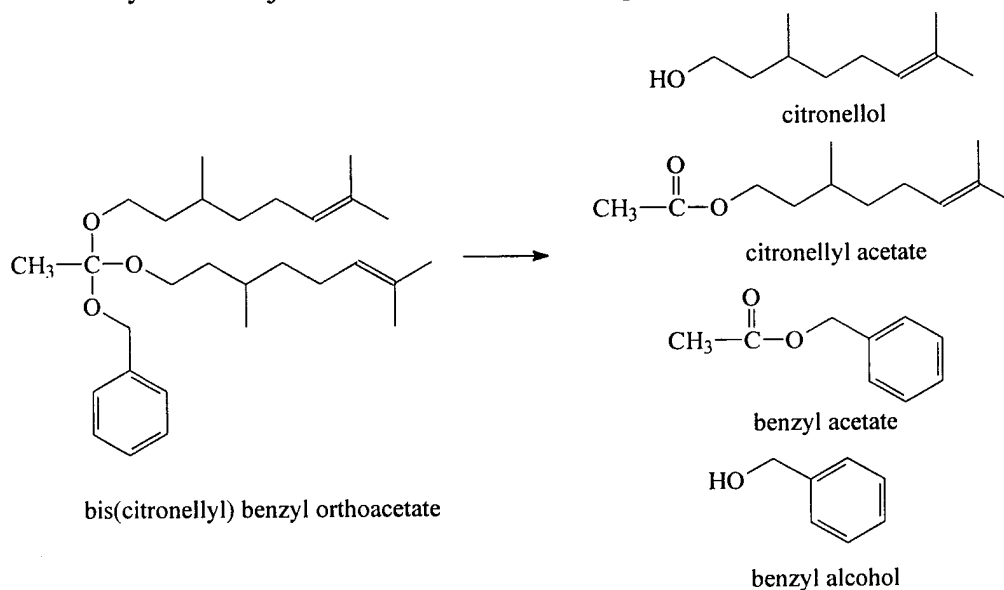
The phenylethyl alcohol/phenylethyl acetate (2:1) binary accord depicted above is useful in delivering to fabric a rose or rose/floral characteristic. As seen in this example, phenylethyl alcohol and phenylethyl acetate are the only fragrance raw materials which are releasable by this binary pro-accord regardless of hydrolysis pathway.

Unsymmetrical Pro-accords

Unsymmetrical pro-accords have the capacity to release fragrance accords more complex than the binary fragrance accords released by symmetrical pro-accords. The composition of the released accord depends on the route of pro-accord hydrolysis. An unsymmetrical pro-accord can be designed by the formulator to release different ratios of fragrance raw materials based not only on the composition of the pro-accord but on the reactivity as well. In addition, unsymmetrical pro-accords can also be used to produce "adjunct pro-accords" useful for releasing low

molecular weight modifiers, fixatives, carriers, astringents, etc., in addition to fragrance raw materials.

An example of an unsymmetrical pro-accord is bis(citronellyl) benzyl orthoacetate capable of releasing the binary fragrance accord of citronellol/citronellyl acetate having a "rose" characteristic together with the benzyl alcohol/benzyl acetate "jasmin" modifiers according to the following scheme:



The above accord can be suitably modified by the formulator to adjust the relative proportions of the accord ingredients. For example, more of the "sweet" character diluent benzyl alcohol can be delivered by adjusting the proportion of citronellol and benzyl alcohol used to formulate the pro-accord. Bis(benzyl) citronellyl orthoacetate delivers the same fragrance raw materials as bis(citronellyl) benzyl orthoacetate, only the relative amounts of the released materials differ.

The present invention also relates to a method for providing a sustained fragrance to fabric comprising the step of contacting fabric with an aqueous solution of a laundry detergent composition comprising:

- a) at least about 0.01%, preferably from about 0.01% to about 10%, more preferably from about 0.1% to about 1% by weight, of a fragrance delivery system comprising one or more pro-accords said pro-accords formed from at least one fragrance raw material and capable of releasing two or more fragrance raw materials wherein provided each pro-accord:
 - i) comprises fragrance raw materials having a molecular weight greater than or equal to 100 g/mol;
 - ii) has a molecular weight greater than or equal to 300 g/mol;

- iii) has a molecular weight at least two times greater than the lowest molecular weight fragrance raw material which comprises said pro-accord; and
- iv) has a fragrance release half-life of less than about 1 hour when measured in a 90:10 dioxane/1 N HCl mixture at pH 0, preferably a fragrance release half-life of less than about 12 hours when measured in NaH_2PO_4 buffer at pH 2.5;
- b) at least about 0.01% by weight, preferably from about 0.1% to about 60%, more preferably from about 0.1% to about 30% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant; and
- c) the balance carriers and adjunct ingredients said 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, dispersants, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, 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.

Surfactant systems

The instant cleaning compositions may contain at least about 0.01 % by weight of a surfactant selected from the group consisting of anionic, cationic, nonionic, ampholytic and zwitterionic surface active agents. Preferably the solid (i.e. granular) and viscous semi-solid (i.e. gelatinous, pastes, etc.) systems of the present invention, surfactant is preferably present to the extent of from about 0.1% to 60 %, more preferably 0.1% to about 30% by weight of the composition.

Nonlimiting examples of surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C_{11} - C_{18} alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C_{10} - C_{20} alkyl sulfates ("AS"), the C_{10} - C_{18} secondary (2,3) alkyl sulfates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^-\text{M}^+)\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^-\text{M}^+)\text{CH}_2\text{CH}_3$ where x and $(y + 1)$ are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10} - C_{18} alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C_{10} - C_{18} alkyl alkoxy carboxylates (especially the EO 1-5

ethoxycarboxylates), the C₁₀-C₁₈ glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides are highly preferred, especially the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are described further herein and are listed in standard texts.

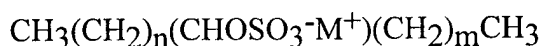
Anionic surfactants can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil

and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

Conventional primary alkyl sulfates (AS), such as those illustrated above, have the general formula $\text{R}\text{OSO}_3\text{-M}^+$ wherein R is typically a linear C8-22 hydrocarbyl group and M is a water solublizing cation. Branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also known; see, for example, Eur. Pat. Appl. 439,316, Smith et al., filed January 21, 1991.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of $m + n$ is typically about 9 to 17, and M is a water-solublizing cation.

The aforementioned secondary alkyl sulfates are those prepared by the addition of H_2SO_4 to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued February 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued December 24, 1991. See also U.S. Patent 5,349,101, Lutz et al., issued September 20, 1994; U.S. Patent 5,389,277, Prieto, issued February 14, 1995.

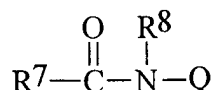
The preferred surfactants of the present invention are anionic surfactants, however, other surfactants useful herein are described below.

The compositions of the present invention can also comprise at least about 0.01%, preferably at least 0.1%, more preferably from about 1% to about 30%, of an nonionic deterative surfactant. Preferred nonionic surfactants such as C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C₆ to C₁₂ alkyl phenols, alkylene oxide condensates of C₈-C₂₂ alkanols and ethylene oxide/propylene oxide block polymers (Pluronic™-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides) can be used in the present compositions. An extensive disclosure

of these types of surfactants is found in U.S. Pat. 3,929,678, Laughlin et al., issued December 30, 1975, incorporated herein by reference.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 Llenado (incorporated herein by reference) are also preferred nonionic surfactants in the compositions of the invention.

More preferred nonionic surfactants are the polyhydroxy fatty acid amides having the formula:



wherein R^7 is C_5 - C_{31} alkyl, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{15} alkyl or alkenyl, or mixtures thereof; R^8 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, preferably methyl or ethyl, more preferably methyl. Q is a polyhydroxyalkyl moiety having a linear alkyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof; preferred alkoxy is ethoxy or propoxy, and mixtures thereof. Preferred Q is derived from a reducing sugar in a reductive amination reaction. More preferably Q is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Q. It should be understood that it is by no means intended to exclude other suitable raw materials. Q is more preferably selected from the group consisting of $-\text{CH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})(\text{CHOH})_{n-1}\text{CH}_2\text{OH}$, $-\text{CH}_2(\text{CHOH})_2-(\text{CHOR}')(\text{CHOH})\text{CH}_2\text{OH}$, and alkoxylated derivatives thereof, wherein n is an integer from 3 to 5, inclusive, and R' is hydrogen or a cyclic or aliphatic monosaccharide. Most preferred substituents for the Q moiety are glycityls wherein n is 4, particularly $-\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$.

$\text{R}^7\text{CO-N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

R^8 can be, for example, methyl, ethyl, propyl, isopropyl, butyl, 2-hydroxy ethyl, or 2-hydroxy propyl.

Q can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

A particularly desirable surfactant of this type for use in the compositions herein is alkyl-N-methyl glucomide, a compound of the above formula wherein R^7 is alkyl (preferably C_{11} - C_{17}), R^8 is methyl and Q is 1-deoxyglucityl.

Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used.

ADJUNCT INGREDIENTS

Builders - Detergent builders 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 typically used in fabric laundering compositions 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. When present, the compositions will typically comprise at least about 1% builder. Formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

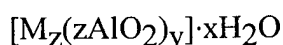
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O 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 the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na₂SiO₅ morphology form of layered silicate. It 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 highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi_xO_{2x+1}·yH₂O 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 herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. 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.

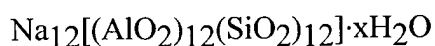
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. 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:



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 an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



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.

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. 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 detergency 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 carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic 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 liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially 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-hexanedioates 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: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can 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. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, 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.

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Other Ingredients - A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solid fillers for bar compositions, etc. Other optional ingredients include enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluoescers, fabric conditioners,

hydrolyzable surfactants, optical brighteners, preservatives, anti-oxidants, chelants, stabilizers, anti-shrinkage agents, anti-wrinkle agents, soil release agents, germicides, fungicides, and anti corrosion agents. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosity in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergent compositions.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Granular Compositions

The pro-accords of the present invention can be used in both low density (below 550 grams/liter) and high density granular compositions in which the density of the granule is at least 550 grams/liter. Granular compositions are typically

designed to provide an in the wash pH of from about 7.5 to about 11.5, more preferably from about 9.5 to about 10.5. Low density compositions can be prepared by standard spray-drying processes. Various means and equipment are available to prepare high density compositions. Current commercial practice in the field employs spray-drying towers to manufacture compositions which have a density less than about 500 g/l. Accordingly, if spray-drying is used as part of the overall process, the resulting spray-dried particles must be further densified using the means and equipment described hereinafter. In the alternative, the formulator can eliminate spray-drying by using mixing, densifying and granulating equipment that is commercially available. The following is a nonlimiting description of such equipment suitable for use herein.

Various means and equipment are available to prepare high density (i.e., greater than about 550, preferably greater than about 650, grams/liter or "g/l"), high solubility, free-flowing, granular detergent compositions according to the present invention. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which often have a density less than about 500 g/l. In this procedure, an aqueous slurry of various heat-stable ingredients in the final detergent composition are formed into homogeneous granules by passage through a spray-drying tower, using conventional techniques, at temperatures of about 175°C to about 225°C. However, if spray drying is used as part of the overall process herein, additional process steps as described hereinafter must be used to obtain the level of density (i.e., > 650 g/l) required by modern compact, low dosage detergent products.

For example, spray-dried granules from a tower can be densified further by loading a liquid such as water or a nonionic surfactant into the pores of the granules and/or subjecting them to one or more high speed mixer/densifiers. A suitable high speed mixer/densifier for this process is a device marketed under the tradename "Lödige CB 30" or "Lödige CB 30 Recycler" which comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. In use, the ingredients for the detergent composition are introduced into the drum and the shaft/blade assembly is rotated at speeds in the range of 100-2500 rpm to provide thorough mixing/densification. See Jacobs et al, U.S. Patent 5,149,455, issued September 22, 1992. The preferred residence time in the high speed mixer/densifier is from about 1 to 60 seconds. Other such apparatus includes the devices marketed under the tradename "Shugi Granulator" and under the tradename "Drais K-TTP 80).

Another process step which can be used to densify further spray-dried granules involves grinding and agglomerating or deforming the spray-dried granules in a moderate speed mixer/densifier so as to obtain particles having lower intraparticle porosity. Equipment such as that marketed under the tradename "Lödige KM" (Series 300 or 600) or "Lödige Ploughshare" mixer/densifiers are suitable for this process step. Such equipment is typically operated at 40-160 rpm. The residence time of the detergent ingredients in the moderate speed mixer/densifier is from about 0.1 to 12 minutes. Other useful equipment includes the device which is available under the tradename "Drais K-T 160". This process step which employs a moderate speed mixer/densifier (e.g. Lödige KM) can be used by itself or sequentially with the aforementioned high speed mixer/densifier (e.g. Lödige CB) to achieve the desired density. Other types of granules manufacturing apparatus useful herein include the apparatus disclosed in U.S. Patent 2,306,898, to G. L. Heller, December 29, 1942.

While it may be more suitable to use the high speed mixer/densifier followed by the low speed mixer/densifier, the reverse sequential mixer/densifier configuration is also contemplated by the invention. One or a combination of various parameters including residence times in the mixer/densifiers, operating temperatures of the equipment, temperature and/or composition of the granules, the use of adjunct ingredients such as liquid binders and flow aids, can be used to optimize densification of the spray-dried granules in the process of the invention. By way of example, see the processes in Appel et al, U.S. Patent 5,133,924, issued July 28, 1992 (granules are brought into a deformable state prior to densification); Delwel et al, U.S. Patent 4,637,891, issued January 20, 1987 (granulating spray-dried granules with a liquid binder and aluminosilicate); Kruse et al, U.S. Patent 4,726,908, issued February 23, 1988 (granulating spray-dried granules with a liquid binder and aluminosilicate); and, Bortolotti et al, U.S. Patent 5,160,657, issued November 3, 1992 (coating densified granules with a liquid binder and aluminosilicate).

In those situations in which particularly heat sensitive or highly volatile detergent ingredients or pro-accords are to be incorporated into the final detergent composition, processes which do not include spray drying towers are preferred. The formulator can eliminate the spray-drying step by feeding, in either a continuous or batch mode, starting detergent ingredients directly into mixing/densifying equipment that is commercially available. One particularly preferred embodiment involves charging a surfactant paste and an anhydrous builder material into a high speed mixer/densifier (e.g. Lödige CB) followed by a moderate speed mixer/densifier (e.g.

Lödige KM) to form high density detergent agglomerates. See Capeci et al, U.S. Patent 5,366,652, issued November 22, 1994 and Capeci et al, U.S. Patent 5,486,303, issued January 23, 1996. Optionally, the liquid/solids ratio of the starting detergent ingredients in such a process can be selected to obtain high density agglomerates that are more free flowing and crisp.

Optionally, the process may include one or more recycle streams of undersized particles produced by the process which are fed back to the mixer/densifiers for further agglomeration or build-up. The oversized particles produced by this process can be sent to grinding apparatus and then fed back to the mixing/densifying equipment. These additional recycle process steps facilitate build-up agglomeration of the starting detergent ingredients resulting in a finished composition having a uniform distribution of the desired particle size (400-700 microns) and density (> 550 g/l). See Capeci et al, U.S. Patent 5,516,448, issued May 14, 1996 and Capeci et al, U.S. Patent 5,489,392, issued February 6, 1996. Other suitable processes which do not call for the use of spray-drying towers are described by Bollier et al, U.S. Patent 4,828,721, issued May 9, 1989; Beerse et al, U.S. Patent 5,108,646, issued April 28, 1992; and, Jolicoeur, U.S. Patent 5,178,798, issued January 12, 1993.

In yet another embodiment, the high density detergent composition of the invention can be produced using a fluidized bed mixer. In this process, the various ingredients of the finished composition are combined in an aqueous slurry (typically 80% solids content) and sprayed into a fluidized bed to provide the finished detergent granules. Prior to the fluidized bed, this process can optionally include the step of mixing the slurry using the aforementioned Lödige CB mixer/densifier or a "Flexomix 160" mixer/densifier, available from Shugi. Fluidized bed or moving beds of the type available under the tradename "Escher Wyss" can be used in such processes.

Another suitable process which can be used herein involves feeding a liquid acid precursor of an anionic surfactant, an alkaline inorganic material (e.g. sodium carbonate) and optionally other detergent ingredients into a high speed mixer/densifier (residence time 5-30 seconds) so as to form agglomerates containing a partially or totally neutralized anionic surfactant salt and the other starting detergent ingredients. Optionally, the contents in the high speed mixer/densifier can be sent to a moderate speed mixer/densifier (e.g. Lödige KM) for further agglomeration resulting in the finished high density detergent composition. See Appel et al, U.S. Patent 5,164,108, issued November 17, 1992.

EXAMPLE 1

Preparation of tris(phenylethyl) orthoformate

To a 500 mL single neck flask assembled with a short path distillation head and a magnetic stirrer is combined phenylethyl alcohol (66 g), triethyl orthoformate (20.2 g) and 3 drops of concentrated sulfuric acid under a nitrogen atmosphere. The reaction mixture is heated for 3 hr at 100° C to distill over ethanol. The reaction progress is monitored by the amount of ethanol generated and by silica gel thin layer chromatography (TLC) eluting with 4% ethyl acetate/petroleum ether and development with iodine stain. Upon completion, the reaction mixture is diluted with diethyl ether (200 mL) and the organic phase washed three times with saturated aqueous sodium carbonate. The organic phase is dried over magnesium sulfate, filtered, and the resulting clear solution is concentrated *in vacuo*. The product is purified by Kugelrohr distillation wherein the fraction in the range 120-140° C, at 0.1 mm Hg is collected to yield 47 g (91%). ¹H NMR (CDCl₃); δ 7.2 (m, 15H); 5.0 (s, 1H); 3.6 (t, 6H); and 2.8 (t, 6H); ¹³C NMR (CDCl₃); δ 138.61, 128.81, 128.17, 126.10, 112.52, 64.76, and 35.89.

EXAMPLE 2

Preparation of tris(9-decenyl) orthoformate:

The procedure described above is suitable for use in preparing tris(9-decenyl) orthoformate using 9-decenol (42.5 g, Rosalva - IFF), and triethyl orthoformate (10 g), to yield 27 g (83 %) of a clear oil isolated by Kugelrohr distillation within the range 140-150° C, at 0.1 mm Hg. ¹H NMR (CDCl₃) δ 5.8 (m, 3H); 5.1 (s, 1H); 4.9 (m, 6H); 3.5 (t, 6H); 2.0 (m, 6H); 1.6 (m, 6H); and 1.35 (m, 30H); ¹³C NMR (CDCl₃) δ 138.87, 113.89, 112.47, 67.74, 33.56, 29.28, 29.19, 29.15, 28.84, 28.68, and 25.52

EXAMPLE 3

Preparation of tris(cis-3-hexenyl) orthoformate:

The procedure described above is suitable for use in preparing tris(cis-3-hexenyl) orthoformate using *cis*-3-hexenol (115 g), and triethyl orthoformate (42.7 g) to yield 79 g (88%) of a clear oil isolated by Kugelrohr distillation at 100° C, 0.1 mm Hg. ¹H NMR (CDCl₃) δ 5.45 (m, 3H); 5.35 (m, 3H); 5.2 (s, 1H); 3.5 (t, 6H); 2.35 (d,t, 6H); 2.05 (d,t, 6H), and 1.0 (t, 9H); ¹³C NMR (CDCl₃) δ 133.57, 124.46, 112.31, 63.51, 27.36, 20.39, and 13.99

EXAMPLE 4

Preparation of Tris(geranyl/neryl) orthoformate

To a 500 mL single neck flask equipped with a short path distillation head and a magnetic stirrer is combined a mixture of geraniol and nerol (52 g, Bush

Boake Allen 70/30), triethyl orthoformate (10 g) and anhydrous citric acid (0.66 g) under a nitrogen atmosphere. (The use of citric acid prevents undesired decomposition of the product). The reaction mixture is heated for 4 hr at 100° C during which time ethanol is removed via distillation. The reaction progress is monitored by the amount of ethanol generated and by silica gel thin layer chromatography (TLC) eluting with 4% ethyl acetate/petroleum ether and development with iodine stain. Upon completion, the reaction mixture is diluted with diethyl ether (200 mL) and the organic phase washed three times with saturated aqueous sodium carbonate. The organic phase was dried over magnesium sulfate, filtered, and the resulting clear solution is concentrated *in vacuo*. The product is purified by Kugelrohr distillation wherein the fraction in the range 140-150° C, at 0.1 mm Hg is collected to yield 23.5 g (73%). ¹H NMR (CDCl₃) δ 5.35 (m, 3H); 5.25 (m, 1H); 5.1 (m, 3H); 4.15 (m, 6H); 2.1 (m, 12H); and 1.8-1.6 (m, 27H); ¹³C NMR (CDCl₃) δ 139.96, 139.75, 131.53, 131.25, 123.73, 123.59, 120.97, 119.99, 111.01, 60.40, 60.05, 39.31, 31.97, 26.48, 26.12, 25.39, 23.19, 17.37, and 16.14.

EXAMPLE 5

Preparation of tris(phenylethyl) orthoacetate:

To a 250 mL three neck flask equipped with a rubber septum fitted with a needle, a drying tube charged with Drierite®, a stopper, and equipped with a magnetic stirrer, is added phenylethyl alcohol (100 g), trimethylorthoacetate (30 g) and 3 drops of concentrated sulfuric acid. Nitrogen is slowly bubbled through the solution over a 4 day period to remove the methanol which is produced. The mixture is then diluted in diethyl ether (300 mL) and washed three times with saturated aqueous sodium carbonate. The organic phase is dried over magnesium sulfate, filtered, and the resulting clear solution is concentrated. The product is purified by Kugelrohr distillation wherein the fraction in the range 150-170° C, at 0.1 mm Hg is collected to yield 72 g (74%). ¹H NMR (CDCl₃) δ 7.2 (m, 15H); 3.6 (t, 6H); 2.8 (t, 6H); and 1.4 (s, 3H); ¹³C NMR (CDCl₃) δ 138.92, 128.93, 128.15, 126.07, 114.18, 63.01, 36.26, and 20.20.

EXAMPLE 6

Preparation of tris(*cis*-3-hexenyl) orthoacetate:

The procedure described above is suitable for use in preparing tris(*cis*-3-hexenyl) orthoacetate using *cis*-3-hexenol (65 g) and trimethyl orthoacetate (22.2 g) and *para*-toluenesulfonic acid monohydrate (0.35 g) over 5 days, to yield 38.6 g (64 %) of a clear oil isolated by Kugelrohr distillation within the range 110-120° C, at 0.1 mm Hg. ¹H NMR (CDCl₃) δ 5.3 (m, 6H), 3.4 (t, 6H), 2.25 (d,t, 6H); 2.0 (d,t,

6H); 1.4 (s, 3H); and 0.9 (t, 9H); ^{13}C NMR (CDCl_3) δ 133.73, 125.03, 113.80, 61.48, 27.54, 20.29, 19.92, and 13.94.

EXAMPLE 7

Preparation of tetrakis(phenylethyl) orthocarbonate:

To a 250 mL three neck flask equipped with a rubber septum fitted with a needle, a drying tube charged with Drierite®, a stopper, and equipped with a magnetic stirrer, is added phenylethyl alcohol (36.7 g), tetraethylorthocarbonate (9.84 g) and *para*-toluenesulfonic acid monohydrate (0.21 g). Nitrogen is slowly bubbled through the solution while stirring over 36 hr to remove the ethanol which is produced. The mixture is then diluted with diethyl ether (300 mL) and washed three times with saturated aqueous sodium carbonate. The organic phase is dried over magnesium sulfate, filtered, and concentrated. The product is purified by Kugelrohr distillation wherein the fraction above 100° C, 0.1 mm Hg is retained to yield 12.8 g (50%) of a clear oil. ^1H NMR (CDCl_3) δ 7.2 (m, 16H); 3.6 (t, 8H); and 2.8 (t, 8H); ^{13}C NMR (CDCl_3) δ 138.84, 128.89, 128.11, 126.03, 119.57, 63.75, and 35.8.

EXAMPLES 8 - 16

The following are examples of granular detergent compositions comprising fragrance pro-accords.

TABLE II

<u>Ingredient</u>	<u>weight %</u>			
	8	9	10	11
Sodium C ₁₁ -C ₁₃ alkylbenzenesulfonate	13.3	13.7	10.4	11.1
Sodium C ₁₄ -C ₁₅ alcohol sulfate	3.9	4.0	4.5	11.2
Sodium C ₁₄ -C ₁₅ alcohol ethoxylate (0.5) sulfate	2.0	2.0	0.0	0.0
Sodium C ₁₄ -C ₁₅ alcohol ethoxylate (6.5)	0.5	0.5	0.5	1.0
Tallow fatty acid	0.0	0.0	0.0	1.1
Sodium tripolyphosphate	0.0	41.0	0.0	0.0
Zeolite A, hydrate (0.1-10 micron size)	26.3	0.0	21.3	28.0
Sodium carbonate	23.9	12.4	25.2	16.1
Sodium Polyacrylate (45%)	3.4	0.0	2.7	3.4
Sodium silicate (1:6 ratio NaO/SiO ₂)(46%)	2.4	6.4	2.1	2.6
Sodium sulfate	10.5	10.9	8.2	15.0
Sodium perborate	1.0	1.0	5.0	0.0
Poly(ethyleneglycol), MW ~4000 (50%)	1.7	0.4	1.0	1.1
Citric acid	0.0	0.0	3.0	0.0

Nonyl ester of sodium p-hydroxybenzene-sulfonate	0.0	0.0	5.9	0.0
Soil release polymer ¹	1.5	0.0	0.0	0.0
Soil release polymer ²	0.0	1.5	0.0	0.0
Soil release polymer ³	0.0	0.5	0.5	0.5
Fragrance pro-accord ⁴	1.0	1.5	0.0	0.0
Fragrance pro-accord ⁵	0.0	0.0	2.5	1.5
Minors ⁶	7.0	2.1	4.1	6.3

1. Soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., issued November 6, 1990.
2. Soil release polymer according to U.S. Patent 5,415,807, Gosselink, Pan, Kellett and Hall, issued May 16, 1995.
3. Soil release polymer according to U.S. Patent 4,702,857, Gosselink, issued October 27, 1987.
4. Pro-accord comprising tris(geranyl) orthoacetate.
5. Pro-accord mixture comprising 80% tris(phenylethyl) orthoacetate and 20% tris(cis-3-hexenyl) orthoformate.
6. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, protease, lipase, cellulase, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including CaCO₃, talc, silicates, etc.

The following are examples of liquid laundry detergent compositions comprising fragrance pro-accords.

TABLE III

Ingredients	Weight %				
	12	13	14	15	16
Polyhydroxy coco-fatty acid amide	3.50	3.50	3.15	3.50	3.00
NEODOL 23-9 ¹	2.00	0.60	2.00	0.60	0.60
C ₂₅ Alkyl ethoxylate sulphate	19.00	19.40	19.00	17.40	14.00
C ₂₅ Alkyl sulfate	--	--	--	2.85	2.30
C ₁₀ -Aminopropylamide	--	--	--	0.75	0.50
Citric acid	3.00	3.00	3.00	3.00	3.00
Tallow fatty acid	2.00	2.00	2.00	2.00	2.00
Ethanol	3.41	3.47	3.34	3.59	2.93
Propanediol	6.22	6.35	6.21	6.56	5.75

Monomethanol amine	1.00	0.50	0.50	0.50	0.50
Sodium hydroxide	3.05	2.40	2.40	2.40	2.40
Sodium p-toluene sulfonate	2.50	2.25	2.25	2.25	2.25
Borax	2.50	2.50	2.50	2.50	2.50
Protease ²	0.88	0.88	0.88	0.88	0.88
Lipolase ³	0.04	0.12	0.12	0.12	0.12
Duramyl ⁴	0.10	0.10	0.10	0.10	0.40
CAREZYME	0.053	0.053	0.053	0.053	0.053
Optical Brightener	0.15	0.15	0.15	0.15	0.15
Fragrance Pro-accord ⁵	1.18	1.18	1.18	1.18	1.75
Soil release agent ⁶	0.22	0.15	0.15	0.15	0.15
Fumed silica	0.119	0.119	0.119	0.119	0.119
Minors, aesthetics, water	balance	balance	balance	balance	balance

1. C₁₂-C₁₃ alkyl E9 ethoxylate as sold by Shell Oil Co.
2. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
4. Disclosed in WO 9510603 A and available from Novo.
5. Pro-accord comprising tris(phenylethyl) orthoacetate.
6. Terephthalate co-polymer as disclosed in U.S. Patent 4,968,451, Scheibel *et al.*, issued November 6, 1990.

EXAMPLE 17

The following is an example of a solid bleaching composition which comprises a pro-accord according to the present invention.

TABLE IV

Ingredients	weight %
Nonanoyloxybenzene sulfonate	7.0
Sodium perborate	20.0
DTPA ¹	10.0
Citric acid (coated)	20.0
Fragrance ²	1.0
Pro-accord ³	2.0
Sodium sulfate	balance

1. Diethylenetriamine pentaacetic acid.
2. Dihydromylenol.

3. Tris(mugetanyl) orthoformate.

EXAMPLE 18

The following is an example of a liquid bleaching composition comprising a pro-accord of the present invention.

TABLE V

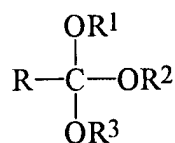
Ingredients	weight %
Sodium hypochlorite	5.25
C ₁₂ Dimethylamine oxide	0.9
Optical brightener ¹	0.3
Fragrance ²	1.0
Pro-accord ³	2.0
Sodium hydroxide	1.0
Water	balance

1. 4,4-bis(4-phenyl-2-H-1,2,3-triazolyl)-(2)-stilbene-2,2-disulfonic acid dipotassium salt.
2. A mixture of linalool (20%), tetrahydrolinalool (30%), Galaxolide (30%), and citral dimethylacetal (20%).
3. Tris(2,6-dimethylnonyl) orthoformate.

What is claimed is:

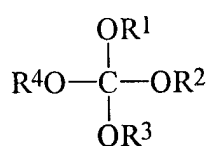
1. A laundry detergent composition having increased fragrance retention and fragrance longevity, comprising:
 - a) at least 0.01% by weight, of a fragrance delivery system comprising one or more pro-accords, provided said pro-accord:
 - i) comprises fragrance raw materials having a molecular weight greater than or equal to 100 g/mol;
 - ii) has a molecular weight greater than or equal to 300 gm/mol;
 - iii) has a molecular weight at least two times greater than the lowest molecular weight fragrance raw material which comprises said pro-accord; and
 - iv) has a fragrance release half-life of less than 1 hour when measured in a 90:10 dioxane/1 N HCl mixture at pH 0, preferably a fragrance release half-life of less than 12 hours when measured in NaH₂PO₄ buffer at pH 2.5;
 - b) at least 0.01% by weight, preferably from 0.1% to 60%, more preferably from 0.1% to 30% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant; and
 - c) the balance carriers and adjunct ingredients.
2. A composition according to Claim 1 wherein said pro-accord is selected from the group consisting of orthoesters, orthocarbonates, and mixtures thereof.
3. A composition according to either Claim 1 or 2 wherein said pro-accord has the formula:

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wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl, and mixtures thereof.

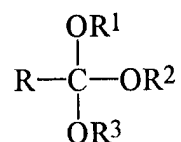
4. A composition according to Claim 2 wherein said pro-accord has the formula:



wherein R¹, R², R³, and R⁴ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof.

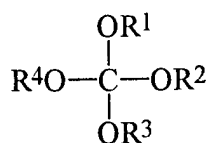
5. A composition according to any of Claims 1-4 wherein the adjunct ingredients are selected from the group consisting of builders, optical brighteners, bleaches, bleach boosters, bleach catalysts, bleach activators, soil release polymers, dye transfer agents, dispersents, enzymes, suds suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, 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.
6. A method for providing fragrance to fabric comprising the step of contacting fabric with an aqueous solution of a laundry detergent comprising:
 - a) at least 0.01%, preferably from 0.01% to 10%, more preferably from 0.1% to 1% by weight, of a fragrance delivery system comprising one or more pro-accords, provided said pro-accord:
 - i) comprises fragrance raw materials having a molecular weight greater than or equal to 100 g/mol;
 - ii) has a molecular weight greater than or equal to 300 gm/mol;
 - iii) has a molecular weight at least two times greater than the lowest molecular weight fragrance raw material which comprises said pro-accord; and
 - iv) has a fragrance release half-life of less than 1 hour when measured in a 90:10 dioxane/1 N HCl mixture at pH 0, preferably a fragrance release half-life of less than 12 hours when measured in NaH_2PO_4 buffer at pH 2.5;
 - b) at least 0.01% by weight, preferably from 0.1% to 60%, more preferably from 0.1% to 30% by weight, of a deterative surfactant selected from the group consisting of anionic, cationic, nonionic, zwitterionic, ampholytic surfactants, and mixtures thereof, preferably said surfactant is an anionic surfactant; and
 - c) the balance carriers and adjunct ingredients.

7. A method according to Claim 6 wherein said pro-accord has the formula:



wherein R is hydrogen, C₁-C₈ linear alkyl, C₄-C₂₀ branched alkyl, C₆-C₂₀ cyclic alkyl, C₆-C₂₀ branched cyclic alkyl, C₆-C₂₀ linear alkenyl, C₆-C₂₀ branched alkenyl, C₆-C₂₀ cyclic alkenyl, C₆-C₂₀ branched cyclic alkenyl, C₆-C₂₀ substituted or unsubstituted aryl, and mixtures thereof; R¹, R² and R³ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀ substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl, and mixtures thereof.

8. A method according to Claim 7 wherein said pro-accord has the formula:



wherein R¹, R², R³, and R⁴ are independently C₁-C₂₀ linear, branched, or substituted alkyl; C₂-C₂₀ linear, branched, or substituted alkenyl; C₅-C₂₀ substituted or unsubstituted cyclic alkyl; C₆-C₂₀ substituted or unsubstituted aryl, C₂-C₄₀ substituted or unsubstituted alkyleneoxy; C₃-C₄₀ substituted or unsubstituted alkyleneoxyalkyl; C₆-C₄₀ substituted or unsubstituted alkylenearyl; C₆-C₃₂ substituted or unsubstituted aryloxy; C₆-C₄₀

substituted or unsubstituted alkyleneoxyaryl; C₆-C₄₀ oxyalkylenearyl; and mixtures thereof.

9. A method according to Claim 8 wherein said pro-accord compound releases a fragrance raw material alcohol selected from the group consisting of 4-(1-methylethyl)cyclohexanemethanol, 2,4-dimethyl-3-cyclohexen-1-ylmethanol, (2,4-dimethylcyclohex-1-yl)methanol, (2,4,6-trimethyl-3-cyclohexen-1-yl)methanol, 2-phenylethanol, 1-(4-isopropylcyclohexyl)-ethanol, 2,2-dimethyl-3-(3-methylphenyl)propan-1-ol, 3-phenyl-2-propen-1-ol, 2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, 3-methyl-5-phenylpentan-1-ol, 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol, 2-methyl-4-phenylpentan-1-ol, *cis*-3-hexen-1-ol, 3,7-dimethyl-6-octen-1-ol, 3,7-dimethyl-2,6-octadien-1-ol, 7-methoxy-3,7-dimethyloctan-2-ol, 6,8-dimethylnonan-2-ol, *cis*-6-nonen-1-ol, 2,6-nonadien-1-ol, 9-decen-1-ol, 4-methyl-3-decen-5-ol, benzyl alcohol, 2-methoxy-4-(1-propenyl)phenol, 2-methoxy-4-(2-propenyl)phenol, and mixtures thereof.
10. A method according to any of Claims 6-9 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 suppressers, dyes, perfumes, colorants, filler salts, hydrotropes, 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.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/07935

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

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	EP 0 771 785 A (PROCTER & GAMBLE) 7 May 1997 see page 20, line 56 - line 58 see page 21, line 26 - line 50 see page 23, line 1 - line 16 see example 4 ---	1, 5, 6, 10
P, X	WO 97 34986 A (PAN ROBERT YA LIN ; MAO HSIANG KUEN (JP); MORELLI JOSEPH PAUL (US);) 25 September 1997 see page 8, line 5 - line 20 see page 9, line 31 - page 10, line 3 see claims 1-14; examples ---	1, 5, 6, 9, 10
A	US 5 378 468 A (SUFFIS ROBERT ET AL) 3 January 1995 cited in the application see column 10, line 50 - line 60; claims -----	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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