(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 006 271**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **79200302.2**

(22) Date of filing: **13.06.79**

(51) Int. Cl.³: **C 11 D 1/835, C 11 D 3/42**

(30) Priority: **20.06.78 GB 2737878**
29.08.78 GB 3490978
15.01.79 US 3567

(43) Date of publication of application: **09.01.80**
Bulletin 80/1

(84) Designated Contracting States: **BE DE FR GB IT NL**

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(54) Washing and softening compositions containing nonionic brightener.

(57) Textile softening detergent compositions comprise a nonionic detergent, a cationic textile softener, builders and a nonionic-type optical brightener, selected from benzoxazole, coumarin, bis(benzimidazolyl) furan and bis-(sulphonamidostyryl)biphenyl types. Preferred compositions also contain a discolouration inhibitor, and are made by spraying a mixture of the nonionic detergent and cationic softener on to spray dried granules comprising at least part of the builders.

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WASHING AND SOFTENING COMPOSITIONS CONTAINING NONIONIC BRIGHTENER

The present invention relates to detergent compositions which have very good cleaning properties and also have textile softening properties.

For many years most heavy duty detergent compositions have been based upon anionic surfactants and they have been observed to cause some harshness in the feel of washed fabrics. Accordingly there have been developed textile softening compositions, and these have been based upon long chained cationic surfactants. As cationic and anionic surfactants are generally incompatible, these softening compositions have been intended for use in the final rinse of a washing process, that is after substantially all the anionic surfactant has been removed. Clearly there is a need for a single composition able both to clean the fabrics and to soften them.

Attempts to incorporate cationic softeners in anionic based detergent compositions, overcoming their ordinary incompatibility, have been described in the art. Another approach has been to use nonionic surfactants with cationic softeners in built detergent compositions, as described in BP 1,079,388, DTAS 1,220,956, USP 3,537,993 and USP 3,607,763. However, products containing a high ratio of nonionic detergent to cationic softener are said to soften inadequately, whereas those with a high ratio of cationic to nonionic are said to clean inadequately. A particular problem in the use of such products has been the discolouration, usually yellowing, of repeatedly washed fabrics.

This problem is believed to arise from three causes. The first is the ineffectiveness of most of the usual optical brighteners when applied in the presence of cationic surfactants due to the failure of the brightener to deposit upon fabrics in such surroundings and/or from an actual quenching of the fluorescence of the brightener in the presence of cationic surfactant. The second main cause of yellowing is build-up of the brightener itself, which in some circumstances can act as a dyestuff at visible wavelengths. The third cause is apparently an interaction between the cationic or nonionic-cationic surfactants and colouring matter in the water used to make up the wash baths. The extent of this problem depends upon the state of the civic water supply, and can vary from place to place and from time to time. Iron content may be one relevant factor but probably organic e.g. peaty colouring matter is more usually the principal cause.

It has been found that the yellowing problems associated with the use of cationic surfactants in textile softening detergent compositions can be largely overcome by selection of certain classes of nonionic brighteners.

According to the invention there is provided a detergent composition which imparts a soft feel to fabrics washed therewith, which comprises:

(A) from 10 to 30% by weight of one or more polyethoxy nonionic detergents having hydrophilic-lipophilic balance in the range from 8 to 15 and having not more than an average of 16 ethoxy units per molecule

(B) from 1 to 15% by weight of one or more cationic textile softeners;

(C) from 0.001 to 3.0% by weight of a nonionic optical brightener selected from one or more of the following types

(a) benzoxazoles
(b) coumarins
(c) 2,5-bis (benzimidazolyl) furans
(d) 4,4'-bis(2-sulphonamido styryl) biphenyls
(D) from 0 to 80% by weight of a detergency builder; and
(E) from 0 to 5% of a discolouration inhibitor,

wherein the weight ratio of anionic surfactant to nonionic surfactant is less than 1:1 and the mol ratio of anionic surfactant to cationic softener is less than 1:1. Anionic surfactant is not an essential component of the invention and may be absent entirely. However, in the preferred form of the invention, viz. granular built detergent compositions, a low level of anionic surfactant is a useful processing aid in producing a satisfactory spray dried granules.

The preferred granular compositions according to this invention, are prepared by first making spray dried carrier granules comprising all or some of the detergency builders, a low level of anionic surfactant, and other non-heat sensitive components of the composition. A moving bed of these carrier granules is then sprayed in suitable mixing equipment with a mixture of the nonionic surfactant and cationic softener. Heat sensitive solid components, e.g. bleaching agent, enzymes, are dry mixed with the carrier granules before or after the spray-on process.

Detailed Description of the Invention

In its broadest aspect, the invention comprises three essential components, i.e. a nonionic detergent (A), a cationic textile softener (B), and a nonionic optical brightener (C).

The Nonionic Detergent

Water-soluble nonionic ethoxylates constitute the principal surfactant component of the present compositions. Such surfactants can be broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic (lipophilic) compound, which may be aliphatic or alkyl-aromatic in nature. The number of ethylene oxide groups condensed with any particular hydrophobic group is adjusted to yield a water-soluble compound having a hydrophilic-lipophilic balance (HLB) of between about 8 and about 15.

Examples of suitable nonionic detergents include:

1. The polyethylene oxide condensates of alkyl phenol, e.g. the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 16 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived, for example, from polymerised propylene, di-isobutylene, octene or nonene. Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; nonylphenol condensed with 9 moles of ethylene oxide per mole of nonylphenol and di-iso-octylphenol condensed with 15 moles of ethylene oxide.

2. The condensation product of primary or secondary aliphatic alcohols having from 8 to 20 carbon atoms, in either straight chain or branched chains configuration, with from 1 to about 16 moles of alkylene oxide per mole of alcohol. Preferably, the aliphatic alcohol comprises between 9 and 15

carbon atoms and is ethoxylated with between 2 and 12, desirably between 3 and 8 moles of ethylene oxide per mole of aliphatic alcohol. Such nonionic surfactants are preferred from the standpoint of providing good to excellent detergency performance on fatty and greasy soils. The preferred surfactants are prepared from primary alcohols which are either linear (such as those derived from natural fats or prepared by the Ziegler process from ethylene, e.g. myristyl, cetyl, stearyl alcohols),or partly branched such as the Dobanols and Neodols which have about 25% 2-methyl branching (Dobanol and Neodol being Trade Names of Shell) or Synperonics, which are understood to have about 50% 2-methyl branching (Synperonic is a Trade Name of I.C.I.) or the primary alcohols having more than 50% branched chain structure sold under the Trade Name Lial by Liquichimica. Specific examples of nonionic surfactants falling within the scope of the invention include Dobanol 45-4, Dobanol 45-7, Dobanol 45-11, Dobanol 91-3, Dobanol 91-6, Dobanol 91-8, Synperonic 6, Synperonic 14, the condensation products of coconut alcohol with an average of between 5 and 12 moles of ethylene oxide per mole of alcohol, the coconut alkyl portion having from 10 to 14 carbon atoms, and the condensation products of tallow alcohol with an average of between 7 and 12 moles of ethylene oxide per mole of alcohol, the tallow portion comprising essentially between 16 and 20 carbon atoms. Secondary linear alkyl ethoxylates are also suitable in the present compositions, especially those ethoxylates of the Tergitol series having from about 9 to 16 carbon atoms in the alkyl group and up to about 11, especially from about 3 to 9, ethoxy residues per molecule.

3. The compounds formed by condensing ethylene oxide with a hydrophobic base formed by the

condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion generally falls in the range of about 1500 to 1800. Such synthetic nonionic detergents are available on the market under the Trade Name of "Pluronic" supplied by Wyandotte Chemicals Corporation.

Preferred nonionic detergents are coconut alcohols with 6 ethoxy residues per molecule, and Dobanol 45-7 (C_{14}-C_{15} primary alcohol containing seven ethoxy groups/mole).

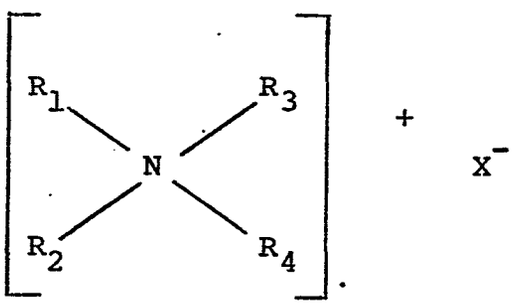
The nonionic detergent comprises from 10% to 30%, preferably from 10% to 20% by weight of the composition.

The Cationic Softener

Any cationic softener may be used in the compositions of the invention.

Among suitable cationic softeners are the conventional substantially water-insoluble quaternary ammonium compounds, and C_{8-25} alkyl imidazolinium salts.

Well-known species of substantially water-insoluble quaternary ammonium compounds have the formula;

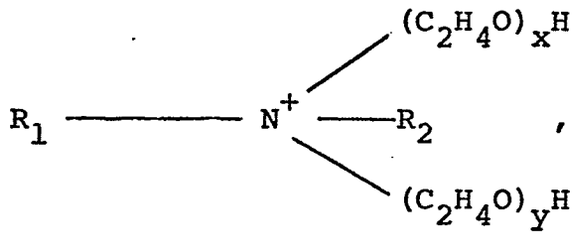


wherein R_1 and R_2 represent hydrocarbyl groups of from about 10 to about 22 carbon atoms; R_3 and R_4 represent hydrocarbyl groups containing from 1 to about 4 carbon atoms, X is an anion such as halide, a C_2-C_4 carboxylate, of an alkyl-or arylsulf(on)ate. Examples of preferred anions include bromide, chloride, methyl sulfate, toluene-, xylene-,

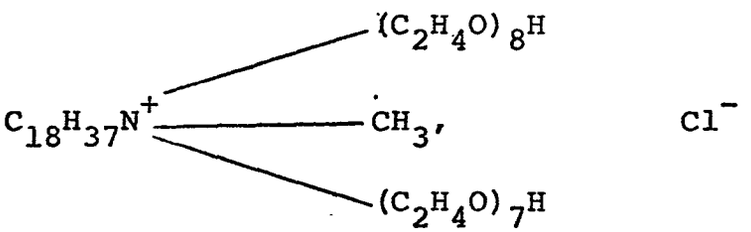
cumene-, and benzene-sulfonate, benzoate, para-hydroxybenzoate acetate, and propionate. Representative examples of quaternary softeners include ditallow dimethyl ammonium chloride; ditallow dimethyl ammonium methyl sulfate; dihexadecyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; dieicosyl dimethyl ammonium chloride; dieicosyl methyl ethyl ammonium chloride; didocosyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methyl sulphate; dihexadecyl diethyl ammonium chloride; dihexadecyl dihydroxyethyl ammonium methyl sulphate; di(coconutalkyl) dimethyl ammonium chloride. Ditallow dimethyl ammonium chloride, di(hydrogenated tallow alkyl) dimethyl ammonium chloride and di-(coconutalkyl) dimethyl ammonium chloride are preferred. Also suitable are the single long chained quaternary ammonium compounds of the above formula wherein R_1 is C_{10} to C_{22} alkyl or alkenyl, preferably C_{16} to C_{20} alkyl, and R_2 R_3 and R_4 are lower alkyl groups, that is C_1 to C_4 alkyl groups especially methyl, or aryl groups, and X is as defined above. Optionally also two or all three of R_2, R_3 and R_4 may together represent a heterocyclic ring. Some representative examples of such compounds are behenyl trimethyl ammonium bromide, oleyl dimethyl benzyl ammonium chloride, myristyl dimethyl ethyl ammonium bromide, cetyl trimethyl ammonium bromide, behenyl trimethyl ammonium methosulfate, oleyl methyl diethyl ammonium chloride, cetyl, stearyl or oleyl pyridinium chloride, behenyl pyridinium bromide, stearyl methyl morpholinium chloride, stearyl

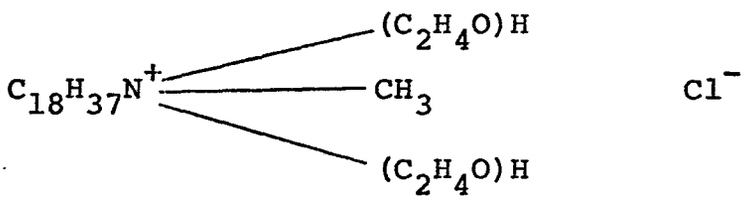
or oleyl ethyl or propyl morpholinium chloride.

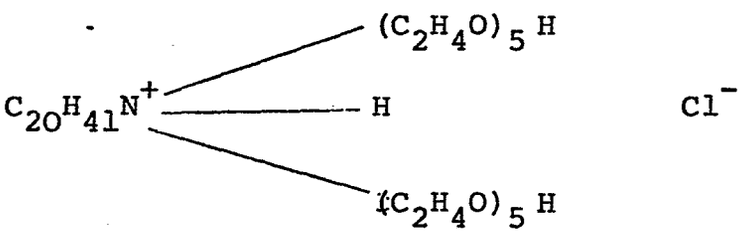
Yet other quaternary ammonium cationic surfactants which may be mentioned have the formula:



wherein R_1 and R_2 are as defined above or R_2 may be hydrogen and x and y are at least 1 and (x + y) is from 2 to 25. Examples are:

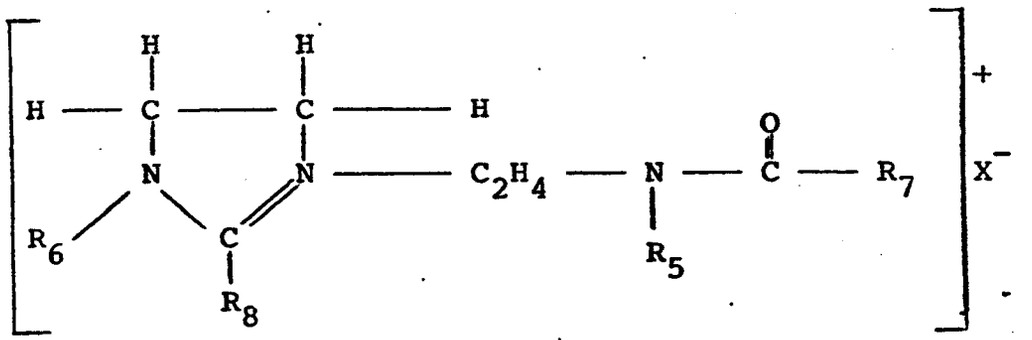






Substances of this sort are sold commercially, for instance under the Trade Name "Ethoquads".

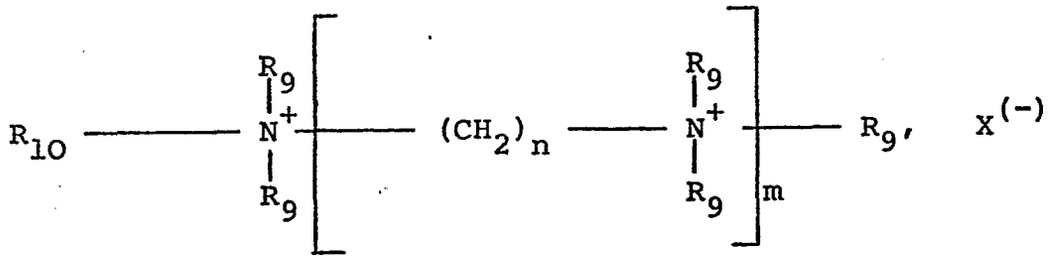
Another class of suitable cationic surfactants can be represented by C_{8-25} alkylimidazolinium salts. Preferred salts are those conforming to the formula;



wherein R_6 is a C_1-C_4 alkyl radical, R_5 is hydrogen or a C_1-C_4 alkyl radical, R_5 is hydrogen or a C_1-C_4 alkyl radical, R_5 is hydrogen or a C_1-C_4 alkyl radical, R_8 is a C_8-C_{25} alkyl radical and R_7 is hydrogen or a C_8-C_{25} alkyl radical. X is a charge balancing ion which has the same meaning as X defined in the quaternary ammonium surfactant above.

A preferred member of this class, believed to have R_6 methyl, R_7 and R_8 tallow alkyl, R_5 hydrogen, is sold under the Trade Name Varisoft 455 or 475 (Ashland Chemical Company), or Steinaquat M5040/H (Chemische Werke Rewo).

Among other suitable cationic surfactants may be mentioned the substituted polyamine salts of general formula:



wherein R_{10} is an alkyl or alkenyl group having from about 10 to 24, preferably 12 to 20, especially from 16 to 18 carbon atoms, the groups R_9 which may be the same or different, each represent hydrogen, a $(C_2H_4O)_pH$, or a $(C_3H_6O)_qH$, or a C_{1-3} alkyl group where p and q may each be 0 or a number such that (p + q) does not exceed 25, n is an integer from 2 to 6, preferably 3, m is from about 1 to 9, preferably from 1 to 4, most preferably 1 or 2, and $X^{(-)}$ represents one or more anions having total charge balancing that of the nitrogen atoms.

Preferred compounds of this class are, most preferred, N-tallow-N,N',N'-trimethyl-1,3-propylene diamine dichloride or di-methosulphate, commercially available under the Trade Names Lilamin 540 EO-3 (Lilachem), Dinoramox SH3, Inopol ODX3 (Pierrefitte-Auby), and N-tallow-N,N,N',N',N'-pentamethyl-1, 3-propylene diamine dichloride, commercially available under the Trade Names Stabiran MS-3 (Pierrefitte-Auby); Duoquad (Armour Hess); Adogen 477 (Ashland Company). Also suitable is the substance sold as Dinormac (Pierrefitte-Auby) or Duomac (Armour Hess) believed to have the formula:

Tallowyl- N^+H_2 - $(CH_2)_3$ - N^+H_3, $2(OCOCH_3)^-$

or the corresponding chloride. Herein Tallowyl represents predominantly C_{16} and C_{18} alkyl groups derived from tallow fatty acids.

It is highly desirable when one or more of R_9 in these components is hydrogen, that the pH of the formulation be such that one or more of the nitrogen atoms is protonated. Other suitable cationic surfactants are disclosed in our copending European Patent Application Nos. 0000234 and 0000235 published January 10th, 1979 and incorporated herein by reference.

Other suitable cationic softeners are described in our co-pending British patent application 22739/77 and USSN 770,487. Some suitable commercially available substances are marketed under the following Trade Names:

Sopa (Pieffefitte-Auby)
Sopapa " "
Lilamin LS33 (Lilachim)
Polyram L 200 (Pierrefitte-Auby)
Taflon - 320A (Diichi Kogyo Seiyaku Co.).

Mixtures of two or more of these cationic softeners may be employed.

Preferred cationic softeners are ditallowyl dimethyl ammonium halides or methosulphate, and imidazolinium salts e.g. Varisoft 455 or 475.

The compositions of the invention contain from 1% to 15%, preferable from 3 to 10%, by weight, of cationic softening agent. It is preferred that the weight ratio of nonionic detergent to cationic softening agent be in the range from 10:1 to 0.5:1, especially from 3:1 to 1:1.

The Optical Brightener

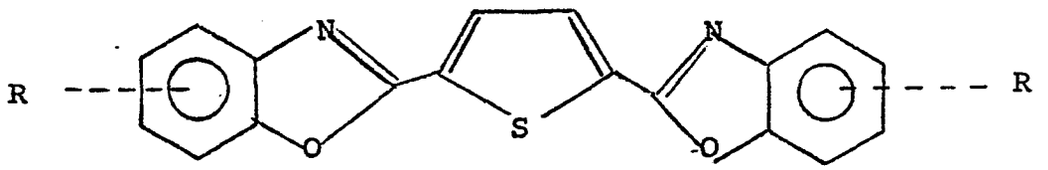
The optical brighteners suitable for compositions of the invention are nonionic in character and are selected from the following groups;

(a) benzoxazoles
(b) coumarins
(c) 2,5-bis(benzimidazolyl) furans
(d) 4,4'-bis-(2-sulphonamido styryl) biphenyls

(a) Benzoxazoles

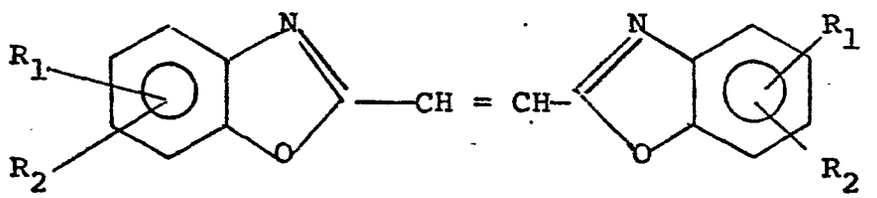
Nonionic benzoxazole brighteners useful in the invention have the following structural formulae :

(i) bis(benzoxazol-2-yl)thiophenes of formula



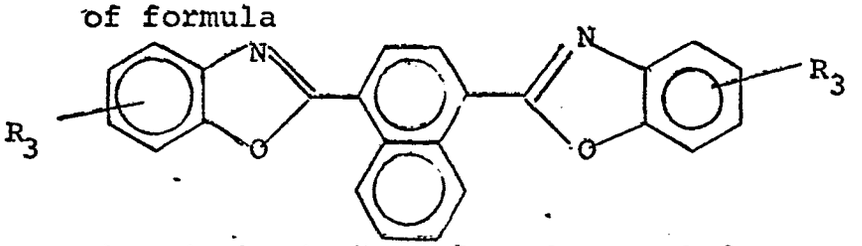
wherein R is H, 5-methyl, 5-dimethylbenzyl, or 5-tertiary butyl;

(ii) 1,2-bis(benzoxazol-2-yl) ethylene of formula



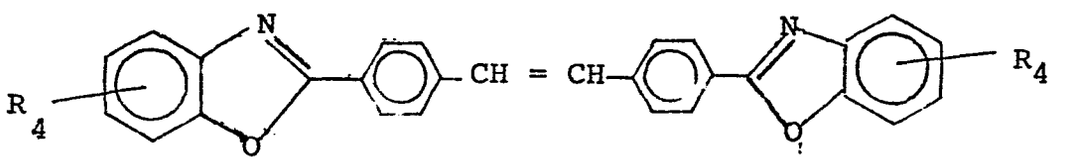
wherein R_1 and R_2 are H, or R_1 is H and R is 5-methyl,

(iii) 1,4-bis(benzoxazol-2-yl) naphthalenes of formula



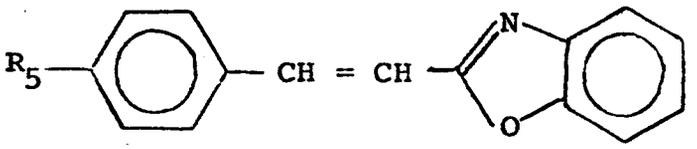
wherein R_3 is H or 5-carboxymethyl;

(iv)4,4'-bis(benzoxazol-2-yl)stilbenes of formula



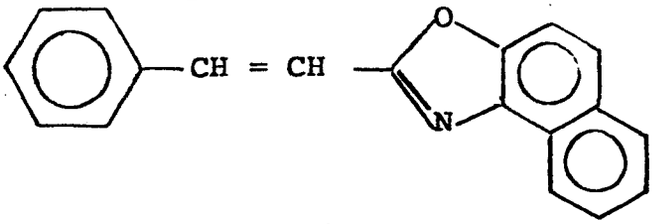
wherein R_4 is H, 5-carboxybutyl or 5-methyl;

(v) 2-(styryl)benzoxazoles of formula

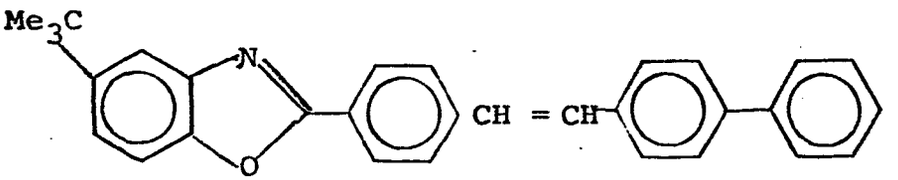


wherein R_5 is H, or carboxymethyl;

(vi) 2-(styryl) naphthoxazole of formula



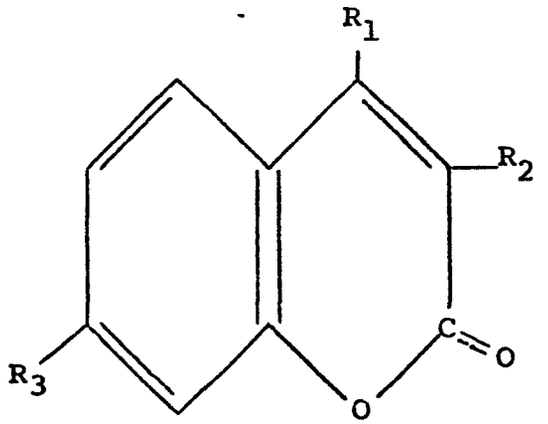
(vii) 2-(4-phenyl stilben-4'-yl)-5-tertbutyl benzoxazole of formula



Preferred are brighteners of classes (i) and (ii) and especially the compound bis(5-methyl benzoxazol-2-yl) thiophene and related structures.

(b) Coumarins

Suitable coumarin derivatives have the formula



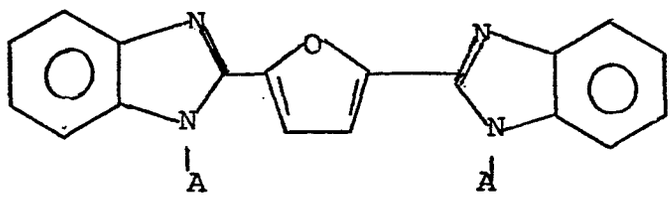
wherein R_1 represent H, a C_{1-4} alkyl or an aralkyl group, R_2 represents H, an aryl or $-COOR_4$, R_3 represents $-OR_4$, $-N(R_4)_2$ or $NHCOCH_3$, and each R_4 independently represents a C_{1-4} alkyl group.

Some compounds of this class are 4-methyl-7-dimethyl amino coumarin, 4-ethyl-7-dimethylamino coumarin, 4-methyl-7-diethylamino coumarin, 4-isopropyl-7-dimethylamino coumarin, 4-isobutyl-7-dimethylamino coumarin, 4-propyl-7-diethylamino coumarin, 3,4-di-methyl-7-dimethylamino coumarin, 4-methyl-7-ethoxy coumarin, 4-ethyl-7-methoxy coumarin, 4-methyl-7-carboxymethylamino coumarin, 4-benzyl-7-dimethyl amino coumarin, 4-benzyl-7-dimethyl amino coumarin, 3-phenyl-7-diethylamino coumarin, 3-carboxymethoxy-4-methyl-7-dimethylamino coumarin.

Especially preferred are the 4-methyl-7-dimethylamino or-7-diethylamino coumarins. Compounds of this type are known in the art, for instance in British Patent Specification 655,296, and a very suitable brightener is sold as Tinopal SWN Conc. (Trade Mark) by Messrs. Ciba-Geigy.

(c) Bis(benzimidazolyl)furans

These have the structure



wherein each A is selected from the group consisting of hydrogen, C_1-C_8 alkyl, C_1-C_8 hydroxyalkyl, C_1-C_8 alkenyl, $-(CH_2)_nOCH_3$, wherein n is from 1 to 8,

$-(CH_2)_nN(CH_3)_2$, wherein n is from 1 to 8,

$-(CH_2\underset{OH}{CH}_2O)_xH$, wherein x is from 2 to 12,

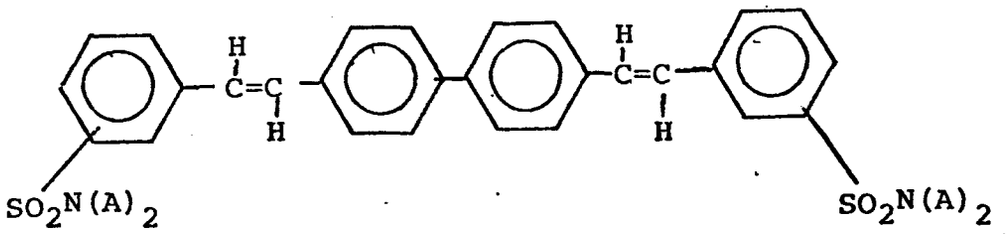
$-(CH_2CHCH_2O)_xH$, wherein x is from 1 to 12,

and $-(\underset{CH_3}{CH}CH_2O)_xH$, wherein x is from 1 to 12,

$-(CH_2CH_2O)_m(CH_2\underset{\underset{OH}{|}}{C}HCH_2O)_yH$, wherein m is from 1 to 12 and y is from 1 to 12. It is preferred that each A is a C_1-C_8 alkyl group, preferably a C_1-C_4 alkyl group, and most preferably a methyl group. In a given compound, the A groups may be both the same (for ease in synthesizing the molecule) or may be chosen so as to be different (to make the molecule substantive to both cotton and synthetic fabrics).

(d) Bis(sulphonamido styryl)biphenyls

These have the structure



wherein A is selected from the group defined under (c) above or where $(A)_2$ forms an oxazine ring containing the N atom.

Mixtures of any of these brighteners may be used and the compositions may contain from about 0.001% to about 3%, preferably from about 0.01 to about 0.5%, and most preferably from about 0.02 to about 0.1% by weight of the specific nonionic optical brighteners described above.

The Detergency Builders

Suitable detergent builder salts useful in the preferred granular compositions herein can be of the polyvalent inorganic and polyvalent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, silicates, and sulfates. Specific examples of such salts include the sodium and potassium tetraborates, bicarbonates, carbonates, tripolyphosphates, pyrophosphates, pentapolyphosphates and hexametaphosphates.

Examples of suitable organic alkaline detergency builder salts are:

(1) water-soluble amino polyacetates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates, N-(2-hydroxyethyl) nitrilodiacetates and diethylenetriamine pentaacetates;

(2) water-soluble salts of phytic acid, e.g., sodium and potassium phytates;

(3) water-soluble polyphosphonates, including sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium, and lithium salts of methylenediphosphonic acid and the like.

(4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethylsuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, cyclopentane-cis, cis, cis - tetracarboxylic acid, mellitic acid and pyromellitic acid.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders

is disclosed in Canadian Patent No. 755,038, e.g. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate, and trisodium ethane-1-hydroxy-1,1-diphosphonate.

Another type of detergency builder material useful in the present compositions and processes comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations preferably in combination with a crystallization seed which is capable of providing growth sites for said reactions product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

Preferred water soluble builders are sodium tripolyphosphate and sodium silicate, and usually both are present. In particular it is preferred that a substantial proportion, for instance from 3 to 15% by weight of the composition of sodium silicate (solids) of ratio (weight ratio SiO_2:Na_2O) from 1:1 to 3.5:1 be employed.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, particularly those described in Belgian Patent 814,874, issued November 12, 1974 incorporated herein by reference. This patent discloses and claims detergent compositions containing sodium aluminosilicates of the formula;

$$Na_z(AlO_2)_z(SiO_2)_yXH_2O$$

wherein Z and Y are integers equal to at least 6, the molar ratio of Z to Y is in the range of from 1.0:1 to about 0.5:1 and X is an integer from about 15 to about 264, said aluminosilicates having a calcium ion exchange capacity of at least 200 mg.eq./gram and a calcium ion exchange rate of at least about 2 grain/minute/gram. A preferred material is $Na_{12}(SiO_2AlO_2)_{12}\ 27H_2O$.

Built granular detergent compositions in

accordance with the invention contain from 10-80% of builder, preferably from 20% to 70% of builder.

Discolouration Inhibitors

Preferably, compositions of the present invention also contain from 0.3% to 5% of a discolouration inhibitor selected from

(a) condensates of C_{10} to C_{20} monohydric alcohols with at least 17 molar proportions of ethylene oxide;

(b) polyethylene glycols of molecular weight from 1,000 to 30,000 and

(c) polyvinyl alcohols of molecular weight from 10,000 to 20,000.

Highly preferred materials of this type are ethoxylated tallow alcohols with from 20 to 100 ethoxy groups, especially 25 or 80 (conveniently abbreviated as TAE_{25}, TAE_{80}).

Also effective are polyethylene glycols of molecular weight from about 1,000 to 30,000, especially from 6,000 to 20,000, and polyvinyl alcohols of molecular weight from 10,000 to 20,000, preferably about 14,000, and polyoxyethylene sorbitan C_{12}-C_{18} fatty acid esters having 17 or more ethylene oxide residues in their constitution.

It is preferred to use from 0.5% to 3.0% of these compounds by weight of the composition.

Other materials can also assist in preventing discolouration, for example by their soil-suspending or sequestering power.

Soil suspending agents such as sodium carboxymethyl cellulose are useful for this purpose, and it is preferred that these should be present at a level from about 0.5% to 1.5% by weight of the composition.

Also useful are methyl vinyl ether - maleic anhydride copolymers or the corresponding acids

and their salts, e.g. sodium salts, such as, for instance, Gantrez AN-119, Gantrez S95 (Trade Name - GAF) and the corresponding acids or salts. When present this component is used at from about 0.5% to 1.5% by weight of the composition.

Sequestering agents effective for chelating especially ferric iron, such as sodium ethylene diamine tetraacetate, diethylene triamine penta acetate, ethylene diamine tetra methylene phosphonate, diethylene triamine pentaphosphonate, and hydroxy-ethane-1,1-di-phosphonate are also useful and may function both as bleach stabilisers and as agents to inhibit yellowing caused by iron in tap water. Preferred agents are ethylene diamine tetra acetates, ethylene diamine tetra methylene phosphonates or both together, especially in the form of the sodium salts.

Furthermore, very low levels (of the order of a few e.g. up to 100 parts per million) of blue or green dyestuffs, such as polar Brilliant blue, ultramarine blue, indigo violet, which serve to mask any residual yellowing caused by the compositions of the invention may be included in the compositions. Especially suitable is a water soluble sulphonate of zinc phthalocyanine having a structure as described in our copending European Patent application No. 79200013.5 filed January 9th, 1979.

Other Optional Ingredients

Other optional components usual in built laundry detergents may of course be present. These include:-

Bleaching agents such as sodium perborate, sodium percarbonate and other perhydrates, at levels from about 5% to 35% by weight of the composition, and activators therefor, such as tetra acetyl ethylene diamine, tetra acetyl glycouril and others known in the art, and stabilisers therefor, such as magnesium silicate.

Suds controlling agents such as mono or di-ethanolamides of fatty acids as suds stabilisers, and C_{16-24} soaps or fatty acids, silicones, micro-crystalline waxes and mixtures thereof as suds depressants.

Proteolytic, amylolytic or lipolytic enzymes, especially proteolytic.

Classes of optical brighteners other than the above described nonionic brighteners.

Colours, non-substantive, and perfumes as required to improve the aesthetic acceptability of the products.

Throughout the description herein, where sodium salts have been employed, potassium, lithium or ammonium or amine salts may be used instead if their extra cost etc. are justified for special reasons.

Making the Composition

The compositions of the present invention may be produced in a variety of forms, including liquid, solid, granular, paste, powder or substrate compositions. Substrate articles may be formulated according to U.S. Patent Application Serial No. 781,378, Flesher et al, filed March 25, 1977, incorporated herein by reference. In a particularly preferred low or zero inorganic builder embodiment, the compositions of the present invention are formulated as liquids and contain up to about 20% of a lower alkyl (C_1 to C_4) alcohol, particularly ethanol. Liquid compositions containing lower levels of such alcohols (i.e., about 7 to 12%) tend to exhibit less phase separation than compositions containing higher alcohol levels.

In making non-liquid products, it has been found that it is important, in order to achieve the best possible softening performance from the compositions of the invention, that the cationic softener

be finely and intimately dispersed. Thus the cationic softener may be mixed in the form of fine solid particles with the rest of the composition, or in the case of spray dried granular products it may be included in the crutcher mix. The nonionic detergent (and optionally the discolouration inhibitor) may also be included in the crutcher mix. However for spray dried granular products it is much preferred to make carrier granules by spray drying a crutcher mix containing at least part, and usually substantially all of the detergency builders, and the other non-heat sensitive components. In order to obtain carrier granules of desired density it is usually desirable to include a low level of anionic surfactant, especially sodium C_{9-16} alkyl benzene sulphonate, in the carrier granules, as described in German Offenlegungschrift 2,617,956, incorporated herein by reference. Other anionic surfactants such as sodium C_{10-20} alkyl sulphates, and the corresponding alkyl ether sulphates with from 1 to 5 ethoxy groups per molecule, C_{10-20} alkane sulphonates and C_{10-20} olefin sulphonates, and C_{10-20} soaps may be employed. However, as stated herein before, the amount of anionic surfactant should be less than the amount of nonionic surfactant and less than the stoichiometric equivalent of the cationic softener in the compositions, and it is usually from 0.1% to 5.0% by weight of the composition, especially about 0.2% to 1.5%. Larger amounts of anionic are undesirable because they impair the cleaning and the softening properties of the compositions.

A moving bed of carrier granules, in any suitable mixing equipment such as a pan granulator, a rotating drum or a fluidised bed, is sprayed with a fluid

mixture comprising the nonionic detergent and the cationic softener, usually melted together, and generally having dissolved or dispersed therein, for instance, the optical brightener, the discolouration inhibitor and the methyl vinyl ether - maleic acid copolymer, and other components if convenient. It has been found to be advantageous to maintain the carrier granules, while they are being sprayed and/or afterwards at a temperature of above 35°C especially about 40°C to 75°C for a period of about ½ to 5 minutes, whereby the free flowing properties of the composition are improved.

Heat sensitive solid, granular or powdery, components are dry mixed with the carrier granules either before or after spray on of the nonionic detergent-cationic softener mixture.

The compositions of the present invention are used in the laundering process by forming an aqueous solution containing from about 0.01% (100 parts per million) to about 1.0% (10,000 parts per million), preferably from about 0.02% to about 0.75%, and most preferably from about 0.2% to about 0.75%, of the detergent compositions defined herein, and agitating the soiled fabrics in that solution. The fabrics are then rinsed and dried. When used in this manner, the compositions of the present invention yield outstanding brightening performance, without discolouring the fabrics upon repeated washing, as well as exceptionally good particulate and greasy/oily soil removal, together with fabric softening, static control, colour fidelity, and dye transfer inhibition benefits, without requiring the use of a conventional fabric softening additive product.

EXAMPLES I TO III

Granular detergent compositions of the following compositions were prepared.

	Composition (per cent by weight)	I	II	III
(c)	Ditallow dimethyl ammonium chloride	6	6	6
(c)	Dobanol 45-7 (1)	12	12	12
(a)	Sodium dodecylbenzene sulphonate	1	1	1
(a)	Sodium tripolyphosphate	33	33	33
(a)	Sodium silicate (2)	4	4	4
(a)	Sodium sulphate	21	20	20
(d)	Sodium perborate tetrahydrate	12	12	12
(a)	Sodium carboxymethyl cellulose	1.4	1.4	1.4
(b)	Gantrez S95 (3)	1	1	1
(d)	Enzyme containing granules	1.3	1.3	1.3
(c)	Optical brightener (4)	0.04	0.04	0.04
(c)	Tallow alcohol-E_{80} (5)	-	1	1
(b)	Dyestuff (6)	-	-	0.002
-	Moisture and impurities	Balance to 100		

(1) C_{14-15} primary alcohols condensed with 7 molar proportions of ethylene oxide

(2) Ratio SiO_2:Na_2 1.6:1 by weight.

(3) Trade Name for the sodium salts of the acid form of methyl vinyl ether - maleic anhydride copolymer

(4) bis(benzoxazol-2-yl) thiophene

(5) Tallow alcohol condensed with 80 molar proportions of ethylene oxide

(6) Irgalite CPVl (Colour Index 51319)

The compositions were prepared by making spray dried granules comprising components (a) with some moisture, spraying these granules with a dispersion in water of components (b), and then spraying them

with a molten mixture comprising components (c). If necessary, some improvements in flow properties of the product can be obtained by heating the granules after the two spray-on steps to from 37-47°C in a fluidised bed, fluidised by hot air, for from 1 to 5 minutes. After cooling (if necessary) the granules are dry mixed with components (d) to form the finished product.

Compositions I, II, and III cleaned fabrics as well as a typical commercial heavy duty anionic detergent composition, and the washed fabrics were as soft as those washed with this detergent composition and treated in the final rinse with a 0.1% dispersion of a typical rinse-added textile softener.

Fabrics washed in Composition I when illuminated by ultraviolet light gave significantly more visual reflected light than those washed in the same composition but lacking optical brightener or containing 0.2% of 1-(4-amino sulphonyl phenyl)-3-(4-chlorophenyl) -2-pyrazoline in place of 0.04% of the benzoxazole brightener of the invention.

Fabrics washed in Composition I were less yellow than fabric washed in the same compositions except containing 0.04% of brighteners:

1-(4-aminosulphonylphenyl)-3-(4-chlorophenyl) -2-pyrazoline

(2-benzimidazolyl)-(N-hydroxyethyl-2-benzimidazolyl) ethylene

Fabrics washed in Compositions II and III were judged to be less yellowed (whiter) than those washed in Composition I.

Similar results are obtained when in the above compositions the DTDMAC is replaced by Varisoft 475, (Trade Mark), an imidazolinium-type softener.

Similar results are obtained when the Dobanol 45-7 is replaced by coconut alcohol - E_6.

Similar results are obtained when the Gantrez S95 is replaced by Gantrez AN 119 (Trade Mark - GAF).

Similar results are obtained when the optical brightener is replaced by between 0.04 and 0.1% of bis(5-methyl benzoxazol-2-yl) thiophene, bis(5-dimethyl benzyl benzoxazol-2-yl)thiophene, bis (5-tert-butyl benzoxazol-2-yl) thiophene, 1,2-bis(benzoxazol-2-yl) ethylene, 1,2-bis(5-methyl benzoxazol-2-yl) ethylene, 1,4-bis(benzoxazol-2-yl) naphthalene 1,4-bis(5-carboxymethyl benzoxazol-2-yl)naphthalene, 4,4'-bis(benzoxazol-2-yl) stilbene, 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene, 4,4'-bis (5-carboxybutylbenzoxazol-2-yl) stilbene, 2-styryl benzoxazole, 2-styryl naphthoxazole, 2-(4-phenyl stilbene-4'-yl) tert-butyl benzoxazole or 4-methyl-7-diethylamino coumarin.

Similar results are obtained when the Tallow alcohol - E_{80} is replaced by Tallow alcohol - E_{25}, polyethylene glycol (M.Wt 6000) or polyvinyl alcohol (M.Wt. 14000).

EXAMPLE IV

An effective textile washing and softening composition has the formula, in parts per cent by weight;-

Coconut alcohol E_6	10
Ditallow dimethyl ammonium chloride	4
Tallow soap	1
Sodium tripolyphosphate	48
Sodium silicate (SiO_2:Na_2O=2:1)	6
Sodium sulphate	18
Sodium carboxymethyl cellulose	0.7
Gantrez AN 119 (Trade Name)	0.7
Polyethylene glycol (M.Wt. 6000)	1.3
1,2-bis(benzoxazol-2-yl)ethylene	0.05
Perfume	0.5
Moisture and impurities	Balance to 100

Similar results are obtained when the brightener is replaced by 4-methyl-7-diethylamino-coumarin.

EXAMPLE V

A detergent composition with pronounced textile softening properties has the formula, in parts per cent by weight:-

Dobanol 45-7	10
Ditallow dimethyl ammonium chloride	9
Sodium dodecylbenzene sulphonate	1
Sodium tripolyphosphate	33
Sodium silicate	4
Sodium sulphate	18
Sodium perborate tetrahydrate	12
Sodium carboxymethyl cellulose	1
Gantrez S95 (Trade Mark)	1
Enzyme containing granules	1
Bis-(5-methyl benzoxazole-2-yl) thiophene	0.05
Tallow alcohol E_{25}	1
Moisture and impurities	Balance to 100

Similar results are obtained when the brightener is replaced by 4-methyl-7-diethylamino coumarin.

EXAMPLE VI

A textile softening heavy duty detergent has the following formula, in parts per cent by weight:-

Dobanol 23-6.5*	20
Ditallow dimethyl ammonium chloride	3
Sodium tripolyphosphate	50
Sodium silicate (SiO_2Na_2O 1.6:1)	4
Sodium carboxy methyl cellulose	0.7
Gantrez S95	0.7
Sodium sulphate	13
Tallow alcohol - E_{80}	1

1,2-bis(5-methyl benzoxazol-2-yl) ethylene	0.1
Perfume	0.5
Moisture and Minors	Balance to 100

* C_{12-13} primary alcohols condensed with 6.5 molar proportions of ethylene oxide.

Similar results are obtained when the brightener is replaced by 3,4,dimethyl-7-methylamino coumarin.

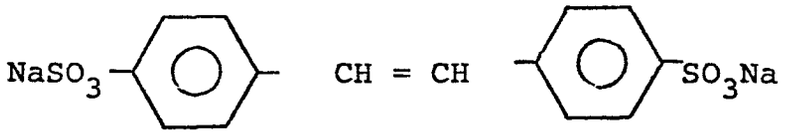
EXAMPLE VII

A granular detergent composition was prepared having the following formula;

Ditallow dimethyl ammonium chloride	6
Dobanol 45-7	12
Sodium dodecyl benzene sulphonate	0.5
Sodium tripolyphosphate	33
Sodium silicate (SiO_2:Na_2O 1.6:1)	4.2
Sodium sulphate	18
Sodium perborate tetrahydrate	12
Sodium carboxymethyl cellulose	0.7
Enzyme-containing granules	1.3
Optical brightener (1)	0.04
Optical brightener (2)	0.2
Tallow alcohol E_{80}	1.0
Sodium ethylenediamine tetraacetate	0.24
Sodium ethylenediamine tetra methylene phosphonate	0.5
Moisture and miscellaneous	Balance to 100

(1) bis(benzoxazol-2-yl)thiophene

(2) brightener of formula;



Fabrics repeatedly washed in each of the products of Examples IV through VII above are notably whiter than fabrics washed in similar compositions employing conventional anionic or nonionic brighteners.

EXAMPLE VIII

A granular detergent composition of the following formula is prepared.

	Composition (per cent by weight)	I
(b)	Ditallow dimethyl ammonium chloride	4.5
(b)	Dobanol 45-7 (1)	10.0
(a)	Sodium dodecylbenzene sulphonate	1
(a)	Sodium tripolyphosphate	33
(a)	Sodium silicate (2)	4
(a)	Sodium sulphate	15
(c)	Sodium perborate tetrahydrate	25
(a)	Sodium carboxymethyl cellulose	1
(c)	Enzyme containing granules	1.3
(b)	Optical brightener (3)	0.04
(b)	Tallow alcohol-E_{80} (4)	1
(a)	Sodium ethylene diamine tetraacetate	0.24
(a)	Sodium ethylene diamine tetra methylene phosphonate	0.50
-	Moisture and impurities	Balance to 100

(1) C_{14-15} primary alcohols condensed with 7 molar proportions of ethylene oxide

(2) Ratio SiO_2:Na_2O 1.6:1 by weight.

(3) Tinopal SWN, believed to be 4-methyl-7-diethyl amino coumarin

(4) Tallow alcohol condensed with 80 molar proportions of ethylene oxide.

The composition is prepared by making spray dried granules comprising components (a) with some moisture, spraying these granules with a molten mixture comprising components (b). After cooling (if necessary) the granules are dry mixed with components (c) to form the finished product.

This composition cleans fabrics as well as a typical commercial heavy duty anionic detergent composition and the washed fabrics are as soft as fabrics so washed and thereafter treated in a final rinse with a 0.1% dispersion of a typical rinse added textile softener composition.

Fabrics washed with the above composition, when illuminated by ultra violet light give significantly more visual reflected light than those washed in the same composition but lacking the optical brightener or containing 0.2% of a typical anionic optical brightener namely 1-(4-amino sulphonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline instead of the 0.04% of coumarin-type brightener.

Comparable results are obtained when in the above composition the ditallow dimethyl ammonium chloride is replaced by the corresponding metho sulphate or by an imidazolinium-type textile softener e.g. Varisoft 475 (Trade Name).

Comparable results are obtained when the Dobanol 45-7 is replaced by a condensate of coconut alcohol with 6 molar proportions of ethylene oxide.

Substantially similar performance is obtained if the Tinopal SWN is replaced by an equivalent weight of 4-methyl-7-dimethylamino coumarin, 4-ethyl-7-dimethylamino coumarin, 4-isopropyl-7-dimethylamino coumarin, 4-isobutyl-7-dimethylamino coumarin, 4-propyl-7-diethylamino coumarin, 3,4-di-methyl-7-dimethylamino coumarin, 4-methyl-7-ethoxy coumarin, 4-ethyl-7-methoxy coumarin, 4-methyl-7-carboxymethylamino coumarin, 4-benzyl-7-dimethylamino coumarin, 3-phenyl-7-diethylamino coumarin, or 3-carbomethoxy-4-methyl-7-dimethyl-amino coumarin.

EXAMPLE IX

A liquid composition of the present invention was as follows:

Component	Weight %
Neodol 45-7[1]	12.0
Neodol 23-6.5[2]	12.0
Unhardened ditallowalkyldimethyl-ammonium chloride	6.4
Ethanol	15.0
Sodium bicarbonate	0.25
Optical brightener	0.41
Perfume	0.35
Dye	0.063
Water	balance to 100

[1]Condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide, commercially available from Shell Chemical Company.

[2]Condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, commercially available from Shell Chemical Company.

[3]The brightener used herein had the formula (c) on page 14, with methyl groups constituting the substituent A.

This composition exhibited excellent removal of particulate and greasy/oily soils and outstanding brightening performance without discolouration problems. It also delivered fabric softening, static control, color fidelity and dye transfer inhibition benefits.

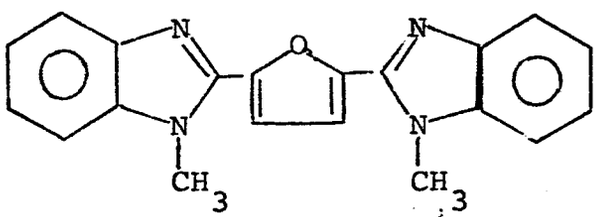
Substantially similar cleaning results are obtained when the cationic surfactant is replaced, in whole or in part, by ditallowalkyldimethylammonium methyl sulfate, ditallowalkyldimethylammonium iodide, dihexacetyl-alkyldimethylammonium chloride, dihexadecylalkyldi-hydroxy ethylammonium methyl sulfate, dioctadecyl-

alkyldimethylammonium chloride, dieicosylalkyl methyl ethyl ammonium chloride, dieicosylalkyl dimethyl-ammonium bromide, methyl (1) tallowalkyl amide ethyl (2) tallowalkyl imidazolinium methyl sulfate, or mixtures of these surfactants.

Substantially similar results are also obtained where the nonionic surfactant in Composition A is replaced, in whole or in part, by the condensation product of C_{14-15} alcohol with 2.25 moles of ethylene oxide; the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide; the condensation product of C_{12-15} alcohol with 9 moles of ethylene oxide; the condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, which is stripped so as to remove lower ethoxylate and nonethoxylated fractions; the condensation product of coconut alcohol with 5 moles of ethylene oxide; the condensation product of coconut alcohol with 6 moles of ethylene oxide; the condensation product of C_{12-15} alcohol with 7 moles of ethylene oxide; the condensation product of tallow alcohol with 9 moles of ethylene oxide; a 1:1 by weight mixture of the condensation product of C_{12-15} alcohol with 7 moles of ethylene oxide and the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide; and other mixtures of those surfactants.

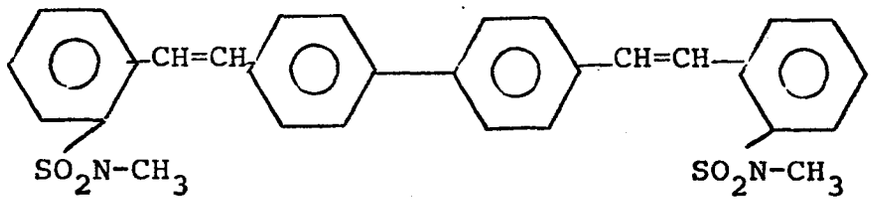
Excellent cleaning results are also obtained where the ratio of nonionic surfactant to cationic surfactant used in is about 2:1, 3:1, 3.5:1, 4.5:1, 5:1, 6:1, or 8:1.

The brightener herein has the formula:



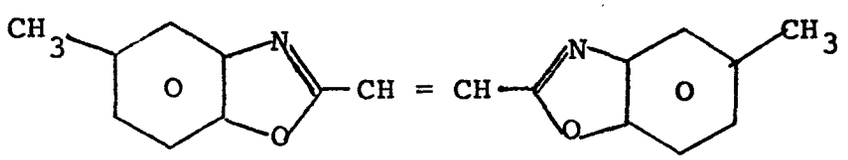
Substantially similar brightening results are obtained when the methyl groups in the above structure are replaced, with C_2, C_4, or C_8 alkyl groups; with hydrogen; with C_2 or C_8 hydroxyalkyl; with C_4 alkenyl; with $-(CH_2)_2OCH_3$; with $-(CH_2)_2N(CH_3)_2$; with $-(CH_2CH_2O)_2H$, $-(CH_2CH_2O)_6H$, or $-(CH_2CH_2O)_{12}H$; with $-(CH_2\underset{OH}{C}HCH_2O)_4H$; $-(\underset{CH_3}{C}HCH_2O)_2H$; or with $-(CH_2CH_2O)_6(CH_2\underset{OH}{C}HCH_2O)_2H$.

Substantially similar brightening results are obtained when the brightener is replaced with a brightener having the formula:



Substantially similar brightening results are obtained when the methyl groups in the above structure are replaced, with C_2, C_4 or C_8 alkyl groups, with hydrogen; with C_2 or C_8 hydroxyalkyl; with C_4 alkenyl; with $-(CH_2)_2OCH_3$; with $-(CH_2)_2N(CH_3)_2$; with $-(CH_2CH_2O)_6H$, or $-(CH_2CH_2O)_{12}H$; with $-(CH_2\underset{OH}{C}HCH_2O)_4H$; $-(\underset{CH_3}{C}HCH_2O)_2H$; or with $-(CH_2CH_2O)_6(CH_2\underset{OH}{C}HCH_2O)_2H$.

Substantially similar brightening results are obtained when the brightener is replaced with a brightener having the formula:



Substantially similar brightening results are obtained when the methyl groups in the above structure are replaced, with C_2, C_4 or C_8 hydroxyalkyl; with C_4 alkenyl; with $-(CH_2)_2OCH_3$; with $-(CH_2)_2N(CH_3)_2$; with $-(CH_2CH_2O)_2H$, $-(CH_2CH_2O)_6H$, or $-(CH_2CH_2O)_{12}H$; with $-(CH_2\underset{OH}{C}HCH_2O)_4H$; $-(\underset{CH_3}{C}HCH_2O)_2H$; or with $-(CH_2CH_2O)_6(CH_2\underset{CH_3}{C}HCH_2O)_2H$.

In a given brightener compound, the substituted groups (the A groups in the general formulae herein) may be both the same (for ease in synthesizing the molecule) or may be chosen so as to be different (to make the molecule substantive to both cotton and synthetic fabrics).

CLAIMS

1. A detergent composition which imparts a soft feel to fabrics washed therewith, which comprises:

(A) from 10 to 30% by weight of one or more polyethoxy nonionic detergent having a hydrophilic-lipophilic balance in the range from 8 to 15 and having not more than an average of 16 ethoxy units per molecule;

(B) from 1 to 15% by weight of one or more cationic textile softeners;

(C) from 0.001 to 3% by weight of a nonionic optical brightener of the following types

(a) benzoxazoles

(b) coumarins

(c) 2,5-bis (benzimidazolyl) furans

(d) 4,4'-bis (2-sulphonamido styryl) biphenyls

(D) from 0 to 80% by weight of a detergency builder;

(E) from 0 to 5% of a discolouration inhibitor;

wherein the weight ratio of anionic surfactant to nonionic surfactant is less than 1:1 and the molar ratio of anionic surfactant to cationic softener is less than 1:1.

2. A composition according to Claim 1 which comprises:

from 10 to 20% by weight of component (A)
from 3 to 10% by weight of component (B)
from 0.01 to 0.5% by weight of component (C)
and from 20 to 70% by weight of component (D)

3. A composition according to Claim 1 to Claim 2 wherein the nonionic detergent is selected from condensates of monohydric branched or unbranched primary or secondary alcohols having from 8 to 20 carbon atoms and condensates of alkyl phenols having

6 to 16 carbon atoms in the alkyl chain, each with from 4 to 16 molar proportions of ethylene oxide, and mixtures thereof.

4. A composition according to any previous claim wherein the cationic softener is selected from

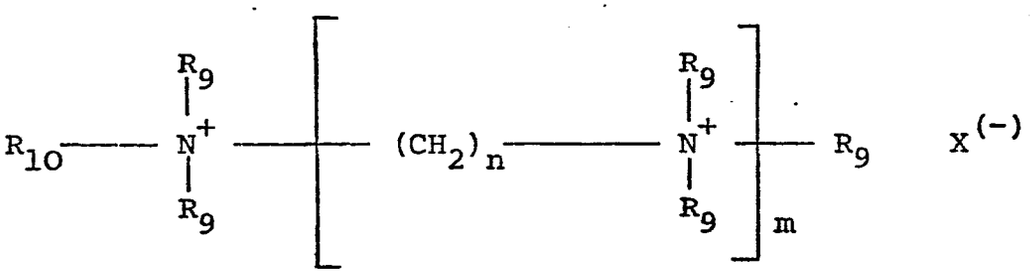
(a) non-cyclic quaternary ammonium salts having at least one C_{12-30} alkyl chain in the molecule

(b) C_{8-25} alkyl imidazolinium salts

(c) C_{12-20} alkyl pyridinium salts

(d) C_{12-20} alkyl morpholinium salts

(e) substituted polyamino salts of general formula



wherein R_{10} is an alkyl or alkenyl group having 10 to 24 carbon atoms, the groups R_9 which may be the same or different each represent hydrogen, $-(C_2H_4O)_pH$, $(C_3H_6O)_qH$, where p and q may be 0 or a number such that (p + q) does not exceed 25, n is an integer from 2 to 6, m is from 1 to 9 and $X^{(-)}$ represents one or more anions having total charge balancing that of the nitrogen atoms and

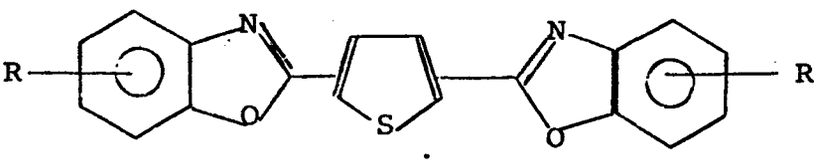
(f) mixtures thereof.

5. A composition according to Claim 5 wherein the cationic softener is selected from ditallow dimethyl ammonium chloride, 2-tallow-1-methyl-1-(tallow amidoethyl) imidazoline methosulphate; or mixture thereof.

6. A composition according to any previous claim wherein the water soluble detergency builder is selected from the group consisting of water soluble alkali metal carbonates, bicarbonates, borates, phosphates, polyphosphates, silicates, sulphates, amino polycarboxylates, phosphonates and mixtures thereof.

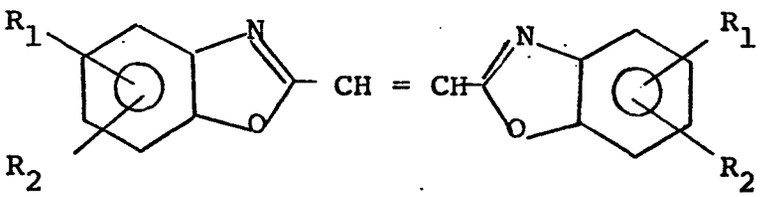
7. A composition according to any previous claim wherein the nonionic optical brightener is selected from benzoxazole brighteners of the classes:

(i) bis(benzoxazol-2-yl) thiophenes of formula



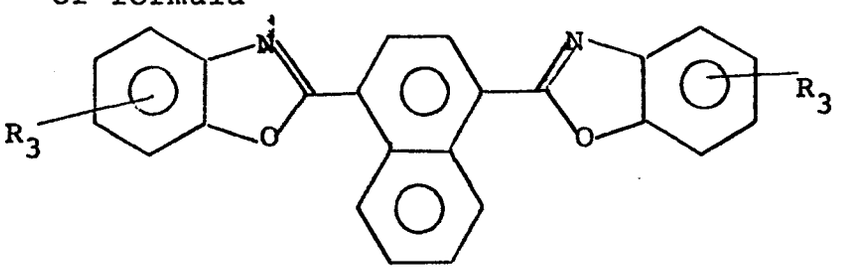
wherein R is H, 5-methyl, 5-dimethylbenzyl, or 5-tertiary butyl;

(ii) 1,2-bis(benzoxazol-2-yl)ethylenes of formula



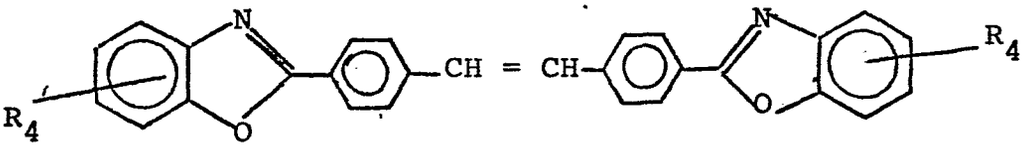
wherein R_1 and R_2 are H, or R_1 is H and R_2 is 5-methyl,

(iii) 1,4-bis (benzoxazol-2-yl) napthalenes of formula



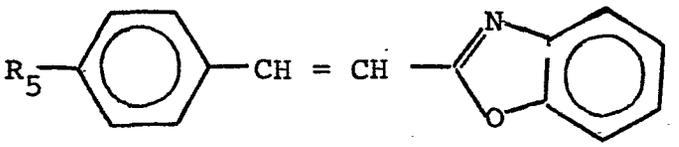
wherein R_3 is H or 5-carboxymethyl;

(iv) 4,4'-bis(benzoxazol-2-yl)stilbenes of formula



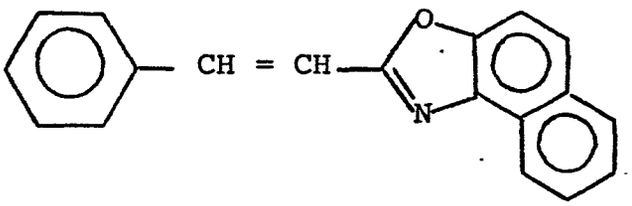
wherein R_4 is H, 5-carboxybutyl or 5-methyl;

(v) 2-(styryl)benzoxazoles of formula

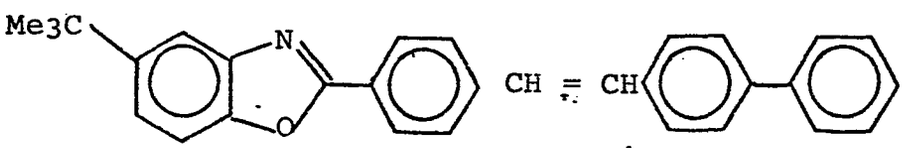


wherein R_5 is H, or carboxymethyl;

(vi) 2-(styryl) napthoxazole of formula

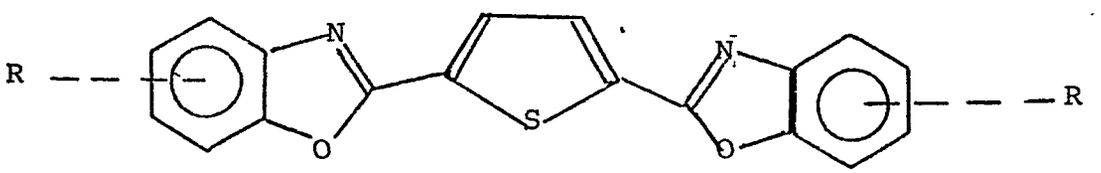


(vii) 2-(4-phenyl stilben-4'-yl)-5-tertbutyl benzoxazole of formula



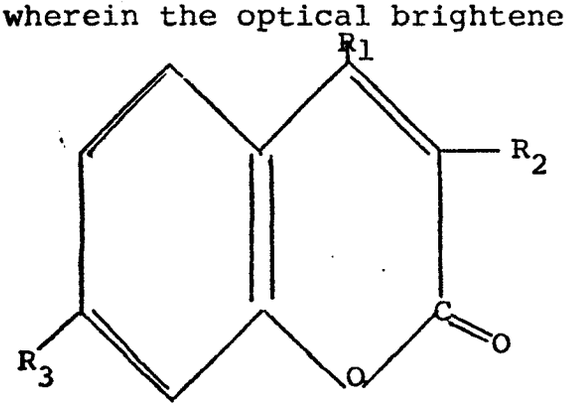
and (viii) mixtures thereof.

8. A composition according to Claim 7 wherein the optical brightener is the compound of formula:



in which R is CH_3

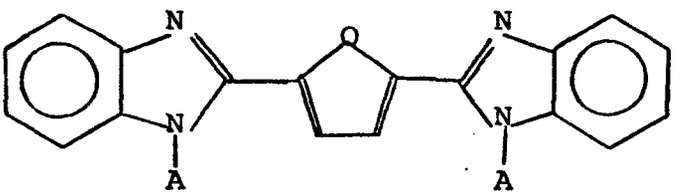
9. A composition according to Claims 1 to 8 wherein the optical brightener has the formula;



wherein R_1 represents H, a C_{1-4} alkyl or an aralkyl group, R_2 represents H, an aryl or $-COOR_4$, R_3 represents $-OR_4$, $-N(R_4)_2$ or $-NHCOCH_3$, and each R_4 independently represents a C_{1-4} alkyl group.

10. A composition according to Claim 9 wherein R_1 is CH_3, R_2 is H, R_3 is $N(CH_3)_2$, or $N(C_2H_5)_2$.

11. A composition according to any one of Claims 1 to 10 wherein the optical brightener has the formula



wherein each A is selected from the group consisting of hydrogen, C_1-C_8 alkyl, C_1-C_8 hydroxyalkyl, C_1-C_8 alkenyl,

$-(CH_2)_nOCH_3$, wherein n is from 1 to 8,

$-(CH_2)_nN(CH_3)_2$, wherein n is from 1 to 8,

$-(CH_2CH_2O)_xH$, wherein x is from 2 to 12,

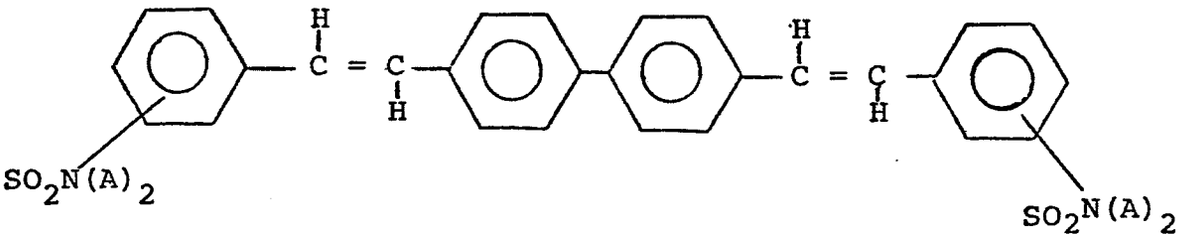
$-(CH_2\underset{OH}{C}HCH_2O)_xH$, wherein x is from 1 to 12 and

$-(\underset{CH_3}{C}HCH_2O)_xH$, wherein x is from 1 to 12,

$-(CH_2CH_2O)_m(CH_2\underset{OH}{C}HCH_2O)_yH$, wherein m is from 1 to 12 and y is from 1 to 12;

12. A composition according to Claim 11 wherein each of the substituent groups A is a methyl group.

13. A composition according to any one of Claims 1 to 12 wherein the optical brightener has the formula (2)



wherein each A is selected from the group defined in Claim 11, or wherein $(A)_2$ is an oxazine ring containing the N atom.

14. A composition according to any one of the preceding claims, wherein the discolouration inhibitor (E) comprises 0.3 to 5% of a material selected from

(a) condensates of C_{10} to C_{20} monohydric alcohols with at least 17 molar proportions of ethylene oxide.

(b) polyethylene glycols of molecular weight from 1000 to 30,000; and

(c) polyvinyl alcohols of molecular weight from 10,000 to 20,000.

European Patent Office

EUROPEAN SEARCH REPORT

0006271
Application number

EP 79 200 302.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 689 424 (M. BERG et al.) * claims 1, 7 to 10; column 3, line 71 to column 4, line 2; column 10, lines 6 to 9; column 11 lines 60 to 75; column 14, lines 71 to 74 *	1,4, 6
X	DE - A - 2 021 678 (HENKEL) * claims 1 to 3, 5 and 7 *	1,6
	DE - B - 1 922 047 (HENKEL) * claim 1; column 9, lines 50 to 53; column 12, example 1 *	1,5
	FR - A - 1 583 335 (SHOWA KAGAKU KOGYO KABUSHIKI KAISHA) * page 9, lines 19 to 29 *	14
A	DE - A - 2 000 231 (UNILEVER) * complete document *	
A	DE - A - 2 308 072 (HENKEL) * complete document *	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 11 D 1/835
C 11 D 3/42

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 11 D 1/00
C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	24-08-1979	SCHULTZE

EPO Form 1503.1 06.78