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(54) **Washing and softening compositions containing nonionic brightener.**

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DE-A- 2 308 072
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Description

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. USP 3,689,424 discloses co-positions of this type in which one or more cationic softeners are mixed with a C₈-C₂₄ fatty acid — hydroxyalkyl polyamine condensation product, which is stated to reduce the incompatibility of the former with anionic surfactants. 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 provided that where the nonionic detergent comprises a tallow alcohol ethoxylate, wherein the tallow alkyl moiety essentially contains from 16-20 carbon atoms, said tallow alcohol ethoxylate shall contain an average of between 7 and 12 moles of ethylene oxide per mole of alcohol ;

(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 ;

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

(F) from 0-5.0 % of an anionic surfactant ;

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 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).

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The Nonionic Detergent

Water-soluble nonionic ethoxylates constitute the principal surfactant component of the present composition. 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 alkylaromatic 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 8 and 15.

Examples of suitable nonionic detergents include :

15 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.

25 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 16 moles of ethylene 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 performances on fatty and greasy soils. The preferred surfactants are prepared from 30 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, and 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. Where ethylene oxide condensation products of tallow alcohol are employed as, or as part of the nonionic detergent they are formed with an average of between 40 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 9 to 16 carbon atoms in the alkyl group and up to 11, especially from 3 to 9, ethoxy residues per molecule.

45 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 1,500 to 1,800. 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 50 Dobanol 45-7 (C₁₄-C₁₅ 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

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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 C₈₋₂₅ alkyl imidazolium salts.

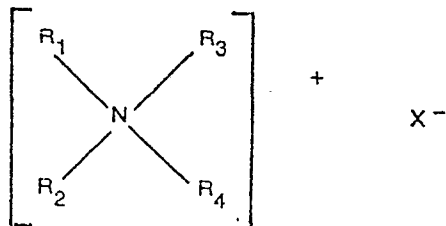
60 Well-known species of substantially water-insoluble quaternary ammonium compounds have the formula ;

(See Scheme p. 4)

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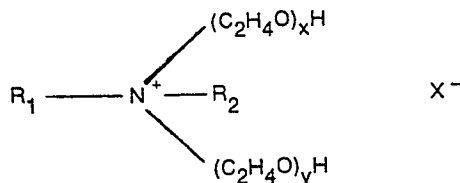
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10 wherein R_1 and R_2 represent hydrocarbyl groups of from 10 to 22 carbon atoms ; R_3 and R_4 represent hydrocarbyl groups containing from 1 to 4 carbon atoms, X is an anion such as halide, a C_2 - C_4 carboxylate, of an alkyl- or arylsulf(on)ate.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

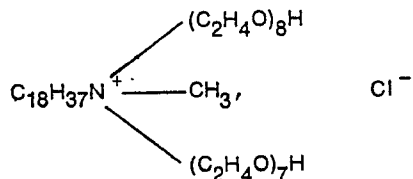
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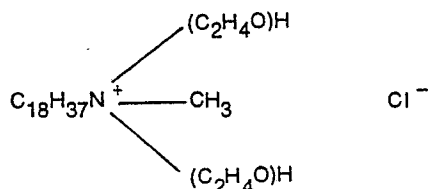
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wherein R_1 and R_2 are as defined above or R_2 may be hydrogen and x and y are at least 1 and $(x+y)$ is from 2 to 25. Examples are :

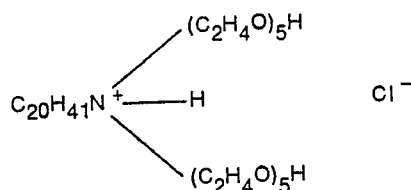
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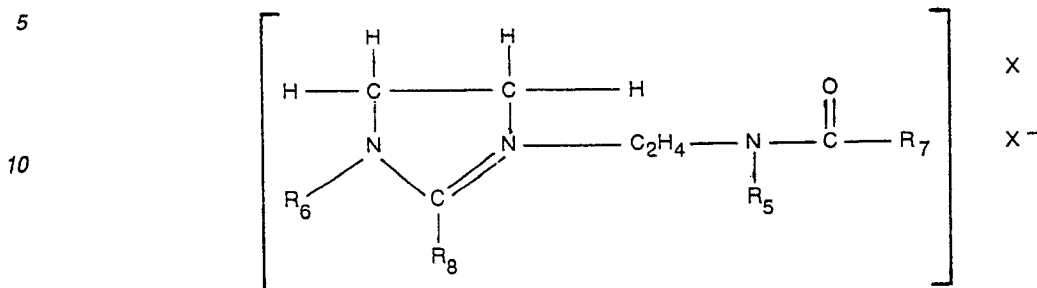
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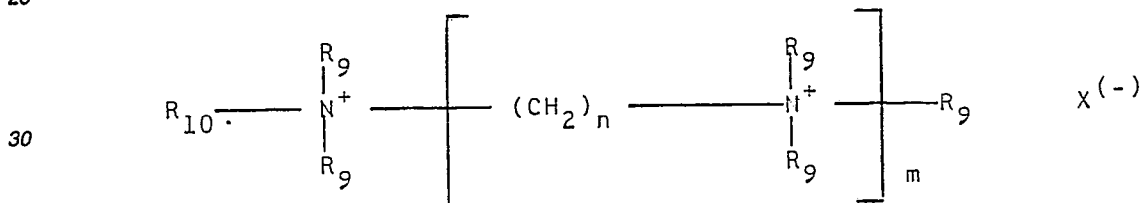
Substances of this sort are sold commercially, for instance under the Trade Name « Ethoquads ». Another class of suitable cationic surfactants can be represented by C₈₋₂₅ alkylimidazolium salts. Preferred salts are those conforming to the formula :



wherein R₆ is a C₁-C₄ alkyl radical, R₅ is hydrogen or a C₁-C₄ alkyl radical, R₅ is hydrogen or a C₁-C₄ alkyl radical, R₈ is a C₈-C₂₅ alkyl radical and R₇ is hydrogen or a C₈-C₂₅ 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 R₆ methyl, R₇ and R₈ tallow alkyl, R₅ hydrogen, in 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 R₁₀ 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 R₉ which may be the same or different, each represent hydrogen, a (C₂H₄O)_pH, or a (C₃H₆O)_qH, or a C₁₋₃ 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⁺H₂-(CH₂)₃-N⁺H₃, 2(OCOCH₃)⁻ or the corresponding chloride. Herein Tallowyl represents predominantly C₁₆ and C₁₈ alkyl groups derived from tallow fatty acids.

It is highly desirable when one or more of the R₉ 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 :

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

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

Preferred cationic softeners are ditallowyl dimethyl ammonium halides or methosulphate, and imidazolium 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 to be in the range from 10 : 1 to 0.5 : 1, especially from 3 : 1 to 1 : 1.

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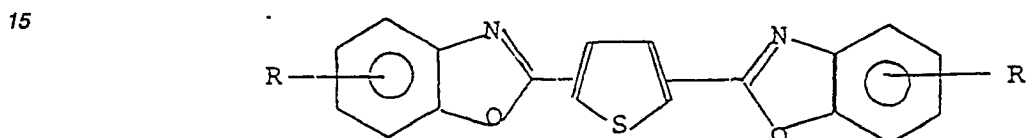
The Optical Brightener

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

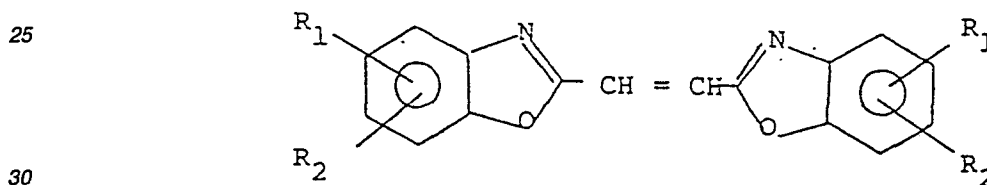
- 5 (a) benzoxazoles
 (b) coumarins
 (c) 2,5-bis(benzimidazolyl)furans
 (d) 4,4'-bis-(2-sulphonamido styryl)biphenyls

- 10 (a) Benzoxazoles

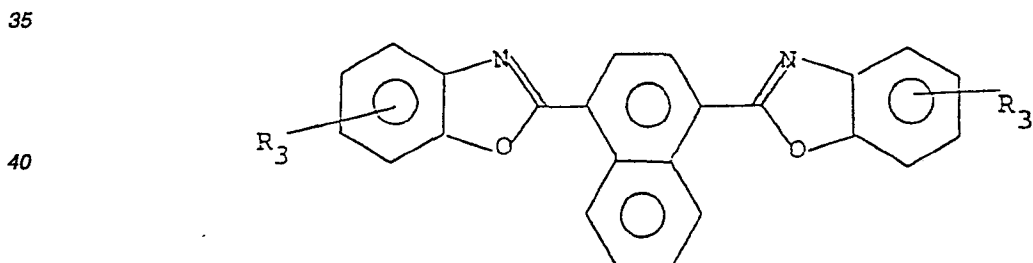
Nonionic benzoxazole brighteners useful in the invention have the following structural formulae :
 (i) bis(benzoxazol-2-yl)thiophenes of formula



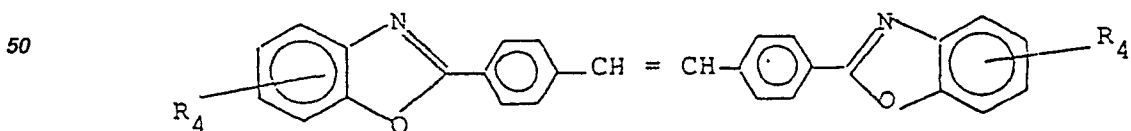
- 20 wherein R is H, 5-methyl, 5-dimethylbenzyl, or 5-tertiary butyl ;
 (ii) 1,2 bis(benzoxazol-2-yl)ethylene of formula



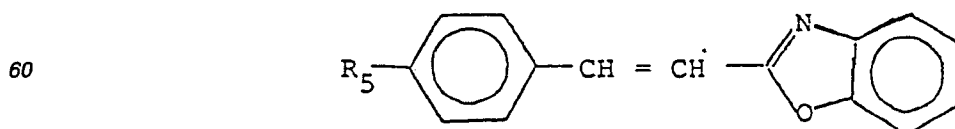
- wherein R₁ and R₂ are H, or R₁ is H and R is 5-methyl,
 (iii) 1,4-bis(benzoxazol-2-yl)naphthalenes of formula



- 45 wherein R₃ is H or 5-carboxymethyl ;
 (iv) 4,4'-bis(benzoxazol-2-yl)stilbenes of formula

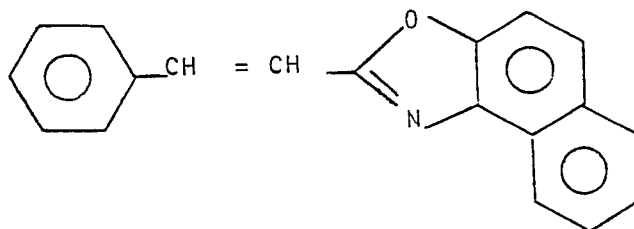


- 55 wherein R₄ is H, 5-carboxybutyl or 5-methyl ;
 (v) 2-(styryl)benzoxazoles of formula



- 65 wherein R₅ is H, or carboxymethyl ;
 (vi) 2-(styryl)naphthoxazole of formula

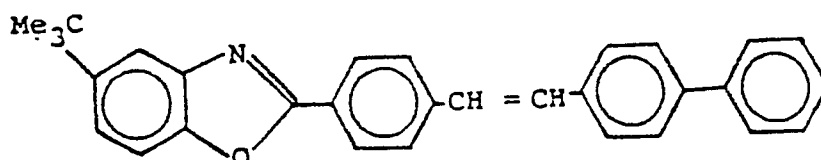
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(vii) 2-(4-phenyl stilben-4'-yl)-5-tertbutyl benzoxazole of formula

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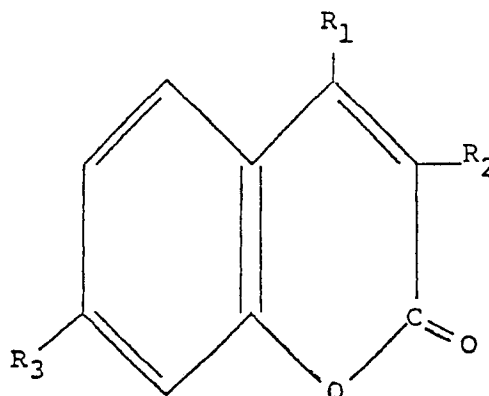
Preferred are brighteners of classes (i) and (ii) and especially the compound bis(5-methyl benzoxazol-2-yl) thiophene and related structures.

(b) Coumarins

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Suitable coumarin derivatives have the formula

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wherein R₁ represent H, a C₁₋₄ alkyl or an aralkyl group, R₂ represents H, an aryl or —COOR₄, R₃ represents —OR₄, —N(R₄)₂ or NHCOCH₃, and each R₄ independently represents a C₁₋₄ alkyl group.

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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-benzyl amino coumarin, 3-phenyl-7-diethylamino coumarin, 3-carboxymethoxy-4-methyl-7-dimethylamino coumarin.

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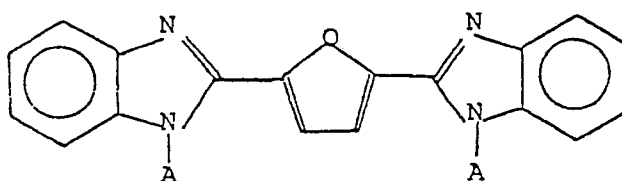
Especially preferred are the 4-methyl-7-dimethylamino or -7-diethylamino coumarins. Compounds of this type are known in the art, for instance in British Patent Specification 655,296, and a very suitable brightener is sold as Tinopal SWN Conc. (Trade Mark) by Messrs. Ciba-Geigy.

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(c) Bis(benzimidazolyl)furans

These have the structure

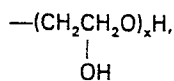
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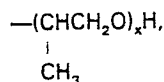
wherein each A is selected from the group consisting of hydrogen, C₁-C₈ alkyl, C₁-C₈ hydroxyalkyl, C₁-C₈ alkenyl, $-(CH_2)_nOCH_3$, wherein n is from 1 to 8, $-(CH_2)_nN(CH_3)_2$, wherein n is from 1 to 8,

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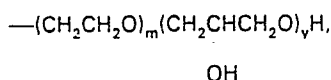


wherein x is from 2 to 12, $-(CH_2CH_2CH_2O)_xH$, wherein x is from 1 to 12, and

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15 wherein x is from 1 to 12,



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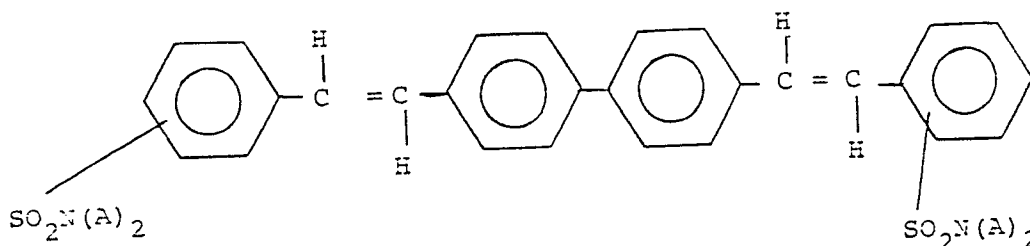
wherein m is from 1 to 12 and y is from 1 to 12. It is preferred that each A is a C₁-C₈ alkyl group, preferably a C₁-C₄ alkyl group, and most preferably a methyl group. In a given compound, the A groups may be both the same (for ease in synthesizing the molecule) or may be chosen so as to be different (to make the molecule substantive to both cotton and synthetic fabrics).

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(d) Bis(sulphonamido styryl)biphenyls

These have the structure

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wherein A is selected from the group defined under (c) above or where (A)₂ forms an oxazine ring containing the N atom.

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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.

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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.

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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 ;

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(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 ;

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(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.

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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
 5 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 $\text{SiO}_2 : \text{Na}_2\text{O}$) from 1 : 1 to 3.5 : 1 be employed.

10 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 :



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
 20 grain/minute/gram. A preferred material is $\text{Na}_{12}(\text{SiO}_2\text{AlO}_2)_{12}\text{27H}_2\text{O}$.

Built granular detergent compositions in accordance with the invention contain from 10-80 % of builder, preferably from 20 % to 70 % of builder.

Discolouration Inhibitors

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

- (a) condensates of tallow alcohols with from 20 to 100 molar proportions of ethylene oxide ;
- (b) polyethylene glycols of molecular weight from 1,000 to 30,000 and
- 30 (c) polyvinyl alcohols of molecular weight from 10,000 to 20,000.

Highly preferred materials of this type are ethoxylated tallow alcohols with 25 or 80 ethoxy groups, (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
 35 14,000, and polyoxyethylene sorbitan $\text{C}_{12}\text{-C}_{18}$ 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.

40 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
 45 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 hydroxyethane-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.
 50 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
 55 suitable is a water soluble sulphionate of zinc phthalocyanine having a structure as described in our copending European Patent application No. 79200013.5 filed January 9th, 1979.

Other Optional Ingredients

60 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
 65 silicate.

Suds controlling agents such as mono or diethanolamides of fatty acids as suds stabilisers, and C₁₆-
 24 soaps or fatty acids, silicones, microcrystalline waxes and mixtures thereof as suds depressants.

Proteolytic, amyolytic or lipolytic enzymes, especially proteolytic.

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

5 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.

10

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
 15 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 (C₁ to C₄) 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
 20 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
 25 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 C₉₋₁₆ alkyl benzen sulphonate, in the carrier granules, as described in German Offenlegungsschrift 2,617,956, incorporated herein by reference. Other anionic surfactants such as sodium C₁₀₋₂₀ alkyl sulphates, and
 30 the corresponding alkyl ether sulphates with from 1 to 5 ethoxy groups per molecule, C₁₀₋₂₀ alkane sulphonates and C₁₀₋₂₀ olefin sulphonates, and C₁₀₋₂₀ 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
 35 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 of 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
 40 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 1/2 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
 45 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
 50 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.

55

(See Table p. 11)

60

65

Examples I to III

Granular detergent compositions of the following compositions were prepared.

Composition (per cent by weight)	I	II	III
(c) Ditalow dimethyl ammonium chloride	6	6	6
(c) Dobanol 45-7 (1)	12	12	12
(a) Sodium dodecylbenzene sulphonate	1	1	1
10 (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
15 (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
20 — Moisture and impurities	Balance to 100		

(1) C₁₄₋₁₅ primary alcohols condensed with 7 molar proportions of ethylene oxide

(2) Ratio SiO₂ : Na₂ 1.6 : 1 by weight

25 (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 CPV1 (Colour Index 51319).

30 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.

35 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.

40 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 :

45 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.

50 Similar results are obtained when the Dobanol 45-7 is replaced by coconut alcohol-E₆.

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

55 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.

60 Similar results are obtained when the Tallow alcohol-E₈₀ is replaced by Tallow alcohol-E₂₅, polyethylene glycol (M.Wt. 6,000) or polyvinyl alcohol (M.Wt. 14,000).

Example IV

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

O 006 271

	Coconut alcohol E ₆	10
	Ditallow dimethyl ammonium chloride	4
	Tallow soap	1
	Sodium tripolyphosphate	48
5	Sodium silicate (SiO ₂ Na ₂ O = 2 : 1)	6
	Sodium sulphate	18
	Sodium carboxymethyl cellulose	0.7
	Gantrez AN 119 (Trade Name)	0.7
	Polyethylene glycol (M.Wt. 6,000)	1.3
10	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-diethylaminocoumarin.

15

Example V

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

20	Dobanol 45-7	10
	Ditallow dimethyl ammonium chloride	9
	Sodium dodecylbenzene sulphonate	1
	Sodium tripolyphosphate	33
25	Sodium silicate	4
	Sodium sulphate	18
	Sodium perborate tetrahydrate	12
	Sodium carboxymethyl cellulose	1
	Gantrez S95 (Trade Mark)	1
30	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 :

40	Dobanol 23-6.5*	20
	Ditallow dimethyl ammonium chloride	3
	Sodium tripolyphosphate	50
	Sodium silicate (SiO ₂ Na ₂ O 1.6 : 1)	4
45	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
50	Perfume	0.5
	Moisture and Minors	Balance to 100

*C₁₂₋₁₃ 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 ;

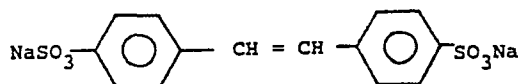
60	Ditallow dimethyl ammonium chloride	6
	Dobanol 45-7	12
	Sodium dodecyl benzene sulphonate	0.5
65	Sodium tripolyphosphate	33

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	Sodium silicate (SiO ₂ : Na ₂ O 1.6 : 1)	4.2
	Sodium sulphate	18
	Sodium perborate tetrahydrate	12
	Sodium carboxymethyl cellulose	0.7
5	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
10	Sodium ethylenediamine tetra methylene phosphonate	0.5
	Moisture and miscellaneous	Balance to 100

- (1) bis(benzoxazol-2-yl)thiophene
 (2) brightener of formula ;

15



20 Fabrics repeatedly washed in each to 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

25

A granular detergent composition of the following formula is prepared.

	Composition (per cent by weight)	
	(b) Ditalow dimethyl ammonium chloride	4.5
30	(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
35	(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
40	(a) Sodium ethylene diamine tetraacetate	0.24
	(a) Sodium ethylene diamine tetra methylene phosphonate	0.50
	— Moisture and impurities	Balance to 100

- 45 (1) C₁₄₋₁₅ primary alcohols condensed with 7 molar proportions of ethylene oxide
 (2) Ratio SiO₂ : Na₂O 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.

50 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.

55 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.

60 Comparable results are obtained when in the above composition the ditalow 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.

65 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

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coumarin, 4-isopropyl-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-diethyl-amino coumarin, or 3-carbomethoxy-4-methyl-7-dimethylamino coumarin.

5

Example IX

A liquid composition of the present invention was as follows :

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

20

(1) Condensation product of C₁₄₋₁₅ alcohol with 7 moles of ethylene oxide, commercially available from Shell Chemical Company.

(2) Condensation product of C₁₂₋₁₃ alcohol with 6.5 moles of ethylene oxide, commercially available from Shell Chemical Company.

25

(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, dihexacetylalkyldimethylammonium chloride, dihexadecylalkyldihydroxy ethylammonium methyl sulfate, dioctadecylalkyldimethylammonium chloride, dieicosylalkyl methyl ethyl ammonium chloride, dieicosylalkyl dimethylammonium bromide, methyl (1) tallowalkyl amide ethyl (2) tallowalkyl imidazolium methyl sulfate, or mixtures of these surfactants.

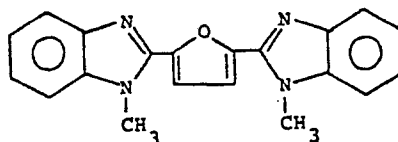
Substantially similar results are also obtained where the nonionic surfactant in Composition A is replaced, in whole or in part, by the condensation product of C₁₄₋₁₅ alcohol with 2.25 moles of ethylene oxide ; the condensation product of C₁₄₋₁₅ alcohol with 7 moles of ethylene oxide ; the condensation product of C₁₂₋₁₅ alcohol with 9 moles of ethylene oxide ; the condensation product of C₁₂₋₁₃ 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 C₁₂₋₁₅ 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 C₁₂₋₁₅ alcohol with 7 moles of ethylene oxide and the condensation product of C₁₄₋₁₅ 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.

50

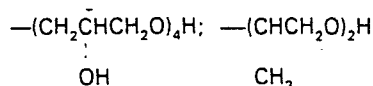
The brightener herein has the formula :

55



Substantially similar brightening results are obtained when the methyl groups in the above structure are replaced, with C₂, C₄, or C₈ alkyl groups ; with hydrogen ; with C₂ or C₈ hydroxyalkyl ; with C₄ alkenyl ; with $-(CH_2)_2OCH_3$; with $-(CH_2)_2N(CH_3)_2$; with $-(CH_2CH_2O)_2H$, $-(CH_2CH_2O)_6H$, or $-(CH_2CH_2)_{12}H$; with

60

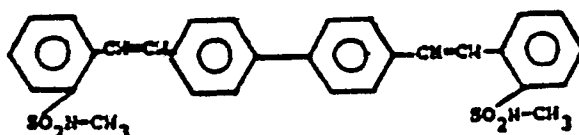


65

or with $-(\text{CH}_2\text{CH}_2\text{O})_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{H}$.

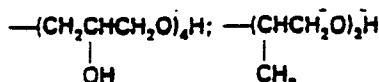
Substantially similar brightening results are obtained when the brightener is replaced with a brightener having the formula :

5



10 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 $-(\text{CH}_2)_2\text{OCH}_3$; with $-(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$; with $-(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$, or $-(\text{CH}_2\text{CH}_2\text{O})_{12}\text{H}$; with

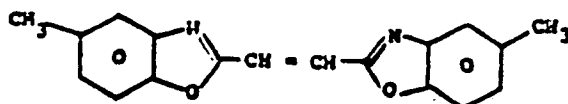
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or with $-(\text{CH}_2\text{CH}_2\text{O})_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{H}$.

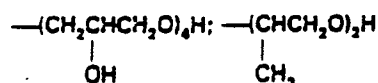
20 Substantially similar brightening results are obtained when the brightener is replaced with a brightener having the formula :

25



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 $-(\text{CH}_2)_2\text{OCH}_3$; with
30 $-(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$; with $-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$, $-(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$, or $-(\text{CH}_2\text{CH}_2\text{O})_{12}\text{H}$; with

35



or with $-(\text{CH}_2\text{CH}_2\text{O})_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2\text{H}$.

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).

40

Claims

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

45 (A) from 10 to 30 % by weight of one or more polyethoxy nonionic detergent having an hydrophilic-lipophilic balance in the range from 8 to 15 and having not more than an average of 16 ethoxy units per molecule provided that where the nonionic detergent comprises a tallow alcohol ethoxylate, wherein the tallow alkyl moiety essentially contains from 16-20 carbon atoms, said tallow alcohol ethoxylate shall contain an average of between 7 and 12 moles of ethylene oxide per mole of alcohol ;

50 (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

55 (d) 4,4'-bis(2-sulphonamide styryl) biphenyls ;

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

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

(F) from 0-5.0 % of an anionic surfactant ;

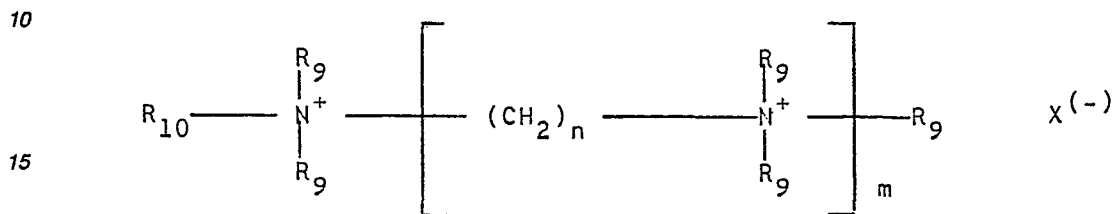
60 wherein the weight ratio of anionic surfactant to nonionic surfactant is less than 1 : 1 and the molar ratio of anionic surfactant to cationic softener is less than 1 : 1.

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)

65 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
- non-cyclic quaternary ammonium salts having at least one C₁₂₋₃₀ alkyl chain in the molecule
 - C₈₋₂₅ alkyl imidazolinium salts
 - C₁₂₋₂₀ alkyl pyridinium salts
 - C₁₂₋₂₀ alkyl morpholinium salts
 - substituted polyamino salts of general formula



wherein R₁₀ is an alkyl or alkenyl group having 10 to 24 carbon atoms, the groups R₉ which may be the same or different each represent hydrogen, -(C₂H₄O)_pH, (C₃H₆O)_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

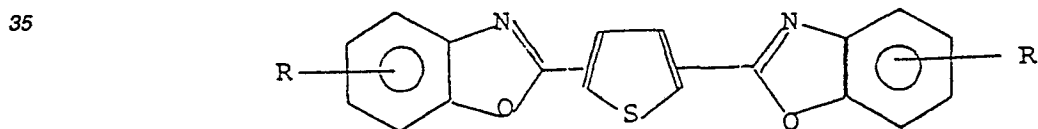
(f) mixtures thereof.

5. A composition according to Claim 4 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.

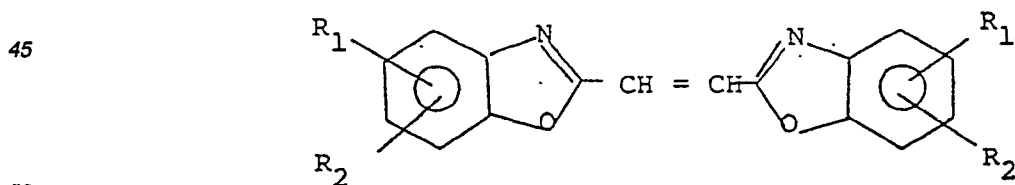
7. A composition according to any previous claim wherein the nonionic optical brightener is selected from benzoxazole brighteners of the classes :

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



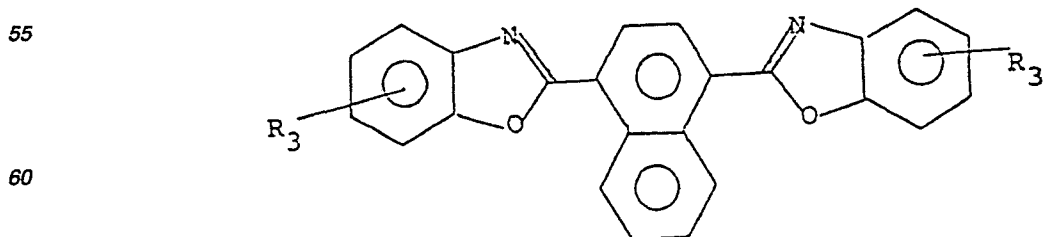
wherein R is H, 5-methyl, 5-dimethylbenzyl, or 5-tertiary butyl ;

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



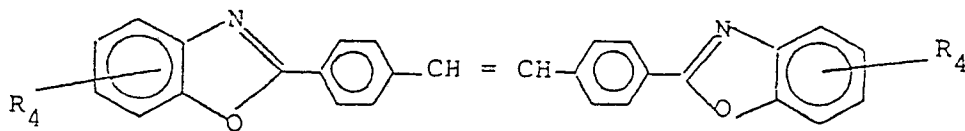
wherein R₁ and R₂ are H, or R₁ is H and R₂ is 5-methyl,

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

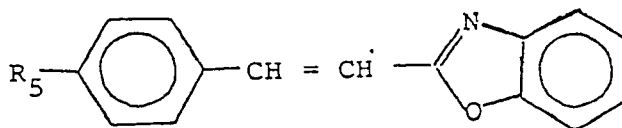


wherein R₃ is H or 5-carboxymethyl ;

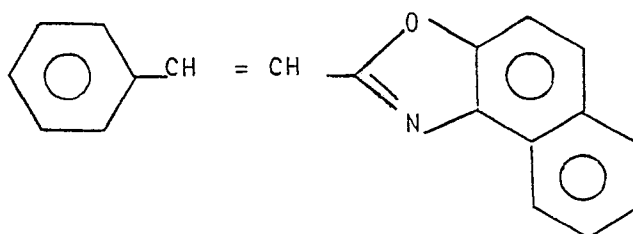
- (iv) 4,4'-bis(benzoxazol-2-yl)stilbenes of formula



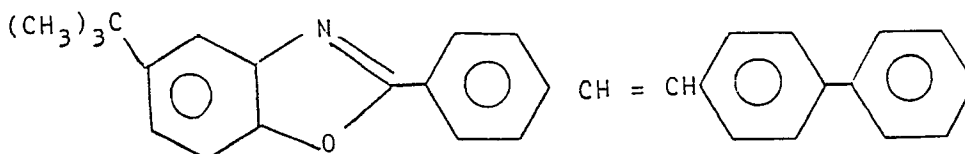
wherein R₄ is H, 5-carboxybutyl or 5-methyl ;
 (v) 2-(styryl)benzoxazoles of formula



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 wherein R₅ is H, or carboxymethyl ;
 (vi) 2-(styryl) naphthoxazole of formula

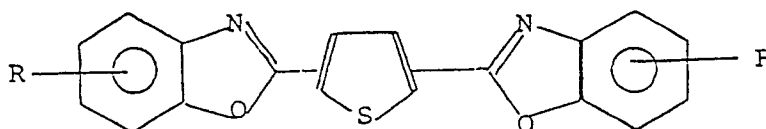


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 (vii) 2-(4-phenyl stilben-4'-yl)-5-tertbutyl benzoxazole of formula



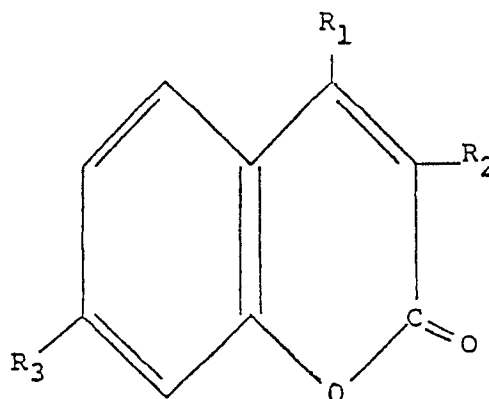
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 and (viii) mixtures thereof.

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



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 in which R is CH₃

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



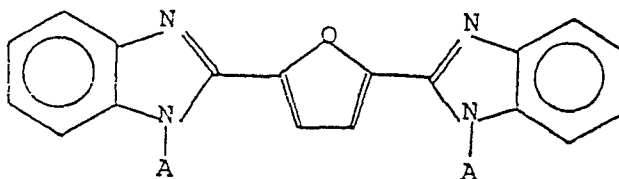
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 wherein R₁ represents H, a C₁₋₄ alkyl or an aralkyl group, R₂ represents H, an aryl or —COOR₄, R₃ represents —OR₄, —N(R₄)₂ or —NHCOCH₃, and each R₄ independently represents a C₁₋₄ alkyl group.

10. A composition according to Claim 9 wherein R₁ is CH₃, R₂ is H, R₃ is N(CH₃)₂, or N(C₂H₅)₂.

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

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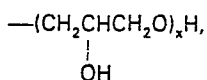


wherein each A is selected from the group consisting of hydrogen, C₁-C₈ alkyl, C₁-C₈ hydroxyalkyl, C₁-C₈ alkenyl,

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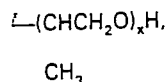
- (CH₂)_nOCH₃, wherein n is from 1 to 8,
- (CH₂)_nN(CH₃)₂, wherein n is from 1 to 8,
- (CH₂CH₂O)_xH, wherein x is from 2 to 12,

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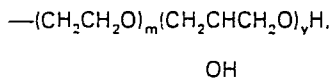
wherein x is from 1 to 12 and

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wherein x is from 1 to 12,

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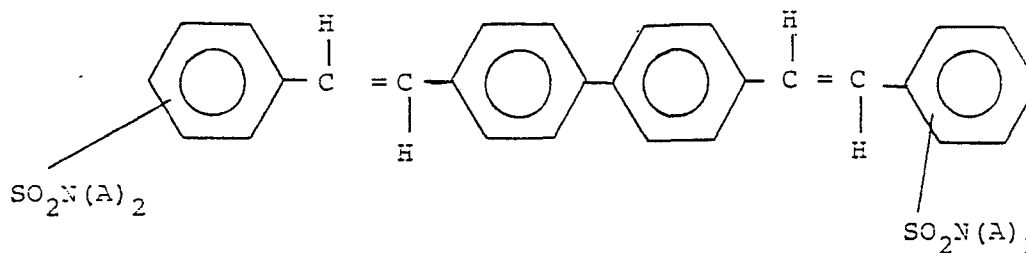
35 wherein m is from 1 to 12 and y is from 1 to 12 ;

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)

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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

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- (a) condensates of tallow alcohols with from 20 to 100 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.

Patentansprüche

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1. Ein Waschmittel, welches damit gewaschenen Textilien einen weichen Griff verleiht, umfassend :
 (A) 10 bis 30 Gew.-% eines oder mehrerer nicht-ionischer Polyethoxydetergentien mit einer Abstimmung von hydrophilen zu lipophilen Gruppen im Bereich von 8 bis 15 und nicht mehr als durchschnittlich 16 Ethoxyeinheiten pro Molekül, mit der Maßgabe, daß dann, wenn das nichtionische Detergens ein Talgalkoholethoxylat umfaßt, worin der Talgalkylanteil im wesentlichen 16 bis 20

Kohlenstoffatome enthält, dieses Talgalkoholethoxylat durchschnittlich zwischen 7 und 12 Mol Ethylenoxid pro Mol Alkohol enthalten soll ;

- (B) 1 bis 15 Gew.-% eines oder mehrerer kationischer Textilweichmacher ;
 (C) 0,001 bis 3 Gew.-% eines nichtionischen optischen Aufhellers der folgenden Typen

- 5 (a) Benzoxazole
 (b) Cumarine
 (c) 2,5-Bis-(benzimidazolyl)-furane
 (d) 4,4'-Bis-(2-sulfonamid-styryl)-biphenyle ;
 10 (D) 0 bis 80 Gew.-% eines Detergensgerüststoffes ;
 (E) 0 bis 5 % eines Verfärbungs-inhibitors ;
 (F) 0 bis 5,0 % eines anionischen oberflächenaktiven Mittels ;

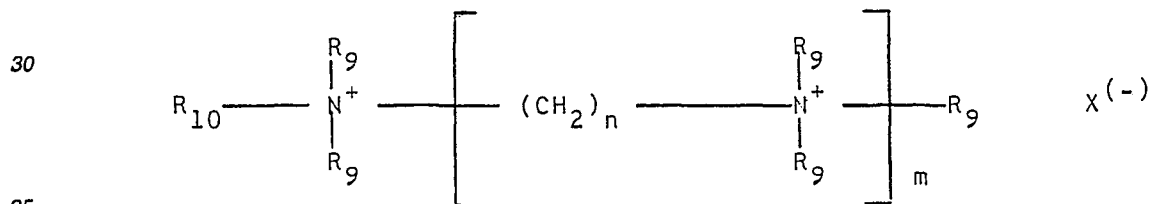
worin das Gewichtsverhältnis von anionischem oberflächenaktivem Mittel zu nichtionischem oberflächenaktivem Mittel weniger als 1 : 1 und das Molverhältnis von anionischem oberflächenaktivem Mittel zu kationischem Weichmacher weniger als 1 : 1 beträgt.

- 15 2. Ein Mittel nach Anspruch 1, umfassend : 10 bis 20 Gew.-% des Bestandteils (A) 3 bis 10 Gew.-% des Bestandteils (B) 0,01 bis 0,5 Gew.-% des Bestandteils (C) und 20 bis 70 Gew.-% des Bestandteils (D).

3. Ein Mittel nach Anspruch 1 bis Anspruch 2, worin das nichtionische Detergens aus Kondensaten von einwertigen, verzweigten oder nicht verzweigten, primären oder sekundären Alkoholen mit 8 bis 20 Kohlenstoffatomen und Kondensaten von Alkylphenolen mit 6 bis 16 Kohlenstoffatomen in der Alkylkette, jeweils mit 4 bis 16 Molanteilen Ethylenoxid, und Gemischen daraus ausgewählt ist.

- 20 4. Ein Mittel nach irgendeinem vorstehenden Anspruch, worin der kationische Weichmacher aus (a) nichtcyclischen quaternären Ammoniumsalzen mit mindestens einer C₁₂₋₃₀-Alkylkette im Molekül

- 25 (b) C₈₋₂₅-Alkylimidazoliumsalzen
 (c) C₁₂₋₂₀-Alkylpyridiniumsalzen
 (d) C₁₂₋₂₀-Alkylmorpholiniumsalzen
 (e) substituierten Polyaminosalzen der allgemeinen Formel



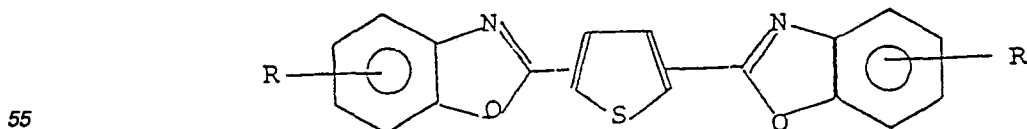
- 35 worin R₁₀ eine Alkyl- oder Alkenylgruppe mit 10 bis 24 Kohlenstoffatomen, die Gruppen R₉, die gleich oder verschieden sein können, jeweils Wasserstoff, -(C₂H₄O)_pH, (C₃H₆O)_qH, worin p und q 0 oder eine solche Zahl sein können, daß (p + q) 25 nicht überschreitet, n eine ganze Zahl von 2 bis 6, m 1 bis 9 und X⁽⁻⁾ eines oder mehrere Anionen, deren Gesamtladung die der Stickstoffatome ausgleicht, bedeuten und
 40 (f) Gemischen daraus ausgewählt ist.

5. Ein Mittel nach Anspruch 4, worin der kationische Weichmacher aus Ditalgdimethylammoniumchlorid, 2-Talg-1-methyl-1-(talgamidoethyl)-imidazolin-methosulfat oder Gemischen daraus ausgewählt ist.

- 45 6. Ein Mittel nach irgendeinem vorstehenden Anspruch, worin der wasserlösliche Detergensgerüststoff aus der Gruppe bestehend aus wasserlöslichen Alkalimetall-carbonaten, -bicarbonaten, -boraten, -phosphaten, -polyphosphaten, -silikaten, -sulfaten, -aminopoly-carboxylaten, -phosphonaten und Gemischen daraus ausgewählt ist.

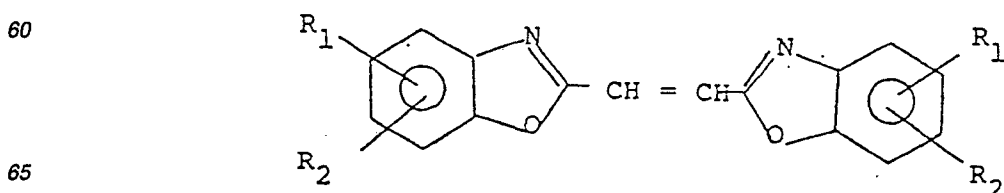
7. Ein Mittel nach irgendeinem vorstehenden Anspruch, worin der nichtionische optische Aufheller aus Benzoxazol-Aufhellern der Klassen :

- 50 (i) Bis-(benzoxazol-2-yl)-thiophenen der Formel .



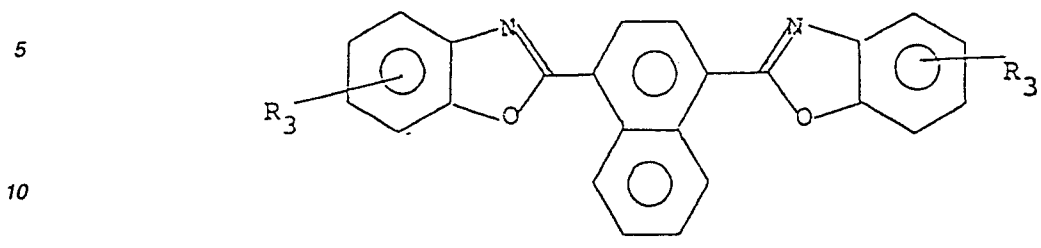
worin R H, 5-Methyl, 5-Dimethylbenzyl oder 5-tert.-Butyl bedeutet ;

- (ii) 1,2-Bis-(benzoxazol-2-yl)-ethylenen der Formel

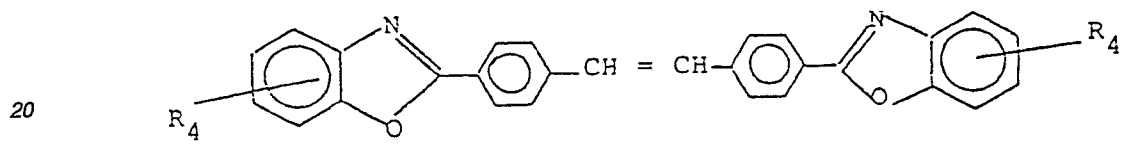


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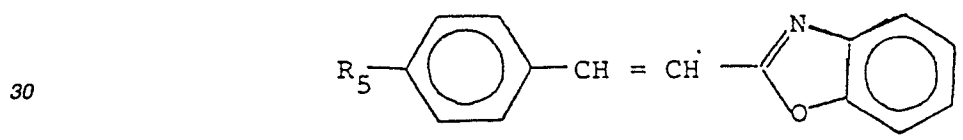
worin R_1 und R_2H sind, oder R_1H und R_2 5-Methyl sind,
 (iii) 1,4-Bis-(benzoxazol-2-yl)-naphthalinen der Formel



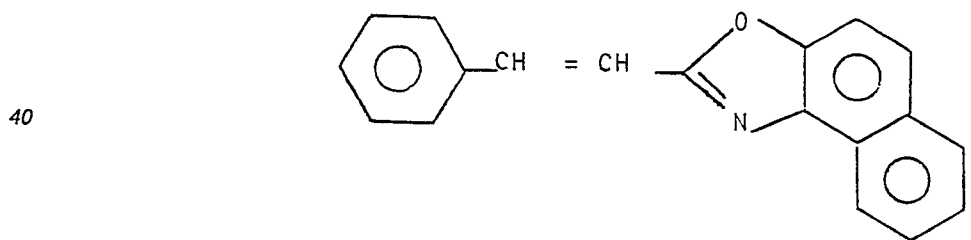
worin R_3H oder 5-Carboxymethyl ist ;
 (iv) 4,4'-Bis-(benzoxazol-2-yl)-stilbenen der Formel



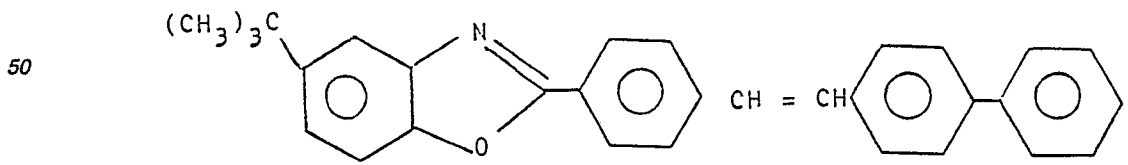
worin R_4H , 5-Carboxybutyl oder 5-Methyl ist ;
 (v) 2-(Styryl)-benzoxazolen der Formel



worin R_5H oder Carboxymethyl ist ;
 (vi) 2-(Styryl)-naphthoxazol der Formel

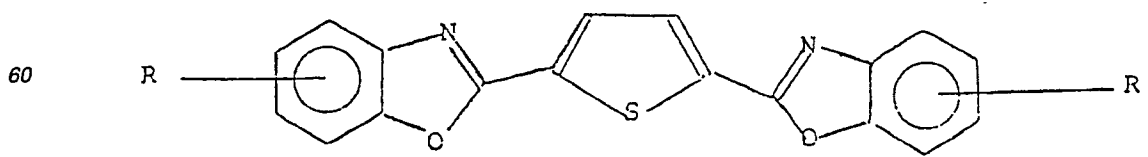


(vii) 2-(4-Phenylstilben-4'-yl)-5-tert.-butyl-benzoxazol der Formel



55 und (viii) Gemischen daraus, ausgewählt ist.

8. Ein Mittel nach Anspruch 7, worin der optische Aufheller die Verbindung der Formel



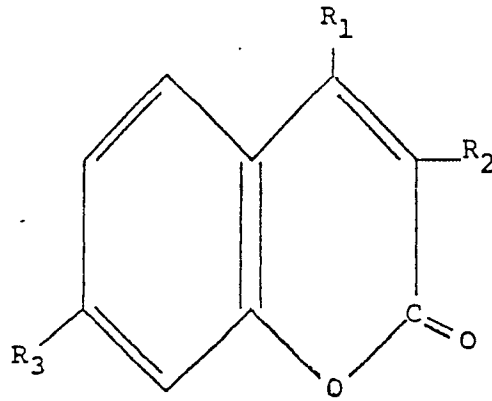
ist, worin R CH_3 ist.

65 9. Ein Mittel nach den Ansprüchen 1 bis 8, worin der optische Aufheller die Formel :

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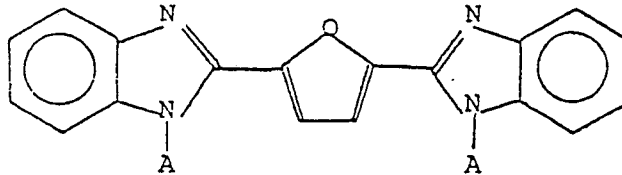
hat, worin R_1 H, eine C_{1-4} -Alkyl- oder eine Aralkyl-gruppe bedeutet, R_2 H, ein Aryl oder $-\text{COOR}_4$ bedeutet, R_3 $-\text{OR}_4$, $-\text{N}(\text{R}_4)_2$ oder $-\text{NHCOCH}_3$ darstellt und jeder R_4 unabhängig eine C_{1-4} -Alkylgruppe bedeutet.

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10. Ein Mittel nach Anspruch 9, worin R_1 CH_3 ist, R_2 H ist, R_3 $\text{N}(\text{CH}_3)_2$ oder $\text{N}(\text{C}_2\text{H}_5)_2$ ist.

11. Ein Mittel nach einem der Ansprüche 1 bis 10, worin der optische Aufheller die Formel

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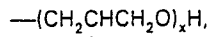
hat, worin jedes A aus der Gruppe bestehend aus Wasserstoff, C_1 - C_8 -Alkyl, C_1 - C_8 -Hydroxyalkyl, C_1 - C_8 -Alkenyl,

$-(\text{CH}_2)_n\text{OCH}_3$, worin n 1 bis 8 ist,

$-(\text{CH}_2)_n\text{N}(\text{CH}_3)_2$, worin n 1 bis 8 ist,

$-(\text{CH}_2\text{CH}_2\text{O})_x\text{H}$, worin x 2 bis 12 ist,

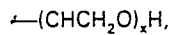
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OH

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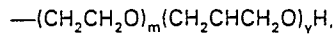
worin x 1 bis 12 ist und



CH₃

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worin x 1 bis 12 ist,



OH

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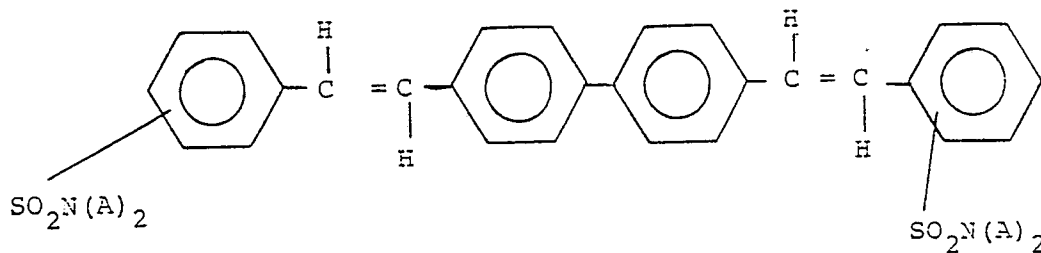
worin m 1 bis 12 ist und y 1 bis 12 ist ; ausgewählt ist.

12. Ein Mittel nach Anspruch 11, worin jede der Substituentengruppen A eine Methylgruppe ist.

13. Ein Mittel nach einem der Ansprüche 1 bis 12, worin der optische Aufheller die Formel (2)

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hat, worin jedes A aus der in Anspruch 11 definierten Gruppe ausgewählt ist oder worin (A)₂ ein das N-Atom enthaltender Oxazinring ist.

14. Ein Mittel nach einem der vorstehenden Ansprüche, worin der Verfärbungsinhibitor (E) 0,3 bis 5 % eines Stoffes ausgewählt aus

- 5 (a) Kondensaten von Talgalkoholen mit 20 bis 100 Molanteilen Ethylenoxid,
 (b) Polyethylenglykolen mit einem Molekulargewicht von 1 000 bis 30 000 ; und
 (c) Polyvinylalkoholen mit einem Molekulargewicht von 10 000 bis 20 000 umfaßt.

10 Revendications

1. Composition détergente qui confère un toucher doux aux tissus lavés avec cette composition, caractérisée en ce qu'elle comprend :

15 (A) de 10 à 30 % en poids d'un ou de plusieurs détergents polyéthoxylés non ioniques ayant un équilibre hydrophile/lipophile de l'ordre de 8 à 15 et n'ayant pas plus qu'une moyenne de 16 unités éthoxy par molécule à condition que, si le détergent non ionique comprend un éthoxylate d'alcool de suif dans lequel la portion alkyle de suif contient de 16 à 20 atomes de carbone, cet éthoxylate d'alcool de suif contient en moyenne entre 7 et 12 moles d'oxyde d'éthylène par mole d'alcool ;

(B) de 1 à 15 % en poids d'un ou de plusieurs adoucissants cationiques pour textiles ;

20 (C) de 0,001 à 3 % en poids d'un agent de blanchiment optique non ionique des types suivants :

- (a) benzoxazoles
 (b) coumarines
 (c) 2,5-bis(benzimidazolyl)furannes
 (d) 4,4'-bis(2-sulfonamide styryl)biphényles

25 (D) de 0 à 80 % en poids d'un adjuvant de détergence ;

(E) de 0 à 5 % en poids d'un inhibiteur de décoloration ;

(F) de 0 à 5,0 % en poids d'un agent tensio-actif anionique

dans laquelle le rapport pondéral de l'agent tensio-actif anionique à l'agent tensio-actif non ionique est inférieur à 1 : 1 et le rapport molaire de l'agent tensio-actif anionique à l'adoucissant cationique est inférieur à 1 : 1.

2. Composition selon la revendication 1, caractérisée en ce qu'elle comprend : de 10 à 20 % en poids du constituant (A), de 3 à 10 % en poids du constituant (B), de 0,01 à 0,5 % en poids du constituant (C), et de 20 à 70 % en poids du constituant (D).

3. Composition selon l'une des revendications 1 et 2, caractérisée en ce que le détergent non ionique est choisi parmi les produits de condensation de monoalcools primaires ou secondaires ramifiés ou non ramifiés ayant de 8 à 20 atomes de carbone et les produits de condensation d'alkyl-phénols ayant de 6 à 16 atomes de carbone dans la chaîne alkyle, chacun contenant de 4 à 16 moles d'oxyde d'éthylène par molécule, et des mélanges de ces produits de condensation.

4. Composition selon l'une quelconque des revendications 1 à 3, caractérisée en ce que l'adoucissant cationique est choisi parmi :

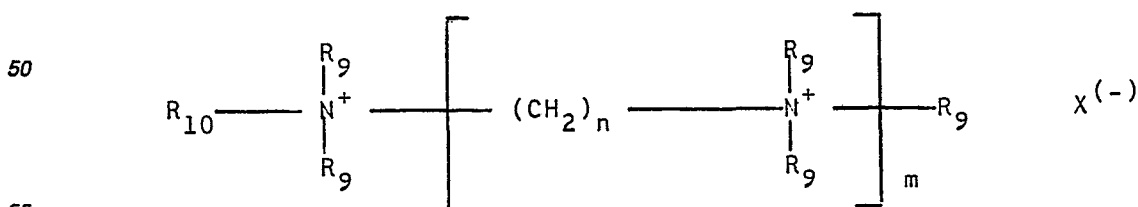
40 (a) les sels d'ammonium quaternaire, non cycliques ayant au moins une chaîne alkyle en C₁₂₋₃₀ dans la molécule

(b) les sels d'alkyl-imidazolinium dans lesquels le groupe alkyle est en C₈₋₂₅

45 (c) les sels d'alkyl-pyridinium dans lesquels le groupe alkyle est en C₁₂₋₂₀

(d) les sels d'alkyl-morpholinium dans lesquels le groupe alkyle est en C₁₂₋₂₀

(e) les sels de polyamines substituées de formule générale :



dans laquelle R₁₀ est un groupe alkyle ou alcényle ayant de 10 à 24 atomes de carbone, les groupes R₉ qui peuvent être identiques ou différents, représentent chacun l'hydrogène, un groupe —(C₂H₄O)_pH, ou —(C₃H₆O)_qH, où p et q peuvent être zéro ou un nombre tel que (p + q) ne dépasse pas 25, n est un nombre entier compris entre 2 et 6, m est compris entre 1 et 9 et X⁽⁻⁾ représente un ou plusieurs anions dont la charge totale équilibre celle des atomes d'azote, et

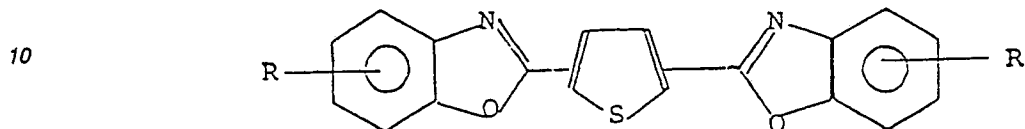
(f) leurs mélanges.

5. Composition selon la revendication 4, caractérisée en ce que l'adoucissant cationique est choisi parmi le chlorure de disulf-diméthyl-ammonium, le méthosulfate de 2-sulf-1-méthyl-1-(sulf-amidoéthyl)imidazoline, ou leurs mélanges.

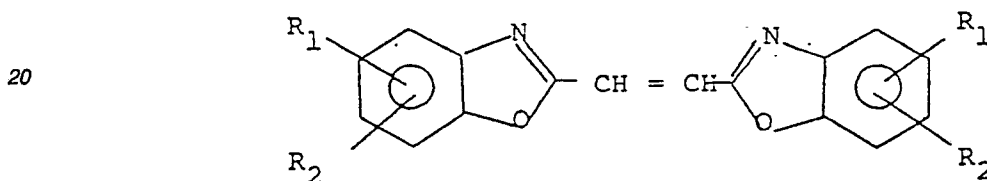
6. Composition selon l'une quelconque des revendications 1 à 5, caractérisée en ce que l'adjuvant de détergence est choisi parmi les carbonates, bicarbonates, borates, phosphates, polyphosphates, silicates, sulfates, amino polycarboxylates, phosphonates, de métaux alcalins, solubles dans l'eau, et les mélanges de ces sels.

5 7. Composition selon l'une quelconque des revendications 1 à 6, caractérisée en ce que l'agent de blanchiment optique, non ionique, est choisi parmi :

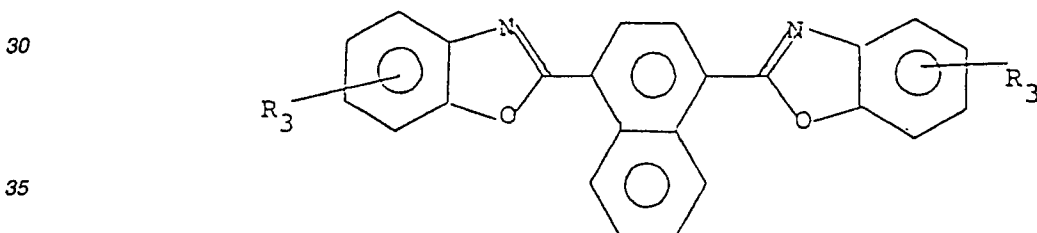
(i) les bis(benzoxazol-2-yl)thiophènes de formule :



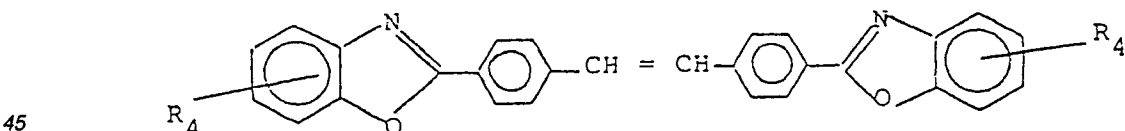
15 dans laquelle R est H, un groupe 5-méthyle, 5-diméthylbenzyle ou 5-butyle tertiaire ;
(ii) les 1,2-bis(benzoxazol-2-yl)éthylènes de formule



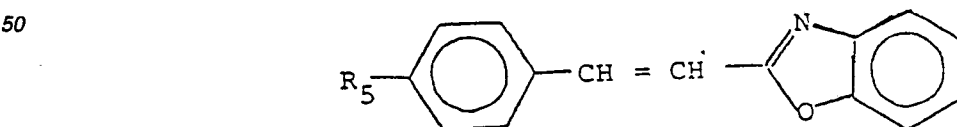
25 dans laquelle R₁ et R₂ sont H, ou R₁ est H et R₂ est un groupe 5-méthyle,
(iii) les 1,4-bis(benzoxazol-2-yl)naphtalènes de formule



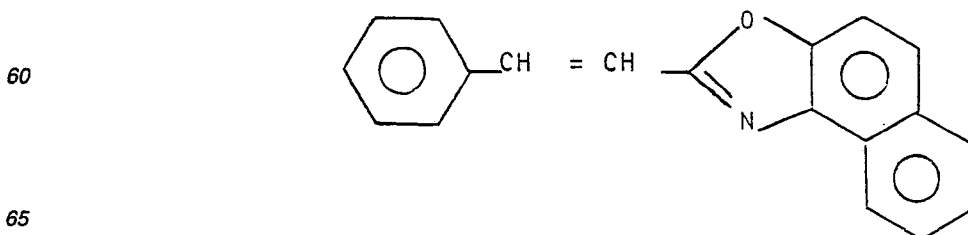
35 dans laquelle R₃ est H ou un groupe 5-carboxyméthyle ;
(iv) les 4,4'-bis-(benzoxazol-2-yl)stilbènes de formule



45 dans laquelle R₄ est H ou un groupe 5-carboxybutyle ou 5-méthyle ;
(v) les 2-(styryl)benzoxazoles de formule

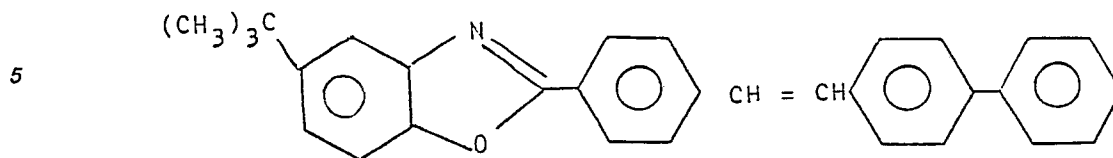


55 dans laquelle R₅ est H ou un groupe carboxyméthyle ;
(vi) le 2-(styryl)naphtoxazole de formule



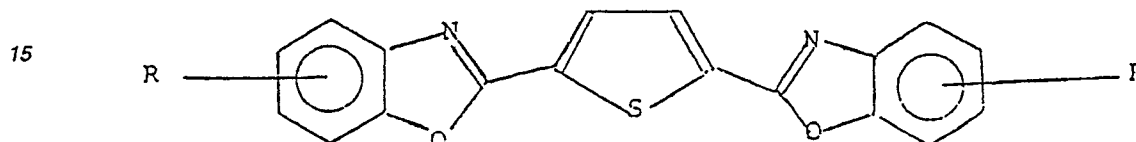
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(vii) le 2-(4-phényl stilbène-4-yl)-5-tert-butyl benzoxazole de formule



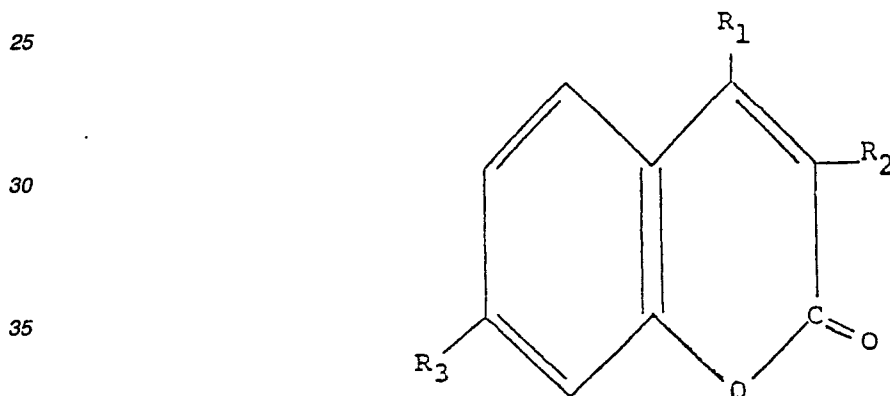
10 et (viii) leurs mélanges.

8. Composition selon la revendication 7, caractérisé en ce que l'agent de blanchiment optique est le composé de formule



20 dans laquelle R est CH₃.

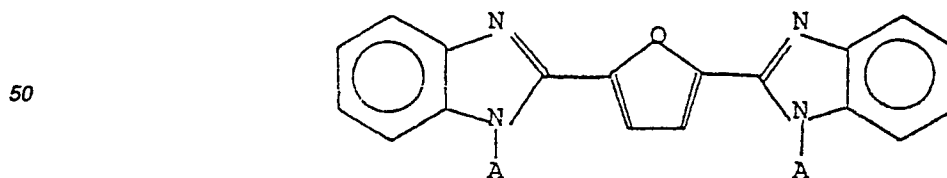
9. Composition selon l'une quelconque des revendications 1 à 8, caractérisée en ce que l'agent de blanchiment optique a la formule



40 dans laquelle R₁ représente H, un groupe alkyle en C₁₋₄ ou un groupe aralkyle, R₂ représente H, un groupe aryle ou —COOR₄, R₃ représente —OR₄, —N(R₄)₂ ou —NHCOCH₃ et chaque substituant R₄ représente indépendamment un groupe alkyle en C₁₋₄.

10. Composition selon la revendication 9, caractérisée en ce que R₁ est CH₃, R₂ est H, R₃ est N(CH₃)₂ ou N(C₂H₅)₂.

45 11. Composition selon l'une quelconque des revendications 1 à 10, caractérisée en ce que l'agent de blanchiment optique a la formule



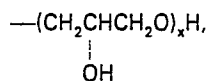
55 dans laquelle chaque A est choisi parmi l'hydrogène, un groupe alkyle en C₁-C₈, hydroxyalkyle en C₁-C₈, alcényle en C₁-C₈,

—(CH₂)_nOCH₃ où n est compris entre 1 et 8,

—(CH₂)_nN(CH₃)₂, où n est compris entre 1 et 8,

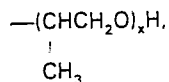
—(CH₂CH₂O)_xH, où x est compris entre 2 et 12,

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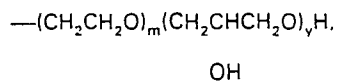


65 où x est compris entre 1 et 12 et

0 006 271



5 où x est compris entre 1 et 12,

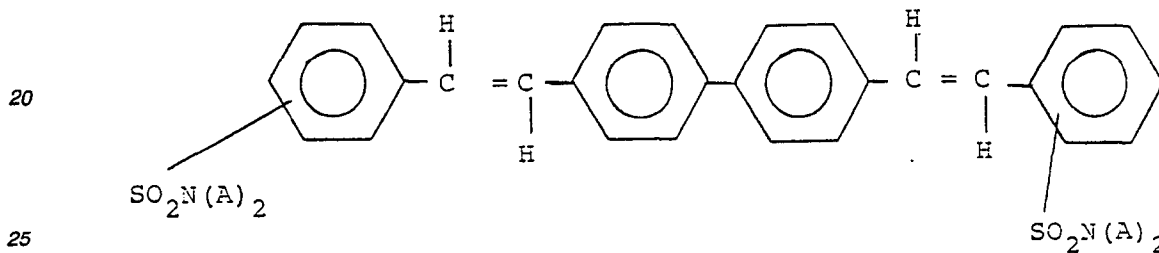


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où m est compris entre 1 et 12 et y est compris entre 1 et 12.

12. Composition selon la revendication 11, caractérisée en ce que chacun des groupes substituants A est un groupe méthyle.

15 13. Composition selon l'une quelconque des revendications 1 à 12, caractérisée en ce que l'agent de blanchiment optique a la formule (2)



dans laquelle chaque A est choisi parmi les groupes définis dans la revendication 11, ou dans laquelle (A)₂ est un noyau d'oxazine contenant l'atome d'azote.

30 14. Composition selon l'une quelconque des revendications 1 à 13, caractérisée en ce que l'inhibiteur de décoloration (E) représente de 0,3 à 5 % d'un matériau choisi parmi :

(a) les produits de condensation d'alcool de suif avec de 20 à 100 en proportions molaires d'oxyde d'éthylène,

(b) les polyéthylène glycols ayant une masse moléculaire comprise entre 1 000 et 30 000 ; et

(c) les alcools polyvinyliques ayant une masse moléculaire comprise entre 10 000 et 20 000.

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