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(54) Title: SOLID CLEANING FORMULATIONS

(57) Abstract: A cleaning composition for improving colour fastness comprises: (a) a dye fixing agent; (b) a dye transfer inhibition agent; and (c) a cellulase enzyme.

SOLID CLEANING FORMULATIONS

The invention relates to a cleaning composition for improving colour fastness on textiles.

Laundry detergents and additive products are generally used to clean, sanitize and remove unpleasant odours from garments. Unfortunately generally products exhibiting good stain removal power exhibit poor colour fastness and in certain cases colour fading effects, especially on dark colours, can be caused. This is due, in most cases, to the presence of bleach ingredients, which apart from removing the coloured part of stains can show detrimental effects, especially after multiple washes, on dyes used on textiles.

In addition to this chemically triggered colour fading effect, textiles are exposed to mechanical action is happening during washes. The abrasion with other garments and drum of washing machines is cause of pills formation which creates a negative appearance. This effect is more evident on cotton fabrics, but also on cotton/polyester textiles.

It is an object of the present invention to obviate / mitigate the problems outlined above.

According to a first aspect of the invention there is provided a cleaning composition for improving colour fastness comprising:-

(a) a dye fixing agent;

(b) a dye transfer inhibition agent; and

(c) a cellulase enzyme.

Compositions in accordance with the first aspect of the invention have been found to reduce colour fading and improve colour maintenance in laundry and laundry additive products which are at the same time effective in stain removal performance.

The dye fixing agent is generally present in the composition in an amount of 0.001 to 30%wt, ideally 0.01 to 10%wt and preferably 0.1 to 5%wt.

A preferred example of a dye fixing agent is a polyamine-amide copolymers. Such polymers are commercially available under the Trade Name Tinofix CL from Ciba.

The dye transfer inhibition agent is generally present in the composition in an amount of 0.001 to 30%wt, ideally 0.01 to 10% wt and preferably 0.1 to 5% wt.

Especially suitable polymeric dye transfer inhibitor agents are polyamine N-oxide polymers, polymers and copolymers of N-vinylpyrrolidone and N-vinylimidazole, vinyloxazolidones, vinylpyridine, vinylpyridine N-oxide, other vinylpyridine derivatives or mixtures thereof.

Polyamine N-Oxide Polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula:

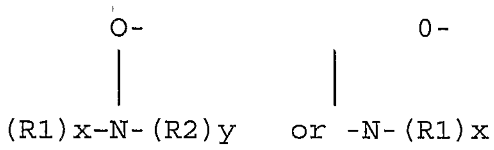
P-Ax-R-N-O

wherein P is a polymerisable unit, whereto the R-N-O group can be attached to, when x is 0, or wherein the R-N-O group forms part of the polymerisable unit or a combination of both;

A is -C(0)0-, -0(C)C-, -C(0)-,-0-,-S-,-N<; and x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures:



$$(R1)x\text{-}\overset{\overset{\displaystyle O\text{-}}{|}}{N}\text{-}(R2)y \quad \text{or} \quad \text{-}\overset{\overset{\displaystyle 0\text{-}}{|}}{N}\text{-}(R1)x$$

wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit P or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof. Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group. Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula above wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof. Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula above wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyiimides, polyacrylates and mixtures thereof. The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of about 10:1 to about 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerisation or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from about 2:3 to about 1:1000000. More preferably from about 1:4 to about 1:1000000, and most preferably from about 1:7 to about 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6. The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired dye-suspending power. Typically, the average molecular weight is within the range of about 500 to about 1,000,000; preferably from about 1,000 to about 50,000, more preferably from about 2,000 to about 30,000, and most preferably from about 3,000 to about 20,000.

Copolymers of N-Vinylpyrrolidone and N-Vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers suitable for use in the present invention have an average molecular weight range from about 5,000 to about 1,000,000, preferably from about 5,000 to about 200,000. Highly preferred polymers for use in the laundry detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from about 5,000 to about 50,000; more preferably from about 8,000 to about 30,000; and most preferably from about 10,000 to about 20,000. The average molecular weight range was determined by light scattering as described in Barth H. G. and Mays J. W. Chemical Analysis Vol 113,"Modern Methods of Polymer Characterisation". Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from about 5,000 to about 50,000; more preferably from about 8,000 to about 30,000; most preferably from about 10,000 to about 20,000. The N-vinylimidazole N-vinylpyrrolidone copolymers characterised by having said average molecular weight range provide excellent soil catcher properties. The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from about 1 to about 0.2, more preferably from about 0.8 to about 0.3, and most preferably from about 0.6 to about 0.4

Polyvinylpyrrolidone

Polyvinylpyrrolidone ("PVP") having an average molecular weight from about 2,500 to about 400,000 can also be utilised; preferably from about 5,000 to about 200,000; more preferably from about 5,000 to about 50,000; and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, N.Y. and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

Polyvinyloxazolidone

One may also utilise polyvinyloxazolidone as a polymeric soil catcher agent. Said polyvinyloxazolidones have an average molecular weight from about 2,500 to about 400,000; preferably from about 5,000 to about 200,000; more preferably from about 5,000 to about 50,000; and most preferably from about 5,000 to about 15,000.

Polyvinylimidazole

One may also utilise polyvinylimidazole as polymeric soil catcher agent. Said polyvinylimidazoles have an average molecular weight from about 2,500 to about 400,000; preferably from about 5,000 to about 200,000; more preferably from about 5,000 to about 50,000; and most preferably from about 5,000 to about 15,000.

Cationic Polymers

Such polymers are those having a cationic group into their polymeric backbone, as shown by the formula:

[P-Catx]n -Zt-CAty

Wherein P represents polymerisable units, Z represents alkyl or aryl groups, oxygen or ester, ether, amide, amine group, Cat represents cationic groups, preferably including quaternised N groups or other cationic units, x=0 or 1, y=0 or 1, t=0 or 1. Preferred cationic polymers are quaternised polyvinylpyridines.

Water insolubility can, in the case of non-cross linked polymers, also be achieved by selecting very high molecular weight range, or by copolymerising, or by varying the degree of oxidation if appropriate, depending on the polymer. Polymers which are water soluble, such as those described in U.S. Pat. No. 5,912,221, may be made insoluble if the molecular weight is increased above 400,000.

Cross-Linked Polymers

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups on the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039. In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in U.S. Pat. No. 5,912,221.

Thus, a cross-linked polymer has one or more individual molecular chains linked by side branches to adjacent chains. The cross-links can be formed: (a) between already existing linear or branched polymers, (b) during the polymerisation of multi-functional monomers, or (c) during the polymerisation of dimeric monomers with traces of multi-functional monomers. The cross-linking can also be achieved by various means known in the art. For instance, the cross-links can be formed using radiation, oxidation and curing agents, such as divinylbenzene, epichlorohydrin and the like. Preferably, cross-linked polymers for the purpose of this invention are those obtained by cross-linking a water-soluble soil catcher polymer described above with divinylbenzene (DVB) cross-linking agent during polymerisation of the soil catcher monomer. Cross-linking degree can be controlled by adjusting the amount of divinylbenzene (DVB) cross-linking agent. Preferably, the degree of cross-linking is between about 0.05% (w/w) of DVB over soil catcher monomer and about 50% of DVB over soil catcher monomer and, more preferably, between about 0.05% (w/w) of DVB over soil catcher monomer and about 25% (w/w) of DVB over soil catcher monomer. Most preferably, the degree of cross-linking is between about 0.1% (w/w) of DVB over soil catcher monomer and about 5% (w/w) of DVB over soil catcher monomer. The cross linking forms soil catcher compound particles, at least 90% (and more preferably at least about 95%) of which have a minimum diameter as measured by conventional methods for particle size distribution evaluation of at least about 1 μm, preferably at least about 50 μm, and more preferably at least about 75 μm, all as measured in their dry state. Most preferably, the cross linking forms soil catcher compounds, at least 90% (and more preferably at least about 95%) of which have a minimum diameter as measured by conventional methods for particle size distribution evaluation of between about 1 μm and about 5 mm, still more preferably between about 50 μm and about 2500 μm, and yet still more preferably between about 75 μm and about 1500 μm, all as measured in their dry state. Preferably, the cross-linked polymer is a polyamine N-oxide or a quaternised polyamine The skilled in the art may conveniently obtain such compounds by oxidising or quaternizing cross-linked polyvinylpyridines from Reilly Industries Inc. commercialised under the name Reillex(TM) 402 or Reillex(TM)425 by methods known in the art. For instance, but not exclusively, the method described in U.S. Pat. No. 5,458,809 can be used to prepare a polyamine N-oxide of interest from the commercially available compounds given above. An example of quaternised polyamine can also be obtained from Reilly Industries under the commercial name Reillex(TM) HPQ.

Cellulases are present in the composition in an amount of, for example, 0.01 to 5%, ideally 0.05 to 1%.

Example of cellulase enzymes useful for present invention are those produced by Humicola insolens. Examples of commercial cellulase products useful for present invention are Carezyme, Celluzyme and Endolase from Novozymes; Puradax and Indiage from Genencor.

Example of anticaking agents useful for present invention are silica powders, magnesium sulfate and sodium xylene sulfonate and cumene sulfonate powders. Among these anticaking agents more preferred are soluble ones which are not leaving residues once dissolved as sodium xylene and cumene sulfonate. They may be present in an amount, for example, 0.01 to 10%, more preferably 0.1 to 1%.

Surfactants may be present in the composition in an amount of, for example, 0.001 to 30% wt, ideally 0.01 to

15% wt and preferably 0.1 to 5% wt. The surfactant is, for example, an anionic or nonionic surfactant or mixture thereof. The nonionic surfactant is preferably a surfactant having a formula $RO(CH_2CH_2O)_nH$ wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from $C_{12}H_{25}$ to $C_{16}H_{33}$ and n represents the number of repeating units and is a number of from about 1 to about 12. Examples of other non-ionic surfactants include higher aliphatic primary alcohol containing about twelve to about 16 carbon atoms which are condensed with about three to thirteen moles of ethylene oxide.

Other examples of nonionic surfactants include primary alcohol ethoxylates (available under the Neodol trade name from Shell Co.), such as C_{11} alkanol condensed with 9 moles of ethylene oxide (Neodol 1-9), C_{12-13} alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C_{12-13} alkanol with 9 moles of ethylene oxide (Neodol 23-9), C12-15 alkanol condensed with 7 or 3 moles ethylene oxide (Neodol 25-7 or Neodol 25-3), C_{14-15} alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), C_{9-11} linear ethoxylated alcohol, averaging 2.5 moles of ethylene oxide per mole of alcohol (Neodol 91-2.5), and the like.

Other examples of nonionic surfactants suitable for use in the present invention include ethylene oxide condensate products of secondary aliphatic alcohols containing 11 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available non-ionic detergents of the foregoing type are C_{11-15} secondary alkanol condensed with either 9 moles of ethylene oxide (Tergitol 15-S-9) or 12 moles of ethylene oxide (Tergitol 15-S-12) marketed by Union Carbide, a subsidiary of Dow Chemical.

Octylphenoxy polyethoxyethanol type nonionic surfactants, for example, Triton X-100, as well as amine oxides can also be used as a nonionic surfactant in the present invention.

Other examples of linear primary alcohol ethoxylates are available under the Tomadol trade name such as, for example, Tomadol 1-7, a C_{11} linear primary alcohol ethoxylate with 7 moles EO; Tomadol 25-7, a C_{12}-C_{15} linear primary alcohol ethoxylate with 7 moles EO; Tomadol 45-7,a C_{14}-C_{15} linear primary alcohol ethoxylate with 7 moles EO; and Tomadol 91-6, a C_9-C_{11} linear alcohol ethoxylate with 6 moles EO.

Other nonionic surfactants are amine oxides, alkyl amide oxide surfactants.

Preferred anionic surfactants are frequently provided as alkali metal salts, ammonium salts, amine salts, aminoalcohol salts or magnesium salts. Contemplated as useful are one or more sulfate or sulfonate compounds including: alkyl benzene sulfates, alkyl sulfates, alkyl ether sulfates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkylsulfonates, alkylamide sulfonates, alkylarylsulfonates, olefinsulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfosuccinamate, alkyl sulfoacetates, alkyl phosphates, alkyl ether phosphates, acyl sarconsinates, acyl isethionates, and N-acyl taurates. Generally, the alkyl or acyl radical in these various compounds comprise a carbon chain containing 12 to 20 carbon atoms.

Other surfactants which may be used are alkyl naphthalene sulfonates and oleoyl sarcosinates and mixtures thereof.

Examples of suitable bleaches are oxygen bleaches. Suitable level of oxygen bleaches is in the range from 0.01 to 90% wt, preferred level is between 0.1 and 60% wt, ideally 10 to 50% wt. As used herein active oxygen concentration refers to the percentage concentration of elemental oxygen, with an oxidation number zero, that being reduced to water would be stoichiometrically equivalent to a given percentage concentration of a given peroxide compound, when the peroxide functionality of the peroxide compound is completely reduced to oxides. The active oxygen sources increase the ability of the compositions to remove oxidisable stains, to destroy malodorous molecules and to kill germs.

The concentration of available oxygen can be determined by methods known in the art, such as the iodimetric method, the permanganometric method and the cerimetric method. Said methods and the criteria for the choice of the appropriate method are described for example in "Hydrogen Peroxide", W. C. Schumo, C. N. Satterfield and R. L. Wentworth, Reinhold Publishing Corporation, New York, 1955 and "Organic Peroxides", Daniel Swern, Editor Wiley Int. Science, 1970.

Suitable organic and inorganic peroxides for use in the compositions according to the present invention include diacyl and dialkyl peroxides such as dibenzoyl peroxide, dilauroyl peroxide, dicumyl peroxide, persulphuric acid and mixtures thereof.

Suitable preformed peroxyacids for use in the compositions according to the present invention include diperoxydodecandioic acid DPDA, magnesium perphthalatic acid, perlauric acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof. Peroxygen bleaching actives useful for this invention are: percarbonates, perborates, peroxides, peroxyhydrates, persulfates. Preferred compound is sodium percarbonate and especially the coated grades that have better stability. The percarbonate can be coated with silicates, borates, waxes, sodium sulfate, sodium carbonate and surfactants solid at room temperature.

Optionally, the compositions may additionally comprise from 0% to 30%, preferably from 2% to 20% of peracid precursors, i.e. compounds that upon reaction with hydrogen peroxide product peroxyacids. Examples of peracid precursors suitable for use in the present invention can be found among the classes of anhydrides, amides, imides and esters such as acetyl triethyl citrate (ATC) described for instance in EP 91 87 0207, tetra acetyl ethylene diamine (TAED), succinic or maleic anhydrides.

The composition may, for example, comprise at least one builder or a combination of them, for example in an amount of from 0.01 to 50%wt, preferably from 0.1 to 20%wt.

Examples of suitable builders are described below:

- the parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures therefore with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.
- borate builders, as well as builders containing borate-forming materials than can produce borate under detergent storage or wash conditions can also be used.
- iminosuccinic acid metal salts
- polyaspartic acid metal salts.
- ethylene diamino tetra acetic acid and salt forms.
- water-soluble phosphonate and phosphate builders are useful for this invention. Examples of phosphate buiders are the alkali metal tripolyphosphates, sodium potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate sodium polymeta/phosphate in which the degree of polymerisation ranges from 6 to 21, and salts of phytic acid. Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from 6 to 21, and salts of phytic acid. Such polymers include the polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates.

Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivates such as the carboxymethloxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, and aminosuccinates described in NL-A-7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in GB-A-1,387,447.

Polycarboxylate containing four carboxy groups include oxydisuccinates disclosed in GB-A-1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates contining sulfo substituents include the sulfosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936448, and the sulfonated pyrolsed citrates described in GB-A-1,439,000.

Alicylic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivates of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB-A-1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Suitable polymer water-soluble compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures of any of thereof.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivates such as the carboxymethloxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, and aminosuccinates described in NL-A-7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in GB-A-1,387,447.

Polycarboxylate containing four carboxy groups include oxydisuccinates disclosed in GB-A-1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarobyxlates. Polycarboxylates contining sulfo substituents include the sulfosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936448, and the sulfonated pyrolsed citrates described in GB-A-1,439,000.

Alicylic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivates of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in GB-A-1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

More preferred polymers are homopolymers, copolymers and multiple polymers of acrylic, fluorinated acrylic, sulfonated styrene, maleic anhydride, methacrylic, isobutylene, styrene and ester monomers.

Examples of these polymers are Acusol supplied from Rohm & Haas, Syntran supplied from Interpolymer and Versa and Alcosperse series supplied from Alco Chemical, a National Starch & Chemical Company.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures therefore with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

In the context of the present application it will be appreciate that builders are compounds that sequester metal ions associated with the hardness of water, e.g. calcium and magnesium, whereas chelating agents are compounds that sequester transition metal ions capable of catalysing the degradation of oxygen bleach systems. However, certain compounds may have the ability to do perform both functions.

Suitable chelating agents to be used herein include chelating agents selected from the group of phosphonate chelating agents, amino carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, and further chelating agents like glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid, or mixtures thereof. Chelating agents when used, are typically present herein in amounts ranging from 0.01% to 50%wt of the total composition and preferably from 0.05% to 10%wt.

Suitable phosphonate chelating agents to be used herein may include ethydronic acid as well as amino phosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates. Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST TM.

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

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'-disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acids is, for instance, commercially available under the trade name ssEDDS TM from Palmer Research Laboratories.

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N-hydroxyethylethylenediamine triacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diacetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS TM and methyl glycine di-acetic acid (MGDA).

Solvents can be used for present invention at levels of 0.01 to 30%wt, preferred level is between 0.1-3% wt. The solvent constituent may include one or more alcohol, glycol, acetate, ether acetate, glycerol, polyethylene glycol with molecular weight ranging from 200 to 1000, silicones or glycol ethers. Exemplary alcohols useful in the compositions of the invention include C_2-C_8 primary and secondary alcohols which may be straight chained or branched, preferably pentanol and hexanol.

Preferred solvents for the invention are glycol ethers and examples include those glycol ethers having the general structure. Preferred solvents for the invention are glycol ethers and examples include those glycol ethers having the general structure $Ra-O-[CH_2-CH(R)-(CH_2)-0]_n-H$, wherein Ra is C_{1-20} alkyl or alkenyl, or a cyclic alkane group of at least 6 carbon atoms, which may be fully or partially unsaturated or aromatic; n is an integer from 1 to 10, preferably from 1 to 5; each R is selected from H or CH_3; and a is the integer 0 or 1. Specific and preferred solvents are selected from propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-propyl ether, ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, diethylene glycol methyl ether, propylene glycol, ethylene glycol, isopropanol, ethanol, methanol, diethylene glycol monoethyl ether acetate, and particularly useful are, propylene glycol phenyl ether, ethylene glycol hexyl ether and diethylene glycol hexyl ether.

The composition may, for example, comprise one enzyme or a combination of them apart cellulases already described, for example in an amount of from 0.01 to 10%wt, preferably from 0.1 to 2%wt. Examples of granular enzymes are proteases, modified proteases stable in oxidisable conditions, amylases and lipases.

Additional, optional, ingredients, selected from a list consisting fragrance, anticaking agent as sodium xylene sulfonate and magnesium sulfate, dye, are present at levels of up to 5% w/v, preferably less then 1% w/v.

According to a second aspect of the invention there is provided a textile washing process comprising the use of the composition of the first aspect of the invention.

The invention is now described with reference to the following non-limiting examples.

EXAMPLES:

The detergent formulations of this invention were prepared by mixing the ingredients in a suitable container. The liquid ingredients were sprayed on top of powder ones during mixing.

The detergent formulations of this invention were tested in terms of stain removal to test the cleaning efficacy and the colour fastness.

STAIN REMOVAL TEST:

The evaluation of stain removal of standard soils was done by considering the reflectance value Y. The X Y Z scale has been used with a spectrophotometer with the UV-filter at 460nm.

Y = 100 means a complete stain removal.

Standard prepared stains have been used for the test.

Standard stains (aged stain):

Soil	Type of soil	Type of fabric	Soil code	Supplier*
Red Wine	Oxidisable	Cotton	WFK 10LI	WFK Institute
Grass	Enzymatic/Oxidi	Cotton	Empa 164	Empa Institute
Cocoa	Enz./Greasy /Oxidisable	Cotton	Empa 112	Empa Institute
Lipstick	Greasy	Cotton	Empa 141	Empa Institute
Make up	Greasy	Cotton	Empa 143	Empa Institute
Sebum	Greasy	Cotton	WFK 10D	WFK Institute
Olive oil	Greasy	Cotton	Empa 101	Empa Institute

*Empa Test Materials in Switzerland
WFK Testgewebe GmbH in Germany

The additive products were added with the detergent in the drawer of washing machine. The cleaning was done using Rex washing machines at, 40°C water temperature, 25 °F water hardness and 3.5 kg ballast. The results are the average of four repetitions.

COLOUR FASTNESS TEST:

Colour fastness was assessed by checking colour maintenance and dye transfer. Colour fastness was evaluated on blue and red direct colours standard swatches provided by WFK by measuring Delta E values with a spectrophotometer and checking performance after 1, 5 and 10 cumulative wash cycles. Dye transfer was considered on white cotton and cotton/polyester swatches by measuring Y-reflectance values after 1 wash cycle.

Products were tested in terg-o-tometer wash cycle at 40°C, 50 rpm and 25 °F water hardness where red and white swatches or blue and white swatches have been mixed during wash.

Examples of compositions in accordance with the present invention are set out below in Table 1 with the various components identified in Table 2.

Table 1

Component	**Ref 2**	**Ex 1**	**Ex 3**	**Ex 4**	**Ex 5**	**Ex 6**	**Ex**
	%	%	%	%	%		
CMC granular			0.5	0.5	0.5		
Celluzyme 0.7 T		0.2	0.1	0.1	0.1	0.2	
Endolase 3.0 T			0.2	0.2	0.2		
Na Percarbonate S 141	55.0	45.0	40.0	45.0	45.0	55.0	45
TAED white		1.0	1.5	1.5	0.8	0.5	1.
Sodium carbonate	38.4	27.2	50.2	50.8	45.2		
Sodium sulfate		20.0					
Na Alkyl sulfate	4.0	3.5	4.0	4.0	4.0	4.0	
Sodium lauroyl sarcosinate	0.5	0.5	0.5	0.5	0.5	0.5	0.
Alcohol ethoxylate	1.5	1.5	1.5	1.5	1.5	1.5	1.
Purafect OX 4000 M	0.3	0.3	0.3	0.3	0.3		
Polyamine-amide copolymers		0.3			1.0		1.
PVP granular		0.3	0.9	0.3	0.3	0.3	0.
Sodium xylene sulfonate	0.3	0.3	0.3	0.3	0.3	0.5	0.
Filler and minors	To 100	To 100	To 100	To 100	To 100	To 100*	T 100

* includes 0.3% protease.

** includes 0.5% lipase, 0.4% amylase.

Table 2

Component	**Description of component**
Sesquicarbonate	Sesquicarbonate from FMC
Sodium carbonate	Sodium carbonate from Solvay
Na Percarbonate S 141	Coated sodium percarbonate from Solvay
Lialet 125-5	Alcohol ethoxylate from Sasol
Crodasinic LS95	Sodium lauroyl sarcosinate from Croda
Stepanol DCX	Alkyl sulfate from Stepan
Etelsol SX93	Sodium xylene sulphonate from Huntsman
Purafect OX 4000 M	Proteases from Genencor
Sodium carbonate	Sodium carbonate from Solvay
Celluzyme 0.7 T	Cellulases from Novozymes
Endolase 3.0 T	Cellulases from Novozymes
CMC granular	Carboxy methyl cellulose from Lamberti
Sodium sulfate	Sodium sulphate from Lenzing
Peractive AC white	TAED from Clariant
Tinofix CL solid	Polyamine-amide copolymers from Ciba
PVP K30 granular	Poly vinyl poly pyrrolidone from Clariant

RESULTS:

The formulations were tested in terms of stain removal performance to show the cleaning efficacy and in terms of colour safety.

STAIN REMOVAL TEST:

The stain removal performance was compared with Reference 1 which is an additive market leader present in Germany and with Persil Megaperls from Henkel as a reference of a leading brand detergent (Reference 2).

Results for stain removal:

Persil Megaperls was used as detergent reference (Ref 1). The dosage used was 67.5 g/load, the same suggested as directed on the packaging.

The additive products, Ref 2 and Ex 1 were dosed at 60 grams in combination with detergent.

For each product/stain the test was repeated four times. The values reported in Table 3 below are averaged.

Table 3

	Red Wine	Grass	Cocoa	Lipstick	Make up	Sebum	Olive oil
Ref 1	82.8	70.8	62.5	49.7	73.2	67.7	36.1
+Ref 2	85.9	74.4	70.3	53.0	74.5	67.5	40.0
+Ex 1	86.6	74.3	72.6	55.2	75.4	71.6	44.5

Ex 1 product is an example of an additive having high cleaning efficacy against detergent alone. It shows stain removal values against Ref 1, detergent alone and better results against a market leader additive.

COLOUR SAFETY TEST:

Additives tested for colour safety were compared to detergent alone (Dash powder from P&G, Ref 3).

Results for colour safety:

The additive products, Ref 3 and Ex 1-5 were dosed at 2 g/1 in combination with detergent (Tables 4a & b).

Table 4a

	Direct Blue			Direct Red		
	1 wash	5 washes	10 washes	1 wash	5 washes	10 washes
Ref 3	2.3	10.5	18.8	2.3	8.9	18.2
Ex 1	2.1	10.8	18.6	1.1	4.6	9.5
Ex 3	2.0	10.0	18.6	1.9	9.0	18.0
Ex 4	2.0	10.5	17.0	2.0	4.7	12.9
Ex 5	2.0	10.3	16.7	2.1	6.5	16.3

The lower the Delta E value, the lower the colour damage. The compositions of the present invention show improved colour fastness.

Table 4b

	Washed with Direct Blue		**Washed with Direct Red**	
	Empa221	**Tic 400**	**Empa221**	**Tic 400**
Ref 3	57.5	55.4	72.8	72.7
Ex 1	70.4	70.8	76.2	75.9
Ex 3	65.5	67.2	74.2	72.9
Ex 4	64.2	64.6	75.9	73.3
Ex 5	71.2	71.7	75.6	75.6

Initial value for Empa 221 is Y=84.2 and for Tic 400 is Y=82.7.

The higher the value the lower the dye transfer. on the measured white samples. The compositions of the present invention show dye transfer.

Claims

1. A cleaning composition for improving colour fastness comprising:-

(a) a dye fixing agent;
(b) a dye transfer inhibition agent; and
(c) a cellulase enzyme.

2. A composition as claimed in claim 1 wherein the dye fixing agent is a polyamine-amide copolymer.

3. A composition as claimed in claim 1 or 2 wherein the dye transfer inhibitor agent is a poly vinyl pyrrolidone polymer.

4. A composition as claimed in claim 1,2 or 3 wherein the cellulase enzyme is present at a level ranging from 0.01 to 5% wt, preferably from 0.1 to 1% wt.

5. A textile washing process comprising the use of the composition of any one of claims 1 to 4.

6. A textile pre-washing process (e.g. before further washing in a washing machine) comprising the use of the composition of any one of claims 1 to 4.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/004315

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/386 C11D3/37

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 01/44423 A (UNILEVER) 21 June 2001 (2001-06-21) pages 15-19; example 1; tables 1,2 claims 1,9,11 ----- -/--	1-6

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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