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(54) Title: METHOD

(57) Abstract: A method of preparing coloured solid particles suitable for use in a cleaning process, comprises dissolving / suspending the material to be coloured in a solvent, colouring the solution and removing the solvent from the solution / suspension.

WO 2007/101978 A1

METHOD

The invention relates to a method of preparing coloured particles of cleaning active materials.

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Standard methods known to colour solid particles generally involve dissolution of the dye in a viscous liquid, such as a non ionic surfactant, and spraying the dye mixture on to the solid particles.

10

This method has at least two disadvantages: lump formation due to particle stickiness and loss of brightness (especially for crystalline particles) due to viscous liquid opaque thin layer formation.

15

Dry mixing colouration of solid particles overcomes some of these issues but suffers from the drawback that it requires particular attention to eliminate any residue of dyeing powder and of coloured fines coming from the process in order to avoid colour release.

20

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

25 In accordance with a first aspect of the invention there is provided a method of preparing coloured solid particles suitable for use in a cleaning process, comprising dissolving / suspending the material to be coloured in a solvent, colouring the solution and removing the solvent
30 from the solution / suspension.

-2-

Solid particles produced through this method are brightly coloured and contribute significantly to the aesthetics of a solid formulation incorporating said crystals.

- 5 It has been found that the colour release from the crystals into the remainder of a composition incorporating same is minimal.

Surprisingly it has been found that the method is useful
10 for colouring particles which are normally insoluble but which are capable of forming a suspension (e.g. pigments, micas or metallic powders).

Preferably (for soluble particles) the solution in the
15 colouring process is at or close to saturation.

Generally the colouring agent (e.g. dye) is added in the liquid form to the solution / suspension of the material to be coloured. For liquid colouring agents they can be
20 added without the need for any additional agent, other colouring agents (e.g. non-liquid colouring agents) may require being dissolved in a suitable solvent to turn them into a liquid form.

- 25 Where a solvent is used (for the dye or the material to be coloured) preferably the solvent is water.

During the colouring process the solution / suspension is preferably stirred using a mixer. The mixing time may
30 vary depending on the material used.

-3-

After colouring the solvent may be removed from the solution using conventional methods. Both the drying time and temperature used is dependent upon the dye / material stability. Typical drying temperatures are in the range
5 20 - 200°C, more preferably between 40 and 150°C and most preferably between 60 and 100°C.

The drying time is connected with the temperature used, and can vary in the range 1 second and 24 hours, more
10 preferably in the range 1 minute and 10 hours.

The drying process may be a multi-stage process. The first stage may be used to provide a solid composition (e.g. crystals) which is then further dried in a second
15 drying step. Clearly the temperatures / times employed in the individual drying steps may differ.

After the drying process the level of solvent remaining in the particles is preferably less than 20wt%, more
20 preferably below 10wt% and most preferably below 5wt%.

Most preferably the coloured detergent particles produced in the method according to the invention are for inclusion in a "complete" detergent composition, e.g. a laundry, a laundry additive, a hard surface or a dish washing
25 solid compositions.

It will be appreciated that the particles provided in accordance with the method of the present invention may
30 comprise an admixture of different components.

Examples of starting materials suitable for being col-

-4-

oured in the method of the present invention are products with good film forming properties that, once dried, produce a bright layer of material easy to break into particles or crystals.

5.

Example of film forming materials useful for this invention to produce crystals are homopolymers, copolymers and multiple polymers of acrylic, fluorinated acrylic, sulfonated styrene, maleic anhydride, metacrylic, isobutylene, styrene and ester monomers. These polymers have good film forming properties and can also be considered actives in detergent formulations as they are used to reduce soil redeposition during the wash cycle, they also improve detergent performances sequestering metal ions that negatively affect other ingredients activity (e.g. surfactants).

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.

Such polymers include 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.

Useful polymers for present invention are Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citra-

-5-

conates as well as succinate derivatives such as the carboxymethoxysuccinates 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 containing sulfo substituents include the sulfosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936,448, and the sulfonated pyrolysed citrates described in GB-A-1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives 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.

25

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

30 Suitable polymer water-soluble compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their

-6-

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.

5

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

10

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 derivatives such as the carboxymethoxysuccinates 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.

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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 containing sulfo substituents include the sul-

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-7-

fosuccinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936,448, and the sulfonated pyrolysed citrates described in GB-A-1,439,000.

5 Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-
10 carboxylates 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
15 molecule, more particularly citrates.

Polymers can be blended with crystalline film forming polymers are for example dye transfer inhibitor polymers, dye fixing agents, non crystalline anti-redeposition
20 agents, soil release polymers.

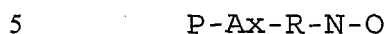
All these polymers can be added in a ratio with crystalline film forming polymers from 0.01 to 1, preferably between 0.05 and 0.5 and more preferably between 0.1 and
25 0.3.

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

-8-

Polyamine N-Oxide Polymers

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



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;

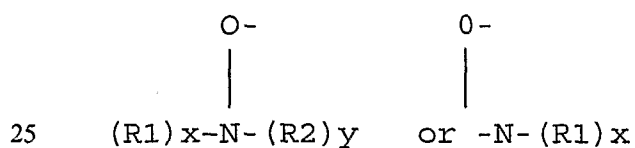
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A is -C(O)O-, -O(C)C-, -C(O)-, -O-, -S-, -N<; and x is 0 or 1;

15 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.

20

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



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.

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-9-

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.

- 5 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-
- 10 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
- 15 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 poly-
- 20 amine 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
- 25 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
- 30 group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

-10 -

Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, 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

-11-

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". 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

-12 -

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).

10 Polyvinylloxazolidone

One may also utilise polyvinylloxazolidone as a polymeric soil catcher agent. Said polyvinylloxazolidones have an average molecular weight from about 2,500 to about 400,000; preferably from about 5,000 to about 200,000; 15 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 20 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.

25

Cationic Polymers

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

30 [P-Catx]_n -Zt-CAty

-13 -

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.

15

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 al-

-14-

ready 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
5 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 ob-
10 tained 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
15 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
20 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
25 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,
30 bly, 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

-15-

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

-16-

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), C_{12-15} 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.

30

Other examples of nonionic surfactants suitable for use in the present invention include ethylene oxide conden-

-17-

sate 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 C₁₁₋₁₅ secondary alcohol 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.

10

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.

15

Other examples of linear primary alcohol ethoxylates are available under the Tomadol trade name such as, for example, Tomadol 1-7, a C₁₁ linear primary alcohol ethoxylate with 7 moles EO; Tomadol 25-7, a C_{12-C15} linear primary alcohol ethoxylate with 7 moles EO; Tomadol 45-7, a C_{14-C15} linear primary alcohol ethoxylate with 7 moles EO; and Tomadol 91-6, a C_{9-C11} linear alcohol ethoxylate with 6 moles EO.

25

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

30

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 sul-

-18-

fates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkylsulfonates, alkylamide sulfonates, alkylarylsulfonates, olefinsulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether
5 sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfo-
succinamate, 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
10 containing 12 to 20 carbon atoms.

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

15 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 ele-
20 mental 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
25 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
30 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 "Hy-

-19 -

drogen 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.

5

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
10 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
15 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
20 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
25 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
30 esters such as acetyl triethyl citrate (ATC) described for instance in EP 91 87 0207, tetra acetyl ethylene diamine (TAED), succinic or maleic anhydrides.

-20 -

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 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 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,

-21-

maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates.

5 Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethoxysuccinates described in GB-A-1,379,241, lactoxysuccinates described in GB-A-1,389,732, and amino-
10 succinates 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
15 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 containing sulfo substituents include the sulfo-succinate derivatives disclosed in GB-A-1,398,421, GB-A-
20 1,398,422 and US-A-3,936448, and the sulfonated pyrolysed citrates described in GB-A-1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadi-
25 enide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives 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-
30 1,425,343.

Of the above, the preferred polycarboxylates are hydroxy-

-22 -

carboxylates 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 derivatives such as the carboxymethoxysuccinates 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.

-23 -

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 containing sulfo substituents include the sulfo-succinate derivatives disclosed in GB-A-1,398,421, GB-A-1,398,422 and US-A-3,936,448, and the sulfonated pyrrolised citrates described in GB-A-1,439,000.

10

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives 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.

20 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.

30 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.

-24 -

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 appreciated 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 tetramethylene phosphonates, and diethylene triamine pentamethylene phosphonates. The phosphonate compounds may be

-25 -

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.

5 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.

10 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.

15 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

20 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.

25

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA), N-hydroxyethylethylenediamine triacetates, nitrilotri-

30 acetates, ethylenediamine tetrapropionates, triethylene-tetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diace-

-26-

tic 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).

10 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, silic-
15 cones or glycol ethers. Exemplary alcohols useful in the compositions of the invention include C₂-C₈ primary and secondary alcohols which may be straight chained or branched, preferably pentanol and hexanol.

20 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-[CH₂-CH(R)-(CH₂)-O]_n-H,
25 wherein Ra is C₁₋₂₀ 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 CH₃; and a is the integer 0 or 1. Specific and preferred solvents are selected from propylene glycol methyl
30 ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-propyl ether, ethyl-

-27 -

ene 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 than 1% w/v.

According to a second aspect of the invention there is provided a textile washing process comprising the use of a composition comprising particles produced in accordance with the first aspect of the invention.

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

EXAMPLES:

Crystals of polyacrylic acid polymer (Acrylic homopolymer Acusol 445N) were prepared from solution. The level of dye (Blue Pigmosol 6900 from Basf) added is was in the

-28 -

range 0.01 - 0.3 %. The mixing was 5 minutes. The polymer solution was spread in a thin layer and dried in oven at 105°C for 5 hours.

- 5 The coloured crystals were evaluated in terms of brightness, soil redeposition, and in terms of colour stability.

Other colours that were used were metallic red / gold, obtained by adding micas directly to the liquid polymer. Red / gold mica were used at a concentration of 0.1%. Only brightness was assessed for these two variants.

15 BRIGHTNESS ASSESSMENT:

Brightness assessment was done by visual evaluation using a quartz crystal as a reference of brightness (rating = 4) and the amorphous polymer as a reference of opacity form (rating = 0). The rating was performed under D65 lamp light (a simulation of sunlight).

Brightness	Description
0	Completely amorphous aspect - opaque
1	Almost opaque solid particles
2	Slightly bright crystal
3	Quite bright crystal
4	Reference of brightness - crystal form

25 SOIL REDEPOSITION TEST:

Anti redeposition properties were assessed using dirt made of red wine, coffee, orange juice, olive oil, choco-

-29 -

late and tomato sauce all mixed together. 1g of the product to be tested was dissolved in 2 litres water then 10g of standard dirt was added to the solutions. The solution was stirred for 10 minutes and then a swatch of terry cotton (15cm x 15cm) was dipped in the solution and stirred for 10 minutes. The cotton swatches are tested in terms of soil redeposition by visual evaluation according to the following rating.

Brightness	Description
0	No soil redeposition, white clean swatch as reference.
1	Very limited soil redeposition, few slightly visible spots.
2	Limited soil redeposition, few well visible spots.
3	Visible soil redeposition, many well visible spots, small visible stains.
4	Strongly visible soil redeposition, big visible stains left.

10

STORAGE STABILITY TEST:

The dyed crystals were added to a laundry powder product and any negative in terms of dye transfer to the white matrix or lump formation were assessed over time at T=40°C and 75%RH. Two visual rating values have been as

-30 -

signed for lump formation and dye transfer.

Dye transfer Rating	Description	Lump Rating	Description
0	No dye transfer. The white matrix remains unchanged	0	Free flowing powder, no lumps
1	Very low dye transfer. The white matrix is almost unchanged	1	Small aggregates present in the matrix
2	Low dye transfer. The white matrix is pale coloured	2	Aggregates present in the matrix
3	Visible dye transfer. The white matrix is visibly coloured	3	Relevant amount of aggregates present in the matrix
4	Complete dye transfer. The white matrix has the colour of the crystals	4	The powder product is all caked

5 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-
 10 filter at 460nm. Y = 90 means a complete stain removal, having white cotton a value of 90.

-31-

Standard prepared stains were used for the test:

Soil	Type of soil	Type of fabric	Soil code	Supplier*
Olive oil	Greasy	Cotton	Empa 101	Empa Institute
Fat	Greasy	Cotton	Empa 120	Empa Institute
Lipstick	Greasy	Cotton	Empa 141	Empa Institute
Make up	Greasy	Cotton	Empa 143	Empa institute
Skin grease	Greasy	Cotton	WFK 10D	WFK institute
Blueberry Juice	Oxidisable	Cotton	CFT CS15	CFT institute
Tea	Oxidisable	Cotton	Empa 167	Empa Institute
Coffee	Oxidisable	Cotton	WFK 10K	WFK institute
Wine	Oxidisable	Cotton	WFK 10LI	WFK institute
Curry	Oxidisable	Cotton	WFK 10U	WFK institute
Soy	Oxidisable	Cotton	WFK 10V	WFK institute
Cocoa	Enzymatic	Cotton	Empa 112	Empa institute
Blood	Enzymatic	Cotton	Empa 116	Empa institute

*Empa Test Materials in Switzerland

WFK Testgewebe GmbH in Germany

5 CFT Institute in the Netherland

The additive products were added (with the detergent) in the drawer of washing machine. The cleaning was done using Bosch washing machines, 40°C water temperature, 12°F
 10 water hardness and 2.5 kg ballast. Results were averaged over four replications.

WHITENESS DEGREE TEST - SOIL REDEPOSITION ASSESSMENT:

15 Whiteness degree was assessed by considering the reflectance value Y. The X Y Z scale was measured with a spectrophotometer. Also the GANZ value was considered for whiteness assessment.

The following fabrics have been used for the test:

- 20
- Table Cloth Cotton
 - Tic 400, standard cotton reference from WFK
 - Popeline

-32 -

- Pes/Cotton

The fabrics were washed together with standard stains for stain removal test in the same conditions.

The results averaged over four replications.

5

EXAMPLES:

To assess lump formation and colour transfer, two powder compositions were prepared by dry mixing starting from a white matrix.

10

To assess soil removal and whiteness degree four formulations were prepared by mixing each ingredient together. The compositions used are set below in Tab 1 with the various components identified in Tab 2.

15

Table1				
Components	Ref 2	Ex 1	Ex 2	Ex 3
	%	%	%	%
Na Percarbonate S 141	92.23	92.23	92.23	92.23
TAED white	1.2	1.2	1.2	1.2
Sodium carbonate	5.9	5.1	5.0	4.5
Bentonite	0.45	0.45	0.45	0.45
Dipropylene glycol	0.1	0.1	0.1	0.1
Blue crystals of Acusol 445N				0.5
CMC granular		0.5	0.3	0.3
PVP granular			0.3	0.3
Sodium xylene sulfonate		0.3	0.3	0.3
FWA	0.1	0.1	0.1	0.1
Perfume	0.02	0.02	0.02	0.02
Filler and minors	To 100	To 100	To 100	To 100

-33 -

Table 2	
Component	Description of component
Sodium carbonate	Sodium carbonate from Solvay
Na Percarbonate S 141	Coated sodium percarbonate from Solvay
Bentonite	Bentonite from SudChemie
Acusol 445N	Acrylic homopolymer from Rohm & Haas
Dipropylene glycol	Dipropylene glycol from Dow Chemical
EtelSol SX93	Sodium xylene sulphonate from Huntsman
CMC granular	Carboxy methyl cellulose from Lamberti
Sodium sulphate	Sodium sulphate from Lenzing
Peractive-AC white	TAED from Clariant
PVP K30 granular	Poly vinyl poly pyrrolidone from Clariant
FWA	Tinopal CBS-X from Ciba
Perfume	Perfume from Givaudan
Blue dye	Blue Pigmosol 6900 from BASF
Red dye	Red Mica from Engelhard
Yellow dye	Golden Mica from Engelhard

RESULTS:

Brightness, Soil Redeposition, Dye Transfer, Lump Forma-
tion assessment

Table 3				
Assessment on crystals				
	Brightness		Dry residue %	
Blue dyed crystals	4		98	
Red dyed crystals	4		97	
Gold dyed crystals	4		98	
Soil redeposition				
Water only	4			
Sokalan CP5	4			
Acusol crystals	1			
Assessment on powder composition				
	Blue dye transfer rating		Lumps rating	
	2 weeks	4 weeks	2 weeks	4 weeks
Matrix without crystals	0	0	0	1
Matrix with crystals	0	0	0	1

-34-

It is evident that the process of the invention is able to provide very bright crystals avoiding or significantly reducing storage issues once the crystals are added to a white matrix.

5

Performance assessment of the two powder formulations in terms of soil removal and whiteness degree:

The performance assessment was done comparing a product containing crystals prepared in accordance with the present invention (Ref 1) compared with a market leader (Ref 2).

RESULTS FOR STAIN REMOVAL:

15

The dosage of detergent used was 35g/load. For test four repetitions were performed and the values obtained were averaged.

	Table 4a (Y - Reflectance)						
	Olive	Fat	Lipstick	Make up	Sebum	Blueberry	Tea
Ref 1	32.18	31.57	42.18	73.83	64.23	68.24	50.93
+Ref 2	33.34	35.42	44.14	74.19	64.64	77.61	66.28
+Ex 1	35.86	32.35	41.3	72.49	63.58	77.69	67.37
+Ex 2	35.3	37.32	44.18	74.03	62.53	77.73	66.85
+Ex 3	37.37	38.39	46.97	74.98	66.92	77.66	67.5

20

	Table 4b (Y - Reflectance)					
	Coffee	Wine	Curry	Soy	Cocoa	Blood
Ref 1	79.54	62.88	81.25	88.28	54.23	42.19
+Ref 2	83.89	72.34	83.35	88.8	55.69	39.16
+Ex 1	83.79	72.85	83.51	88.84	57.69	38.81
+Ex 2	83.94	72.1	83.29	88.84	55.4	39.95
+Ex 3	84.01	72.5	83.5	89.03	56.75	39.79

-35 -

It is evident that the introduction of crystals in the formula has brought an increase in terms of soil removal performance against products currently available on the market. The results show also that the crystals give better results against Ex 2 and Ex 3, formulations already containing CMC and PVP.

RESULTS FOR WHITENESS DEGREE:

10

	Table 5 - Whiteness degree (Ganz)				
	Polyamide	Table cloth cotton	Tic 400	Popeline	Pes/Cotton
Ref 1	246.3	135.6	159	187.9	260.4
Ref 2	246.5	140.1	168.4	193	262.6
Ex 1	246.8	138.6	165.1	191.2	261.5
Ex 2	247.6	140.5	166	194.6	263.4
Ex 3	248	147	168.2	194.2	264.1

The superiority of Ex 3 against Ref 2 is evident. Ex 3 is generally better or equal than all the other product tested.

15

-36-

Claims

1. A method of preparing coloured solid particles suitable for use in a cleaning process, comprising dissolving / suspending the material to be coloured in a solvent, colouring the solution and removing the solvent from the solution / suspension.
2. A method according to claim 1, wherein the solution in the colouring process is at or close to saturation.
3. A method according to claim 1 or 2, wherein the colouring agent (e.g. dye) is added in the liquid form to the solution / suspension of the material to be coloured.
4. A method according to claim 1, 2 or 3, wherein the solvent is water.
5. A method according to any one of the preceding claims, wherein after colouring the solvent is be removed from the solution / suspension.
6. A method according to claim 5, wherein the solvent is removed at a temperature are in the range 20 - 200°C.
7. A method according to claim 5 or 6, wherein the solvent is removed over a time period of from 1 second to 24 hours.
8. Coloured solid particles produced in accordance with any one of claims 1 to 7.

-37 -

9. A detergent composition comprising the particles according to claim 8.

5 10. A textile washing process comprising the use of a composition according to claim 8 or 9.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2007/000646

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D3/40 C11D17/00 C09C3/08 C08J3/20

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D C08J C09C

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 770 692 A (MILLER D [US]) 6 November 1973 (1973-11-06) column 2, lines 11-16; claims; examples	1-8
X	EP 0 565 417 A (L'OREAL [FR]) 13 October 1993 (1993-10-13) page 4, lines 45-47; claims 1,4,5,8,9; examples	1-8
X	EP 1 421 167 A (UNILEVER PLC [GB]; UNILEVER NV [NL]) 26 May 2004 (2004-05-26) claims; examples	8-10
X	US 6 281 187 B1 (SMERZNAK MARK ALLEN [US]) 28 August 2001 (2001-08-28) column 1, lines 9-14; claims; examples	8-10

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

☒ See patent family annex.

* Special categories of cited documents :

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Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2007/000646

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