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(54) **AN UNCOLOURED LAUNDRY ADDITIVE MATERIAL FOR PROMOTION OF ANTI REDEPOSITION OF PARTICULATE SOIL**

UNGEFÄRBTE WÄSCHEZUSATZMATERIAL ZUR FÖRDERUNG DER ANTI-WIEDERABLAGERUNG VON PARTIKELFÖRMIGEM DRECK

MATÉRIAU ADDITIF DE LESSIVE NON COLORÉ POUR LA PROMOTION D'ANTIREDEPOSITION DE PARTICULES DE SALETÉ

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**EP-A1- 1 524 314** **WO-A1-2006/079626**  
**WO-A1-2011/047987** **US-A- 5 565 145**

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**Description**TECHNICAL FIELD

5 **[0001]** This invention relates to uncoloured laundry additive materials for promotion of anti redeposition of particulate soil, in particular to anti-redeposition polymers (ARPs).

BACKGROUND

10 **[0002]** A crosslinked PEI possibly suitable as a laundry anti redeposition polymer is taught by Zhang & Lonnie (Chinese J. Chem., Vol 21 p 460-5, 2003) discusses the preparation of PEI-PEO block copolymers and their clay dispersancy. The polymers are triblock polymers formed from divalently modified PEG (dimesyl). This forms a PEO crosslink between two PEI groups. We have determined that EPEI is much preferred over PEI for several reasons. A major factor in the selection is the poor performance of PEI on nylon elastane based fabrics. PEI tends to deposit soil onto such fabrics.

15 Crosslinked PEI does not solve that problem satisfactorily.  
**[0003]** EPEI does not suffer from the same nylon- elastane negatives as PEI and has consequently been widely used in laundry compositions. However, it would be desirable to improve the performance of EPEI as an ARP.

**[0004]** For EPEI that has all available amine nitrogens substituted by alkoxy chains it is not feasible to use the crosslinking strategy proposed for PEIs.

20 **[0005]** EP-A-1 524 314 describes a laundry detergent builder obtained by copolymerisation of a polyalkyleneimine unsaturated monomer, having an oxyalkylene group, and an unsaturated carboxylic acid monomer.

**[0006]** There is a need to improve the ARP performance of alkoxyated polyethyleneimines.

SUMMARY OF THE INVENTION

25 **[0007]** According to a first aspect of the present invention there is provided an uncoloured laundry additive material for promotion of anti redeposition of particulate soil, the material having a maximum extinction coefficient in  $L\ mol^{-1}\ cm^{-1}$  of less than 800, preferably less than 100, in the wavelength range 400 to 750 nm and comprising at least two poly-alkoxyated polyethyleneimines, which can be the same or different, cross-linked to one another by a difunctional un-  
 30 coloured aromatic cross linker which also has a maximum extinction coefficient in  $L\ mol^{-1}\ cm^{-1}$  of less than 800, preferably less than 100, in the wavelength range 400 to 750 nm, said cross linker containing an aromatic group comprising at least one aromatic ring and two reactive groups selected from  $-SO_2CH_2CH_2OSO_3Na$  and  $NHCOCH=CH_2$ .

**[0008]** The aromatic group may confer rigidity to the cross link, which prevents the polyalkoxyated PEIs folding together and failing to function as intended. Preferably the difunctional aromatic cross-linker contains 2 or 3 aromatic groups, the  
 35 aromatic groups covalently bound to each other by a single covalent bond, or via a  $-CH_2-$  or  $-NH-$  group. Preferably the functional (reactive) groups will be identical. More preferably one or more of the aromatic groups is a phenyl group. Most preferably one or more of the aromatic groups is a 1,3,5 triazine.

**[0009]** The polyalkoxylation is preferably polyethoxylation, to thereby form ethoxyated polyethyleneimine (EPEI).

40 **[0010]** Dicarbamate functional groups on the cross linkers are preferred because the EPEI may then be cross-linked by the very simple process of mixing the EPEI and the aromatic cross-linker in warm water. The aromatic cross-linker is itself uncoloured. By uncoloured it is meant that the material is not strongly coloured which is the case provided that it has a maximum extinction coefficient in  $L\ mol^{-1}\ cm^{-1}$  of less than 800, preferably less than 100, in the wavelength range 400 to 750 nm. Amino functional materials can have a slight yellowness and such slight  
 45 yellowness is uncoloured for the purposes of this invention provided that the extinction coefficient criterion is met.

**[0011]** According to a second aspect of the invention there is provided a process to manufacture the uncoloured crosslinked polyethoxyated polyethyleneimine material comprising the steps of mixing the uncoloured cross linker with EPEI in warm aqueous solution, preferably at 320 to 360 K.

**[0012]** According to a third aspect there is provided a laundry detergent composition comprising 2 to 60 wt % of a  
 50 detersive surfactant system and 0.1 to 10 wt % of the uncoloured cross linked polyalkoxyated polyethyleneimine according to the first aspect.

**[0013]** According to a fourth aspect there is provided use of the material according to the first aspect to prevent particulate soil redeposition during a fabric washing process.

**[0014]** According to a fifth aspect there is provided a laundry process wherein a wash liquor comprising at least 5 ppm  
 55 of the material of the first aspect and at least 0.3 g/L of detersive surfactant dispersed in water is used to wash a mixed load of fabrics selected from at least 2 of: cotton, polycotton, polyester and nylon elastane, provided that nylon elastane is present.

DETAILED DESCRIPTION OF THE INVENTIONPolyalkoxylated Polyethyleneimines

5 **[0015]** A polyalkoxylated polyethyleneimine (EPEI polymer) is a known organic compound. If the cross-linker is intended to react with a hydroxyl group it is necessary that at least some of the alkoxy chains are terminated with hydroxyl groups. Alternatively, if the cross linker is intended to react with the primary or secondary amine to substitute its hydrogen then it is essential that the polyethyleneimine has at least one NH group remaining after polyalkoxylation. This unsubstituted primary or secondary amine then permits the formation of a covalent bond between its nitrogen and the aromatic cross-linker.

10 **[0016]** Preferred polyalkoxylation is polyethoxylated and/or polypropoxylated. Most preferably polyethoxylated. When propoxylation is present it is preferred that it is in a minority of the polyalkoxylation and that it is adjacent to the nitrogens, the remaining polyalkoxylation being polyethoxylation and being more remote from the nitrogen.

15 **[0017]** Polyethyleneimine (PEI) materials are usually highly branched polyamines characterized by the empirical formula  $(C_2H_5N)_n$  with a molecular mass of 43.07 (as repeating units). They are commercially prepared by acid-catalyzed ring opening of ethyleneimine, also known as aziridine.

20 **[0018]** PEIs may be alkoxyated to form polyalkoxylated polyethyleneimines whereby polyalkoxy chains are provided in place of some or all of the hydrogen moieties found on the primary and secondary amines in the PEI. The alkylene oxide used in this reaction can be a single type (for example ethylene oxide) or a mixture. The resulting polyalkoxylation can be a homopolymer, a random copolymer or a block copolymer.

**[0019]** The alkoxy groups are preferably selected from ethoxy and propoxy groups. The polyalkylene oxide chains preferably have repeat units of alkoxy moieties in the range from 5 to 30, preferably 12 to 22.

25 **[0020]** The polyalkylimine core, preferably PEI, of the material preferably has a weight average molecular weight of 180-60000, more preferably 400-2000, most preferably 500-1000. The polyalkylimine core may be branched or linear, preferably branched.

**[0021]** It is preferred that the polyalkoxylation consists entirely of ethylene oxide units (polyethoxylation).

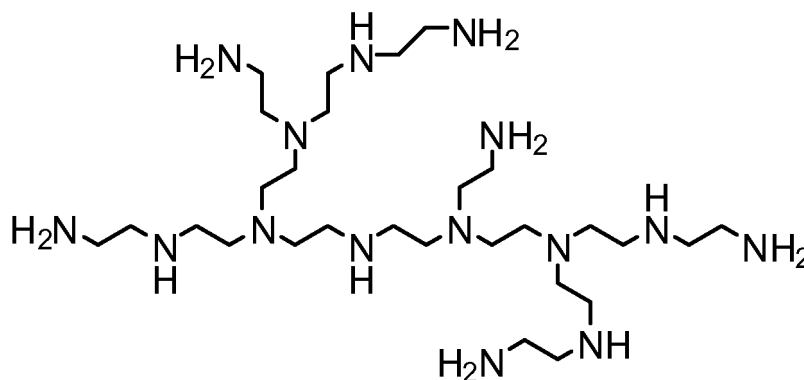
**[0022]** It is preferred that the PEI is not modified except by polyalkoxylation prior to crosslinking, for example it is not oxidised to make NO groups and the Nitrogens are not quaternised.

30 **[0023]** The weight average molecular weights,  $M_w$ , are suitably determined by dynamic light scattering using a Zetasizer Nano (Malvern).

**[0024]** EPEIs are commercially available from the BASF Corporation and from Nippon Shokubai.

**[0025]** Suitable EPEIs for crosslinking may be found in: WO2007/083262; WO 2006/113314; EP760846; US4597898; WO 2009/060409; WO 2008/114171; WO 2008/007320; EP 760846; WO 2009/065738; WO 2009/060409; WO 2005/063957; EP 996701; EP 918837; EP 917562; EP 907703; and, 6,156,720.

35 **[0026]** An example PEI core is shown below:



**[0027]** The polymer contains 15 Nitrogens of which 6 are primary amines ( $NH_2$ ); 5 are secondary amines (NH) and 4 are tertiary amines.

Aromatic Cross-linker

55 **[0028]** The aromatic cross-linker (ACL) is an organic chemical which contains an aromatic group comprising at least one aromatic ring and two reactive groups that react with alcohols, primary amines, or secondary amines to form a covalent bond. Preferably the aromatic group is phenyl or 1, 3, 5-triazine. Preferably the aromatic cross-linker contains

2 or 3 aromatic rings that are directly linked to each other by a single covalent bond, or linked by a divalent CH<sub>2</sub> or NH group. The aromatic rings may be further substituted by nonaromatic organic groups.

[0029] The reactive groups are selected from (-SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>Na) and NHCOCH=CH<sub>2</sub>. When the reactive group is not -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>Na, the aromatic cross linker is preferably sulphonated.

[0030] Preferably the aromatic cross-linker is ACL 2, ACL 3, ACL 4, most preferably ACL 3 and ACL 4, as hereafter described.

[0031] The ACL is preferably cross-linked via the OH groups of the alkoxy chain or via the NH and NH<sub>2</sub> groups of the core PEI. Most preferably the cross-link is via the OH groups of the alkoxy chain.

[0032] Preferably the mole ratio of aromatic cross-linker to polyalkoxylated polyamines is from 1:5 to 1:2.

[0033] The aromatic cross-linker is itself uncoloured by which is meant that it has a maximum extinction coefficient in L mol<sup>-1</sup> cm<sup>-1</sup> of less than 800, preferably less than 100, in the wavelength range 400 to 750 nm.

[0034] The detergent compositions may take any suitable form. For example they may be powders, tablets, liquids or gels and in the case of liquids they may be contained in a water soluble capsule to allow for ease of use. Preferred compositions are liquids due to the compatibility of the polyalkoxylated PEI ARP materials with ingredients typically found in liquid detergents.

### Surfactants

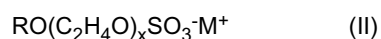
[0035] Surfactants assist in removing soil from the textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor. Blends of anionic and nonionic surfactants are a preferred feature of the compositions. The amount of anionic surfactant is preferably at least 5 wt%, more preferably at least 10wt%.

#### *Anionic*

[0036] Preferred anionic surfactants are alkyl sulphonates especially alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C<sub>8</sub>-C<sub>15</sub>. The counter ion for the anionic surfactants may be an alkali metal, typically sodium, or another counter-ion for example MEA, TEA or ammonium can be used.

[0037] Suitable linear alkyl benzene sulphonate surfactants include Detal LAS with an alkyl chain length of from 8 to 15, more preferably 12 to 14.

[0038] It is further desirable that the composition comprises an alkyl polyethoxylate sulphate anionic surfactant of the formula (II):



where R is an alkyl chain having from 10 to 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from 1 to 15.

[0039] Preferably R is an alkyl chain having from 12 to 16 carbon atoms, M is Sodium and x averages from 1 to 3, preferably x is 3; This is the anionic surfactant sodium lauryl ether sulphate (SLES). It is the sodium salt of lauryl ether sulphonic acid in which the predominantly C<sub>12</sub> lauryl alkyl group has been ethoxylated with an average of 3 moles of ethylene oxide per mole.

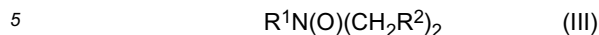
#### *Nonionic*

[0040] Nonionic surfactants include primary and secondary alcohol ethoxylates, especially C<sub>8</sub>-C<sub>20</sub> aliphatic alcohol ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy amides (glucamide). Mixtures of nonionic surfactant may be used. When included therein the composition contains from 0.1 to 20 wt% preferably 1 wt% to 15 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant, for example alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside, alkyl dimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl derivatives of glucosamine ("glucamides").

[0041] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C<sub>8</sub>-C<sub>20</sub> aliphatic alcohols ethoxylated with an average of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol.

*Amine Oxide*

[0042] The composition may comprise up to 10 wt% of an amine oxide of the formula (III):



[0043] In which R<sup>1</sup> is a long chain moiety each CH<sub>2</sub>R<sup>2</sup> are short chain moieties. R<sup>2</sup> is preferably selected from hydrogen, methyl and -CH<sub>2</sub>OH. In general R<sup>1</sup> is a primary or branched hydrocarbonyl moiety which can be saturated or unsaturated, preferably, R<sup>1</sup> is a primary alkyl moiety. R<sup>1</sup> is a hydrocarbonyl moiety having chain length of from about 8 to about 18.

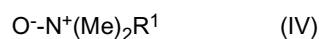
10 [0044] Preferred amine oxides have R<sup>1</sup> is C<sub>8</sub>-C<sub>18</sub> alkyl, and R<sup>2</sup> is H. These amine oxides are illustrated by C<sub>12-14</sub> alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

[0045] A preferred amine oxide material is Lauryl dimethylamine oxide, also known as dodecyldimethylamine oxide or DDAO. Such an amine oxide material is commercially available from Huntsman under the trade name Empigen® OB.

15 [0046] Amine oxides suitable for use herein are also available from Akzo Chemie and Ethyl Corp. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

[0047] Whereas in preferred embodiments R<sup>2</sup> is H, it is possible to have R<sup>2</sup> slightly larger than H. Specifically, R<sup>2</sup> may be CH<sub>2</sub>OH, for example: hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide.

20 [0048] Preferred amine oxides have the formula (IV):



where R<sup>1</sup> is C<sub>12-16</sub> alkyl, preferably C<sub>12-14</sub> alkyl; Me is a methyl group.

25 *Zwitterionic*

[0049] A preferred zwitterionic material is a carbobetaine available from Huntsman under the name Empigen® BB. Betaines and / or amine oxides, improve particulate soil detergency in the compositions.

30 **Additional surfactants**

[0050] Other surfactants than the preferred LAS, SLES, nonionic and amine oxide/ carbobetaine) may be added to the mixture of detergent surfactants. However cationic surfactants are preferably substantially absent.

35 [0051] Although less preferred, some alkyl sulphate surfactant (PAS) may be used, especially the non-ethoxylated C<sub>12-15</sub> primary and secondary alkyl sulphates. A particularly preferred material, commercially available from BASF, is Sulfofon 1214G.

**Polymers**40 **Polyester soil release polymer**

[0052] The compositions may include 0.5 wt% or more of a soil release polymer which is substantive to polyester fabric. Such polymers typically have a fabric substantive midblock formed from propylene terephthalate repeat units and one or two end blocks of capped polyalkylene oxide, typically PEG 750 to 2000 with methyl end capping.

45 **Other polymer types**

[0053] In addition to a polyester soil release polymer there may be used dye transfer inhibition polymers, and cotton soil release polymers, especially those based on modified cellulosic materials.

50 **Hydrotrope**

55 [0054] A hydrotrope is a solvent that is neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components in the aqueous liquid to render it isotropic. Among suitable hydrotropes there may be mentioned as preferred: MPG (monopropylene glycol), glycerol, sodium cumene sulphonate, ethanol, other glycols, e.g. di propylene glycol, diethers and urea.

**Enzymes**

**[0055]** It is preferable that at least one or more enzymes may be present in the compositions. Preferably at least two, more preferably at least three different classes of enzymes are used in combination. Preferred enzyme cocktails are selected from the group comprising: lipase, Phospholipase, protease, Cutinase, Amylase, Cellulase, Peroxidases/oxidase, Pectate Lyase, and Mannanase.

**[0056]** Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol for example propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative for example 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708. Alternatively, or additionally, the enzymes may be protected by encapsulation

**[0057]** When a lipase enzyme is included a lignin compound may be used in the composition. Preferably the lignin compound comprises a lignin polymer and more preferably it is a modified lignin polymer. A modified lignin polymer as used herein is lignin that has been subjected to a chemical reaction to attach chemical moieties to the lignin covalently. The attached chemical moieties are preferably randomly substituted.

**Fluorescent Agents**

**[0058]** It may be advantageous to include fluorescer in the compositions. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.5 wt %.

Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra, Tinopal 5BMGX, and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

**[0059]** Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

**Bleach Catalyst**

**[0060]** Compositions may comprise a weight efficient bleach system. Such systems typically do not utilise the conventional percarbonate and bleach activator approach. An air bleach catalyst system is preferred. Suitable complexes and organic molecule (ligand) precursors for forming complexes are available to the skilled worker, for example, from: WO 98/39098; WO 98/39406, WO 97/48787, WO 00/29537; WO 00/52124, and WO00/60045, incorporated by reference.

An example of a preferred catalyst is a transition metal complex of MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1-,1-bis(pyridin-2-yl)-1-aminoethane). Suitable bispidon catalyst materials and their action are described in WO02/48301. The bleach catalyst may be encapsulated to reduce interaction with other components of the liquid during storage.

**[0061]** Photobleaches may also be employed. A "photobleach" is any chemical species that forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction. Preferred photo-bleaches include singlet oxygen photo-bleaches and radical photo-bleaches. Suitable singlet oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO<sub>3</sub>X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba).

**[0062]** When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10 wt%, preferably about 0.001 to about 5 wt%.

**Perfume**

**[0063]** The composition will normally include one of more perfume components. Free oil and encapsulated perfumes may be used, and mixtures thereof.

**[0064]** A particularly preferred way of ensuring that perfume is employed efficiently is to use an encapsulated perfume. Use of a perfume that is encapsulated reduces the amount of perfume vapour that is produced by the composition before it is diluted. This is important when the perfume concentration is increased to allow the amount of perfume per wash to be kept at a reasonably high level.

**[0065]** It is even more preferable that the perfume is not only encapsulated but also that the encapsulated perfume is provided with a deposition aid to increase the efficiency of perfume deposition and retention on fabrics. The deposition aid is preferably attached to the encapsulate by means of a covalent bond, entanglement or strong adsorption.

**Further Optional Ingredients**

5 [0066] The compositions may contain one or more other ingredients. Such ingredients include viscosity modifiers, foam boosting agents, preservatives (e.g. bactericides), pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents and ironing aids. The compositions may further comprise colorants, pearlisers and/or opacifiers, and shading dye.

**Shading dyes**

10 [0067] Shading dye can be used to improve the performance of the compositions. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself. Examples of shading dyes are alkoxyated thiophene dyes, acid violet 50, direct violet 35, direct violet 99, direct violet 9, solvent violet 13, disperse violet 28, disperse blue 165.

15 [0068] Shading dye can be used in the absence of fluorescer, but it is especially preferred to use a shading dye in combination with a fluorescer, for example in order to reduce yellowing due to chemical changes in adsorbed fluorescer.

**Builders and sequestrants**

20 [0069] The detergent compositions may also optionally contain relatively low levels of organic detergent builder or sequestrant material. Examples include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other examples are DEQUEST™, organic phosphonate type sequestering agents sold by Monsanto and alkanehydroxy phosphonates.

25 [0070] Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, for example those sold by BASF under the name SOKALAN™.

30 [0071] If utilized, the organic builder materials may comprise from about 0.5% to 20 wt%, preferably from 1 wt% to 10 wt%, of the composition. The preferred builder level is less than 10 wt% and preferably less than 5 wt% of the composition. A preferred sequestrant is HEDP (1-Hydroxyethylidene -1,1,-diphosphonic acid), for example sold as Dequest 2010. Also suitable but less preferred as it gives inferior cleaning results is Dequest® 2066 (Diethylenetriamine penta(methylene phosphonic acid or Heptasodium DTPMP).

**Buffers**

35 [0072] The presence of some buffer is preferred for pH control; preferred buffers are MEA, and TEA. If present they are preferably used in the composition at levels of from 1 to 15 wt%.

**External Structurants**

40 [0073] The compositions may have their rheology modified by use of a material or materials that form a structuring network within the composition. Suitable structurants include hydrogenated castor oil, microfibrinous cellulose and natural based structurants for example citrus pulp fibre. Citrus pulp fibre is particularly preferred especially if lipase enzyme is included in the composition.

**Visual Cues**

45 [0074] The compositions may comprise visual cues of solid material that is not dissolved in the composition. Preferably they are used in combination with an external structurant to ensure that they remain in suspension. Preferred visual cues are lamellar cues formed from polymer film and possibly comprising functional ingredients that may not be as stable if exposed to the alkaline liquid. Enzymes and bleach catalysts are examples of such ingredients. Also perfume, particularly microencapsulated perfume.

[0075] The invention will now be further described with reference to the following nonlimiting examples.

**EXAMPLES**

55 [0076] The following polymers were synthesised:

Standard EPEI polymer

[0077] A 600 molecular weight branched PEI with 15 ethoxylate groups per NH (e.g. the primary amine functionality  $-NH_2$  has become  $-N(15EO)_2$ ). The polyethoxylate chains of this polyethoxylated polyethyleneimine polymer (EPEI) are OH capped.

Cross-linked polyethoxylated PEI

[0078] The aromatic cross-linkers detailed in Table 1 were used to cross-link the standard polyethoxylated polyethyleneimine polymer.

Table 1

Resultant (ARP) polymer name	Aromatic Cross-linker (ACL)
CLAP 1 Reference	
CLAP 2	
CLAP 3	
CLAP 4	

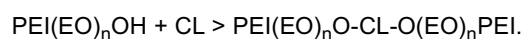
NB. CLAP 4 is a cross-linked EPEI without any sulphonates.

Using the nomenclature:

CL = crosslinker

PEI = PEI

$(EO)_nOH$  = ethoxylate chain



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**[0079]** Typically one adds on to the double bonds of the crosslinker. For the vinyl sulphone, it loses the sulphone group at high pH to give an alkene, which then reacts.

**[0080]** In all cases 5 wt% of the cross-linker was mixed with the standard polymer for 4 days at 293 K. For CLAP 1, CLAP 2 and CLAP 3 the aqueous solution was then heated to 333 K and stirred for 3 hours; then the temperature was raised to 353 K and the solution stirred for a further 24 hours and cooled before use. For CLAP 4 the solution was then heated to 333 K and stirred for 3 hours then 2.5 wt% Na<sub>2</sub>CO<sub>3</sub> added and stirred at 333 K for a further 24 hours, cooled and used.

**[0081]** The polymers were added to the base detergent composition given in Table 2 at levels of 0.44 and 3.5 wt% to make detergent compositions A and B.

Table 2

	Wt%
NaLAS	4.9
NI(7EO)	7.3
SLES(3EO)	2.4
Alkyl Betaine	0.9
1,2-propanediol	15
Triethanolamine	2
Free oil perfume	1.4
Water	to 100

NaLAS is sodium C<sub>11</sub> to C<sub>15</sub> alkyl benzene sulphonate.

NI(7EO) is R-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH, where R is an alkyl chain of C<sub>12</sub> to C<sub>15</sub>, and n is 7.

**[0082]** SLES(3EO) is sodium lauryl ether sulphate with 3 ethoxy groups.

The Alkyl Betaine used was Empigen® BB (ex Huntsman).

**[0083]** Alkaline (pH approx 8.3) wash liquors made using Compositions A and B were used to wash a mixture of white fabrics: woven cotton, micro-fibre polyester, woven polycotton and knitted nylon-elastane at Liquor to cloth ratio of 10:1 in a Linitester™. Each piece was the same area, 2 pieces of cotton, and 1 each of the rest. 26° French hard water at room temperature was used and each wash lasted 20 minutes and was followed by 2 rinses in 75 ml water. This procedure was repeated twice in the composition without the addition of polymer, the cloths were then dried. The procedure was repeated three times with the test formulation. Addition of soil strips to each wash to simulate soiling. The weight ratio of soil strips to the white fabrics was 8.6:1. The soil strips used were SBL 2004 Soil Ballast Fabrics (ex wfk Testgewebe GmbH) and a Stanley Clay strip on cotton (ex Warwick Equest UK) in the weight ratio of 1:1.

**[0084]** The detergent compositions were each used at 2.3 g/L.

**[0085]** The white cotton cloths were removed, dried and the reflectance spectrum then measured using a reflectometer with the UV filter in place. The enhancement in cleaning was measured via ΔR<sub>460</sub> which is given by:

$$\Delta R_{460} = R_{460}(\text{polymer}) - R_{460}(\text{control-no polymer}).$$

**[0086]** The cleaner the cotton cloth the higher the reflectance, therefore the larger ΔR<sub>460</sub> is the greater the increase in cleanliness of the cloth verses the control. The overall effectiveness is shown by the performance on cotton. The results are given in Table 3.

Table 3

	ΔR <sub>460</sub> Cotton	
	A = 0.44 wt%	B = 3.5 wt%
Standard polymer	1.0	2.6
CLAP 1 *	2.0	3.2
CLAP 2	1.7	3.0

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(continued)

	$\Delta R_{460}$ Cotton	
	A = 0.44 wt%	B = 3.5 wt%
CLAP 3	3.4	4.9
CLAP 4	3.5	4.1
* Reference		

[0087] The cross-linked samples all gave a larger increase in  $\Delta R_{460}$  than the uncross-linked standard EPEI polymer. CLAP 3 and CLAP 4 cross-linked polymers gave the best performance.

[0088] Table 4 is a detergent composition according to the invention.

Table 4

	wt% (solids)
NaLAS	4.9
NI(7EO)	7.3
SLES(3EO)	2.4
Alkyl Betaine	0.9
1,2-propanediol	15.0
Triethanolamine	2.0
Free oil perfume	1.4
CLAP 3	0.5
Lipase	0.002
Cellulase	0.002
Amylase	0.002
Acid Violet 50	0.002
Fluorescer	0.1
Water	to 100

[0089] Enzyme levels are expressed as pure protein. The lipase used was Lipoclean™ (Novozymes); the cellulose used was Celluclean™ (Novozymes); the amylase used was Stainzyme™ (Novozymes).

### Claims

1. An uncoloured laundry additive material for promotion of anti redeposition of particulate soil, the material having a maximum extinction coefficient in  $L \text{ mol}^{-1} \text{ cm}^{-1}$  of less than 800, preferably less than 100, in the wavelength range 400 to 750 nm and comprising at least two polyalkoxylated polyethyleneimines, which can be the same or different, cross-linked to one another by a difunctional uncoloured aromatic cross linker which also has a maximum extinction coefficient in  $L \text{ mol}^{-1} \text{ cm}^{-1}$  of less than 800, preferably less than 100, in the wavelength range 400 to 750 nm, said cross linker containing an aromatic group comprising at least one aromatic ring and two reactive groups selected from  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$  and  $\text{NHCOCH}=\text{CH}_2$ .
2. A material according to claim 1 wherein the polyalkoxylation consists of a polyethoxyl chain terminated by a hydroxyl group and wherein the material is cross-linked by reaction of the crosslinker with the terminal hydroxyl groups on two otherwise discrete polyalkoxylated polyethyleneimines.
3. A material according to claim 2 wherein all amine hydrogens are replaced with such a chain.

4. A material according to claim 2 or 3 wherein the polyethoxyl chain consists of from 12 to 22 ethylene oxide units.
5. A material according to any preceding claim, wherein the aromatic cross-linker comprises at least one heteroaromatic or homoaromatic group.
- 5 6. A material according to any preceding claim in which the difunctional aromatic cross-linker contains 2 or 3 aromatic groups, the aromatic groups covalently bound to each other by a single covalent bond, or via a -CH<sub>2</sub>- or -NH- group.
- 10 7. A material according to any preceding claim in which the functional (reactive) groups on the cross linker are identical.
8. A material according to any preceding claim in which one or more of the aromatic groups of the cross linker is a phenyl group.
- 15 9. A material according to claim 8 in which one or more of the aromatic groups is a 1,3,5 triazine.
10. A process to manufacture the crosslinked polyalkoxylated polyethyleneimine material according to any preceding claim comprising the steps of mixing the uncoloured aromatic cross linker with EPEI in warm aqueous solution.
- 20 11. A laundry detergent composition comprising 2 to 60 wt % of a deterative surfactant system and 0.1 to 10 wt % of the cross linked alkoxylated polyethyleneimine according to any one of claims 1 to 9.
12. Use of the material according to any one of claims 1 to 9 to prevent particulate soil redeposition during a fabric washing process.
- 25 13. A laundry process wherein a wash liquor comprising at least 5 ppm of the material according to any one of claims 1 to 9 and at least 0.3 g/L of deterative surfactant dispersed in water is used to wash a mixed load of fabrics selected from at least 2 of: cotton, polycotton, polyester and nylon elastane, provided that nylon elastane is present.

30 **Patentansprüche**

1. Ungefärbtes Waschmittelzusatzmaterial zur Förderung der Anti-Wiederablagerung von teilchenförmigem Schmutz, wobei das Material einen maximalen Extinktionskoeffizienten in L mol<sup>-1</sup> cm<sup>-1</sup> von weniger als 800, vorzugsweise von weniger als 100, in dem Wellenlängenbereich von 400 bis 750 nm aufweist und mindestens zwei polyalkoxylierte Polyethylenimine umfasst, die gleich oder verschieden sein können, miteinander durch einen difunktionellen ungefärbten aromatischen Vernetzer vernetzt, der ebenfalls einen maximalen Extinktionskoeffizienten in L mol<sup>-1</sup> cm<sup>-1</sup> von weniger als 800, vorzugsweise von weniger als 100, in dem Wellenlängenbereich von 400 bis 750 nm aufweist, wobei der Vernetzer eine aromatische Gruppe enthält, die mindestens einen aromatischen Ring und zwei reaktive Gruppen, ausgewählt aus -SO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>Na und NHCOCH=CH<sub>2</sub>, umfasst.
- 35 2. Material nach Anspruch 1, wobei die Polyalkoxylierung aus einer Polyethoxyl-Kette besteht, die durch eine Hydroxy-Gruppe terminiert ist, und wobei das Material durch die Umsetzung des Vernetzers mit den terminalen Hydroxy-Gruppen auf zwei sonst diskreten polyalkoxylierten Polyethylenimininen vernetzt wird.
- 40 3. Material nach Anspruch 2, wobei sämtliche Aminwasserstoffe durch eine solche Kette ersetzt sind.
4. Material nach Anspruch 2 oder 3, wobei die Polyethoxyl-Kette aus 12 bis 22 Ethylenoxid-Einheiten besteht.
5. Material nach irgendeinem vorhergehenden Anspruch, wobei der aromatische Vernetzer mindestens eine heteroaromatische oder homoaromatische Gruppe umfasst.
- 50 6. Material nach irgendeinem vorhergehenden Anspruch, in welchem der difunktionelle aromatische Vernetzer 2 oder 3 aromatische Gruppen aufweist, wobei die aromatischen Gruppen miteinander durch eine einzige kovalente Bindung oder über eine -CH<sub>2</sub>- oder -NH-Gruppe kovalent gebunden sind.
- 55 7. Material nach irgendeinem vorhergehenden Anspruch, in welchem die funktionellen (reaktiven) Gruppen auf dem Vernetzer identisch sind.

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8. Material nach irgendeinem vorhergehenden Anspruch, in welchem eine oder mehrere der aromatischen Gruppen des Vernetzers eine Phenyl-Gruppe darstellen.
- 5 9. Material nach Anspruch 8, in welchem eine oder mehrere der aromatischen Gruppen ein 1,3,5-Triazin darstellen.
10. Verfahren zur Herstellung des vernetzten polyalkoxylierten Polyethylenimin-Materials nach irgendeinem vorhergehenden Anspruch, umfassend die Schritte des Vermischens des ungefärbten aromatischen Vernetzers mit EPEI in warmer wässriger Lösung.
- 10 11. Waschmittelzusammensetzung, umfassend 2 bis 60 Gew.-% eines Waschtensid-Systems und 0,1 bis 10 Gew.-% des vernetzten alkoxylierten Polyethylenimins nach irgendeinem der Ansprüche 1 bis 9.
12. Verwendung des Materials nach irgendeinem der Ansprüche 1 bis 9 zum Verhindern der Wiederablagerung von teilchenförmigem Schmutz während eines Textilwaschverfahrens.
- 15 13. Waschverfahren, bei dem eine Waschflüssigkeit, umfassend mindestens 5 ppm des Materials nach irgendeinem der Ansprüche 1 bis 9 und mindestens 0,3 g/l Waschtensid, dispergiert in Wasser, verwendet wird, um eine gemischte Beladung mit Textilien, ausgewählt aus mindestens 2 von Baumwolle, Polycotton, Polyester und Nylon-Elastan, unter der Voraussetzung, dass Nylon-Elastan vorliegt, zu waschen.
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### Revendications

- 25 1. Matériau d'additif de lessive non coloré pour une promotion d'antiredéposition de saleté particulaire, le matériau ayant un coefficient d'extinction maximal en  $L \text{ mol}^{-1} \text{ cm}^{-1}$  inférieur à 800, de préférence inférieur à 100, dans l'intervalle de longueur d'onde de 400 à 750 nm et comprenant au moins deux polyéthylèneimines polyalcoylées, lesquelles peuvent être identiques ou différentes, réticulées l'une à l'autre par un agent de réticulation aromatique non coloré difonctionnel qui présente également un coefficient d'extinction maximal en  $L \text{ mol}^{-1} \text{ cm}^{-1}$  inférieur à 800, de préférence inférieur à 100, dans l'intervalle de longueur d'onde de 400 à 750 nm, ledit agent de réticulation
- 30 contenant un groupe aromatique comprenant au moins un noyau aromatique et deux groupes réactifs choisis parmi  $-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$  et  $\text{NHCOCH}=\text{CH}_2$ .
- 35 2. Matériau selon la revendication 1, dans lequel la polyalcoylation consiste en une chaîne polyéthoxyle terminée par un groupe hydroxyle et dans lequel le matériau est réticulé par réaction de l'agent de réticulation avec les groupes hydroxyle terminaux sur deux polyéthylèneimines polyalcoylées par ailleurs discrètes.
3. Matériau selon la revendication 2, dans lequel tous les hydrogènes d'amines sont remplacés avec une telle chaîne.
- 40 4. Matériau selon la revendication 2 ou 3, dans lequel la chaîne polyéthoxyle est constituée de 12 à 22 unités d'oxyde d'éthylène.
5. Matériau selon l'une quelconque des revendications précédentes, dans lequel l'agent de réticulation aromatique comprend au moins un groupe hétéroaromatique ou homoaromatique.
- 45 6. Matériau selon l'une quelconque des revendications précédentes, dans lequel l'agent de réticulation aromatique difonctionnel contient 2 ou 3 groupes aromatiques, les groupes aromatiques liés par covalence les uns aux autres par une liaison simple covalente, ou via un groupe  $-\text{CH}_2-$  ou  $-\text{NH}-$ .
- 50 7. Matériau selon l'une quelconque des revendications précédentes, dans lequel les groupes fonctionnels (réactifs) sur l'agent de réticulation sont identiques.
8. Matériau selon l'une quelconque des revendications précédentes, dans lequel un ou plusieurs des groupes aromatiques de l'agent de réticulation est un groupe phényle.
- 55 9. Matériau selon la revendication 8, dans lequel un ou plusieurs des groupes aromatiques est une 1,3,5-triazine.
10. Procédé de fabrication du matériau de polyéthylèneimine polyalcoylée réticulée selon l'une quelconque des revendications précédentes comprenant les étapes de mélange de l'agent de réticulation aromatique non coloré avec

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EPEI dans une solution aqueuse chaude.

5 **11.** Composition de détergent de lessive comprenant de 2 à 60 % en masse d'un système de tensioactif détersif et de 0,1 à 10 % en masse de la polyéthylèneimine alcoylée réticulée selon l'une quelconque des revendications 1 à 9.

**12.** Utilisation du matériau selon l'une quelconque des revendications 1 à 9 pour éviter une redéposition de saleté particulaire pendant un procédé de lavage de textile.

10 **13.** Procédé de lessive, dans lequel une liqueur de lavage comprenant au moins 5 ppm du matériau selon l'une quelconque des revendications 1 à 9 et au moins 0,3 g/L de tensioactif détersif dispersé dans l'eau est utilisée pour laver une charge mixte de textiles choisis parmi au moins 2 de : coton, polycoton, polyester et nylon élastane, à condition que le nylon élastane soit présent.

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