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(54) Title: DYE POLYMERS

(57) Abstract: The present invention provides dye polymers for use in laundry applications.

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DYE POLYMERS

FIELD OF INVENTION

The present invention concerns the provision and use of laundry shading dye polymers.

BACKGROUND OF THE INVENTION

WO2005/003274, to Unilever, discloses that shading dyes may be included in detergent formulations to enhance the whiteness of garments.

WO09/090125 discloses cationic dyes covalently linked to polymers.

Synthesis of synthetic organic shading dye-polymers required synthesis of the dye monomer and then subsequent polymerisation reaction. It would be desirable to have a simpler synthetic route.

SUMMARY OF THE INVENTION

The dye polymers of the present invention may be used to shade textiles or provide colour cues for laundry detergent and fabric conditioners. The dye polymers are easily synthesised. The dye polymers also provide soil removal benefits.

In one aspect the present invention provides a method for obtaining a dye-polymer, the method comprising the step of reacting a polymer with a primary amine of a dye to form the dye-polymer, wherein the polymer has a group for reacting with the primary amine, the group selected from: isocyanate; oxazolone; epoxide; ester, and anhydride, preferably epoxide or anhydride, most preferably anhydride.

In another aspect the present invention provides a laundry treatment composition comprising:
(i) from 2 to 70 wt% of a surfactant; and,
(ii) from 0.0001 to 20.0 wt%, preferably 0.01 to 2wt%, of the dye-polymer.

In a further aspect the present invention provides a method of treating a laundry textile, the method comprising the steps of:

(i) treating a textile with an aqueous solution of the dye-polymer, the aqueous solution comprising from 10 ppb to 100 ppm of the dye-polymer (preferably 0.1 to 5ppm, most preferably 0.5 to 2ppm); and, from 0.0 g/L to 3 g/L, preferably 0.3 to 2 g/L, of a surfactant;
(ii) optionally rinsing; and,
(iii) drying the textile.

The present invention also extends to the dye-polymers obtainable from the method.

DETAILED DESCRIPTION OF THE INVENTION

REACTION DESCRIPTION

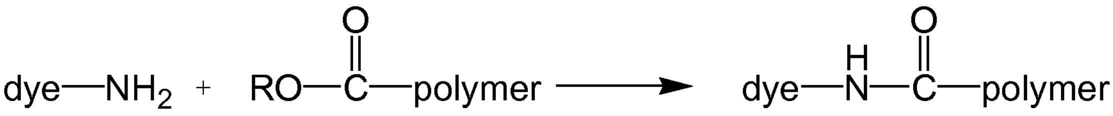
Post-polymerization modification dye polymers are made using reactive polymers, which carry functional reactive groups that react with the NH_2 group of a dye.

The NH_2 group of a dye is reacted with the isocyanate; oxazolone, epoxide, ester, and/or anhydride of the reactive polymer. Of the ester classes, activated esters are preferred.

Post-polymerization modification using reactive polymers is described in detail in Gauthier, M.A., Gibson, M.I., and Klok H-A., *Angew. Chem. Int. Ed* **2009** *48*, 48058.

The following are examples of reacting a dye with a polymer in accordance with the present invention. Preferably the polymer does not contain a primary amine.

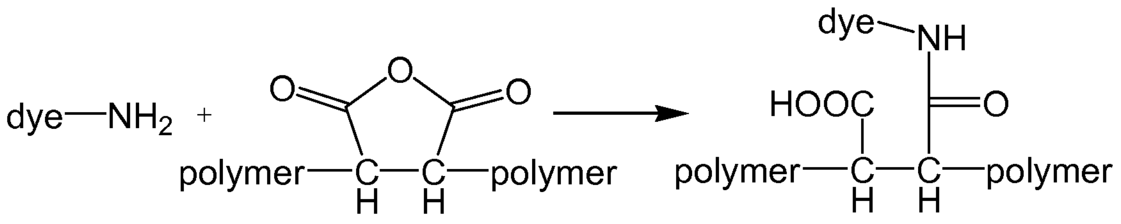
Reaction (a)



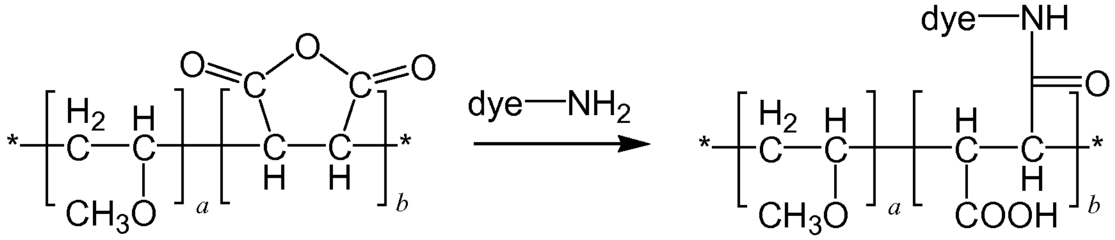
$$\text{dye}{-}NH_2 + RO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\text{polymer} \longrightarrow \text{dye}{-}\overset{H}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\text{polymer}$$

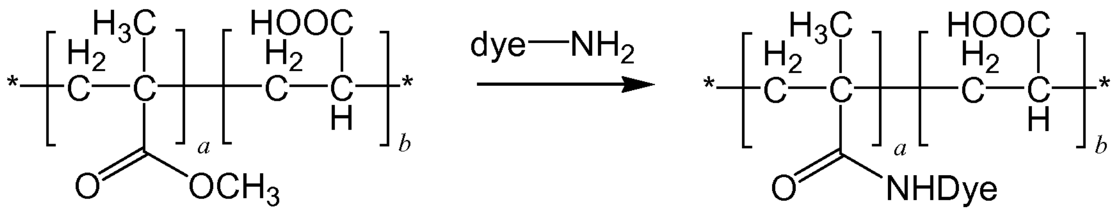
Where R is H, alkyl, aryl or selected so that the COOR group forms an anhydride.

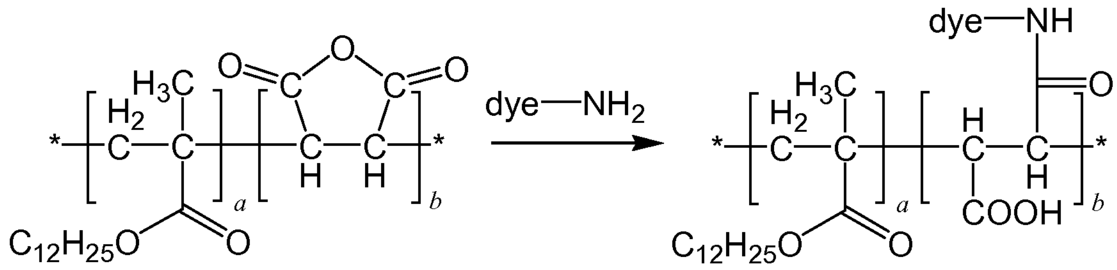
Most preferably the reaction is of the form:

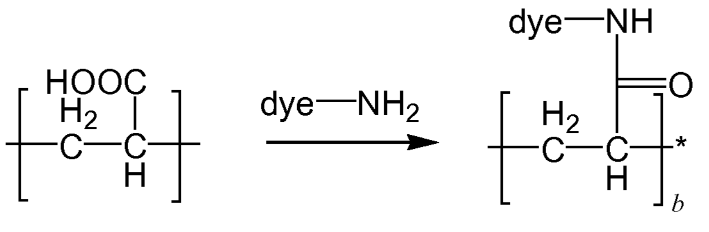


Non-limiting examples of polymers formed by such reactions are:





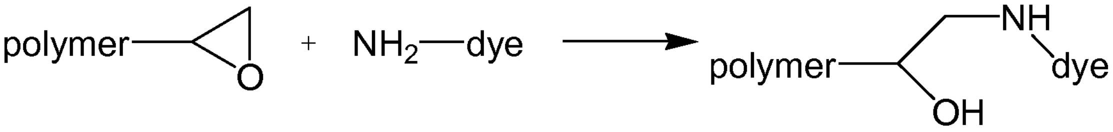




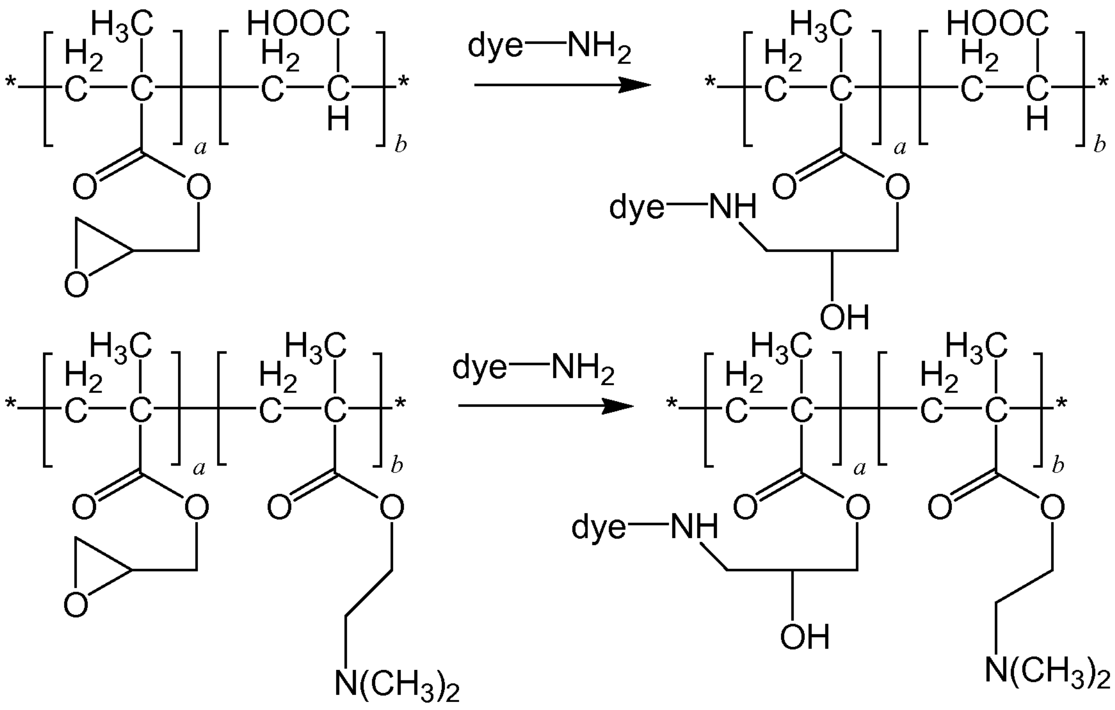
Catalysts may be used to accelerate the reactions.

Such reactions are discussed in Macromolecules 1994, 27, 7121-7126.

Reaction (b)



Non-limiting Examples of polymers formed by such reactions:



Dye description

Dyes are described in Industrial Dyes (K.Hunger ed, Wiley VCH 2003). Many dyes are listed in the colour index (Society of Dyers and Colourists and American Association of Textile Chemists and Colorists).

The dye having a primary amine may be any colour but the dye is preferably blue or violet. Preferably, the polymer is reacted with the same dye moiety. In another aspect different types of dye moieties may be reacted with the polymer, for example blue and red dyes may be reacted with the polymer to provide a good shade whilst minimising dullness. To minimise dullness whilst providing a good shade the weight ratio of the blue dye: the red dye is from 10:1 to 10:4, preferably 10:1 to 10:2.

The dye does not contain reactive groups or polymerisable double bonds. A dye containing a reactive groups is made up of a chromophore which is linked to a reactive group that undergoes addition or substitution reactions with –OH, -SH and $-NH_2$ groups to form covalent bonds. Reactive dyes are described in Industrial Dyes (K.Hunger ed, Wiley VCH 2003). Many Reactive dyes are listed in the colour index (Society of Dyers and Colourists and American Association of Textile Chemists and Colorists). Reactive groups are, for example, dichlorotriazinyl, difluorochloropyrimidine, monofluorotrazinyl, dichloroquinoxaline, vinylsulfone, difluorotriazine, monochlorotriazinyl, bromoacrlyamide and trichloropyrimidine.

Dyes are organic molecules that have an absorption coefficient of greater than 4000, preferably greater than 10 000 mol^{-1} L cm^{-1} at any wavelength in the range 400-700nm, preferably 540 to 640nm. Molar absorption coefficients are preferably measured in an organic solvent, preferably propan-2-ol, using a 1, 5 or 10 cm cell.

Anionic and neutral dyes are preferred. The dye is anionic and neutral in aqueous solution at a pH in the range from 4 to 10. The dyes are most preferably anionic.

The dye is preferably selected from organic dyes selected from the following chromophore classes: anthraquinone, azo, oxazine, azine, triphenodioxazine, triphenyl methane, xanthene and phthalocyanin, more preferably azo, anthraquinone and azine chromophore classes, most preferably azo and anthraquinone. The dye of preference is an anthraquinone. The dye must contain an NH_2 group which is covalently bound to an aromatic ring of the dye.

Preferably the dye polymer is blue or violet. Preferably the dye polymer gives a blue or violet colour to the cloth with a hue angle of 240 to 345, more preferably 265 to 330, most preferably 270 to 300. The cloth used to determine the hue angle is white bleached non-mercerised woven cotton sheeting.

Preferred dyes containing $-NH_2$ groups for such reactions are selected from: acid violet 1; acid violet 3; acid violet 6; acid violet 11; acid violet 13; acid violet 14; acid violet 19; acid violet 20; acid violet 36; acid violet 36:1; acid violet 41; acid violet 42; acid violet 43; acid violet 50; acid violet 51; acid violet 63; acid violet 48; acid blue 25; acid blue 40; acid blue 40:1; acid blue 41; acid blue 45; acid blue 47; acid blue 49; acid blue 51; acid blue 53; acid blue 56; acid blue 61; acid blue 61:1; acid blue 62; acid blue 69; acid blue 78; acid blue 81:1; acid blue 92; acid blue 96; acid blue 108; acid blue 111; acid blue

215; acid blue 230; acid blue 277; acid blue 344; acid blue 117; acid blue 124; acid blue 129; acid blue 129:1; acid blue 138; acid blue 145; direct violet 99; direct violet 5; direct violet 72; direct violet 16; direct violet 78; direct violet 77; direct violet 83; food black 2; direct blue 33; direct blue 41; direct blue 22; direct blue 71; direct blue 72; direct blue 74; direct blue 75; direct blue 82; direct blue 96; direct blue 110; direct blue 111; direct blue 120; direct blue 120:1; direct blue 121; direct blue 122; direct blue 123; direct blue 124; direct blue 126; direct blue 127; direct blue 128; direct blue 129; direct blue 130; direct blue 132; direct blue 133; direct blue 135; direct blue 138; direct blue 140; direct blue 145; direct blue 148; direct blue 149; direct blue 159; direct blue 162; direct blue 163; food black 2; food black 1 wherein the acid amide group is replaced by NH_2; Basic Violet 2; Basic Violet 5; Basic Violet 12; Basic Violet 14; Basic Violet 8; Basic Blue 12; Basic Blue 16; Basic Blue 17; Basic Blue 47; Basic Blue 99; disperse blue 1; disperse blue 5; disperse blue 6; disperse blue 9; disperse blue 11; disperse blue 19; disperse blue 20; disperse blue 28; disperse blue 40; disperse blue 56; disperse blue 60; disperse blue 81; disperse blue 83; disperse blue 87; disperse blue 104; disperse blue 118; disperse violet 1; disperse violet 4, disperse violet 8, disperse violet 17, disperse violet 26; disperse violet 28; solvent violet 26; solvent blue 12; solvent blue 13; solvent blue 18; solvent blue 68; and, solvent blue 76.

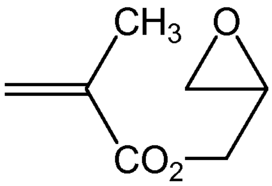
Further preferred dyes are selected from mono-azo dyes which contain a phenyl group directly attached to the azo group, wherein the phenyl group has an NH_2 groups covalent bound to it.

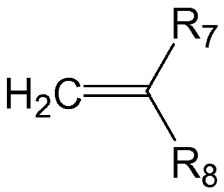
Examples of suitable dyes of other colours are acid red 33, acid red 30, acid red 34, acid yellow, acid green 20, acid green 33, acid brown 4, acid brown 9.

POLYMER DESCRIPTION

The polymer is an organic polymer which is colourless, that is to say when the polymer is dissolved in an organic solvent it has a maximum molar absorption extinction coefficient of less than 100 mol^{-1} L cm^{-1} in the range 400 to 700nm, preferably less than 10 mol^{-1} L cm^{-1}.

Suitable polymers may be formed by polymerisation reaction of a monomer containing a reactive group, with further co-monomers. The co-monomer does not contain primary amines.

Preferably the polymer is obtained by polymerisation of maleic anhydride or  and a comonomer of the form:



wherein R_7 and R_8 are organic groups independently selected from: H; C1-C8alkyl; OC1-C8alkyl; C(O)OH; CO_2C1-C18alkyl; CO_2C1-C4N(C1-C4alkyl)$_2$; -C(O)N(C1-C18alkyl)2; -C(O)N(C1-C18alkyl)H; -C(O)NH2; heteroaromatic; phenyl; benzyl; polyether; pyrrolidone; imidazole; cyano; Cl and F. Preferably, R_7 is selected from; H and CH3 and R_8 is selected from: –OMe and OEt.

Where C1-C18 is specified a preferred range is C1 to C4.

Further examples of co-polymer formed by polymerisation of a reactive monomer with acrylates; methacrylates; mixtures of ethyl acrylate, methyl methacrylate and methacrylic acid ; mixtures of vinylpyrrolidone with long-chain olefins; mixtures of vinylpyrrolidone and dimethylaminoethyl methacrylates; mixtures of vinylpyrrolidone and aminopropyl methacrylamides; mixtures of vinyl- pyrrolidone/aminopropyl; mixtures of vinylpyrrolidones and quaternised aminoethyl methacrylates; mixtures of vinylcaprolactam/vinyl-pyrrolidone/aminoethyl methacrylates; mixtured ofcaprolactam/vinyl- pyrrolidone/aminoethyl methacrylates; mixtures of styrene and acrylic acid; acrylic acids; mixtures of, co-maleic acid with unsaturated hydrocarbons; mixtures of maleic acid, vinylpyrrolidone, vinylimidazole and/or hydrophobic monomer; mixtures of vinylpyrrolidone with vinyl acetate; mixtures of maleic/acrylic acid copolymers; mixtures of lauryl methacrylate/acrylic acid copolymers; further mixtures of the above mentioned monomers.

DYE POLYMER

Preferably, the dye polymer is blue or violet in colour. Preferably the dye polymer gives a blue or violet colour to the cloth with a hue angle of 240 to 345, more preferably 265 to 330, most preferably 270 to 300. The cloth used to determine the hue angle is white bleached non-mercerised woven cotton sheeting.

Preferably the polymer contains 0.1 to 30 Molar% dye, more preferably 1 to 15 Molar% dye monomers units, most preferably 2 to 10 Molar%.

The monomers within the polymer may be arranged in any suitable manner. For example as Alternating copolymers possess regularly alternating monomer residues; Periodic copolymers have monomer residue types arranged in a repeating sequence; Random copolymers have a random sequence of monomer residue types; Statistical copolymers have monomer residues arranged according to a known statistical rule; Block copolymers have two or more homopolymer subunits linked by covalent bonds. Most preferably the polymer is a random copolymer. The polymer should have a molecular weight 2000 and greater. Preferred ranges are from 2000 to 8000000, more preferred ranges are from 2000 to 5000000, most preferably 20000 to 3000000. In this context the molecular weight is the number average molecular weight. This is the ordinary arithmetic mean of the molecular weights of the individual macromolecules. It is determined by measuring the molecular weight of j polymer molecules, summing the weights, and dividing by *j*. Molecular weights are determined by Gel Permeations Chromatography.

SURFACTANT

The laundry composition comprises between 2 to 70 wt percent of a surfactant, most preferably 10 to 30 wt %. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. Preferably the surfactants used are saturated.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C_6 to C_{22} alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C_{11} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C_{16} to C_{18} primary alcohol sulphate together with a C_{12} to C_{15} primary alcohol 3 to 7 EO ethoxylate.

The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt % of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40 wt % of the surfactant system.

In another aspect which is also preferred the surfactant may be a cationic such that the formulation is a fabric conditioner.

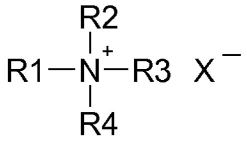
CATIONIC COMPOUND

When the present invention is used as a fabric conditioner it needs to contain a cationic compound.

Most preferred are quaternary ammonium compounds.

It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C_{12} to C_{22} alkyl chain.

It is preferred if the quaternary ammonium compound has the following formula:



$$R1-\overset{\overset{\textstyle R2}{|}}{\underset{\underset{\textstyle R4}{|}}{N^{+}}}-R3 \quad X^{-}$$

in which R^1 is a C_{12} to C_{22} alkyl or alkenyl chain; R^2, R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl quaternary ammonium bromide.

A second class of materials for use with the present invention are the quaternary ammonium of the above structure in which R^1 and R^2 are independently selected from C_{12} to C_{22} alkyl or alkenyl chain; R^3 and R^4 are independently selected from C_1 to C_4 alkyl chains and X^- is a compatible anion.

A detergent composition according to claim 1 in which the ratio of (ii) cationic material to (iv) anionic surfactant is at least 2:1.

Other suitable quaternary ammonium compounds are disclosed in EP 0 239 910 (Proctor and Gamble).

It is preferred if the ratio of cationic to nonionic surfactant is from 1:100 to 50:50, more preferably 1:50 to 20:50.

The cationic compound may be present from 1.5 wt % to 50 wt % of the total weight of the composition. Preferably the cationic compound may be present from 2 wt % to 25 wt %, a more preferred composition range is from 5 wt % to 20 wt %.

The softening material is preferably present in an amount of from 2 to 60% by weight of the total composition, more preferably from 2 to 40%, most preferably from 3 to 30% by weight.

The composition optionally comprises a silicone.

BUILDERS OR COMPLEXING AGENTS

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

The composition may also contain 0-65 % of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate) are preferred builders.

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15%w. Aluminosilicates are materials having the general formula:

$$0.8\text{-}1.5\ M_2O.\ \ Al_2O_3.\ \ 0.8\text{-}6\ \ SiO_2$$

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to alumuminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

Preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt% of phosphate. Preferably the laundry detergent formulation is carbonate built.

FLUORESCENT AGENT

The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. 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 0.1 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 and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[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-sulfostyryl)biphenyl.

It is preferred that the aqueous solution used in the method has a fluorescer present. When a fluorescer is present in the aqueous solution used in the method it is preferably in the range from 0.0001 g/l to 0.1 g/l, preferably 0.001 to 0.02 g/l.

PERFUME

Preferably the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, most preferably 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

Perfume and top note may be used to cue the whiteness benefit of the invention.

It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

OTHER POLYMERS

The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Polymers present to prevent dye deposition, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole), are preferably absent from the formulation.

ENZYMES

One or more enzymes are preferred present in a composition of the invention and when practicing a method of the invention.

Preferrably the level of each enzyme is from 0.0001 wt% to 0.1 wt% protein.

Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a

Pseudomonas lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens*, *Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202, WO 00/60063.

Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ (Novozymes A/S).

The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids. Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A_1 and A_2 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

The enzyme and the shading dye may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme or shading dye and/or other segregation within the product.

Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

The method of the invention may be carried out in the presence of cutinase (classified in EC 3.1.1.74). The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a special strain of *B. licheniformis*, described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila,* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

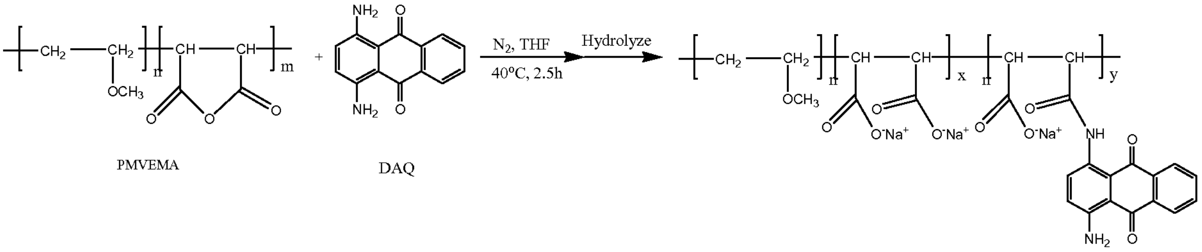
ENZYME STABILIZERS

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as 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 such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.
The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise.

Example 1 Post-polymerisation modification

Reaction scheme:



1,4-Diaminoanthraquinone (DAQ) (90% technical grade) and Poly (methyl vinyl ether-alt-maleic anhydride) (PMVEMA, CAS: 9011-16-9, Mn=80000, Mw=210000) were obtained from Aldrich and used as received. 2.044g of PMVEMA (0.013 mol maleic anhydride) and 40ml dry THF was charged into a 100ml threenecked round bottle equipped with a condenser and a magnetic stirring bar. The mixture was purged with N_2 stream and stirred at 40°C for 15min. Then 0.284g DAQ (0.0012 mol) dissolved in 20 ml THF was added slowly into the reactor and the reaction carried out at 65°C for 8 hours. Cooled reaction mixture was poured into 500mL petroleum ether for precipitation. The resultant polymer was further washed by $CHCl_3$ for three times to remove the non-reacted dyes and vacuum dried at r.t. over night thereafter. Finally, the resultant polymer containing non-reacted maleic anhydride underwent hydrolyzation treatment producing carbonic acid groups of moderate acidity.

The synthesis was repeated with different amounts of DAQ to give polymers with varying levels of dye substitution.

Example 2 UV-VIS of dye polymers

The UV-Vis spectra of the dye polymers of example 2 were recorded in demineralised water at 1g/L dye polymer. The UV-Vis spectra of the dye polymers of example 3 were recorded in demineralised water at 1g/L dye polymer and containing 1g/L of linear alky benzene sulphonate surfactant (LAS). The results are given in the tables below and an identifying code given to each polymer.

Nominal inclusion level of DAQ	Code	λmax in range 400-700nm	Absorbance (1cm) @ λmax for 1g/L in water
0.64	P1	540	0.16
2.4	P2	540	0.45
4.8	P3	540	1.12
9.6	P4	540	1.34

Example 3 wash deposition

Knitted white polyester (microfiber), knitted nylon-elastane (80:20) and white woven non-mercerised cotton fabrics were used together in 4g/L of a detergent which contained 15% Linear Alkyl benzene sulfonate (LAS) surfactant, 30% Na_2CO_3, 40% NaCl, remainder minors included calcite and fluorescer and moisture. Washes were conducted in 6° French Hard water at room temperature with a liquor to cloth ratio of 30:1, for 30 minutes. This was then repeated once more to accomplish 2 washes in total. Following the washes the cloths were rinsed twice in water, dried, their reflectance spectrum measured on a reflectometer and the colour expressed as CIE L* a* b* values (UV-excluded).

The experiment was repeated with the addition of the dye polymers of example 2. The polymers were added to give 5ppm in the wash solution. The deposition of the dye-polymers to the fabrics was expressed as the Δb value such that

Δb = b(control) -b(dye polymer)

+ve values indicate a blueing of the fabric, due to dye-polymer deposition.

Dye-polymer	Δb 4th wash	
	Cotton	Nylon elastane
P2	0.4	2.9
P4	0.5	5.0

The dye-polymers deposit to nylon-elastane and cotton fabrics.

An added advantage is that the dye-polymer also facilitates soil removal and alter fabric feel.

<u>Example 4 soil removal</u>

Knitted white polyester (microfiber), white woven non-mercerised cotton fabrics and a sebum stain monitor [WFK 10 D (Cotton). (Supplied by WFK-Testgewebe GmbH, Adlerstr. 42, D-4150)] were washed together in 4g/L of a detergent which contained 15% Linear Alkyl benzene sulfonate (LAS) surfactant, 30% Na_2CO_3, 40% NaCl, remainder minors included calcite and fluorescer and moisture. Washes were conducted in 6° French Hard water at room temperature with a liquor to cloth ratio of 30:1, for 30 minutes. Following the washes the cloths were rinsed twice in water, dried, their reflectance spectrum measured on a reflectometer (UV-excluded).

The experiment was repeated with the addition of 1ppm in the wash solution of dye polymer P4 of example 3.

The soil removal on the WFK10D cloth was measured as the change in %Reflectance at 460nm before and after washing: $\Delta R_{460} = R_{460}$(after wash) - R_{460}(before wash).

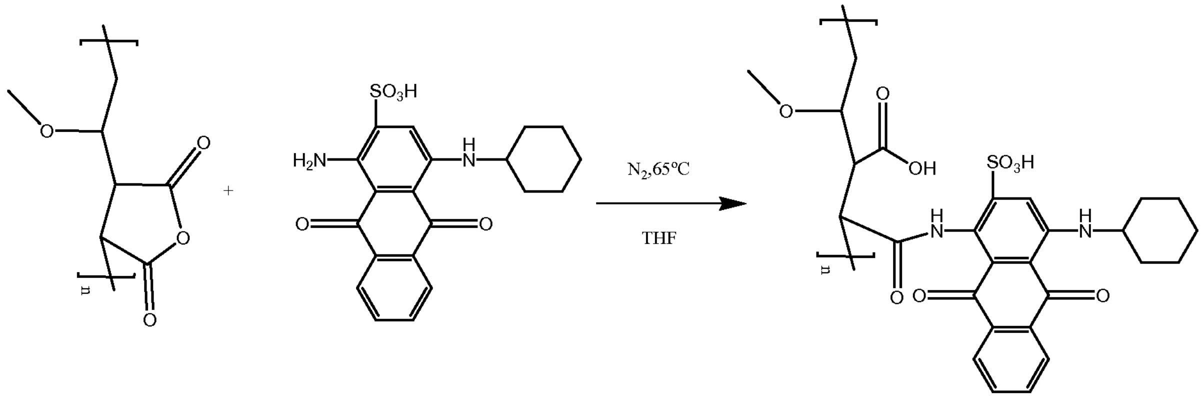
The experiments were repeated 4 times and the average values of ΔR_{460} calculated. The results were

ΔR_{460} (control) = 5.1
ΔR_{460} (P4) = 6.2

The dye polymer p4 increases the soil removal.

Example 5 post-polymer modified dye polymers with anionic dye.

The reaction of example 1 was repeated using the anionic charged dye Acid Blue 62 (AB62).



1g of the polymer was mixed with 0.1g of the dye in 50ml of tetrahydrofuran and heated at 65°C for 8 hours. The resultant dye polymer was precipitate in petroleum ether and dried in a vacuum. The reaction was conducted twice with polymers of initial molecular weights (Mw) of 200,000 and 2,000,000 and the resultant dye polymers coded P5 and P6. Polymers were obtained from ISP (Gantrez™ AN 119 and An169, respectively).

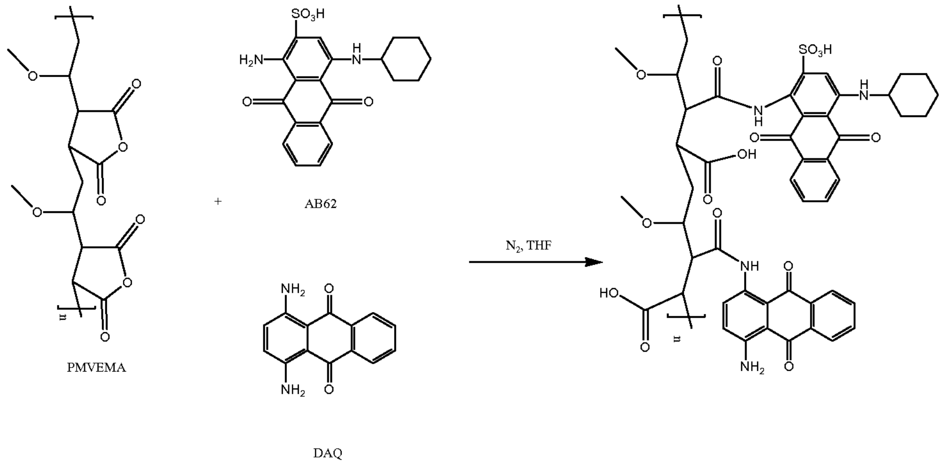
The resultant dye polymers were blue in colour.

The wash experiment of example 3 was repeated with the current dye polymers.

Dye-polymer	Δb 4th wash	
	Cotton	Nylon elastane
P5	1.0	2.4
P6	0.9	2.6

Example 6 post-polymer modified dye polymers with both anionic and uncharged dyes.

The reaction of example 5 was repeated using AB62 and DAQ.



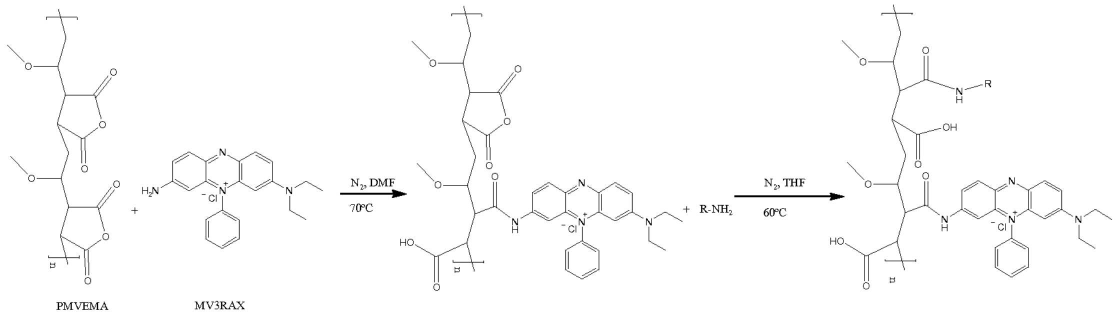
1g of the polymer (PMVEMA, CAS: 9011-16-9, Mn=80000, Mw=210000) was mixed with 0.069g acid blue 62 and 0.030 g DAQ of the dye in 50ml of tetrahydrofuran and heated at 65°C for 8 hours. The resultant dye polymer was precipitate in petroleum ether and dried in a vacuum. The resultant dye polymer was coded P7.

The wash experiment of example 3 was repeated with P7.

Dye-polymer	Δb 4th wash	
	Cotton	Nylon elastane
P7	1.1	4.4

Example 7 post-polymer modified dye polymers with cationic dye.

The reaction of example 5 was repeated using the cationic azine dye MV3RAX. The dye polymers were prepared, for two a further reaction step was included, which involved binding an alkylamine to anhydride groups in a manner analogous to the dye.



1g of the polymer (PMVEMA, CAS: 9011-16-9, Mn=80000, Mw=210000) was mixed with 0.05g MV3RAX dye in 15ml of dimethylformamide and heated at 70°C for 6 hours. The resultant dye polymer was precipitate in petroleum ether, hydrolyzed in water at 50°C and dried in a vacuum. The resultant dye polymers was coded P8.

Two further dye polymers were synthesised. Here, instead of hydrolyzing in water the dye polymer was dissolved in tetrahdyofuran and heated with 0.038g of $C_8H_{17}NH_2$ or 0.055g of $C_{12}H_{25}NH_2$ for 12 hours at 60°C. The resultant dye polymer was precipitate in petroleum ether, hydrolyzed in water at 50°C and dried in a vacuum. The polymers were coded P9 and P10 respectively.

The wash experiment of example 3 was repeated with P8, P9 and P10.

Dye-polymer	Δb 2nd wash Cotton
P8	0.5
P9	0.3
P10	0.3

We claim:

1. A method for obtaining a dye-polymer, the method comprising the step of reacting a polymer with a primary amine of a dye to form the dye-polymer, wherein the polymer has a group for reacting with the primary amine, the group selected from: isocyanate; oxazolone; epoxide; ester, and anhydride.

2. A method according to claim 1, wherein the group for reacting with the primary amine selected from: epoxide; and, anhydride.

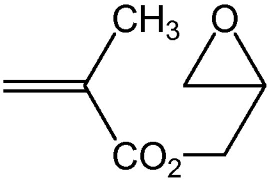
3. A method according to claim 2, wherein the group for reacting with the primary amine is anhydride.

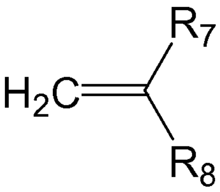
4. A method according to claim 1, 2 or 3, wherein the dye is selected from: anthraquinone, azo, oxazine, azine, triphenodioxazine, triphenyl methane, xanthene and phthalocyanin.

5. A method according to claim 3, wherein the dye is selected from: anthraquinone; azine; and azo,

6. A method according to claim 5, wherein the dye is selected from: anthraquinone; and azo.

7. A method according to claim 6, wherein the dye is anthraquinone.

8. A method according to any one of claims 2 to 7, wherein the polymer is obtained by polymerisation of maleic anhydride or  and a comonomer of the form:



wherein R_7 and R_8 are organic groups independently selected from: H; C1-C8alkyl; OC1-C8alkyl; C(O)OH; CO_2C1-C18alkyl; CO_2C1-C4N(C1-C4alkyl)$_2$; -C(O)N(C1-C18alkyl)2; -C(O)N(C1-C18alkyl)H; -C(O)NH2; heteroaromatic; phenyl; benzyl; polyether; pyrrolidone; imidazole; cyano; Cl and F.

9. A method according to claim 8, wherein R_7 is selected from; H and CH3 and R_8 is selected from: -OMe and OEt.

10. A method according to any preceding claim 1 to 9, wherein the dye is selected from: acid violet 1; acid violet 3; acid violet 6; acid violet 11; acid violet 13; acid violet 14; acid violet 19; acid violet 20; acid violet 36; acid violet 36:1; acid violet 41; acid violet 42; acid violet 43; acid violet 50; acid violet 51; acid violet 63; acid violet 48; acid blue 25; acid blue 40; acid blue 40:1; acid blue 41; acid blue 45; acid blue 47; acid blue 49; acid blue 51; acid blue 53; acid blue 56; acid blue 61; acid blue 61:1; acid blue 62; acid blue 69; acid blue 78; acid blue 81:1; acid blue 92; acid blue 96; acid blue

108; acid blue 111; acid blue 215; acid blue 230; acid blue 277; acid blue 344; acid blue 117; acid blue 124; acid blue 129; acid blue 129:1; acid blue 138; acid blue 145; direct violet 99; direct violet 5; direct violet 72; direct violet 16; direct violet 78; direct violet 77; direct violet 83; food black 2; direct blue 33; direct blue 41; direct blue 22; direct blue 71; direct blue 72; direct blue 74; direct blue 75; direct blue 82; direct blue 96; direct blue 110; direct blue 111; direct blue 120; direct blue 120:1; direct blue 121; direct blue 122; direct blue 123; direct blue 124; direct blue 126; direct blue 127; direct blue 128; direct blue 129; direct blue 130; direct blue 132; direct blue 133; direct blue 135; direct blue 138; direct blue 140; direct blue 145; direct blue 148; direct blue 149; direct blue 159; direct blue 162; direct blue 163; food black 2; food black 1 wherein the acid amide group is replaced by NH_2; Basic Violet 2; Basic Violet 5; Basic Violet 12; Basic Violet 14; Basic Violet 8; Basic Blue 12; Basic Blue 16; Basic Blue 17; Basic Blue 47; Basic Blue 99; disperse blue 1; disperse blue 5; disperse blue 6; disperse blue 9; disperse blue 11; disperse blue 19; disperse blue 20; disperse blue 28; disperse blue 40; disperse blue 56; disperse blue 60; disperse blue 81; disperse blue 83; disperse blue 87; disperse blue 104; disperse blue 118; disperse violet 1; disperse violet 4, disperse violet 8, disperse violet 17, disperse violet 26; disperse violet 28; solvent violet 26; solvent blue 12; solvent blue 13; solvent blue 18; solvent blue 68; and, solvent blue 76.

11. A dye-polymer obtainable from the method as defined in any preceding claim.

12. A laundry treatment composition comprising:
(i) from 2 to 70 wt% of a surfactant; and,
(ii) from 0.0001 to 20.0 wt% of the dye-polymer as defined in anyone of claims 1 to 10.

13. A method of treating a laundry textile, the method comprising the steps of:

(i) treating a textile with an aqueous solution of the dye-polymer as defined in anyone of claims 1 to 10, the aqueous solution comprising from 10 ppb to 100 ppm of the dye-polymer (preferably 0.1 to 5ppm, most preferably 0.5 to 2ppm); and, from 0.0 g/L to 3 g/L, preferably 0.3 to 2 g/L, of a surfactant;

(ii) optionally rinsing; and,

(iii) drying the textile.