

(19)



(11)

EP 3 421 583 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

02.01.2019 Bulletin 2019/01

(51) Int Cl.:

C11D 3/00 (2006.01)

C11D 3/37 (2006.01)

C11D 11/00 (2006.01)

(21) Application number: **17177768.3**

(22) Date of filing: **26.06.2017**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

MA MD

(71) Applicant: **BASF SE**

67056 Ludwigshafen am Rhein (DE)

(72) Inventors:

- **Lee, Yungi**
106-6121, Tokyo (JP)
- **Lamprou, Alexandros**
200137 Shanghai (CN)
- **Tran-Thien, Hoang Trang**
33098 Paderborn (DE)

(74) Representative: **BASF IP Association**

BASF SE

G-FLP-C006

67056 Ludwigshafen (DE)

(54) **USE OF CATIONIC VINYL CARBOXAMIDE/VINYLAMINE COPOLYMERS AS A COLOR CARE AGENT FOR LAUNDERING FORMULATIONS**

(57) The use of a cationic vinylcarboxamide/vinylamine copolymer as a color care agent for laundering, to liquid laundering formulations comprising such cationic vinylcarbox-amide/vinylamine copolymer as a color care agent and to a method for preparing them.

EP 3 421 583 A1

Description**Technical Field**

[0001] The present invention relates to use of at least one cationic vinylcarboxamide/vinylamine copolymer as a color care agent for laundering, especially as a dye transfer inhibitor (DTI) and/or a dye fixation agent (DFA), to a method for preparation of liquid laundering formulations by incorporation of the at least one cationic vinylcarboxamide/vinylamine copolymer as a color care agent, and thus to liquid laundering formulations comprising at least one cationic vinylcarboxamide/vinylamine copolymer.

Background

[0002] Liquid detergent compositions contribute more and more proportionately to the portfolio of washing compositions for textiles today. Liquid washing compositions comprise surfactants as a main component, including cationic, anionic, nonionic and amphoteric surfactants. Further essential components used in liquid washing compositions are builders selected from for example polycarboxylates, and solubilizers selected from for example ethanol, glycerol or propanediol. In general, additional additive components are also comprised, typically in small concentrations, including different active substances such as foam regulators, graying inhibitors, soil release polymers, enzymes, optical brighteners and color care agents, such as dye transfer inhibitors and dye fixation agents. During washing process, dye molecules are often detached from colored textiles, often called as "bleeding"; these can in turn attach to other textiles, often called as "dye transferring". In order to counteract these undesired bleeding and dye transferring, color care agents such as dye transfer inhibitors (DTI) and dye fixation agents (DFA) are often used. Dye transfer inhibitors and dye fixation agents have long been an important constituent of textile laundry detergents and cleaners of state of the art.

Different polymers have been proposed as dye fixation agents, as dye transfer inhibitors or for similar purposes, for example, in US 2007/0277327A1, US 2008/0103081A1, US 2008/0318830A1, US 2008/0103080A1, US 2009/0048137A1, US 2008/0096788A1, US 2002/0193280A1, US 2003/0171249A1, US 2010/0017973 A1, DE 4235798A1, DE 19621509A1, WO 98/30664A1, WO 2006/100246A1, EP 0753566A1, and JP H07316590A.

[0003] US 2007/0277327A1 describes detergents and cleaning agents that contain a soil-release polymer and a dye fixative selected from (a) reaction products of polyamines and cyanamides and organic and/or inorganic acids, or cyanamides and aldehydes and ammonium salts, or cyanamides and aldehydes and amines, or amines and epichlorohydrin, (b) the group containing polyamines and polyamine derivatives, (c) the group containing polyimines and polyimine derivatives, (d) the group of cationic polyelectrolytes, (e) the group containing polymers that comprise imidazoline units or (f) the group containing bis(chloromethyl)biphenyl polyquat.

[0004] US 2008/0103081A1 describes a liquid washing and cleaning composition comprising a) an anionic surfactant and d) a dye fixative selected from the group consisting of a homo- or a copolymer of diallyldimethylammonium chloride, a reaction product of cyanamides with aldehydes and ammonium salts, a reaction product of cyanamides with aldehydes and monoamines, a reaction product of monoamines and/or polyamines with epichlorohydrin, a reaction product of polyamines with cyanamides and amidosulfuric acid, and mixtures thereof. The same dye fixative species were also proposed to be used in liquid washing and cleaning compositions in US 2008/0318830A1, US 2008/0103080A1, US 2009/0048137A1 and US 2008/0096788A1.

[0005] US 2002/0193280A1 describes a laundry detergent comprising dye-transfer-inhibiting dye fixatives which are obtained by reacting a) amines with epichlorohydrin or b) cyanamide with amines and formaldehyde.

[0006] US 2003/0171249A1 describes a laundry detergent comprising dye-transfer-inhibiting dye fixatives which are obtained by reacting a) polyamines with cyanamides and amidosulfuric acid or b) cyanamides with aldehydes and ammonium salts or c) amines with epichlorohydrin.

[0007] US 2010/0017973A1 describes use of hydrophobically modified polyalkylenimines as dye transfer inhibitors.

[0008] DE 4235798A1 describes copolymers of 1-vinylpyrrolidone, 1-vinylimidazole, 1-vinylimidazolium compounds or mixtures thereof; further nitrogen-containing, basic ethylenically unsaturated monomers; and, if appropriate, other monoethylenically unsaturated monomers, and their use for inhibiting dye transfer during the washing process. Similar copolymers are described for this purpose in DE 19621509A1 and WO 98/30664A1.

[0009] WO 2006/100246A1 describes use of cationic polycondensation products as additives for fixing colours and/or inhibiting the running of colours, for washing products and washing aftertreatment products. The cationic polycondensation products can be produced by the condensation of (A1) non-cyclic amines obtained by the reaction of (A1a) mono(N,N-dialkylaminoalkyl)amines with (A1b) bifunctional compounds selected from the group containing urea, thiourea, dialkyl carbonates, aliphatic and aromatic dicarboxylic acids, and aliphatic and aromatic diisocyanates, in a molar ratio 1.2: 1 to 2.1: 1, or (A2) mixtures of non-cyclic amines (A1) and cyclic amines (A3) in a molar ratio 10: 1 to 1: 10 with (B) bifunctional compounds selected from the group containing alkylene di-halogenides, dihalogen alkyl ethers, halomethyl oxiranes, and bisepoxides, in a molar ratio (B) to (A1) or (B) to (A2) from 0.6: 1 to 1.3: 1.

[0010] EP 0753566A1 describes a fabric washing composition for inhibiting dye deposition, which comprises a dye deposition inhibiting polymer comprising vinyl amide monomer(s) and optionally vinyl ester monomer(s), acrylamide monomer(s) and ethylenically unsaturated monomer(s).

[0011] JP H07316590A describes a composition containing a water-soluble polymer comprising a (co)polymer of a specific amino group-containing monomer, effective for washing colored clothes and white clothes in the same bath, not requiring to select the kind of a surfactant, and not causing the problem of iron adsorption.

[0012] Use of certain cationic nitrogen-containing polymers in liquid washing compositions for color care purpose is typically accompanied by a problem resulted from poor compatibility of the cationic nitrogen-containing polymers with anionic surfactants comprised in the liquid washing compositions, which leads to flocculation, precipitation or phase separation in the liquid washing compositions. On the other hand, anionic surfactants, such as linear alkylbenzenesulfonates (LAS), fatty alcohol sulfates (FAS), secondary alkanesulfonates (SAS) and in some cases also fatty alcohol ether sulfates (FAES), are basically indispensable in washing compositions due to their almost unique good washing performances.

[0013] There is always a need to provide a color care agent in liquid washing composition formulations for textiles, which shows good color care efficacy through dye fixation and/or dye transfer inhibition properties and is also further compatible with anionic surfactants.

[0014] Cationic vinylcarboxamide/vinylamine copolymers as described in the present application have never been proposed as a color care agent, especially as a dye transfer inhibitor (DTI) or a dye fixation agent (DFA), for a liquid laundry detergent formulation. On several occasions, uses of copolymers of vinylcarboxamide and vinylamine or similar polymers for other purposes have been described.

[0015] WO 2005/026220A1 describes use of polymers containing polyvinylamine and polyvinylamide in order to prevent smell in dishwashers.

[0016] WO 1998/025981A1 describes a new amphiphilic graft polymer based on N-vinyl carboxamide units for use e.g. as paper strengthening agents, dispersants for pigments or plant protectants and thickeners in cosmetics.

[0017] EP 0753570A1 describes a composition useful in a washing process containing at least one vinyl amide polymer containing from 5 to 100 % by weight of at least one vinyl amide monomer and from 0 to 95 % by weight of one or more vinyl ester monomers. The polymer is taught to be used for purpose of removing soil from an article, inhibiting soil deposition, or providing soil resistance to an article.

[0018] CH 690401A5 describes a process for fixing substantive dyes in textile industry onto cellulose-containing fibre materials comprises treating the fibre material before, during or after dyeing in a liquor containing a homo- or copolymer obtained by polymerisation of N-vinylformamide or N-vinylacetamide and optionally one or more copolymerisable monomers selected from allylamine or diallylamine derivatives, (meth)acrylic acid, maleic acid, N-vinylpyrrolidone, N-vinyl-N-methyl-formamide, N-vinyl-N-methylacetamide, N-vinyl-N-ethyl-acetamide, vinyl acetate, vinyl propionate, hydroxy-C₂-C₄-alkyl(meth)acrylate, (meth)acrylic acid-C₁-C₂₂-alkyl ester, (meth)acrylonitrile, (meth)acrylamide, N-mono/N,N-di-C₁-C₁₀-alkyl-(meth)acrylamide and N,N-di-C₁-C₂-alkylamino-C₂-C₄-alkyl-(meth)acrylate and subsequent hydrolysis of the (co)polymer. Similarly, US 6039768A describes a process for fixing reactive or substantive dyes on cellulosic fiber materials. The process comprises treating the fiber before, during or after dyeing with a solution of homo- or copolymers of nitrogen-containing monomers, e.g. N-vinylformamide, N-vinylimidazole, N-vinylpyrrolidone and the like.

[0019] WO 97/032477A1 describes use of polymers containing vinylamine or ethyleneimine units and optionally units from other monomers, for example N-vinyl carboxamides as biocides.

[0020] WO 95/025759A1 describes graft polymers in which monoethylenically unsaturated monomers are grafted onto the grafting base which is a polymer which contains N-vinylcarboxamides and N-vinylamines and the grafting base and use of the graft polymers as dispersants for pigments, as additives for detergents and cleaning agents, and strength agents for paper and as soil stabilizers and for fertilizer compaction.

WO 2014/148465A1 describes a cationizing agent for cationizing a cloth prior to the firm fixing of water-insoluble particles onto the cloth, the cationizing agent comprising a polymer derived from vinyl amine monomer.

[0021] WO 95/16815A1 describes a dye fixation agent for cellulosic fibers dyed with reactive dyes, comprising a homopolymer of vinylamine or a copolymer of vinylamine with diallylamine or vinyl compound. The polymers are proposed to be used for treating cellulose fibers dyed with a reactive dye in order to improve chlorine fastness and wet fastness of cellulose fibers dyed with a reactive dye.

[0022] A color care effect of the cationic vinylcarboxamide/vinylamine copolymers as described in the present application during laundering has not yet been described in prior art.

Summary of the Invention

[0023] It is an object of the present invention to provide a color care agent with not only a good dye transfer inhibiting and/or dye fixing effect during laundering, but also a good compatibility with conventional detergent components, especially anionic surfactants, in the case of liquid laundering compositions, resulting in stable formulations.

[0024] The object of the present invention is surprisingly achieved by cationic vinylcarboxamide/vinylamine copolymers which comprise (1a) 30 to 95 mol% of vinylamine derived units, (1b) 5 to 70 mol % of vinylcarboxamide derived units and optionally (1c) 0 to 5mol % of units derived from one or more ethylenically unsaturated monomers, described in detail hereinafter. The cationic vinylcarboxamide/vinylamine copolymers according to the present invention are well compatible with anionic surfactants in a liquid laundering formulation, which formulation is both, physically and chemically, stable at a pH from about pH 4.5 to about pH 11, and especially from about pH 7.0 to about 8.5, more preferably at a neutral pH of about 7, and without deterioration in cleaning or treatment performance of the laundering formulation.

[0025] Accordingly, the present invention relates to use of at least one cationic vinylcarboxamide/vinylamine copolymer according to the present invention as a color care agent, especially as a dye transfer inhibitor (DTI) and/or a dye fixation agent (DFA), in laundering formulations, especially liquid laundering formulations.

[0026] Accordingly, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention also show good compatibility with anionic surfactants, especially LAS surfactants widely used in laundering formulations, which will not result in any deterioration in cleaning or caring performance of the laundering formulations.

[0027] Thus, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention show a color care effect, particularly, a dye (or color) fixing effect and/or a dye transfer inhibiting effect during laundering without any deterioration in cleaning or caring performance of the laundering formulations.

[0028] In the context of the present invention, the dye fixing effect refers to an effect of preventing dyes from fading out of colored textiles during laundering or reducing the amount of the dyes fading out of colored textiles during laundering.

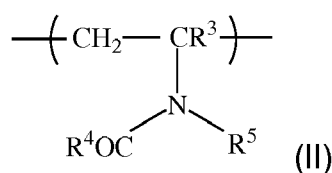
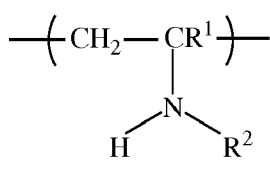
[0029] In the context of the present invention, the dye transfer inhibiting effect refers to an effect of preventing dyes fading out of darker colored textiles from transferring to lighter colored textiles during laundering.

[0030] These and other aspects are achieved according to the present invention by:

The use of at least one cationic vinylcarboxamide/vinylamine copolymer of a number average molecular weight (M_n) of up to 400,000 g/mol as a color care agent in laundering formulations, especially liquid laundering formulations, wherein the cationic vinylcarboxamide/vinylamine copolymer comprises

(1a) 30 to 95 mol% of vinylamine derived units represented by formula (I),

(1 b) 5 to 70 mol % of vinylcarboxamide derived units represented by formula (II),



wherein

R1 and R3, which are identical, each represent H or methyl, preferably H,
R2 and R5, which are identical, each represent H or C1-6 alkyl, preferably H, and
R4 represents H or C₁₋₆ alkyl, preferably H or methyl, and optionally

(1c) 0 to 5 mol % of units derived from one or more ethylenically unsaturated monomers; the sum of units (1a), (1b) and (1c) being 100%,

and provided that

if the M_n is below 25,000 g/mol, the content of unit (1a) is equal to or higher than 40 mol%, and

if the M_n is equal to or above 25,000 g/mol, the content of unit (1a) is equal to or less than 80 mol%.

[0031] Further, the cationic vinylcarboxamide/vinylamine copolymer used for the purpose of the present invention is a hydrolysate of copolymers or homopolymers comprising the vinylcarboxamide derived units represented by formula (II), especially a hydrolysate of homopolymers of N-vinylformamide or N-vinylacetamide.

[0032] Furthermore, the cationic vinylcarboxamide/vinylamine copolymer for the purpose of the present invention is prepared and obtained from a polyvinylformamide (PVF) with a number average molecular weight M_n of from 1,000 to 100,000, preferably from 3,000 to 60,000 and most preferably from 5,000 to 45,000. Preferably it is prepared and obtained from a polyvinylformamide (PVF) with a number average molecular weight M_n of less than 50,000.

[0033] The laundering formulations according to the present invention comprise in addition to the cationic vinylcarboxamide/vinylamine copolymer of the present invention at least one anionic surfactant. Preferably such anionic sur-

factant is selected from linear alkylbenzenesulfonate anionic surfactants. The present invention also comprises methods for preparing such laundering formulations by incorporating such anionic surfactant, especially linear alkylbenzenesulfonate anionic surfactants.

[0034] The laundering formulations according to the present invention show good compatibility anionic surfactants at a pH from about pH 4.0 to about pH 11.0, and especially preferably from about pH 7.0 to about pH 8.5.

[0035] The cationic vinylcarboxamide/vinylamine copolymers for the purpose of the present invention can be applied as dye transfer inhibitor agents in laundering formulations and/or as dye fixation agents in laundering formulations.

[0036] Thus the present invention also relates to methods for preparing laundering formulations, especially liquid laundering formulations, by incorporating at least one cationic vinylcarboxamide/vinylamine copolymer of the present invention as a color care agents, acting as dye transfer inhibitor and/or as dye fixation agent.

Detailed Description of the Invention

[0037] The present invention relates to use of at least one cationic vinylcarboxamide/vinylamine copolymer as a color care agent in laundering formulations, particularly liquid laundering formulations.

[0038] Hereinafter, when the at least one cationic vinylcarboxamide/vinylamine copolymer useful as the color care agent in laundering formulations according to the present invention are to be mentioned, the expression "the cationic vinylcarboxamide/vinylamine copolymer(s) according to the present invention" or "the cationic copolymer(s) according to the present invention" or "the vinylcarboxamide/vinylamine copolymer(s) according to the present invention" or the "cationic vinylcarboxamide/vinylamine copolymer(s)" are used. Furthermore the terms used for the cationic vinylcarboxamide/vinylamine copolymer(s) according to the present invention may be interpreted with the single meaning of one "copolymer" as well as with the plural meaning of more than one "copolymers".

It is to be understood that the cationic vinylcarboxamide/vinylamine copolymer(s) may optionally be at least partly in form of salt with any suitable counterions. Counterions that may be present in the salt are not particularly limited. Suitable counterions are for example, but not limited to, halide anions such as chloride, bromide, iodide anions, as well as polyatomic anions, such as chlorate, chlorite, hypochlorite, sulfate, sulfonate, hydroxide, hydrogen sulfate, hydrogen bisulfate, sulfide, sulfite, phosphate, hydrogen phosphate, dihydrogen phosphate, phosphonate, nitride, nitrite, nitrate, carbonate, hydrogen carbonate, hydrogen bicarbonate, acetate anions.

Embodiments of the invention

[0039] According to an embodiment of the present invention, the cationic vinylcarboxamide/vinylamine copolymers of a number average molecular weight (M_n) of up to 400,000 g/mol useful as a color care agent in laundering formulations comprise

- (1a) 30 to 95 mol% of vinylamine derived units represented by formula (I),
 (1 b) 5 to 70 mol % of vinylcarboxamide derived units represented by formula (II),



wherein

- R1 and R3, which are identical, each represent H or methyl, preferably H,
 R2 and R5, which are identical, each represent H or C1-6 alkyl, preferably H, and
 R4 represents H or C1-6 alkyl, preferably H or methyl, and optionally

- (1c) 0 to 5 mol % of units derived from one or more ethylenically unsaturated monomers, the sum of units (1a), (1b) and (1c) being 100%,

provided that

- if the M_n is below 25,000 g/mol, the content of unit (1a) is equal to or higher than 40 mol%, and
 if the M_n is equal to or above 25,000 g/mol, the content of unit (1a) is equal to or less than 80 mol%.

[0040] It is to be understood, as discussed above, at least part of nitrogen atoms in the units represented by formula

(I) and formula (II) may be in form of ammonium salt with suitable anions which are not shown in the formulae. Suitable counterions are for example, but not limited to, halide anions such as chloride anion, sulfate anion and sulfonate anions.

[0041] In the context of the present invention, the expression "alkyl" comprises straight-chain or branched alkyl groups, in particular C₁-C₆-alkyl. Examples for C₁-C₆-alkyl are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-pentyl, neo-pentyl, n-hexyl, and position isomers thereof.

[0042] As the ethylenically unsaturated co-monomers from which units (1c) are derived, any co-monomers having an ethylenically unsaturated bond can be used. The ethylenically unsaturated co-monomers from which units (1c) are derived may be nitrogenous monomers polymerizable via vinyl or allyl groups, for example N-vinylpyrrolidone, N-vinylimidazole, N-vinylcaprolactam, 4-vinylpyridine, N-vinylpyridine, diallyldimethylammonium chloride, allylamine, (meth)acrylamide, N-substituted and N,N-substituted (meth)acrylamide. The ethylenically unsaturated co-monomers from which units (1c) are derived may also be nitrogen-free monomers, for example, vinyl formate and vinyl acetate (which after polymerization may be completely or partially hydrolyzed to the vinyl alcohol unit); C₂-C₂₄-olefins, preferably ethylene, propylene, butylene; diisobutene; vinylbenzene (styrene); vinyl chloride; (meth)acrylic acid and also its esters with aliphatic, alicyclic, aromatic alcohols R-OH where R = C₁-C₁₈-alkyl, benzyl, ethylphenyl, cyclohexyl or phenyl, preferably with methanol, ethanol or propanol; vinylsulfonic acid; allylsulfonic acid.

[0043] In a preferable embodiment, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention comprises

(1 a) 40 to 80 mol% of vinylamine derived units represented by formula (I),

(1 b) 20 to 60 mol % of vinylcarboxamide derived units represented by formula (II),



wherein

R¹ and R³, which are identical, each represent H or methyl, preferably H,

R² and R⁵, which are identical, each represent H or C₁₋₆ alkyl, preferably H, and

R⁴ represents H or C₁₋₆ alkyl, preferably H or methyl, and

(1c) 0 to 5 mol % of units derived from one or more ethylenically unsaturated co-monomers, the sum of units (1a), (1b) and (1c) being 100%.

[0044] In a more preferable embodiment, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention consist of (1a) 30 to 95 mol% of vinylamine derived units represented by formula (I), and (1 b) 5 to 70 mol % of vinylcarboxamide derived units represented by formula (II), wherein the unit described under (1c) hereinabove is not present and the formula (I) and formula (II) are as described hereinabove, provided that if the M_n is below 25,000 g/mol, the content of unit (1a) is equal to or higher than 40 mol%, and if the M_n is equal to or above 25,000 g/mol, the content of unit (1 a) is equal to or less than 80 mol%.

[0045] In a more preferable embodiment, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention consist of (1a) 40 to 80 mol% of vinylamine derived units represented by formula (I), and (1 b) 20 to 60 mol % of vinylcarboxamide derived units represented by formula (II), wherein the unit described under (1c) hereinabove is not present and the formula (I) and formula (II) are as described hereinabove.

[0046] According to the embodiments of the present invention, both R¹ in formula (I) and R³ in formula (II) are H. Additionally or alternatively, both R² in formula (I) and R⁵ in formula (II) are H. Additionally or alternatively, R⁴ in formula (II) is preferably H or methyl.

In a preferred embodiment, both R¹ in formula (I) and R³ in formula (II) are H and both R² in formula (I) and R⁵ in formula (II) are H. In a more preferred embodiment, both R¹ in formula (I) and R³ in formula (II) are H, both R² in formula (I) and R⁵ in formula (II) are H, and R⁴ in formula (II) is H.

[0047] The cationic vinylcarboxamide/vinylamine copolymers according to the present invention have a number average molecular weight (M_n) of up to 400,000.

[0048] The cationic vinylcarboxamide/vinylamine copolymers according to the present invention have a number average molecular weight (M_n) of preferably of from 1,000 to 100,000.

[0049] The cationic vinylcarboxamide/vinylamine copolymers according to the present invention have a number av-

verage molecular weight (M_n) of more preferably from 3,000 to 60,000.

[0050] The cationic vinylcarboxamide/vinylamine copolymers according to the present invention have a number average molecular weight (M_n) of most preferably of less than 50,000.

[0051] In particular the cationic vinylcarboxamide/vinylamine copolymers according to the present invention have a number average molecular weight (M_n) of from 5,000 to 45,000.

[0052] The cationic vinylcarboxamide/vinylamine copolymers according to the present invention preferably have a dispersity PDI (M_w/M_n) in the range from 1.1 to 4.0, more preferably from 2.0 to 3.0.

[0053] In a still preferable embodiment, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention are hydrolysates of copolymers or homopolymers comprising the vinylcarboxamide derived units represented by formula (II) which is as described hereinabove. Most preferably, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention are hydrolysates of homopolymers of N-vinylformamide or N-vinylacetamide. In the preferable embodiments wherein the cationic vinylcarboxamide/vinylamine copolymers according to the present invention are hydrolysates as described above, the hydrolysis degree of the copolymers is equal to or higher than 40 mol% if the M_n is below 25,000 g/mol, and the hydrolysis degree of the copolymers is equal to or less than 80 mol% if the M_n is equal to or above 25,000 g/mol.

Preparation of the cationic vinylcarboxamide/vinylamine copolymers

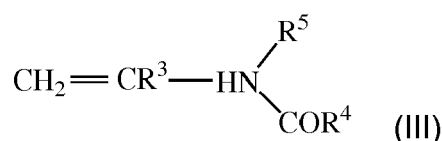
[0054] The cationic vinylcarboxamide/vinylamine copolymers according to the present invention are obtainable or obtained by polymerization of monomers from which the units (1a), (1b) and (1c) are derived.

[0055] In particular, the monomers are selected from substituted or non-substituted N-vinylcarboxamides from which both units (1a) and (1b) are derived by hydrolysis.

[0056] Particularly, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention can be prepared by a process which comprises

(i) polymerizing monomers consisting of

- 95 to 100 mol% of a N-vinylcarboxamide monomer of formula (III)



wherein

R^3 represents H or methyl, preferably H,

R^4 represents H or C_{1-6} alkyl, preferably H or methyl, and

R^5 represent H or C_{1-6} alkyl, preferably H, and optionally

- 0 to 5 mol% one or more ethylenically unsaturated co-monomers, and

(ii) partially removing the group $-\text{COR}^4$ from the obtained polymers by hydrolysis to an extent such that the units (1a) as described hereinabove are present in the polymer in an amount of 30 to 95 mol%, preferably 40 to 80 mol%.

[0057] In such a process, the units (1a) and units (1b) contained in the cationic vinylcarboxamide/vinylamine copolymers according to the present invention are both derived from the N-vinylcarboxamide monomer of formula (III).

[0058] Particularly, the units (1a) are derived from the N-vinylcarboxamide monomer of formula (III) through polymerization thereof and subsequent hydrolysis.

[0059] Suitable ethylenically unsaturated co-monomers for the polymerization are as described hereinabove for the ethylenically unsaturated co-monomers from which units (1c) are derived.

[0060] The polymerization of the monomers in the process for preparing the cationic vinylcarboxamide/vinylamine copolymers is not particularly limited, and various known polymerization methods can be applied, for example but not limited to, bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization and the like, e.g. as described in Principles of Polymerization, G. Odian, 4th Ed. (2004), Wiley, New jersey.

[0061] It is possible to use one or more free radical polymerization initiators in polymerization. As the radical polymerization initiator, a redox initiator, azo initiator, peroxide, etc. can be exemplified. Polymerization can be carried out

continuously or batchwise. The polymerization can optionally be initiated solely by the action of energy-rich radiation, e.g. electron beams or UV rays. In case of presence of a free radical polymerization initiator, an amount of from 0.01 to 20% by weight, preferably 0.05 to 5% by weight, based on the monomers can be applied.

[0062] The polymerization can be carried out in the presence or absence of inert solvents or diluents. Since polymerization in the absence of inert solvents or diluents usually leads to inhomogeneous polymers, polymerization in an inert solvent or diluent is preferred. Suitable inert diluents are, for example, those in which the N-vinylcarboxamides are soluble, for example, methanol, ethanol, isopropanol, n-propanol, n-butanol, sec-butanol, tetrahydrofuran, dioxane, water and any mixtures thereof.

[0063] The polymerization of the monomers is customarily carried out in an inert gas atmosphere with exclusion of atmospheric oxygen. In the case of smaller batches in which safe dissipation of the heat of polymerization is guaranteed, the monomers can be copolymerized batchwise by heating the reaction mixture to the polymerization temperature and then allowing the reaction to proceed. In this case, these temperatures are in the range from 40 to 180 °C. The polymerization can be carried out under normal pressure (i.e. about 1.0 bar), reduced pressure (for example, about 0.5 bar) or elevated pressure (for example, about 2 bar).

[0064] In order to avoid hydrolysis of the monomeric N-vinylcarboxamides during the polymerization when the polymerization is carried out in aqueous solution, the aqueous solution is preferably adjusted to a pH in the range of from 4 to 9, in particular from 5 to 8. In many cases, it is recommended to carry out the polymerization in the presence of buffers, e.g. to add primary or secondary sodium phosphate to the aqueous phase.

The hydrolysis to partially remove the group -COR⁴ from the obtained polymers is preferably carried out in the presence of water under the action of acids, bases or enzymes.

[0065] In the case of using an acid for the hydrolysis, a strong acid such as hydrochloric acid or sulfuric acid is preferable. During hydrolysis with acids, the pH is in the range of from 0 to 5. In the case of using a base for the hydrolysis, a strong base such as sodium hydroxide, potassium hydroxide or ammonia is preferable. During hydrolysis with bases, the pH is in the range of from 8 to 14. The acid or base is generally used in an amount of from 0.05 to 1.5 equivalents, preferably of from 0.4 to 1.2 equivalents, per acyl group equivalent in the cationic vinylcarboxamide/vinylamine copolymers according to the present invention.

[0066] Hydrolysis in the presence of acid or base is carried out, for example, at a temperature in the range of 30 to 170 °C or, preferably 50 to 120 °C. The reaction time differs depending on temperature, which however is normally about 2 to 8, preferably 3 to 5 hours. A procedure has proven particularly suitable in which, for hydrolysis, the bases or acids are added in aqueous solution. After hydrolysis, neutralization is preferably carried out such that the pH of the hydrolyzed polymer solution is in the range of from 2 to 8, preferably 3 to 7, in order to obtain the desired hydrolysis degree, that is relative to the contents of the units (1a) and the units (1b). The hydrolysis can also be carried out with the aid of enzymes. The degree of hydrolysis of the polymers can easily be determined analytically by conventional methods known in the art.

[0067] It is to be understood that the preparation of the cationic vinylcarboxamide/vinylamine copolymers is not limited to the above process. The cationic vinylcarboxamide/vinylamine copolymers can also be prepared by any other processes known in the art, for example, deriving the units (1a) from arylamide monomers through polymerization and Hoffman reaction as described in EP 2977 507A1.

Formulations

[0068] As a care color agent, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention can be used generally in all types of formulations for laundering, for example, various detergents such as laundry detergents, especially color care detergents, heavy-duty detergents, mild detergents, specialty detergents for black textiles, detergents for jeans, and wool detergents, or laundry after-treatment formulations. The laundering formulations in which the cationic vinylcarboxamide/vinylamine copolymers according to the present invention can be used in semi-liquid form or in liquid form, but most preferably in liquid form.

[0069] Typically, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention may be used in a laundering formulation in a conventional amount known in the art for a dye transfer inhibitor or a dye fixation agent. Generally, the cationic vinylcarboxamide/vinylamine copolymers are used in an amount of from 0.01 % to 20.0 % by weight, preferably from 0.05 to 10.0 % by weight, particularly from 0.05 % to 5.0 % by weight and especially from 0.1 % to 2.0 % by weight, based on the total weight of the formulation.

[0070] The laundry detergent formulations, after-treatment formulations and the like may have any known compositions in the field of laundering and may contain in addition to or in place of conventional care color agents, such as dye transfer inhibitors or dye fixation agents, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention as a color care agent.

[0071] For example, liquid laundry detergent formulations may comprise following components:

- (a) 0.01 to 20% by weight of at least one cationic vinylcarboxamide/vinylamine copolymer as described above,

(b) 0.5 to 70% by weight of at least one nonionic, anionic and/or cationic surfactant,

(c) 0 to 10% by weight of an organic builder,

(d) 0.1 to 60% by weight of other customary ingredients, such as sodium carbonate, enzymes, perfume, complexing agents, corrosion inhibitors, bleaches, bleach activators, bleach catalysts, further color protection additives and dye transfer inhibitors, graying inhibitors, soil release polyesters, fiber protection additives, silicones, dyes, bactericides and preservatives, organic solvents, solubility promoters, hydrotropes, foam regulators, thickeners and/or alkanolamines, and

(e) a balance of water.

[0072] Laundry after-treatment formulations, in particular laundry care rinse formulations generally comprise

(a) 0.01 to 20% by weight of at least one cationic vinylcarboxamide/vinylamine copolymers as described above,

(b) 0.1 to 40% by weight of at least one cationic surfactant,

(c) 0 to 30% by weight of at least one nonionic surfactant,

(d) 0.1 to 30% by weight of other customary ingredients, such as silicones, other lubricants, wetting agents, film-forming polymers, fragrances and dyes, stabilizers, fiber protection additives, further color protection additives and dye transfer inhibitors, complexing agents, viscosity modifiers, soil release additives, solubility promoters, hydrotropes, corrosion protection additives, bactericides and preservatives, and

(e) a balance of water.

[0073] It is to be understood that the above formulations are provided just to exemplify compositions of formulations in which the cationic vinylcarboxamide/vinylamine copolymers according to the present invention may be used, without any limitation to the application of the cationic vinylcarboxamide/vinylamine copolymers according to the present invention.

[0074] Suitable nonionic surfactants include, for example:

- alkoxyated C₈-C₂₂-alcohols, such as fatty alcohol alkoxyates, oxo alcohol alkoxyates and Guerbet alcohol ethoxyates: the alkoxylation can take place with ethylene oxide, propylene oxide and/or butylene oxide. Per mole of alcohol, they usually comprise 2 to 50 mol, preferably 3 to 20 mol, of at least one alkylene oxide. A preferred alkylene oxide is ethylene oxide. The alcohols preferably have 10 to 18 carbon atoms;
- alkylphenol alkoxyates, in particular alkylphenol ethoxyates, which comprise C₆-C₁₄-alkyl chains and 5 to 30 mol of alkylene oxide/mol;
- alkyl polyglucosides which comprise C₈-C₂₂-, preferably C₁₀-C₁₈-alkyl chains and as a rule 1 to 20, preferably 1.1 to 5, glucoside units;
- N-alkylglucamides, fatty acid amide alkoxyates, fatty acid alkanolamide alkoxyates, long-chain amine oxides, polyhydroxy(alkoxy) fatty acid derivatives, such as, for example, polyhydroxy fatty acid amides, gemini surfactants, and block copolymers of ethylene oxide, propylene oxide and/or butylene oxide; and
- mixtures thereof.

[0075] Suitable anionic surfactants include, for example:

- sulfates of (fatty) alcohols having 8 to 22, preferably 10 to 18, carbon atoms, in particular C₉C₁₁-alcohol sulfates, C₁₂C₁₄-alcohol sulfates, C₁₂-C₁₈-alcohol sulfates, lauryl sulfate, cetyl sulfate, myristyl sulfate, palmityl sulfate, stearyl sulfate and tallow fatty alcohol sulfate;
- sulfated alkoxyated C₈-C₂₂-alcohols (alkyl ether sulfates): compounds of this type are prepared, for example, by firstly alkoxyating a C₈-C₂₂-, preferably a C₁₀-C₁₈-alcohol, e.g. a fatty alcohol, and then sulfating the alkoxylation

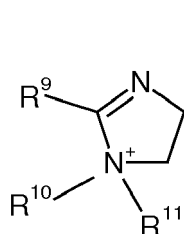
product. For the alkoxylation, ethylene oxide is preferably used;

- linear C₈-C₂₀-alkylbenzenesulfonates, preferably linear C₉-C₁₃-alkylbenzenesulfonates and alkyltoluenesulfonates;
- alkanesulfonates, in particular C₈-C₂₄-, preferably C₁₀-C₁₈-alkanesulfonates;
- olefinsulfonates;
- fatty acid and fatty acid ester sulfonates;
- soaps, such as the Na and K salts of C₈-C₂₄-carboxylic acids; and
- mixtures thereof.

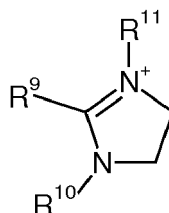
[0076] The anionic surfactants are preferably added to the laundry formulations in the form of salts. Suitable salts here are, for example, alkali metal salts, such as sodium, potassium and lithium salts, and ammonium salts, such as hydroxyethylammonium, di(hydroxyethyl)ammonium and tri(hydroxyethyl)ammonium salts.

[0077] Suitable cationic surfactants include, for example:

- C₇-C₂₅-alkylamines;
- N,N-dimethyl-N-(hydroxy-C₇-C₂₅-alkyl)ammonium salts;
- mono- and di(C₇-C₂₅-alkyl)dimethylammonium compounds quaternized with alkylating agents;
- ester quats, in particular quaternary esterified mono-, di- and trialkanolamines which have been esterified with C₈-C₂₂-carboxylic acids;
- imidazoline quats, in particular 1-alkylimidazolinium salts of the formulae II or III



II



III

in which the variables have the following meaning:

R⁹ is C₁-C₂₅-alkyl or C₂-C₂₅-alkenyl;

R¹⁰ is C₁-C₄-alkyl or hydroxy-C₁-C₄-alkyl;

R¹¹ is C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl or a radical R¹-(CO)-X-(CH₂)_m- wherein X is -O- or -NH-; m is 2 or 3),

where at least one radical R⁹ is C₇-C₂₂-alkyl; and

- mixtures thereof.

[0078] Amphoteric surfactants may also be used in the laundry formulations, for example, alkylbetaines, alkylamido-betaines, aminopropionates, aminoglycinates and amphoteric imidazolium compounds.

[0079] The advantages of the cationic vinylcarboxamide/vinylamine copolymers according to the present invention are notable especially in those detergent formulations which comprise only anionic surfactants as surface active compounds or a major fraction of anionic surfactants, especially linear alkylbenzenesulfonates (LAS) anionic surfactants.

[0080] In general, a detergent formulation comprising the cationic vinylcarboxamide/vinylamine copolymers according to the present invention may contain a total of 0.5 to 70% % by weight of surfactants. Preferably, the total percentage

of surfactants ranges from 10 to 40 % by weight in a detergent formulation according to the present invention.

[0081] A higher ratio of anionic surfactant can be incorporated into the final detergent formulation without affecting the compatibility of the components. For instance, a fraction of anionic surfactants of up to 90 % by weight, based on the total amount of surfactants in the laundering formulation, may be tolerated without negative impact on the formulation.

In case the anionic surfactants are linear alkylbenzenesulfonates (LAS), a total a fraction of up to 25 % by weight, based on the total amount of surfactants in the laundering formulation, may still result in stable formulations.

[0082] Suitable organic builders include, for example:

- low molecular weight carboxylic acids, such as citric acid, hydrophobically modified citric acid, e.g. agaricic acid, malic acid, tartaric acid, gluconic acid, glutaric acid, succinic acid, imidodisuccinic acid, oxydisuccinic acid, propanetricarboxylic acid, butanetetracarboxylic acid, cyclopentanetetracarboxylic acid, alkyl- and alkenylsuccinic acids and aminopolycarboxylic acids, e.g. nitrilotriacetic acid, β -alaninediacetic acid, ethylenediaminetetraacetic acid, serinediacetic acid, isoserinediacetic acid, N-(2-hydroxyethyl)iminoacetic acid, ethylenediaminedisuccinic acid and methyl- and ethylglycinediacetic acid or alkali metal salts thereof;
- oligomeric and polymeric carboxylic acids, such as homopolymers of acrylic acid and aspartic acid, oligomaleic acids, copolymers of maleic acid with acrylic acid, methacrylic acid or C_2 - C_{22} -olefins, e.g. isobutene or long-chain α -olefins, vinyl C_1 - C_8 -alkyl ethers, vinyl acetate, vinyl propionate, (meth)acrylic acid esters of C_1 - C_8 -alcohols and styrene. Preference is given to the homopolymers of acrylic acid and copolymers of acrylic acid with maleic acid. The oligomeric and polymeric carboxylic acids are used in acid form or as sodium salt;
- phosphonic acids, such as, for example, 1-hydroxyethylene(1,1-diphosphonic acid), aminotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid) and diethylenetriaminepenta(methylenephosphonic acid) and alkali metal salts thereof.

[0083] Suitable graying inhibitors are, for example, carboxymethylcellulose and graft polymers of vinyl acetate onto polyethylene glycols.

[0084] Suitable bleaches are, for example, adducts of hydrogen peroxide onto inorganic salts, such as sodium perboratemonohydrate, sodium perboratetetrahydrate and sodium carbonate perhydrate, and percarboxylic acids, such as phthalimidopercaproic acid.

[0085] Suitable bleach activators are, for example, N,N,N',N'-tetraacetyethylenediamine (TAED), sodium p-nonanoyloxybenzenesulfonate and N-methylmorpholinium acetonitrile methyl sulfate.

[0086] Enzymes preferably used in detergents are proteases, lipases, amylases, cellulases, oxidases and peroxidases.

[0087] Suitable further dye transfer inhibitors include, for example, homopolymers, copolymers and graft polymers of 1-vinylpyrrolidone, 1-vinylimidazole or 4-vinylpyridine N-oxide. Homopolymers and copolymers of 4-vinylpyridine reacted with chloroacetic acid are also suitable as dye transfer inhibitors. Such dye transfer inhibitors are commercially available, for example polyvinylpyrrolidones, vinylpyrrolidone-vinylimidazole copolymers, poly(4-vinylpyridine N-oxides) or poly(4-vinylpyridine N-carboxymethyl)betaines.

[0088] Detergent ingredients are otherwise generally known. Detailed descriptions can be found, for example, in Liquid Detergents, Editor: Kuo-Yann Lai, Surfactant Sci. Ser., Vol. 67, Marcel Decker, New York, 1997, p. 272-304 or in patent (application) publications such as WO 99/06524A1.

[0089] The incorporation of the cationic vinylcarboxamide/vinylamine copolymers according to the present invention into the respective formulations can be carried out in a manner known per se, the cationic vinylcarboxamide/vinylamine copolymers often being used in liquid form, i.e. dissolved or dispersed form. The cationic vinylcarboxamide/vinylamine copolymers can also be used in powder or granule form.

[0090] Accordingly, the present invention relates to a method for preparation of a laundering formulation, especially a liquid laundering formulation by incorporation of the cationic vinylcarboxamide/vinylamine copolymers according to the present invention, as a color care agent. More particularly, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention functions as dye transfer inhibitor agent or dye fixation agent in the prepared laundering formulations.

[0091] It is to be understood that the liquid laundering formulation is intended to include any fluid forms of formulation, including liquid and semi-liquid formulations, for example liquids, gels and pastes.

[0092] In the method for preparation of a laundering formulation, the cationic vinylcarboxamide/vinylamine copolymers according to the present invention are mixed with surfactants such as nonionic, anionic and/or cationic surfactants and other conventional ingredients for a laundering formulation, in a solvent, preferably water. As described above, the other conventional ingredients include, for example but not limited to, organic builder, enzymes, perfume, complexing agents, corrosion inhibitors, amphoteric surfactants, bleaches, bleach activators, bleach catalysts, further color protection additives and dye transfer inhibitors, graying inhibitors, soil release polyesters, fiber protection additives, silicones, dyes,

bactericides and preservatives, organic solvents, solubility promoters, hydrotropes, foam regulators, thickeners and/or alkanolamines.

Application, methods and uses

[0093] In the context of the present invention, the expression "laundering" is intended to comprise washing, rinsing, after-treatment and any other possible operations for laundry. Accordingly, laundering formulations comprise any formulations that may be used during laundering methods, for example, washing, rinsing, after-treatment and the like.

[0094] The present invention further relates to a method for color care of colored textiles during laundering, wherein the cationic vinylformamide/vinylamine copolymers according to the present invention are brought into contact with the textiles.

[0095] In one particularly embodiment, the present invention relates to a method for fixing dyes on colored textiles during laundering, wherein the cationic vinylformamide/vinylamine copolymers according to the present invention are brought into contact with the textiles. In another embodiment, the present invention relates to a method for preventing and inhibiting dye transfer from colored textiles to white or lighter colored textiles during laundering, wherein the cationic vinylformamide/vinylamine copolymers according to the present invention are brought into contact with the textiles.

[0096] The methods for color care of colored textiles during laundering according to the present invention can be applied to textiles of various sources, for example, cotton, linen, silk and synthetic fiber materials, preferably to textiles of cotton and cotton blends.

[0097] The colored textiles that can be treated by the method for color care according to the present invention are preferably those colored with reactive dyes or direct dyes.

[0098] The colored textiles, that can be treated by the method for color care according to the present invention, are for example dyed with direct dyes selected from, including but not limited to, C.I. Direct Yellow 11, C.I. Direct Yellow 12, C.I. Direct Orange 26, C.I. Direct Orange 39, C.I. Direct Red 23, C.I. Direct Red 28, C.I. Direct Red 31, C.I. Direct Red 13, C.I. Direct Red 83.1 C.I. Direct Red 227, C.I. Direct Green 6, C.I. Direct Green 26, C.I. Direct Blue 6, C.I. Direct Blue 15, C.I. Direct Blue 71, C.I. Direct Blue 151, C.I. Direct brown 1, C.I. Direct Brown 2, C.I. Direct Brown MM, C.I. Direct Brown RN, C.I. Direct Violet 66, C.I. Direct Black 38, C.I. Direct Black 19, C.I. Direct Black 22, C.I. Direct Black 168 or C.I. Direct Black 17.

[0099] The colored textiles, that can be treated by the method for color care according to the present invention, are for example dyed with reactive dyes selected from, including but not limited to, C.I. Reactive Yellow 2, C.I. Reactive Yellow 125, C.I. Reactive Yellow 158, C.I. Reactive Yellow 14, C.I. Reactive Red 1, C.I. Reactive Red 120, C.I. Reactive Red 241, C.I. Reactive Red 158, C.I. Reactive Red 35, C.I. Reactive Green 6, C.I. Reactive Green 8, C.I. Reactive Blue 19, C.I. Reactive Blue 181, C.I. Reactive Blue 162, C.I. Reactive Blue 221, C.I. Reactive Orange 5, C.I. Reactive Orange 13, C.I. Reactive Orange 127, C.I. Reactive Orange 122, C.I. Reactive Brown 11, C.I. Reactive Brown 23, C.I. Reactive Brown 7, C.I. Reactive Violet 4, C.I. Reactive Violet 33, C.I. Reactive Violet 12, C.I. Reactive Black 8, C.I. Reactive Black 5 or C.I. Reactive Black 11.

[0100] The present invention is further demonstrated and exemplified in the following Examples, however, without being limited to the embodiments described in the Examples.

Examples

Preparation Examples

1. Preparation of Cationic Vinylcarboxamide/Vinylamine Copolymers

[0101] Several cationic vinylcarboxamide/vinylamine copolymers (CVVC) according to the present invention were prepared according to the preparation method described herein below, under the conditions and parameters as specified in the respective lines of Table 1.

[0102] A 35% wt. aqueous solution of polyvinylformamide (PVF) with a number average molecular weight M_n as specified Table 1, at pH of 8.0 and a density of 1.1 g/cm³ was placed inside a Systag FlexyCuybe automated glass reactor and heated under stirring at 200 rpm. After temperature equilibration at 80°C, 40% wt. aqueous sodium bisulfite and/or 50% wt. aqueous NaOH solutions in amounts as specified in Table 1 as vinylformamide (VFA) equivalents were fed inside the reactor within 1 h. The hydrolysis reaction was left to proceed for the time as specified in Table 1, after which the reactor was rapidly cooled down to room temperature. Subsequently, a 23% wt. aqueous HCl solution was fed inside the reactor over 2.5 h, in order to adjust the pH in the range of from 7.0 to 7.5 and the stirring was maintained for an additional 30 min.

Table 1 Parameters for CVVCs according to the Present Invention

Copolymers	Number average molecular weight (M_n) [g/mol] of starting PVF	Number average molecular weight (M_n) [g/mol] of final Copolymers (calculated)	NaHSO ₃ solution, VFA eq.	NaOH solution, VFA eq.	reaction time [h]	Degree of hydrolysis, [mol%]
CVVC 3	10,000	8,300	0	0.8	6.0	43
CVVC 4	10,000	7,900	0	0.8	4.5	54
CVVC 5	10,000	7,200	0.02	0.8	3.0	70
CVVC 6	10,000	6,300	0.02	1.05	6.0	95
CVVC 8	45,000	39,700	0.02	0.35	3.0	30
CVVC 9	45,000	32,600	0.02	0.8	3.0	70
CVVC 10	45,000	30,800	0	1.1	4.0	80
CVVC 12	400,000	352,700	0.02	0.35	3.0	30

[0103] Comparative vinylcarboxamide/vinylamine copolymers were prepared according to the preparation method described hereinabove and under the conditions and parameters as specified in the respective lines of Tables 2.1 and 2.2.

Table 2.1 Parameters for Comparative CVVCs showing no color care effect

Copolymers	Number average molecular weight (M_n) [g/mol] of starting PVF	Number average molecular weight (M_n) [g/mol] of final Copolymers (calculated)	NaHSO ₃ solution, VFA eq.	NaOH solution, VFA eq.	reaction time [h]	Degree of hydrolysis, [mol%]
CVVC 1 (Comp.)	10,000	10,000	0	0	0	0
CVVC 2 (Comp.)	10,000	8,800	0.02	0.35	3.0	30
CVVC 7 (Comp.)	45,000	45,000	0	0	0	0

Table 2.2 Parameters for Comparative CVVCs showing no compatibility with anionic surfactants

Copolymers	Number average molecular weight (M_n) [g/mol] of starting PVF	Number average molecular weight (M_n) [g/mol] of final Copolymers (calculated)	NaHSO ₃ solution, VFA eq.	NaOH solution, VFA eq.	reaction time [h]	Degree of hydrolysis, [mol%]
CVVC 11 (Comp.)	45,000	28,200	0.02	1.05	6.0	95
CVVC 13 (Comp.)	400,000	250,400	0.02	1.05	6.0	95

[0104] The number average molecular weights of the starting polyvinylformamide (PVF) for preparing cationic vinylcarboxamide/vinylamine copolymers CVVC 1 to CVVC 13 as shown above (according to Tables 1, 2.1 and 2.2) were determined by Size-Exclusion Chromatography (SEC), using an Agilent 1200 chromatograph, equipped with a binary pump, a refractive index detector and a PSS Novema Max Ultrahigh analytical column. Poly(2-vinylpyridine) was used as standard and water comprising 0.1 w/w% trifluoroacetic acid and 0.1 mol/l NaCl was used as effluent under following conditions:

Temperature of the column: 25°C,

Injection volume: 100 μL (μliter),
 Concentration: 1.5 mg/mL, and
 Flow rate: 0.8 mL/min.

[0105] The hydrolysis degrees of the cationic vinylcarboxamide/vinylamine copolymers CVVC 1 to CVVC 13 as prepared above according to Tables 1, 2.1 and 2.2 were determined by the ratio of the peak area of the released formic acid protons over the sum of the peak areas of the released formic acid protons plus the unhydrolyzed formyl protons as measured by ^1H NMR.

[0106] The number average molecular weight of the final copolymers after hydrolysis was estimated and calculated based on the weight of the leaving formyl groups and the weight of protons combined that correspond to the respective degree of hydrolysis. Specifically, the corresponding weight of the formyl groups released during hydrolysis was subtracted, while the corresponding weight of the protons combined during hydrolysis was added to the number average molecular weight of the polymer before hydrolysis.

2. Preparation of Detergent Formulations

[0107] For washing application tests in a washing machine, four detergent model formulations as shown in Table 3 were prepared at a pH between 7.0 and 8.0, to which respectively one of the cationic vinylcarboxamide/vinylamine copolymers CVVC 1 to CVVC 13 (as prepared and shown above in Tables 1, 2.1 and 2.2) was additionally included as the color care agent.

Table 3 Detergent Model Formulations

	Composition, % by weight			
Components	Formulation A	Formulation B	Formulation C	Formulation D
¹ Linear alkyl benzene sulfonate	6.0	2.0	4.0	4.8
² Alkyl ether sulfate	-	4.5	16.0	14.4
³ Alkyl ether ethoxylate (7 EO)	24.0	-	-	-
⁴ Alkyl ether ethoxylate (9 EO)	-	17.5	4.0	4.8
Sodium citrate	0.5	0.1	-	0.1
Mono propylene glycol	5.0	1.0	-	1.0
Ethanol	1.5	-	-	-
Toluene sulfonic acid	-	-	-	0.2
Deionized water	Add to 100			
• The surfactants used in formulations A to D: • ¹Linear alkyl benzene sulfonate: Linear C₁₀C₁₃-alkylbenzene sulfonates, sodium salt • ²Alkyl ether sulfate: Sodium laureth sulfate + 2 mole ethylene oxide • ³Alkyl ether ethoxylate (7EO): C₁₂C₁₄-fatty alcohol + 7 mole ethylene oxide • ⁴Alkyl ether ethoxylate (9EO): C₁₂C₁₄ fatty alcohol + 9 mole ethylene oxide				

Materials

[0108] Following dyed textile samples (also called dye bleeders) were used as textile samples for testing potential dye bleeding during laundering:

- C.I. Direct Red 83.1 on cotton (Empa 130: commercially available from Swisstest, Swisstest Testmaterialien AG, Switzerland);
- C.I. Direct Blue 71 on cotton (Empa 133: commercially available from Swisstest, Swisstest Testmaterialien AG, Switzerland);
- C.I. Direct Orange 39 on cotton (Empa 134: commercially available from Swisstest, Swisstest Testmaterialien AG, Switzerland);

- C.I. Reactive Brown 7 on cotton (Empa 136: commercially available from Swisstatest, Swisstatest Testmaterialien AG, Switzerland);
- C.I. Direct Green 26 on cotton
- C.I. Direct Violet 66 on cotton
- C.I. Direct Red 227 on cotton

[0109] Following white textile samples were used as textile samples for testing potential staining by dyes fading out from dye bleeders during laundering:

- white acceptor - standard cotton (Wfk 10 A: commercially available from wfk Testgewebe GmbH) Germany,
- white acceptor- cotton knit (Wfk 80 A: commercially available from wfk Testgewebe GmbH, Germany)
- white acceptor- Polyester/cotton (65%/35%) (Wfk 20 A: commercially available from wfk Testgewebe GmbH, Germany).

3. Application of the Cationic Vinylcarboxamide/Vinylamine Copolymers

Color Measurement and Test Result Evaluation:

[0110] The textiles were instrumentally assessed with a Datacolor reflection spectrometer Model Type ELREPHO before and after washing. From the reflection data readings L^* , a^* , b^* , Y were derived and further expressed in ΔE and ΔY values.

[0111] The higher values of ΔE are observed for the acceptor textiles in comparison to the initial whiteness before the test, the higher dye transfer is found; and the higher values of ΔY are observed for the Dye bleeder textiles in comparison to the initial lightness before the test, the higher dye bleeding and lower dye fixing is found.

[0112] For dye transfer inhibiting effect, ΔE is adopted as conventionally used in the art. ΔE is calculated as CIE 1976 color difference according to DIN EN ISO 11664-4 (June 2012) in accordance with following equation:

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

in which

$$\Delta L^* = L^*_{\text{washed}} - L^*_{\text{initial}};$$

$$\Delta a^* = a^*_{\text{washed}} - a^*_{\text{initial}};$$

and

$$\Delta b^* = b^*_{\text{washed}} - b^*_{\text{initial}}.$$

[0113] The values L^*_{initial} , a^*_{initial} , and b^*_{initial} are measured on white acceptor textile before washing. The values L^*_{washed} , a^*_{washed} and b^*_{washed} are measured on the white acceptor textile after washing. Standard colorimetric measurement was used to obtain L^* , a^* and b^* values.

[0114] For dye fixing effect, ΔY is adopted for characterization, which is calculated from Y value for lightness according to CIE 1931 XYZ color space in accordance with following equation:

$$\Delta Y = Y_{\text{washed}} - Y_{\text{initial}}$$

1) Color Care Test in a Simple System

[0115] 2g dye bleeder textile was immersed into 200 mL washing solution prepared from water and respective surfactants and the cationic vinylcarboxamide/vinylamine copolymer CVVC 5, as shown in Table 4. After 24 hours, the textiles were removed from water, rinsed and dried.

Table 4 Color Care Test Results for Simple System

No.	Ingredients, % by weight				Dye bleeder	
	¹ Linear alkyl benzene sulfonate	² Alkyl ether sulfate	³ Alkyl ether ethoxylate (7 EO)	CVVC 5	ΔY of Empa 130 (Direct Red 83.1)	ΔY of Empa 133 (Direct Blue 71)
1	0	0	0	0	1.36	0.80
2	0	0	0	0.025	0.04	0.54
3	1	0	0	0	1.23	1.57
4	1	0	0	0.025	1.16	1.12
5	0	1	0	0	1.34	1.55
6	0	1	0	0.025	1.11	1.22
7	0	0	1	0	0.87	0.98
8	0	0	1	0.025	-0.14*	0.60
* ΔY with a negative value represents darker in color. • ¹ Linear alkyl benzene sulfonate: Linear C ₁₀ C ₁₃ -alkylbenzene sulfonates, sodium salt • ² Alkyl ether sulfate: Sodium laureth sulfate + 2 mole ethylene oxide • ³ Alkyl ether ethoxylate (7EO): C ₁₂ C ₁₄ -fatty alcohol + 7 mole ethylene oxide						

[0116] As shown in Table 4 above, solutions containing CCVC 5 copolymer according to the present invention show a lower ΔY value of the dye bleeder compared to solutions without the inventive copolymers respectively, thereby demonstrating a better dye fixation performance in presence of the CCV5 copolymer of the present invention for each solution.

2) Color Care Test in a Washing Machine

[0117] In a Launder-Ometer (SDL ATLAS) washing machine, dye bleeder (2 g) and white acceptor textiles (18 g) were washed with 200 ml washing solutions prepared from water with a hardness of 250 ppm and 3.25 g/L of a detergent of a model formulation (specified above) to which 0.5 % by weight of color care agent based on the weight of the detergent has been added, at 40°C for 30 min. After washing, the textiles were rinsed with tap water and dried at 37°C in an oven.

[0118] For multi-cycle color care test wherein washing cycle was repeated for several times, dye bleeder textile was kept during the whole cycles, while white acceptor textile was replaced with fresh textiles in each cycle.

i) Color Care Test with Various Copolymers as Color Care Agents

[0119]

Table 5 Color Care Test Results in Detergent Model Formulation A

	Empa 130 (Direct Red 83.1)		Empa 133 (Direct Blue 71)	
	ΔY of dye bleeder	ΔE of wfk 10 A	ΔY of dye bleeder	ΔE of wfk 10 A
Nil	0.34	4.80	0.12	7.6
CVVC 1 (Comp.)	0.54	7.09	0.29	11.36
CVVC 2 (Comp.)	0.46	5.97	0.46	10.80
CVVC 3	0.48	3.77	0.07	7.05

(continued)

	Empa 130 (Direct Red 83.1)		Empa 133 (Direct Blue 71)	
	ΔY of dye bleeder	ΔE of wfk 10 A	ΔY of dye bleeder	ΔE of wfk 10 A
CVVC 4	0.50	4.56	0.11	7.14
CVVC 5	0.13	1.68	0.13	2.16
CVVC 6	0.10	1.65	-0.04	1.28
CVVC 7 (Comp.)	0.54	6.71	0.29	5.72
CVVC 8	0.30	3.88	0.18	4.83
CVVC 9	0.54	1.58	0.19	1.18

[0120] Color care performance of copolymers according to the present invention is confirmed via a lower ΔY (better dye fixation performance) and/or lower ΔE (better dye transfer inhibition performance) in comparison to the the blank sample ("Nil"). As shown in Table 5 above, the Comparative Examples show both, higher ΔY and ΔE values, thereby demonstrating no color care performance, while the copolymers according to the present inventions show at least either a lower ΔY (better dye fixation) or a lower ΔE (better dye transfer inhibition), or even a lower ΔY (better dye fixation) and a lower ΔE (better dye transfer inhibition) at the same time, thereby demonstrating the color care performance of copolymers according to the present invention.

ii) Color Care Test for Multi-cycle Washing

[0121]

Table 6 Multi-cycle washing test results for EMPA 130

	EMPA 130 (Direct Red 83.1)					
	1 cycle		3 cycles		5 cycles	
	ΔY of dye bleeder	ΔE of wfk 10A	ΔY of dye bleeder	ΔE of wfk 10A	ΔY of dye bleeder	ΔE of wfk 10A
Nil	0.39	4.81	0.73	3.36	0.79	2.32
CVVC 5	0.23	1.32	0.28	1.38	0.28	1.24

[0122] Color care performance of copolymers according to the present invention is confirmed via a lower ΔY value (better dye fixation performance) and/or a lower ΔE value (better dye transfer inhibition performance) in comparison to the the blank sample ("Nil"). As shown in Table 6 above, CVVC 5 copolymer according to the present invention shows a lower ΔY value as well as a lower ΔE value in comparison to the blank sample ("Nil"), thereby demonstrating the color care performance of copolymers according to the present invention during multiple washing cycles.

Table 7 Multi-cycle washing test results for EMPA 133

	EMPA 133 (Direct Blue 71)					
	1 cycle		3 cycles		5 cycles	
	ΔY of dye bleeder	ΔE of wfk 10A	ΔY of dye bleeder	ΔE of wfk 10A	ΔY of dye bleeder	ΔE of wfk 10A
Nil	0.16	6.66	0.43	4.69	0.50	3.04
CVVC 5	0.18	2.28	0.46	2.16	0.49	2.14

[0123] Color care performance of copolymers according to the present invention is confirmed via a lower ΔY value (better dye fixation performance) and/or a lower ΔE value (better dye transfer inhibition performance) in comparison to the blank sample ("Nil"). As shown in Table 7 above, CVVC 5 copolymer according to the present invention shows a lower ΔE value compared to the blank sample ("Nil"), thereby demonstrating the color care performance, especially the dye transfer inhibition performance, of copolymers according to the present invention during multiple washing cycles.

3) Color Care Test for Various Dye Bleeders

[0124]

Table 8 Test Results for Various Dye Bleeders

	Nil		CVVC 5	
Dye bleeder	ΔY of Dye bleeder	ΔE of Wfk 10A	ΔY of Dye bleeder	ΔE of Wfk 10A
Empa 134 (Direct Orange 39)	0.44	16.07	0.29	10.12
Cotton with Direct Green 26	0.36	4.40	0.27	1.36
Cotton with Direct Violet 66	0.42	8.43	0.29	1.92
Cotton with Direct Red 227	0.23	12.25	0.14	4.31
Empa 136 (Reactive Brown 7)	0.69	1.73	0.16	0.57

[0125] Color care performance of copolymers according to the present invention is confirmed via a lower ΔY value (better dye fixation performance) and/or a lower ΔE value (better dye transfer inhibition performance) in comparison to the blank sample ("Nil"). As shown in Table 8 above, CVVC 5 copolymer according to the present invention shows a lower ΔY and a lower ΔE value compared to the blank sample ("Nil"), thereby demonstrating the color care performance of copolymers according to the present invention for various dye bleeders.

4) Test of Compatibility of Various Copolymers with Surfactants

[0126] 0.5 % by weight of the polymer as color care agent was added in each aqueous surfactant solution or each formulation during the conventional formulation process. Each sample with the color care agent was kept for 1 week and its appearance was visually checked.

Table 9 Compatibility of Copolymers in Anionic Surfactant Solutions

	Stability and optical appearance	
aqueous surfactant solution	24 % by weight of ¹ Linear alkyl benzene sulfonate	24 % by weight of ² Alkyl ether sulfate
Nil	Stable (transparent)	Stable (transparent)
CVVC 3	Stable (transparent)	Stable (transparent)
CVVC 4	Stable (transparent)	Stable (transparent)
CVVC 5	Stable (transparent)	Stable (transparent)
CVVC 6	Stable (translucent)	Stable (transparent)
CVVC 8	Stable (transparent)	Stable (transparent)
CVVC 11 (Comp.)	Unstable (phase separation)	-
CVVC 13 (Comp.)	Unstable (phase separation)	Unstable (phase separation)
• ¹ Linear alkyl benzene sulfonate: Linear C ₁₀ C ₁₃ -alkylbenzene sulfonates, sodium salt • ² Alkyl ether sulfate: Sodium laureth sulfate + 2 mole ethylene oxide		

Table 10 Compatibility of Copolymers in Anionic Surfactant Solutions

	Stability and optical appearance	
aqueous surfactant solution	15 % by weight of ¹ Linear alkyl benzene sulfonate	15 % by weight of ² Alkyl ether sulfate
Nil	Stable (transparent)	Stable (transparent)

(continued)

	Stability and optical appearance	
CVVC 12	Stable (translucent)	Stable (transparent)
CVVC 13 (Comp.)	Unstable (phase separation)	Unstable (phase separation)
• ¹Linear alkyl benzene sulfonate: Linear C₁₀C₁₃-alkylbenzene sulfonates, sodium salt • ²Alkyl ether sulfate: Sodium laureth sulfate + 2 mole ethylene oxide		

Table 11 Compatibility of Copolymers in Model Formulations

	Stability and optical appearance			
Formulation	A	B	C	D
Nil	Stable (transparent)	Stable (transparent)	Stable (transparent)	Stable (transparent)
CVVC 3	Stable (transparent)		Stable (transparent)	
CVVC 4	Stable (translucent)	-	Stable (transparent)	-
CVVC 5	Stable (translucent)	Stable (transparent)	Stable (translucent)	Stable (translucent)
CVVC 6	Stable (Translucent)	-	Stable (opaque)	-
CVVC 8	Stable (transparent)	-	Stable (transparent)	-
CVVC 10	Stable (translucent)	Stable (transparent)	-	-
CVVC 11 (Comp.)	-	-	Unstable (phase separation)	-
CVVC 13 (Comp.)	Unstable (phase separation)	-	Unstable (phase separation)	-

[0127] Compatibility of the cationic vinylcarboxamide/vinylamine copolymers according to the present invention with anionic surfactants is demonstrated under different concentrations such as 15 wt% as shown in Table 10 and up to 24 wt% as shown in Table 9. The results in Table 11 show compatibility of the cationic vinylcarboxamide/vinylamine copolymers according to the present invention in liquid detergent of various model formulations, thereby demonstrating the cationic vinylcarboxamide/vinylamine copolymers according to the present invention can be applied widely in liquid detergent formulations, especially those containing an anionic surfactant.

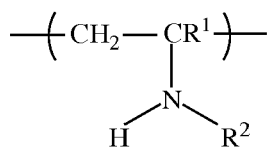
[0128] With the cationic vinylcarboxamide/vinylamine copolymers according to the present invention, a good balance between the improved dye transfer inhibiting and/or dye fixation performance of the copolymers and the compatibility of the copolymers with anionic surfactants commonly contained in liquid detergent formulations are successfully achieved.

Claims

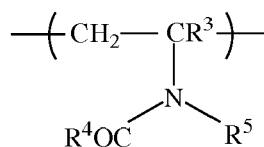
1. Use of at least one cationic vinylcarboxamide/vinylamine copolymer of a number average molecular weight (Mn) of up to 400,000 g/mol as a color care agent in laundering formulations, especially liquid laundering formulations, wherein the cationic vinylcarboxamide/vinylamine copolymer comprises

(1a) 30 to 95 mol% of vinylamine derived units represented by formula (I),

(1 b) 5 to 70 mol % of vinylcarboxamide derived units represented by formula (II),



(I)



(II)

wherein

R¹ and R³, which are identical, each represent H or methyl, preferably H,
 R² and R⁵, which are identical, each represent H or C₁₋₆ alkyl, preferably H, and
 R⁴ represents H or C₁₋₆ alkyl, preferably H or methyl, and optionally

(1c) 0 to 5 mol % of units derived from one or more ethylenically unsaturated monomers;

the sum of units (1a), (1b) and (1c) being 100%,
 and provided that

if the M_n is below 25,000 g/mol, the content of unit (1a) is equal to or higher than 40 mol%, and
 if the M_n is equal to or above 25,000 g/mol, the content of unit (1a) is equal to or less than 80 mol%.

2. The use according to claim 1, wherein the cationic vinylcarboxamide/vinylamine copolymer has a number average molecular weight M_n from 1,000 to 100,000, preferably from 3,000 to 60,000, more preferably of less than 50,000, and most preferably from 5,000 to 45,000.

3. The use according to claim 1 or 2, wherein the cationic vinylcarboxamide/vinylamine copolymer comprises

(1a) 40 to 80 mol% of vinylamine derived units represented by formula (I),
 (1 b) 20 to 60 mol % of vinylcarboxamide derived units represented by formula (II), and
 (1c) 0 to 5 mol % of units derived from one or more ethylenically unsaturated co-monomers, the sum of units (1a), (1b) and (1c) being 100%.

4. The use according to claim 1 or 2, wherein the cationic vinylcarboxamide/vinylamine copolymer consists of

(1a) 30 to 95 mol%, preferably 40 to 80 mol% of vinylamine derived units represented by formula (I), and
 (1 b) 5 to 70 mol %, preferably 20 to 60 mol % of vinylcarboxamide derived units represented by formula (II).

5. The use according to any of preceding claims, wherein the cationic vinylcarboxamide/vinylamine copolymer is a hydrolysate of copolymers or homopolymers comprising the vinylcarboxamide derived units represented by formula (II).

6. The use according to any of preceding claims, wherein the cationic vinylcarboxamide/vinylamine copolymer is a hydrolysate of homopolymers of N-vinylformamide or N-vinylacetamide.

7. The use according to any of preceding claims, wherein the cationic vinylcarboxamide/vinylamine copolymer is prepared and obtained from a polyvinylformamide (PVF) with a number average molecular weight M_n of from 1,000 to 100,000, preferably from 3,000 to 60,000, more preferably of less than 50,000, and most preferably from 5,000 to 45,000.

8. The use according to any of preceding claims, wherein the laundering formulations comprise at least one anionic surfactant, preferably a linear alkylbenzenesulfonate anionic surfactants.

9. The use cationic vinylcarboxamide/vinylamine copolymer according to any of preceding claims as a dye transfer inhibitor agent and/or as a dye fixation agent in laundering formulations.

10. The use according to any of preceding claims, wherein the cationic vinylcarboxamide/vinylamine copolymer is applied during laundering to textiles including, cotton, linen, silk and synthetic fiber materials, preferably to textiles of cotton and cotton blends.

11. The use according to any of preceding claims, wherein the cationic vinylcarboxamide/vinylamine copolymer is applied during laundering to textiles coloured with colored with reactive dyes and/or direct dyes; wherein the direct dyes are preferably selected from, including but not limited to, C.I. Direct Yellow 11, C.I. Direct Yellow 12, C.I. Direct Orange 26, C.I. Direct Orange 39, C.I. Direct Red 23, C.I. Direct Red 28, C.I. Direct Red 31, C.I. Direct Red 13, C.I. Direct Red 83.1 C.I. Direct Red 227, C.I. Direct Green 6, C.I. Direct Green 26, C.I. Direct Blue 6, C.I. Direct Blue 15, C.I. Direct Blue 71, C.I. Direct Blue 151, C.I. Direct brown 1, C.I. Direct Brown 2, C.I. Direct Brown MM, C.I. Direct Brown RN, C.I. Direct Violet 66, C.I. Direct Black 38, C.I. Direct Black 19, C.I. Direct Black 22, C.I. Direct

Black 168 or C.I. Direct Black 17; and the reactive dyes are preferably selected from, including but not limited to, C.I. Reactive Yellow 2, C.I. Reactive Yellow 125, C.I. Reactive Yellow 158, C.I. Reactive Yellow 14, C.I. Reactive Red 1, C.I. Reactive Red 120, C.I. Reactive Red 241, C.I. Reactive Red 158, C.I. Reactive Red 35, C.I. Reactive Green 6, C.I. Reactive Green 8, C.I. Reactive Blue 19, C.I. Reactive Blue 181, C.I. Reactive Blue 162, C.I. Reactive Blue 221, C.I. Reactive Orange 5, C.I. Reactive Orange 13, C.I. Reactive Orange 127, C.I. Reactive Orange 122, C.I. Reactive Brown 11, C.I. Reactive Brown 23, C.I. Reactive Brown 7, C.I. Reactive Violet 4, C.I. Reactive Violet 33, C.I. Reactive Violet 12, C.I. Reactive Black 8, C.I. Reactive Black 5 or C.I. Reactive Black 11.

12. A method for preparation of laundering formulations, especially liquid laundering formulations, by incorporation of the at least one cationic vinylcarboxamide/vinylamine copolymer as defined in any of claims 1 to 7 as a color care agent, wherein the cationic vinylcarboxamide/vinylamine copolymer is incorporated as a dye transfer inhibitor or a dye fixation agent.

13. The method according claim 12, wherein the laundering formulations comprise at least one anionic surfactant, preferably a linear alkylbenzenesulfonate anionic surfactants.

14. Laundering formulations, preferably liquid laundering formulations, which comprise the at least one cationic vinylcarboxamide/vinylamine copolymer as defined in any of claims 1 to 7 and at least one anionic surfactant, the latter preferably a linear alkylbenzenesulfonate anionic surfactant.

15. Laundering formulations according to claim 14, wherein the laundering formulations has a pH from about pH 4.0 to about pH 11.0, preferably from about pH 7.0 to about pH 8.5.



EUROPEAN SEARCH REPORT

Application Number
EP 17 17 7768

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 2 295 531 A1 (PROCTER & GAMBLE [US]) 16 March 2011 (2011-03-16) * paragraphs [0034], [0046]; claims 1-3 *	14,15	INV. C11D3/00 C11D3/37 C11D11/00
Y,D	JP H07 316590 A (LION CORP) 5 December 1995 (1995-12-05) * paragraphs [0018] - [0020], [0034], [0052]; claims; example 12; table 1 *	1-15	
Y	EP 1 670 986 A1 (BASF AG [DE]) 21 June 2006 (2006-06-21) * polyvinylformamide P4; page 3, lines 4-6; claim 1; tables 1, 2 * * paragraphs [0004], [0005], [0019] - [0021], [0050] *	1-15	
A	US 2016/047087 A1 (CREPET BERNARD [FR] ET AL) 18 February 2016 (2016-02-18) * paragraphs [0023], [0027] - [0032]; claims 1, 2; example 1 *	1-15	
T	R. Rathinamoorthy et al: "Optimization of dye transfer inhibition properties of Polyvinylpyrrolidone for reactive dye on cotton fabric", Indian Journal of Fibre & Textile Research, vol. 41 December 2016 (2016-12), pages 432-439, XP002776536, Retrieved from the Internet: URL: http://nopr.niscair.res.in/bitstream/123456789/39043/1/IJFTR%2041%284%29%20432-439.pdf [retrieved on 2017-12-08]	1-15	TECHNICAL FIELDS SEARCHED (IPC) C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 8 December 2017	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 17 17 7768

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-12-2017

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2295531 A1	16-03-2011	AR 078365 A1	02-11-2011
		CA 2770036 A1	17-03-2011
		EP 2295531 A1	16-03-2011
		ES 2623840 T3	12-07-2017
		HU E031936 T2	30-10-2017
		JP 5722328 B2	20-05-2015
		JP 2013503948 A	04-02-2013
		PL 2295531 T3	31-07-2017
		US 2011065624 A1	17-03-2011
		US 2015105311 A1	16-04-2015
		WO 2011031712 A2	17-03-2011

JP H07316590 A	05-12-1995	NONE	

EP 1670986 A1	21-06-2006	AT 519887 T	15-08-2011
		BR PI0414662 A	21-11-2006
		EP 1670986 A1	21-06-2006
		JP 2007507620 A	29-03-2007
		PE 07402005 A1	29-09-2005
		PT 1670986 E	05-09-2011
		TW 200521287 A	01-07-2005
		WO 2005033402 A1	14-04-2005

US 2016047087 A1	18-02-2016	FR 3004198 A1	10-10-2014
		US 2016047087 A1	18-02-2016
		WO 2014167208 A1	16-10-2014

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20070277327 A1 [0002] [0003]
- US 20080103081 A1 [0002] [0004]
- US 20080318830 A1 [0002] [0004]
- US 20080103080 A1 [0002] [0004]
- US 20090048137 A1 [0002] [0004]
- US 20080096788 A1 [0002] [0004]
- US 20020193280 A1 [0002] [0005]
- US 20030171249 A1 [0002] [0006]
- US 20100017973 A1 [0002] [0007]
- DE 4235798 A1 [0002] [0008]
- DE 19621509 A1 [0002] [0008]
- WO 9830664 A1 [0002] [0008]
- WO 2006100246 A1 [0002] [0009]
- EP 0753566 A1 [0002] [0010]
- JP H07316590 A [0002] [0011]
- WO 2005026220 A1 [0015]
- WO 1998025981 A1 [0016]
- EP 0753570 A1 [0017]
- CH 690401 A5 [0018]
- US 6039768 A [0018]
- WO 97032477 A1 [0019]
- WO 95025759 A1 [0020]
- WO 2014148465 A1 [0020]
- WO 9516815 A1 [0021]
- EP 2977507 A1 [0067]
- WO 9906524 A1 [0088]

Non-patent literature cited in the description

- **G. ODIAN.** Principles of Polymerization. Wiley, 2004 [0060]
- Liquid Detergents. Surfactant Sci. Ser. Marcel Dekker, 1997, vol. 67, 272-304 [0088]