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(54) NOVEL FLUORINATED COPOLYMERS, THEIR USE FOR COATING AND IMPREGNATING SUBSTRATES, AND RESULTING TREATED SUBSTRATES

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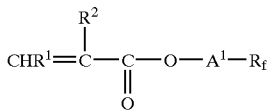
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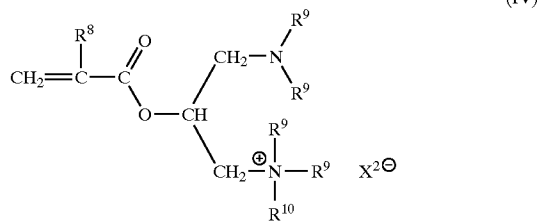
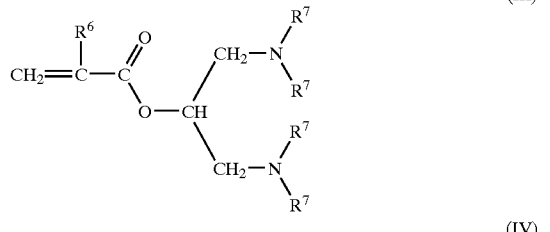
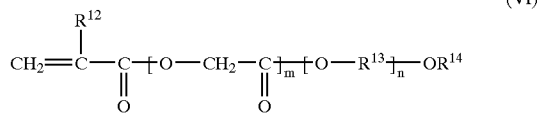
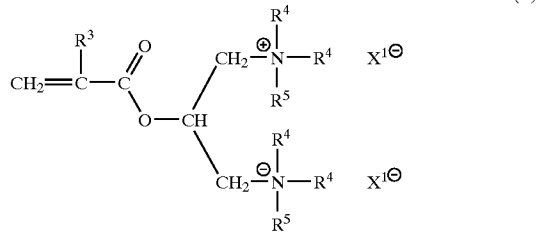
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(57) ABSTRACT

This cationic fluorocopolymer is obtained from a composition comprising, per 100 parts by weight (pw): 5 to 92 pw of at least one polyfluorinated monomer (I); 0.10 to 25 pw of at least one monomer (II), (III) or (IV) ; 0 to 20 pw of at least one anionic monomer or monomer potentially anionic by varying the pH; 0 to 25 pw of at least one vinyl monomer (V) : CH₂=CHR¹¹; 0 to 60 pw of at least one monomer (VI); 0 to 10 pw of at least one monomer capable of causing postcrosslinking of the fluorocopolymer during or after the said fluorocopolymer has formed a coating on a substrate; and 0 to 25 parts by weight of at least one monomer (VII):



-continued



R¹, R²=H or one of them =H and the other =C₁-C₄ alkyl; A=divalent linking group linked to O by a carbon atom and possibly comprising one or more oxygen and/or sulphur and/or nitrogen atoms; R_f=C₂-C₂₀ perfluorinated radical with a straight or branched chain; R, R, R_s, R¹=H or -CH₃; R⁴, R⁵, R⁷, R⁹, R¹⁰=H, C₁-C₁₈ is alkyl, benzyl or hydroxyethyl; X¹, X²=monovalent anion; R¹¹=C₁-C₁₈ alkyl carboxylate, alkyl ether or alkyl; m=0 or 1; R¹³=C₁-C₆ alkylene possibly substituted with at least one halogen; m=0 or an integer from 1 to 11, limits inclusive; R¹⁴=C₁-C₃₂ alkyl possibly substituted with at least one halogen, or cycloalkyl possibly substituted with at least one halogen; R¹⁵=H or C-C₄ alkyl; A²=C₁-C₄ linear or branched alkylene; R¹⁶, R¹⁷=H, C₁-C₁₈ linear or branched alkyl, or hydroxyethyl or benzyl, or R¹⁶ and R¹⁷ together with the nitrogen atom to which they are linked form a morpholino, piperidino or pyrrolidinyl radical.

NOVEL FLUORINATED COPOLYMERS, THEIR USE FOR COATING AND IMPREGNATING SUBSTRATES, AND RESULTING TREATED SUBSTRATES

[0001] The subject of the present invention is novel fluorocopolymers and their use for the coating and the impregnation of various substrates, such as textiles, leather, wood, non-wovens, metal, concrete and, more particularly, paper and similar articles as well as textiles, for the purpose of making them oleophobic and hydrophobic. The invention also relates to the substrates thus treated.

[0002] To achieve this objective, many cationic fluoroderivatives have already been proposed, these having three types of presentation:

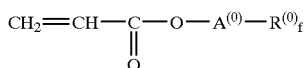
[0003] (1) in the form of a latex or emulsion (a dispersion in water of polymer particles stabilized by surfactants);

[0004] (2) in the form of a solution in a water/solvent mixture; or

[0005] (3) in the form of an aqueous dispersion after removing the solvent in presentation (2).

[0006] European Patent EP-B-0 234 601 thus teaches cationic fluorocopolymers having a presentation in the form of a latex or emulsion, and obtained by copolymerization of:

[0007] (a) 60 to 80% by weight of acrylate fluoromonomer of formula:



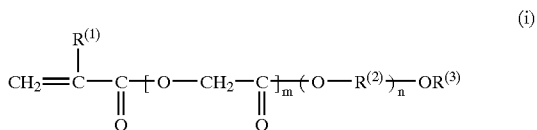
[0008] in which:

[0009] $\text{R}^{(0)_f}$ is an aliphatic perfluorinated radical having from 3 to 20 carbon atoms; and

[0010] $\text{A}^{(0)}$ is a divalent linking group;

[0011] (b) 1 to 30% by weight of:

[0012] (i) an alkyl or alkoxyalkyl (meth)acrylate monomer of formula (i):



[0013] in which:

[0014] $\text{R}^{(1)}$ is H or methyl;

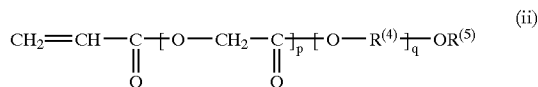
[0015] $\text{R}^{(2)}$ is a C_1 - C_6 alkylene group, the $\text{R}^{(2)}$ groups being identical or different;

[0016] $\text{R}^{(3)}$ is a C_1 - C_{20} alkyl or cycloalkyl group;

[0017] m is 0 or 1; and

[0018] n is 0 to 10, provided that when n is 0, $\text{R}^{(3)}$ is a C_1 - C_{16} alkyl or cycloalkyl group; or

[0019] (ii) a halogenated alkyl or alkoxyalkyl acrylate monomer of formula (ii):



[0020] in which:

[0021] $\text{R}^{(4)}$ is a C_1 - C_6 alkylene or haloalkylene group, the $\text{R}^{(4)}$ groups being identical or different;

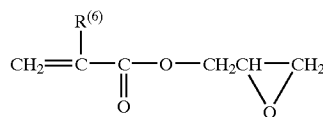
[0022] $\text{R}^{(5)}$ is a C_1 - C_{20} alkyl, cycloalkyl, haloalkyl or halocycloalkyl group;

[0023] at least one R or R group containing a halogen atom;

[0024] p is 0 or 1; and

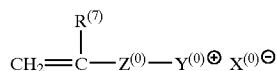
[0025] q is 0 to 10, provided that when q is 0, $\text{R}^{(5)}$ is a C_1 - C_{16} haloalkyl or halocycloalkyl group;

[0026] (c) 2 to 15% by weight (when the copolymer comprises units deriving from monomer (i)) or 1 to 15% by weight (when the copolymer comprises units deriving from monomer (ii)) of a monomer of formula:



[0027] in which $\text{R}^{(6)}$ is H or methyl;

[0028] (d) 1 to 6% by weight of a cationic monomer of formula:



[0029] in which:

[0030] $\text{R}^{(7)}$ represents H or methyl;

[0031] $\text{Z}^{(0)}$ is an electron-withdrawing divalent group which activates the radical polymerization;

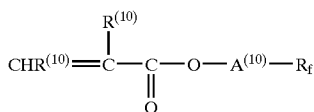
[0032] $\text{Y}^{(0)+}$ is a cationic monovalent group; and

[0033] $\text{X}^{(0)-}$ is an anion; and

[0034] (e) 0 to 20% by weight of vinylidene chloride.

[0035] International Application WO 98/23657 relates to cationic fluorocopolymers having a presentation in the form of a solution in a water/solvent (N-vinylpyrrolidone) mixture, which are obtained by the polymerization of:

[0036] (a) 50 to 92% by weight of one or more poly-fluoromonomers of general formula:



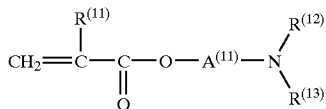
[0037] in which:

[0038] $\text{A}^{(10)}$ represents a divalent linking group which is linked to C by a carbon atom and which may comprise one or more oxygen, sulphur and/or nitrogen atoms;

[0039] one of the symbols $\text{R}^{(10)}$ represents a hydrogen atom and the other a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms; and

[0040] R_f represents a perfluorinated radical, having a straight or branched chain, containing 2 to 20 carbon atoms, preferably 4 to 16 carbon atoms,

[0041] (b) 1 to 25% by weight of one or more monomers of general formula:



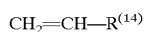
[0042] in which:

[0043] $\text{R}^{(11)}$ represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms;

[0044] $\text{A}^{(11)}$ represents a linear or branched alkylene radical containing 1 to 4 carbon atoms; and

[0045] the symbols $\text{R}^{(12)}$ and $\text{R}^{(13)}$, which are identical or different, each represent a hydrogen atom, a linear or branched alkyl radical containing 1 to 18 carbon atoms or a hydroxyethyl or benzyl radical, or $\text{R}^{(12)}$ and $\text{R}^{(13)}$ together with the nitrogen atom to which they are linked form a morpholino, piperidino or pyrrolidin-1-yl radical;

[0046] (c) 1 to 25% by weight of a vinyl derivative of general formula:



[0047] in which $\text{R}^{(14)}$ may be an alkyl carboxylate or alkyl ether group containing from 1 to 18 carbon atoms; and

[0048] (d) 0 to 10% of any monomer other than the monomers of the above three formulae.

[0049] The copolymerization reaction leading to the fluorocopolymers described by that international application is carried out in solution in a water-miscible organic solvent or solvent mixture and is followed by a step of dilution with an aqueous solution of a mineral or organic acid. This dilution step is carried out in the presence of hydrogen peroxide or is followed by a treatment by means of an aqueous hydrogen peroxide solution.

[0050] After the said dilution step, it is necessary to carry out a vacuum distillation or to flush with an inert gas, for example nitrogen, in order to remove the volatile compounds and to obtain a composition that can be sold and applied to the substrate to be treated.

[0051] The solvents exemplified in that application are, mostly, mixtures based on N-methylpyrrolidone. Because of their boiling point, these solvents are not completely removed by the distillation operation so that significant quantities of them remain in the commercial composition.

[0052] This commercial composition is thus in the form of a solution in a water/solvent (N-methylpyrrolidone) mixture, thereby giving it stability properties which are highly advantageous for its transportation and its storage.

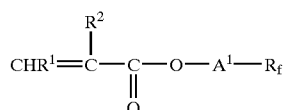
[0053] However, for some applications, and especially for the treatment of papers or similar articles intended for the field of packaging food products, the presence of an organic solvent liable to come into contact with these food products is a drawback because of the health risks.

[0054] International Application WO 98/23657 mentions (cf. page 5 lines 14-15) that the use of light solvents makes it possible to obtain, after distillation, a composition containing no organic solvent, that is to say in the form of an aqueous copolymer dispersion.

[0055] The tertiary or quaternary amino monomers used for the preparation of the cationic fluorocopolymers described in the above documents possess a single tertiary amino group or a single quaternary amino group per molecule. Unlike these known structures, it has now been found that other monomers having two tertiary amino groups, or two quaternary amino groups or one quaternary amino group combined with one tertiary amino group can be used to prepare novel cationic fluorocopolymers which give various substrates, and especially paper and textiles, the same hydrophobic and oleophobic properties and which, in addition, may be in the form of aqueous compositions, especially in the form of a latex, emulsion or dispersion, or in the form of a solution in a water/solvent mixture.

[0056] The subject of the present invention is therefore firstly a cationic fluorocopolymer, characterized in that it is obtained from a monomer composition comprising, per 100 parts by weight:

[0057] (A) 5 to 92 parts by weight, in particular 40 to 90 parts by weight, of at least one polyfluorinated monomer of formula (I):



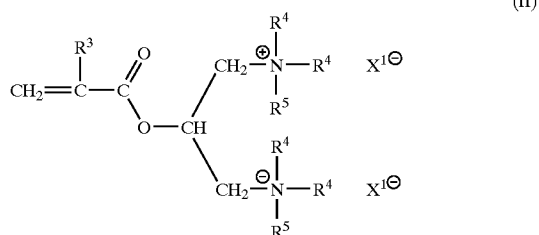
[0058] in which:

[0059] R^1 and R^2 both represent a hydrogen atom or one of them represents a hydrogen atom and the other a C_1 - C_4 alkyl radical;

[0060] A^1 represents a divalent linking group which is linked to O by a carbon atom and may comprise one or more oxygen and/or sulphur and/or nitrogen atom; and

[0061] R_f represents a C_2 - C_{20} perfluorinated radical with a straight or branched chain;

[0062] (B) 0.10 to 25 parts by weight, in particular 1 to 18 parts by weight, of at least one monomer chosen from those of the following formulae (II), (III) and (IV):

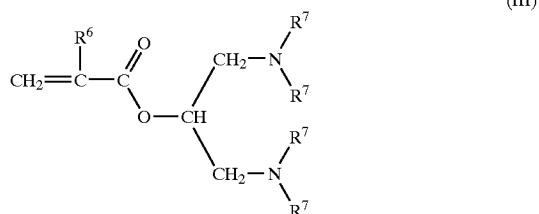


[0063] in which:

[0064] R^3 represents H or $-\text{CH}_3$;

[0065] R^4 and R^5 , which are identical or different, each independently represent H, C_1 - C_{18} alkyl, benzyl or hydroxyethyl; and

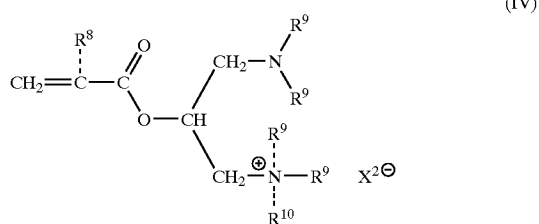
[0066] x^1 represents a monovalent anion;



[0067] in which:

[0068] R^6 represents H or $-\text{CH}_3$; and

[0069] R^7 represents H, C_1 - C_{18} alkyl, benzyl or hydroxyethyl;



[0070] in which:

[0071] R^8 represents H or $-\text{CH}_3$;

[0072] R^9 and R^{10} , which are identical or 20 different, each independently represent hydrogen, C_1 - C_{18} alkyl, benzyl or hydroxyethyl; and

[0073] X^2 represents a monovalent anion;

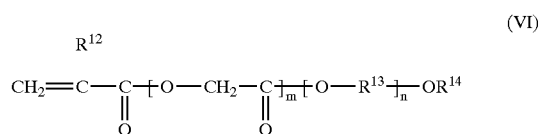
[0074] (C) 0 to 20 parts by weight, in particular 1 to 10 parts by weight, of at least one anionic monomer or a monomer which is potentially anionic by varying the

[0075] (D) 0 to 25 parts by weight, in particular 2 to 10 parts by weight, of at least one vinyl monomer of general formula (V):



[0076] in which R^1 represents a C_1 - C_{18} alkyl or an alkyl carboxylate or alkyl ether group;

[0077] (E) 0 to 60 parts by weight of at least one monomer of formula (VI):



[0078] in which:

[0079] R^{12} represents H or $-\text{CH}_3$;

[0080] m is 0 or 1;

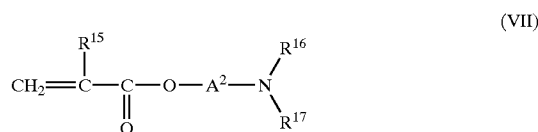
[0081] R^{13} represents a C_1 - C_6 alkylene residue possibly substituted with at least one halogen;

[0082] m is 0 or is an integer from 1 to 11, limits inclusive;

[0083] R^{14} represents a C_1 - C_{32} alkyl residue possibly substituted with at least one halogen, or a cycloalkyl residue possibly substituted with at least one halogen;

[0084] (F) 0 to 10 parts by weight of at least one monomer capable of causing the postcrosslinking of the fluorocopolymer during or after the said fluorocopolymer has formed a coating on a substrate; and

[0085] (G) 0 to 25 parts by weight of at least one monomer of general formula (VII):



[0086] in which:

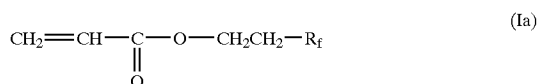
[0087] R^{15} represents a hydrogen atom or an alkyl radical containing 1 to 4 carbon atoms;

[0088] A^2 represents a linear or branched alkylene radical containing 1 to 4 carbon atoms;

[0089] the symbols R^{16} and R^{17} , which are identical or different, each represent a hydrogen atom, a linear or branched alkyl radical containing 1 to 18 carbon atoms or a hydroxyethyl or benzyl radical, or R^{16} and

R¹⁷ together with the nitrogen atom to which they are attached form a morpholino, piperidino or pyrrolidin-1-yl radical.

[0090] The monomer or monomers (A) of formula (I) are especially those for which R_f is a C₄-C₁₆ perfluoroalkyl radical. More particularly, the monomer or monomers (A) of formula (I) are chosen from those of formula (Ia):



[0091] in which R_f represents a C₄-C₁₆ perfluoroalkyl radical.

[0092] The monomer or monomers (B) of formula (II) are chosen especially from those for which:

[0093] R³ represents H;

[0094] R⁴ represents —CH₃;

[0095] R⁵ represents —CH₃ or benzyl; and

[0096] X¹ represents Cl.

[0097] The monomer (B) of formula (III) is especially that for which:

[0098] R⁶ represents H; and

[0099] R⁷ represents —CH₃.

[0100] The monomer or monomers (B) of formula (IV) are chosen especially from those for which:

[0101] R⁸ represents H;

[0102] R⁹ represents —CH₃;

[0103] R¹⁰ represents —CH₃ or benzyl; and

[0104] X² represents Cl.

[0105] In the case of the copolymers according to the invention which are obtained in an emulsion, it will be preferred to use, as compound(s) (B), a compound (II) in which R³=H; R⁴=—CH₃; R⁵=—CH₃ or —CH₂-C₆H₅ and X¹=Cl. and/or a compound (IV) in which R⁸=H; R⁹=—CH₃; R¹⁰=—CH₃ or —CH₂-C₆H₅ and X²=Cl.

[0106] In the case of the copolymers according to the invention which are obtained in solution, it will be preferred to use, as compound(s) (B), a compound (III) in which R⁶=H and R⁷=—CH₃ and/or a compound (IV) in which R⁸=H; R⁹=—CH₃; R¹⁰=—CH₃ or —CH₂-C₆H₅ and X²=Cl.

[0107] The anionic monomer(s) or monomer(s) potentially anionic by varying the pH (monomers (C)) are especially chosen from ethylenically unsaturated carboxylic acids and salts thereof and ethylenically unsaturated sulphonated monomers and salts thereof.

[0108] The ethylenically unsaturated carboxylic acid is especially methacrylic acid and the ethylenically unsaturated sulphonated monomers are especially chosen from 2-acrylamido-2-methylpropanesulphonic acid and salts thereof. It is preferred to use methacrylic acid as monomer (C).

[0109] The monomer (D) is especially vinyl acetate.

[0110] The monomer or monomers (E) are especially chosen from behenyl acrylate, stearyl methacrylate, methoxyethyl acrylate and methoxyethyl methacrylate.

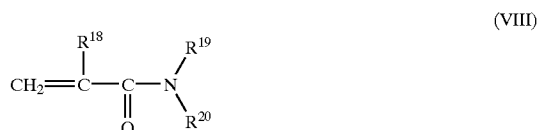
[0111] The monomer or monomers (F), which can cause postcrosslinking of the polymer during or after the fluorocopolymer has formed a coating on the substrate, are especially chosen from:

[0112] (F1), ethylenically unsaturated silane monomers;

[0113] (F2), 2-hydroxy-3-chloropropyl (meth)acrylate;

[0114] (F3), (meth)acrylates with an epoxy functional group;

[0115] (F4), monomers of formula (VIII):

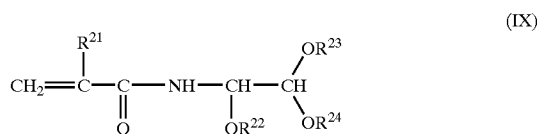


[0116] in which:

[0117] R¹⁸ represents H or —CH₃; and

[0118] R¹⁹ and R²⁰, which are identical or different, each independently represent H or a C₁-C₅ alkyl, which possibly includes one or more OH groups, or a (C₁-C₅)alkoxy-(C₁-C₅)alkyl; and

[0119] (F5), monomers of formula (IX):



[0120] in which:

[0121] R²¹ represents H or —CH₃; and

[0122] R²², R²³ and R²⁴, which are identical or different, each represent H or a C₁-C₄ alkyl.

[0123] The monomer (F4) is especially N-methylolacrylamide. The monomer (F5) of formula (IX) is especially that for which:

[0124] R² and R²² each represent H; and

[0125] R²³ and R²⁴ each represent —CH₃.

[0126] The monomer (G) is especially dimethylaminoethyl methacrylate.

[0127] Depending on the final presentation of the polymer, the fluorocopolymers according to the present invention are prepared by radical copolymerization of the monomers using two polymerization techniques, especially emulsion polymerization (to obtain a polymer in latex or emulsion form) or solution polymerization (to obtain the polymer in

solution form in a water/solvent mixture or in the form of an aqueous dispersion after solvent removal).

Emulsion Polymerization

[0128] In the case of emulsion polymerization, to carry out the reaction one or more water-miscible organic solvents must be used. The present invention describes the composition of the water/solvent(s) mixture which can result in a-product with a flash point above 100° C. =p The organic solvents are compounds which can be at least partially diluted with water, such as propylene glycol, ethylene glycol, ethyl glycol, methoxypropanol, ethylene carbonate, propylene carbonate, the ethylic ether of ethylene glycol, the methyl ether of propylene glycol, N-methylpyrrolidone, acetone, methyl ethyl ketone, acetic acid, propionic acid, tetrahydrofuran, diacetone alcohol, methyl alcohol, ethyl alcohol, isopropyl alcohol and γ -butyrolactone.

[0129] The amounts to be used in the water/solvent(s) mixture may vary between 40 and 95% by weight in the case of water and from 5 to 60% by weight in the case of the solvent mixture.

[0130] The following solvents are preferably used:

[0131] propylene glycol, N-methylpyrrolidone, the methyl ether of propylene glycol or acetic acid; in this case, the polymerization is not followed by a distillation as the solvent mixture does not result in a flash point between 0 and 100° C.;

[0132] acetone; the water/acetone mixture results in a flash point between 0 and 100° C.; in this case, the distillation is carried out until the solvent is removed from the emulsion.

[0133] The emulsion copolymerization is carried out in the presence of cationic surfactants which may or may not be combined with nonionic surfactants in an amount from 1 to 10% by weight with respect to the monomer mixture. The total concentration of monomers in the reaction mixture (water/solvent/monomers/surfactants) may range from 15 to 70% by weight and is preferably between 30 and 60% by weight.

[0134] The molecular masses are adjusted by means of chain transfer agents, such as mercaptans, in an amount from 0.01 to 0.5% by weight with respect to the monomer mixture, or by the monomer introduction technique.

[0135] The copolymerization may be initiated between 20 and 150° C. by means of initiators of the peroxide type (such as hydrogen peroxide) or persalt (such as persulphates) or of the azo type, such as 4,4'-azobis(4-cyano pentanoic acid) or azobis(aminidinopropane) hydro-chloride. They are used in an amount from 0.1 to 4% by weight with respect to the monomer mixture.

[0136] The amount of water-miscible solvent to be used may vary within wide limits and is generally between 10 and 80 parts by weight per 100 parts of the total of the monomers. For the emulsion of the monomers, high-energy emulsifying means may possibly be used, such as ultrasound or homogenizers of the Manton-Gaulin type.

[0137] The polymerization step may be followed by a solvent distillation step so as to obtain an emulsion in water without any organic solvent.

Solution Polymerization

[0138] This type of polymerization is used for copolymers having at least one tertiary amino group which is quaternized or salified by an acid at the end of polymerization. The solution polymerization is carried out in a water-miscible organic solvent or in a mixture of such solvents. Preferably, a distillable solvent will be used, in the form of a mixture with water in order to obtain a solventless product. The reaction mixture is then diluted with water in the presence of a mineral or organic acid in order to salify the macromolecules.

[0139] According to a preferred variant of the invention, this dilution step is carried out in the presence of hydrogen peroxide or is followed by a treatment by means of an aqueous hydrogen peroxide solution.

[0140] As water-miscible organic solvents distillable as a mixture with water, in which solvents the copolymerization is carried out, mention may be made, by way of non-limiting examples, of ketones (for example, acetone and methyl ethyl ketone), alcohols (for example, isopropanol) and ethers (for example, methyl ether).

[0141] To implement the invention, it is preferred to use as solvent methyl isobutyl ketone or methyl ethyl ketone, or a mixture of these with acetone.

[0142] As water-miscible organic solvents not distillable as a mixture with water, in which solvents the copolymerization is carried out, mention may be made by way of a non-limiting example of N-vinylpyrrolidone.

[0143] The total concentration of monomers in the organic solvent or organic solvent mixture may range from 15 to 70% by weight and is preferably between 30 and 60% by weight.

[0144] The copolymerization is carried out in the presence of at least one initiator, used in an amount from 0.1 to 2% by weight with respect to the total weight of monomers. As initiators, it is possible to use peroxides, such as benzoyl peroxide, lauroyl peroxide, succinyl peroxide and tert-butyl perpivalate, or azo compounds such as, for example, 2,2'-azobis(isobutyronitrile), 4-4'-azobis(4-cyanopentanoic acid) and azobis(aminidinopropane). The copolymerization step may be carried out at a temperature ranging from 40° C. up to the boiling point of the reaction mixture. Preferably, it is carried out between 60 and 90° C.

[0145] The dilution step consists in adding, to the organic solution of the copolymer, an aqueous solution of a strong or moderately strong organic or mineral acid, that is to say one whose dissociation constant or the first dissociation constant is greater than 10^{-5} .

[0146] As examples of such acids, mention may be made of hydrochloric, hydrobromic, sulphuric, nitric, phosphoric, acetic, formic, propionic and lactic acids, but it is preferred to use acetic acid. The amount of aqueous solution to be used and its acid concentration must be sufficient, on the one hand, to completely salify the amine functional groups provided by the monomer(s) of formulae (III), (IV) and (VII) and, on the other hand, to obtain a final copolymer solution having a solids content between 5 and 30% by weight, preferably between 20 and 30% by weight. For complete salification of the amine functional groups, the amount of acid is advantageously between 0 and 5 acid

equivalents with respect to the monomer(s) of formulae (III), (IV) and (VII), preferably between 1 and 2 equivalents.

[0147] The amount of hydrogen peroxide used is between 0 and 10% by weight, preferably from 0.5 to 4% by weight with respect to the total initial weight of monomers. The treatment is carried out between 25 and 100° C., preferably from 70 to 85° C.

[0148] These emulsion or solution fluorocopolymers can be applied to various substrates, such as leather, non-wovens, building materials, paper and paperboard. In particular, they can be applied to textiles or to paper using various techniques (in a size-press or throughout the bulk of the material), thus giving the substrate excellent hydrophobic and oleophobic properties without requiring additives (sequestrants, retention agents, fixing resins).

[0149] The subject of the present invention is also a solid substrate comprising at least one fluorocopolymer according to the invention, as defined above.

[0150] As substrates capable of being made oleophobic and hydrophobic with the products according to the invention, it is preferred to use paper, paperboard and similar materials. It is also possible to use other highly varied materials such as, for example, woven or non-woven articles based on cellulose or regenerated cellulose, on natural, artificial or synthetic fibres such as cotton, cellulose acetate, wool, silk, polyamide, polyester, polyolefin, polyurethane or polyacrylonitrile fibres, leather, plastics, glass, wood, metals, porcelain and painted surfaces. It may also be advantageous to treat building materials such as concrete, stone, brick and tiles with the products according to the invention.

[0151] The compositions comprising a fluorocopolymer according to the invention are mainly applied diluted in an aqueous medium or in a mixture of water and solvents using known techniques, for example by coating, impregnation, immersion, spraying, brushing, padding or film-coating.

[0152] The products according to the invention can be applied in aqueous solution to paper, either onto the surface of the already completed substrate (preferably in an amount of 0.05 to 0.2% fluorine with respect to the weight of paper) or into the body of the material, that is to say into the paper pulp (preferably in an amount of 0.2 to 0.4% fluorine with respect to the weight of pulp).

[0153] The substrates thus treated exhibit good oleophobic and hydrophobic properties after simple drying at room temperature or at high temperature, optionally followed by a heat treatment which can range, depending on the nature of the substrate, up to 200° C.

[0154] To obtain good attachment of the fluorocopolymers according to the invention to the substrates to which they have been applied, and, in addition, to confer a specific effect, it is sometimes advantageous to combine them with certain additives, polymers, thermocondensable products and catalysts capable of promoting their crosslinking with the substrate. Mention may be made, as such, of urea-formaldehyde or melamine-formaldehyde condensates or precondensates, epoxy derivatives, such as diglycidylglycerol, polyamine-epichlorohydrin resins, glyoxal and its derivatives, polyvinyl alcohols and cationic, oxidized and amphoteric starches.

[0155] It may also be advantageous to combine the fluorocopolymers according to the invention with one or more nonionic and/or cationic surfactants in order to improve the wetting of the substrate. The weight of this or these surfactants with respect to the total weight of copolymer may vary from 0 to 100%.

[0156] The following tests were used to evaluate the performance of the treated substrates according to the invention:

Grease Resistance Test or Kit Test Value

[0157] This test, described in TAPPI, Vol. 50, No. 10, pages 152A and 153A and in the RC338 and UM511 standards, makes it possible to measure the grease resistance of substrates using mixtures of castor oil, toluene and heptane. These mixtures contain variable amounts of these three products:

Kit Test value	Volume of castor oil	Volume of toluene	Volume of heptane
1	200	0	0
2	180	10	10
3	160	20	20
4	140	30	30
5	120	40	40
6	100	50	50
7	80	60	60
8	60	70	70
9	40	80	80
10	20	90	90
11	0	100	100
12	0	90	110

[0158] The test consists in gently depositing drops of these mixtures on the treated paper. The drops are left on the paper for 15 seconds and then the appearance of the paper or paperboard is carefully observed and the wetting or penetration revealed by a browning of the surface is recorded. The number corresponding to the mixture containing the highest percentage of heptane, which does not penetrate or wet the paper, is the Kit Test value of the paper and is regarded as being the degree of oleophobicity of the treated paper. The higher the Kit Test value, the better the oleophobicity of the paper.

Cobb Test

[0159] The Cobb test [NF EN 20535-ISO 535 (1994)] consists in measuring the weight (in g) of water absorbed during one minute by a square metre of paper supporting a water height of one centimetre.

Oleophobicity Test

[0160] The oleophobicity was measured on certain substrates using the method described in "AATCC Technical Manual", Test Method 118-1972, which evaluates the non-wettability of the substrate using a series of oily liquids numbered 1 to 8:

[0161] No. 1: liquid paraffin

[0162] No. 2: liquid paraffin/n-hexadecane (64/35)

[0163] No. 3: n-hexadecane

[0164] No. 4: n-tetradecane

[0165] No. 5: n-dodecane

[0166] No. 6: n-decane

[0167] No. 7: n-octane

[0168] No. 8: n-heptane.

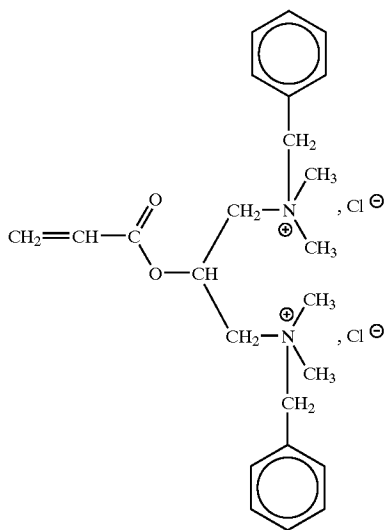
[0169] The test consists in depositing drops of these mixtures on the treated substrates and then in observing the effect of the drop after 30 seconds of contact. The rating is given by the number of the last drop of liquid which has neither penetrated nor wetted the substrate.

Hydrophobicity Test

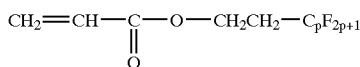
[0170] This test, called a spray test, is fully described by the AATCC 22-1989 standard. It consists in pouring, over a treated fabric, fixed to a substrate inclined at 45° C, 250 ml of water from a funnel fitted with a sprinkle rose over about twenty seconds and from a height of approximately 15 cm. The test reading is a visual one, the rating going from 0 (for a completely wetted fabric) to 100 (for a completely dry fabric).

[0171] The following examples illustrate the invention without, however, limiting the scope thereof. The parts and percentages given are by weight, unless otherwise indicated, and the following abbreviation has been used:

[0172] S-ADAMQUAT 2BZ: a compound of formula:



[0173] In Examples 1 and 2, a mixture of polyfluoroacrylates of formula:



[0174] was used, in which p is equal to 8, 10, 12 and 14 in respective proportions by weight of 63/25/10/2.

EXAMPLE 1

[0175] A reactor comprising 1000 parts by volume, heated by a thermostatted jacket and fitted with an anchor stirrer and with a reflux condenser, was charged with the following:

[0176] 383 parts of demineralized water;

[0177] 140 parts of acetone;

[0178] 3.75 parts of trimethyloleylammonium chloride;

[0179] 3.43 parts of a mixture of ethoxylated alkylphenols (HLB=15);

[0180] 176.9 parts of the mixture of polyfluorinated acrylates defined above;

[0181] 43.2 parts of methoxyethyl acrylate;

[0182] 25 parts of 48% N-methylolacrylamide in water;

[0183] 12.8 parts of an aqueous 75% S-ADAMQUAT 2BZ solution; and

[0184] 0.48 parts of n-dodecylmercaptan.

[0185] After inerting with nitrogen and heating to 70° C., the polymerization was initiated using 1.2 parts of azobis (amidinopropane) hydrochloride dissolved in 8 parts of water. After 2 hours of polymerization at 70° C., 796 parts of an emulsion having a solids content of 30.2% was obtained.

[0186] Next, the acetone was distilled off at 90° C., resulting in a latex having a solids content of 36%; this was then diluted with water in order to obtain a perfectly stable emulsion having a solids content of 25%. This product did not have a flash point between 0 and 100° C. in the closed cup test (using the Setaflash N.F.T.300.50 method).

EXAMPLE 2

[0187] A reactor comprising 1000 parts by volume, heated by a thermostatted jacket and fitted with an anchor stirrer and with a reflux condenser, was charged with the following:

[0188] 257.4 parts of demineralized water;

[0189] 91.8 parts of acetone;

[0190] 8.98 parts of trimethyloleylammonium chloride;

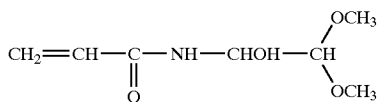
[0191] 8.22 parts of a mixture of ethoxylated alkylphenols (HLB=15);

[0192] 118.7 parts of the mixture of polyfluorinated acrylates defined above;

[0193] 50.3 parts of behenyl acrylate;

[0194] 5.74 parts of 48% N-methylolacrylamide in water;

[0195] 7.30 parts of a 50% solution of the monomer of formula:



[0196] 2.80 parts of an aqueous 75% S-ADAM-QUAT 2BZ solution;

[0197] 8.45 parts of methyl acrylate; and

[0198] 0.18 parts of n-dodecylmercaptan.

[0199] After inerting with nitrogen and heating to 70° C., the polymerization was initiated using 0.9 parts of azobis (amidinopropane) hydrochloride dissolved in 9 parts of water. After 2 hours of polymerization at 70° C., 573 parts of an emulsion having a solids content of 36% was obtained.

[0200] Next, the acetone was distilled off at 90° C., resulting in a latex having a solids content of 40%; this was then diluted with water in order to obtain a perfectly stable emulsion having a solids content of 20%. This product did not have a flash point between 0 and 100° C. in the closed cup test (using the Setaflash NF.T.300.50 method).

EXAMPLE 3

[0201] An aqueous size-press bath containing 16 g/l of the emulsion obtained in Example 1 was prepared.

[0202] This composition was applied in the size press to a 70 g/m² gummed paper composed of bleached pulp. The degree of application was about 70%. After drying for 1 minute at 120° C., the paper thus treated was stored for one day at room temperature and then subjected to the various tests.

[0203] The results are given in Table 1 below:

TABLE 1

TESTS	PAPER TREATED	
	WITH THE BATH	UNTREATED PAPER
KIT TEST VALUE	12	0
COBB VALUE (g/m ²)	17	>20

[0204] The cationic fluorocopolymer of the invention gives the treated paper excellent oleophobic and hydrophobic properties.

EXAMPLE 4

[0205] A padding bath containing 20 g/l of the emulsion obtained in Example 2 and 1.5 g/l of acetic acid in water was prepared at room temperature. A polyester fabric was then padded in this bath, with 40% expression. After drying, the fabric was heat-set for 1 minute at 160° C. in a BENZ-type heat setter.

[0206] The hydrophobicity and oleophobicity of the fabric were then tested. The results obtained are given in Table 2 below:

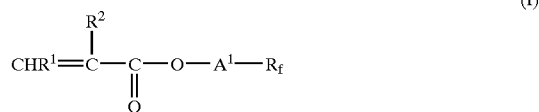
TABLE 2

TESTS	FABRIC TREATED	
	WITH BATH	UNTREATED FABRIC
SPRAY TEST	100	0
OLEOPHOBICTY	5	0

[0207] The cationic fluorocopolymer of the invention gives the treated fabric excellent oleophobic and hydrophobic properties.

1. Cationic fluorocopolymer, characterized in that it is obtained from a monomer composition comprising, per 100 parts by weight:

(A) 5 to 92 parts by weight of at least one polyfluorinated monomer of formula (I):



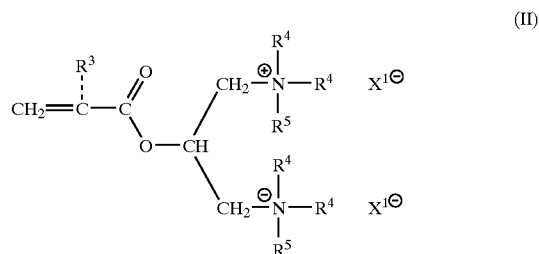
in which:

R¹ and R² both represent a hydrogen atom or one of them represents a hydrogen atom and the other a C₁-C₄ alkyl radical;

A¹ represents a divalent linking group which is linked to O by a carbon atom and may comprise one or more oxygen and/or sulphur and/or nitrogen atom; and

R_f represents a C₂-C₂₀ perfluorinated radical with a straight or branched chain;

(B) 0.10 to 25 parts by weight of at least one monomer chosen from those of the following formulae (II), (III) and (IV):



in which:

R³ represents H or —CH₃;

R⁴ and R⁵, which are identical or different, each independently represent H, C₁-C₁₈ alkyl, benzyl or hydroxyethyl; and

X¹. represents a monovalent anion;

R⁵ represents —CH₃ or benzyl; and

x¹ represents Cl;

the monomer (B) of formula (III) is that for which:

R⁶ represents H;

R⁷ represents —CH₃; and

the monomer or monomers (B) of formula (IV) are chosen from those for which:

R⁸ represents H;

R⁹ represents —CH₃;

R¹⁰ represents —CH₃ or benzyl; and

x² represents Cl.

7. Cationic fluorocopolymer according to one of claims 1 to 6, characterized in that the monomer or monomers (C) represent 1 to 10 parts by weight per 100 parts by weight of total monomer.

8. Cationic fluorocopolymer according to one of claims 1 to 7, characterized in that the monomer or monomers (C) are chosen from ethylenically unsaturated carboxylic acids and salts thereof and ethylenically unsaturated sulphonated monomers and salts thereof.

9. Cationic fluorocopolymer according to claim 8, characterized in that the ethylenically unsaturated carboxylic acid is methacrylic acid and the ethylenically unsaturated sulphonated monomers are chosen from 2-acrylamido-2-methylpropanesulphonic acid and salts thereof.

10. Cationic fluorocopolymer according to one of claims 1 to 9, characterized in that the monomer or monomers (D) represent 2 to 10 parts by weight per 100 parts by weight of total monomer.

11. Cationic fluorocopolymer according to one of claims 1 to 10, characterized in that the monomer (D) is vinyl acetate.

12. Cationic fluorocopolymer according to one of claims 1 to 11, characterized in that the monomer or monomers (E) are chosen from behenyl acrylate, stearyl methacrylate, methoxyethyl acrylate and methoxyethyl methacrylate.

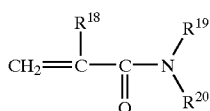
13. Cationic fluorocopolymer according to one of claims 1 to 12, characterized in that the monomer or monomers (F) are chosen from:

(F1), ethylenically unsaturated silane monomers;

(F2), 2-hydroxy-3-chloropropyl (meth)acrylate;

(F3), (meth)acrylates with an epoxy functional group;

(F4), monomers of formula (VIII):



(VIII)

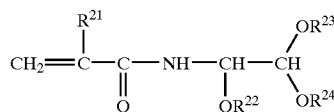
in which:

R¹⁸ represents H or —CH₃; and

R¹⁹ and R²⁰, which are identical or different, each independently represent H or a C₁-C₅ alkyl, which

possibly includes one or more OH groups, or a (C₁-C₅)alkoxy-(C₅)alkyl; and

(F5), monomers of formula (IX):



(IX)

in which:

R²¹ represents H or —CH₃; and

R²², R²³ and R²⁴, which are identical or different, each represent H or a C₁-C₄ alkyl.

14. Cationic fluorocopolymer according to claim 13, characterized in that the monomer (F4) is N-methylolacrylamide

15. Cationic fluorocopolymer according to claim 13, characterized in that the monomer (F5) of formula (IX) is that for which:

R²¹ and R²² each represent H; and

R²³ and R²⁴ each represent —CH₃.

16. Cationic fluorocopolymer according to one of claims 1 to 15, characterized in that the monomer (G) of formula (VII) is dimethylaminoethyl methacrylate.

17. Cationic fluorocopolymer according to one of claims 1 to 16, characterized in that it was obtained by emulsion copolymerization in at least one water-miscible organic solvent, the said copolymerization possibly being followed by a solvent distillation step so as to obtain an emulsion in water without any organic solvent.

18. Cationic fluorocopolymer according to one of claims 1 to 16, characterized in that it was obtained by solution copolymerization in a water-miscible organic solvent or a mixture of water-miscible organic solvents, and being followed by a step of dilution with an aqueous solution of a mineral or organic acid, the said step possibly being carried out in the presence of hydrogen peroxide or having been followed by a treatment by means of an aqueous hydrogen peroxide solution.

19. Application of the cationic fluorocopolymer as defined in one of claims 1 to 18 for the oleophobic and hydrophobic treatment of solid substrates, particularly of paper and paperpaperboard.

20. Application according to claim 19 to the surface of a paper in an amount from 0.05 to 0.2% of fluorine with respect to the weight of the paper.

21. Application according to claim 19 into the bulk of a paper pulp in an amount from 0.2 to 0.4% of fluorine with respect to the weight of pulp.

22. Solid substrate comprising at least one fluorocopolymer as defined in one of claims 1 to 18.

23. Solid substrate according to claim 22, characterized in that it is made of paper or paperpaperboard.

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