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(54) Title: AQUEOUS DISPERSIONS CONTAINING ANTIMICROBIALS IN A HYBRID NETWORK

(57) Abstract: The invention relates to a method of preparing a composition comprising (a) reacting a binder component (B) comprising at least one alkoxysilane (B2), and a polymer dispersion (PD), thus obtaining a prepolymer and subsequently (b) mixing or hydrolyzing and polycondensing said prepolymer in the presence of water and at least one antimicrobial agent (Z) comprising at least one antimicrobial active (Z1) and optionally a particulate carrier substance (Z2), wherein the at least one antimicrobial agent (Z) is unreactive during step (b).



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## AQUEOUS DISPERSIONS CONTAINING ANTIMICROBIALS IN A HYBRID NETWORK

### Description

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The invention relates to a method of preparing a composition comprising

- (a) reacting
- a binder component (B) comprising at least one alkoxy silane (B2), and a polymer dispersion (PD), thus obtaining a prepolymer and subsequently
- (b) mixing or hydrolyzing and polycondensing said prepolymer in the presence of
- water and
  - at least one antimicrobial agent (Z) comprising at least one antimicrobial active (Z1) and a particulate carrier substance (Z2) which is selected from the group consisting of zeolites and polymer hydrogels,
- wherein the at least one antimicrobial agent (Z) is unreactive during step (b) and comprises silver ions as antimicrobial active (Z1).

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The present invention furthermore relates to compositions obtainable by said method, to coatings comprising said compositions and to a kit of parts comprising a curable composition containing said components (B) and (Z) for joint application. The present invention also relates to a hybrid network of acrylate copolymers (Polymer P) and silica chemically linked to each other via Si-containing groups comprising an antimicrobial agent, wherein the antimicrobial active (Z1) is not covalently linked to said network but the carrier substance (Z2) has functional groups that can react with the organosilane in the polymer dispersion to form the silica network (hybrid network). The present invention furthermore concerns the use of said compositions for preparing antimicrobial coatings.

Coating applications are becoming increasingly more demanding in terms of performance, safety and environmental compliance. Coatings based on acrylate copolymer dispersions are known to provide high chemical resistance, flexibility,

abrasion resistance, weathering and impact resistance. The protection afforded by such coatings is of particular significance in the automotive, construction, marine and chemical sectors.

- 5 There is a need in the art to develop coatings with the above mentioned advantages with at the same time having long-term antimicrobial properties. Consequently, several different coatings have been suggested in the prior art.

10 The use of alumino-silicates or zeolites that contain ions of certain metals in antimicrobial coatings is known for example from US-patents No. 452,410 and 5,556,699. However, coatings comprising zeolites or aluminosilicates are not transparent and their use is often limited to coatings with less than 15 micron thickness.

15 It is known from US-A-6,596,401 to use a composition comprising a silane copolymer and an antimicrobial agent wherein the copolymer is the reaction product of at least one polyisocyanate, an organo-functional silane and a polyol. However, US-P 6,596,401 does not disclose hybrid networks.

20 US Patent No. 6,572,926 discloses polymer substrates which are exposed to a polymerizable quaternary ammonium salts such as dimethyloctadecyl-[3-(trimethoxy silyl)propyl]ammonium chloride dissolved in a solvent. The quaternary salt in the solvent is adsorbed by the polymeric substrate and polymerized thereby creating a substrate impregnated with an antimicrobial on its surface. The  
25 polymerized antimicrobial also penetrates the surface to some depth forming an interpenetrating network.

The method is limited to the penetration or swelling of a polymer substrate by certain mixtures of polymerizable quaternary ammonium salts and a solvent. In  
30 another embodiment the addition of polymerizable quaternary ammonium salts to commercially available coatings is disclosed so that an interpenetrating network forms in situ. Nevertheless, leaching out of the coating can only be avoided by means of polymerizing the antimicrobial. Also, the disclosed coatings still do not exhibit sufficient antimicrobial activity against *E. Coli*.

35 It is an object of the present invention to provide antimicrobial compositions where the antimicrobial active does not leach out of the composition. It is a related object of the present invention to provide coatings where the antimicrobial activity

## 2a

is long-lasting, in particular over a period of five years under weathering. The antimicrobial coatings ought to be usable for a broad range of antimicrobials.

- 5 It is another object of the present invention to provide antimicrobial compositions, in particular coatings, which show high efficacy against *Staphylococcus aureus* and *Escherichia Coli*. Furthermore, the antimicrobial coatings ought to efficiently kill these bacteria within a period of twenty four hours or less at room temperature.
- 10 At the same time it is an object of the present invention to provide antimicrobial coatings which are resistant to chemicals and weathering and exhibit high optical quality, sufficient flame retardancy, good adhesion to polycarbonate and aluminum substrates, and high abrasion resistance.
- 15 Accordingly at least one of the before-mentioned problems are solved and/or objects achieved by the inventive method and by compositions and coatings obtained by the method. Preferred embodiments are outlined in the following and in the claims. Combinations of preferred embodiments do not leave the scope of the present invention.

The inventive method for preparing compositions comprises steps (a) and (b) as defined above. The steps (a) and (b) are outlined in more detail in the following. It is preferred if the compositions according to the present invention are present as coatings.

5     Step (a)

According to the invention, step (a) comprises reacting

- a binder component (B) comprising at least one alkoxysilane (B2), and a polymer dispersion (PD)

10    thus obtaining a prepolymer.

A prepolymer is referred to as a polymeric system which still contains reactive groups or sites which can be further polymerized and/or crosslinked. In the present case, the alkoxysilane (B2) contains hydrolyzable groups which according to step (b) form an inorganic network as part of a resulting hybrid network. The cross linking to form inorganic/silica network occurs when the dispersion gets dried.

Each average value referring to the functionality refers to a number-weighted average.

20    Binder component (B)

According to the invention, the binder component (B) comprises at least one alkoxysilane (B2), and a polymer dispersion (PD).

25    In a preferred embodiment, the binder component (B) comprises at least one binder (B1) which is incapable of reacting in step (b), and (B2) at least one alkoxysilane.

Preferably, the binder (B1) incapable of reacting in step (b) is a binder which has no alkoxysilane groups.

30

Polymer dispersion PD

The polymer P, comprising at least two monomers M, has a glass transition temperature  $T_g$  in the range from -20 to +60°C. The polymer dispersion (PD) is obtained by free-radical emulsion polymerization of at least one ethylenically unsaturated monomer M.

Generally speaking, polymer P is a copolymer obtained by copolymerizing two or more monomers M. The skilled worker is able in this case, through a skilful choice of monomer composition, to prepare polymers having a glass transition temperature in the range from -20 to +60°C.

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According to Fox (see Ullmanns Enzyklopädie der technischen Chemie, 4th edition, volume 19, Weinheim (1980), pp. 17, 18), it is possible to estimate the glass transition temperature  $T_g$ . The glass transition temperature of copolymers with little or no crosslinking is given at high molar mass in good approximation by:

5

$$\frac{1}{T_g} = \frac{X^1}{T_g^1} + \frac{X^2}{T_g^2} + \dots \frac{X^n}{T_g^n}$$

where  $X^1, X^2, \dots, X^n$  are the mass fractions 1, 2, ..., n and  $T_g^1, T_g^2, \dots, T_g^n$  are the glass transition temperatures of the polymers synthesized in each case only from one of the monomers 1, 2, ..., n, in degrees Kelvin. The latter are known, for example, from Ullmann's Encyclopedia of Industrial Chemistry, VCH, 5th ed., Weinheim, vol. A 21 (1992) p. 169 or from J. Brandrup, E.H. Immergut, Polymer Handbook 3<sup>rd</sup> ed., J. Wiley, New York 1989.

15 In general the monomers M are selected from esters of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with  $C_1$ - $C_{20}$  alkanols and  $C_5$ - $C_{10}$  cycloalkanols, vinylaromatics, esters of vinyl alcohol with  $C_1$ - $C_{30}$  monocarboxylic acids, ethylenically unsaturated nitriles, vinyl halides, vinylidene halides, monoethylenically unsaturated carboxylic and sulfonic acids, phosphorus monomers, esters of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with  $C_2$ - $C_{30}$  alkanediols, amides of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with  $C_2$ - $C_{30}$  amino alcohols containing a primary or secondary amino group, primary amides of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic acids and their N-alkyl and N,N-dialkyl derivatives, N-vinyl lactams, open-chain N-vinylamide compounds, esters of allyl alcohol  
25 with  $C_1$ - $C_{30}$  monocarboxylic acids, esters of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids of amino alcohols, amides of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with diamines which contain at least one primary or secondary amino group, N,N-diallyl amines, N,N-diallyl-N-alkyl amines, vinyl- and allyl-substituted nitrogen heterocycles, vinyl ethers,  $C_2$ - $C_8$  monoolefins, nonaromatic hydrocarbons having at least two conjugated double bonds, polyether  
30 (meth)acrylates, monomers containing urea groups, or mixtures thereof.

Where (meth)acrylates are referred to in the context of this application, what are meant are not only the corresponding acrylates, in other words the derivatives of acrylic acid,  
35 but also the methacrylates, the derivatives of methacrylic acid.

Examples of suitable monomers include the following:

(a): Esters of  $\alpha, \beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids  
40 with  $C_1$ - $C_{20}$  alkanols, especially the esters of acrylic acid, methacrylic acid, and ethacrylic acid, such as methyl (meth)acrylate, methyl ethacrylate, ethyl

- (meth)acrylate, ethyl ethacrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, tert-butyl ethacrylate, n-hexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 1,1,3,3-tetramethylbutyl (meth)acrylate, ethylhexyl (meth)acrylate, n-nonyl (meth)acrylate, n-decyl (meth)acrylate, n-undecyl (meth)acrylate, tridecyl (meth)acrylate, myristyl (meth)acrylate, pentadecyl (meth)acrylate, palmityl (meth)acrylate, heptadecyl (meth)acrylate, nonadecyl (meth)acrylate, arachinyl (meth)acrylate, behenyl (meth)acrylate, lignoceryl (meth)acrylate, cerotinyl (meth)acrylate, melissyl (meth)acrylate, palmitoleyl (meth)acrylate, oleyl (meth)acrylate, linolyl (meth)acrylate, linolenyl (meth)acrylate, stearyl (meth)acrylate and lauryl (meth)acrylate.
- (b): Vinylaromatics, preferably styrene, 2-methylstyrene, 4-methylstyrene, 2-(n-butyl)styrene, 4-(n-butyl)styrene, 4-(n-decyl)styrene, and  $\alpha$ -methylstyrene, and more preferably styrene and  $\alpha$ -methylstyrene.
- (c): Esters of vinyl alcohol with C<sub>1</sub>-C<sub>30</sub> monocarboxylic acids, such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl stearate, vinyl propionate and vinyl esters of Versatic acid.
- (d): Ethylenically unsaturated nitriles such as acrylonitrile and methacrylonitrile.
- (e): Vinyl halides and vinylidene halides such as vinyl chloride, vinylidene chloride, vinyl fluoride, and vinylidene fluoride.
- (f): Ethylenically unsaturated carboxylic acids and sulfonic acids or their derivatives are acrylic acid, methacrylic acid, ethacrylic acid,  $\alpha$ -chloroacrylic acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, fumaric acid, the monoesters of monoethylenically unsaturated dicarboxylic acids, having 4 to 10, preferably 4 to 6, C atoms, e.g., monomethyl maleate, vinylsulfonic acid, allylsulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-acryloyloxypropylsulfonic acid, 2-hydroxy-3-methacryloyloxypropylsulfonic acid, styrenesulfonic acids, and 2-acrylamido-2-methylpropanesulfonic acid. Suitable styrenesulfonic acids and derivatives thereof are styrene-4-sulfonic acid and styrene-3-sulfonic acid and the alkaline earth metal or alkali metal salts thereof, e.g. sodium styrene-3-sulfonate and sodium styrene-4-sulfonate. Particularly preferred are acrylic acid and methacrylic acid.
- (g): Phosphorus monomers such as vinylphosphonic acid and allylphosphonic acid. Further suitable are the monoesters and diesters of phosphonic acid and phos-



- phoric acid with hydroxyalkyl (meth)acrylates, especially the monoesters. Suitable additionally are diesters of phosphonic acid and phosphoric acid which have been esterified singly with a hydroxyalkyl (meth)acrylate and also singly with a different alcohol, an alkanol, for example. Suitable hydroxyalkyl (meth)acrylates for these
- 5 esters are those specified as separate monomers below, more particularly 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, etc. Corresponding dihydrogen phosphate ester monomers comprise phosphoalkyl (meth)acrylates, such as 2-phosphoethyl (meth)acrylate, 2-phosphopropyl (meth)acrylate, 3-phosphopropyl (meth)acrylate, phosphobutyl
- 10 (meth)acrylate, and 3-phospho-2-hydroxypropyl (meth)acrylate. Also suitable are the esters of phosphonic acid and phosphoric acid with alkoxylated hydroxyalkyl (meth)acrylates, examples being the ethylene oxide condensates of (meth)acrylates such as  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{P}(\text{OH})_2$  and  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2\text{CH}_2\text{O})_n\text{P}(=\text{O})(\text{OH})_2$ , in which  $n$  is 1 to 50. Additionally suitable
- 15 are phosphoalkyl crotonates, phosphoalkyl maleates, phosphoalkyl fumarates, phosphodialkyl (meth)acrylates, phosphodialkyl crotonates, and allyl phosphates. Further suitable monomers containing phosphorus groups are described in WO 99/25780 and US 4,733,005, hereby incorporated by reference.
- 20 (h): Esters of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids, with  $\text{C}_2$ - $\text{C}_{30}$  alkanediols such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl ethacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 3-hydroxybutyl acrylate, 3-hydroxybutyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl methacrylate, 6-hydroxyhexyl acrylate, 6-hydroxyhexylmethacrylate, 3-hydroxy-2-ethylhexyl acrylate, and 3-hydroxy-2-ethylhexyl methacrylate.
- 25 (i): Primary amides of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic acids such as acrylamide and methacrylamide.
- 30 (k): N-Alkylamides and N,N-dialkylamides of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic acids such as N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N-propyl(meth)acrylamide, N-(n-butyl)(meth)acrylamide, N-(tert-butyl)(meth)acrylamide, N-(n-octyl)(meth)acrylamide, N-(1,1,3,3-tetramethylbutyl)(meth)acrylamide, N-ethylhexyl(meth)acrylamide, N-(n-nonyl)(meth)acrylamide, N-(n-decyl)(meth)acrylamide, N-(n-undecyl)(meth)acrylamide, N-tridecyl(meth)acrylamide, N-myristyl(meth)acrylamide, N-pentadecyl(meth)acrylamide, N-palmityl(meth)acrylamide, N-heptadecyl(meth)acrylamide, N-nonadecyl(meth)acrylamide, N-arachinyl(meth)acrylamide, N-behenyl(meth)acrylamide, N-lignoceryl(meth)acrylamide, N-
- 35
- 40

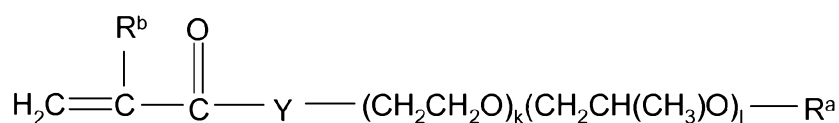
cerotinyl(meth)acrylamide, N-melissinyl(meth)acrylamide,  
 N-palmitoleyl(meth)acrylamide, N-oleyl(meth)acrylamide, N-  
 linolyl(meth)acrylamide, N-linolenyl(meth)acrylamide, N-stearyl(meth)acrylamide,  
 N-lauryl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, N,N-  
 5 diethyl(meth)acrylamide, and morpholinyl(meth)acrylamide.

(o): Esters of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids  
 with amino alcohols such as N,N-dimethylaminomethyl(meth)acrylate,  
 N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminoethyl acrylate,  
 10 N,N-dimethylaminopropyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate,  
 and N,N-dimethylaminocyclohexyl (meth)acrylate.

(p): Amides of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids  
 with diamines which contain at least one primary or secondary amino group, such  
 15 as N-[2-(dimethylamino)ethyl]acrylamide, N-[2-  
 (dimethylamino)ethyl]methacrylamide, N-[3-(dimethylamino)propyl]acrylamide, N-  
 [3-(dimethylamino)propyl]methacrylamide, N-[4-(dimethylamino)butyl]acrylamide,  
 N-[4-(dimethylamino)butyl]methacrylamide, N-[2-(diethylamino)ethyl]acrylamide,  
 N-[4-(dimethylamino)cyclohexyl]acrylamide, and  
 20 N-[4-(dimethylamino)cyclohexyl]methacrylamide.

(s): C<sub>2</sub>-C<sub>8</sub> monoolefins and nonaromatic hydrocarbons having at least two conjugated  
 double bonds, such as ethylene, propylene, isobutylene, isoprene, and butadi-  
 25 ene.

(t): Polyether (meth)acrylates are compounds of the general formula (A)



(A)

30 in which

the sequence of the alkylene oxide units is arbitrary,

k and l independently of one another are an integer from 0 to 100, the sum of k  
 35 and l being at least 3,

R<sup>a</sup> is hydrogen, C<sub>1</sub>-C<sub>30</sub> alkyl, C<sub>5</sub>-C<sub>8</sub> cycloalkyl or C<sub>6</sub>-C<sub>14</sub> aryl,

$R^b$  is hydrogen or  $C_1-C_8$  alkyl,

Y is O or  $NR^c$ ,  $R^c$  being hydrogen,  $C_1-C_{30}$ -alkyl or  $C_5-C_8$  cycloalkyl.

- 5 Polyether (meth)acrylates are, for example, the polycondensation products of the  
aforementioned  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and/or dicarboxylic  
acids and their acid chlorides, amides, and anhydrides with polyetherols. Suitable  
polyetherols can easily be prepared by reacting ethylene oxide, 1,2-propylene ox-  
10 ide and/or epichlorohydrin with a starter molecule, such as water or a short-chain  
alcohol  $R^a-OH$ . The alkylene oxides can be used individually, in alternating suc-  
cession or as a mixture. The polyether acrylates can be used alone or in mixtures  
for preparing the emulsion polymers used in accordance with the invention. Suit-  
able polyether (meth)acrylates are available commercially, in the form for exam-  
15 ple of various products under the name Bisomer® from Laporte Performance  
Chemicals, UK. These include, for example, Bisomer® MPEG 350 MA, a meth-  
oxypolyethylene glycol monomethacrylate.

Preferred compounds of the formula (A) are those in which Y is O, in other words  
an ether bridge.

- 20 Preferred compounds of the formula (A) are those in which k is an integer from 3  
to 50, more particularly 4 to 25. Likewise preferred are compounds of the formula  
(A) in which l is an integer from 3 to 50, more particularly 4 to 25. Particularly pre-  
ferred compounds are those in which Y is O,  $R^b$  is hydrogen or methyl, l is 0  
25 (zero), and k is an integer from 3 to 15, preferably 4 to 12. Particular preference  
is additionally given to compounds in which Y is O,  $R^b$  is hydrogen or methyl, k is  
0 (zero), and l is an integer from 3 to 15, preferably 4 to 12.

- 30 Preferably  $R^a$  in the formula (A) is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-  
butyl, sec-butyl, n-pentyl, n-hexyl, octyl, 2-ethylhexyl, decyl, lauryl, palmityl or  
stearyl.

- 35 Preferably  $R^b$  in the formula (A) is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-  
butyl, sec-butyl, tert-butyl, n-pentyl or n-hexyl, more particularly hydrogen, methyl  
or ethyl. With particular preference  $R^b$  is hydrogen or methyl.

- (u): Suitable monomers containing urea groups, such as N-vinyl or N-allylurea or de-  
40 rivatives of imidazolidin-2-one. These include N-vinyl- and N-allylimidazolidin-2-  
one, N-vinyloxyethylimidazolidin-2-one, N-(2-(meth)acrylamidoethyl)imidazolidin-  
2-one, N-(2-(meth)acryloyloxyethyl)imidazolidin-2-one (= 2-ureido(meth)acrylate,  
(UMA), and N-[2-((meth)acryloyloxy)acetamido]ethylimidazolidin-2-one. Pre-  
ferred monomers containing urea groups are N-(2-acryloyloxyethyl)imidazolidin-

2-one and N-(2-methacryloyloxyethyl)imidazolidin-2-one. Particular preference is given to N-(2-methacryloyloxyethyl)imidazolidin-2-one (2-ureidomethacrylate, UMA).

5

- (v): Alkoxysilyl group-containing monomers such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriisopropoxysilane, vinyltris(0-methoxyethoxy)silane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinyldimethylmethoxysilane, vinyldimethylethoxysilane, 3-methacryloypropyltrimethoxysilane, 3-methacryloypropyltriethoxysilane, 3-methacryloypropylmethyldimethoxysilane, 3-methacryloypropylmethyldiethoxysilane, tris(2-acetoxyethyl dimethylsiloxy) silylpropyl acrylate and methacrylate tris(2-carboxyethyl dimethylsiloxy) silylpropyl acrylate and methacrylate tris(3-hydroxypropyl dimethylsiloxy) silylpropyl acrylate and methacrylate functional, fluorosubstituted alkyl/aryl siloxanes such as: tris(3,3,3 trifluoropropyl dimethylsiloxy) silyl propyl acrylate and methacrylate tris[3-heptafluoroisopropoxy propyl] dimethylsiloxy silylpropyl acrylate and methacrylate tris(pentafluorophenyl dimethylsiloxy) silyl propyl acrylate and methacrylate

20

The aforementioned monomers M can be used individually, in the form of mixtures within one class of monomers, or in the form of mixtures from different classes of monomer, provided the polymer P has a glass transition temperature  $T_g$  in the range from -20 to +60°C, preferably -10 to + 50 °C, more particularly 0 to 30°C.

25

The monomers M generally comprise at least 80%, preferably at least 85%, more preferably at least 90%, by weight, of a monoethylenically unsaturated monomer M1 (principal monomer) having a water solubility < 30g/l at 25°C and 1 bar. These include, in particular, the monomers of classes (a), (b), (c) and (s). Preferred as principal monomers M1 are monomers of classes (a) and (b).

30

For the emulsion polymerization it is preferred to use at least 80%, more preferably at least 85%, and in particular at least 90%, by weight, based on the overall weight of the monomers M, of at least one monomer M1, which is preferably selected from esters of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with  $C_1$ - $C_{20}$  alcohols and vinylaromatics. The monomers M1 are used preferably in an amount of up to 99.9%, more preferably up to 99.5%, and in particular up to 99%, by weight, based on the overall weight of the monomers M, for the emulsion polymerization.

35

40 The principal monomers M1 are preferably selected from methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate,

n-butyl(meth)acrylate, sec-butyl(meth)acrylate, tert-butyl(meth)acrylate, n-pentyl(meth)acrylate, n-hexyl(meth)acrylate, n-heptyl(meth)acrylate, n-octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, styrene, 2-methylstyrene, and mixtures thereof.

5

In addition to at least one principal monomer M1, the free-radical emulsion polymerization for preparing (PD) can be carried out using at least one further monomer M2, which has a water solubility  $\geq 30$  g/l, especially  $\geq 50$  g/l, at 25°C and 1 bar. These monomers M2 are generally present in minor proportions (secondary monomers). Preferred monomers M2 are monomers of classes (f), (g), (h), and (i).

10

For the emulsion polymerization it is preferred to use up to 20%, more preferably up to 15%, in particular up to 10%, by weight, based on the overall weight of the monomers M, of at least one monomer M2, which is preferably selected from ethylenically unsaturated monocarboxylic and dicarboxylic acids and the anhydrides and monoesters of ethylenically unsaturated dicarboxylic acids, (meth)acrylamides, C<sub>1</sub>-C<sub>10</sub> hydroxyalkyl(meth)acrylates, C<sub>1</sub>-C<sub>10</sub> hydroxyalkyl(meth)acrylamides, and mixtures thereof. The monomers M2, where present, are used preferably in an amount of at least 0.1%, more preferably at least 0.5%, in particular at least 1%, by weight, based on the overall weight of the monomers M, for the emulsion polymerization.

15

20

The monomers M2 are selected with particular preference from acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, maleic anhydride, acrylamide, methacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethylacrylamide, 2-hydroxyethylmethacrylamide, and mixtures thereof.

25

Particularly suitable combinations of principal monomers M1 for the process of the invention are, for example:

30

n-butyl acrylate and methyl methacrylate;  
n-butyl acrylate, methyl methacrylate, and styrene;  
n-butyl acrylate and styrene;  
n-butyl acrylate and ethylhexyl acrylate;  
n-butyl acrylate, ethylhexyl acrylate, and styrene.

35

The aforementioned particularly suitable combinations of principal monomers M1 can be combined with particularly suitable monomers M2, which are preferably selected from acrylic acid, methacrylic acid, acrylamide, methacrylamide, and mixtures thereof.

40

In one specific embodiment the free-radical emulsion polymerization for the preparation of (PD) is carried out using, in addition to M1 and, if present, M2, at least one polyether (meth)acrylate. The latter is used preferably in an amount of 0.5% up to 15%, prefera-

bly 1% to 10%, and more particularly 1% to 5%, by weight, based on the overall weight of the monomers M. Suitable polyether methacrylates are the abovementioned compounds of polymer class (t). Preferably the polyether (meth)acrylate is selected from compounds of the general formula (A) in which Y is O, R<sup>b</sup> is hydrogen or methyl, l is 0 (zero), and k is an integer from 3 to 15, preferably 4 to 12, and also from compounds of the general formula (A) in which Y is O, R<sup>b</sup> is hydrogen or methyl, k is 0 (zero) and l is an integer from 3 to 15, preferably 4 to 12.

10 In the preparation of the polymer dispersions of the invention it is possible, in addition to the aforementioned monomers M, to use at least one crosslinker. Monomers which possess a crosslinking function are compounds having at least two polymerizable, ethylenically unsaturated, nonconjugated double bonds in the molecule. Crosslinking may also take place, for example, through photochemical activation. For that purpose, 15 for preparation of PD, it is possible additionally to use at least one monomer having photoactivatable groups. Photoinitiators can also be added separately. Crosslinking may also take place, for example, through functional groups which are able to enter into a chemical crosslinking reaction with functional groups that are complementary to them. These complementary groups may both be attached to the emulsion polymer, 20 and crosslinking effected using a crosslinker capable of entering into a chemical crosslinking reaction with functional groups of the emulsion polymer.

Examples of suitable crosslinkers include acrylic esters, methacrylic esters, allyl ethers or vinyl ethers of at least dihydric alcohols. The OH groups of the parent alcohols may be wholly or partly etherified or esterified; however, the crosslinkers comprise at least two ethylenically unsaturated groups.

Examples of the parent alcohols are dihydric alcohols such as 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 2,3-butanediol, 1,4-butanediol, but-2-ene-1,4-diol, 1,2-pentanediol, 1,5-pentanediol, 1,2-hexanediol, 1,6-hexanediol, 1,10-decanediol, 1,2-dodecanediol, 1,12-dodecanediol, neopentyl glycol, 3-methylpentane-1,5-diol, 2,5-dimethyl-1,3-hexanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,4-bis(hydroxymethyl)cyclohexane, hydroxypivalic acid neopentyl glycol monoester, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis[4-(2-hydroxypropyl)phenyl]propane, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 3-thiapentane-1,5-diol, and also polyethylene glycols, polypropylene glycols, and polytetrahydrofurans having molecular weights of in each case 200 to 10 000 g/mol. Apart from the homopolymers of ethylene oxide or propylene oxide it is also possible to use block copolymers of ethylene oxide or propylene oxide, or copolymers comprising ethylene oxide groups and propylene oxide groups incorporated. Examples of parent alcohols having more than two OH groups are trimethylolpropane, glycerol, pentaerythritol, 1,2,5-

pentanetriol, 1,2,6-hexanetriol, cyanuric acid, sorbitan, sugars such as sucrose, glucose, and mannose. Of course it is also possible for the polyhydric alcohols to be used after reaction with ethylene oxide or propylene oxide, as the corresponding ethoxylates or propoxylates, respectively. The polyhydric alcohols may also first be converted to  
5 the corresponding glycidyl ethers by reaction with epichlorohydrin.

Further suitable crosslinkers are the vinyl esters or the esters of monohydric unsaturated alcohols with ethylenically unsaturated C<sub>3</sub>-C<sub>6</sub> carboxylic acids, examples being acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid. Examples of  
10 such alcohols are allyl alcohol, 1-buten-3-ol, 5-hexen-1-ol, 1-octen-3-ol, 9-decen-1-ol, dicyclopentenyl alcohol, 10-undecen-1-ol, cinnamyl alcohol, citronellol, crotyl alcohol or cis-9-octadecen-1-ol. An alternative possibility is to esterify the monohydric unsaturated alcohols with polybasic carboxylic acids, examples being malonic acid, tartaric acid, trimellitic acid, phthalic acid, terephthalic acid, citric acid or succinic  
15 acid.

Further suitable crosslinkers are esters of unsaturated carboxylic acids with the above-described polyhydric alcohols, examples being those of oleic acid, crotonic acid, cinnamic acid or 10-undecenoic acid.  
20

Further suitable as crosslinkers are straight-chain or branched, linear or cyclic, aliphatic or aromatic hydrocarbons which possess at least two double bonds, which in the case of aliphatic hydrocarbons must not be conjugated, for example, divinylbenzene, divinyltoluene, 1,7-octadiene, 1,9-decadiene, 4-vinyl-1-cyclohexene, trivinylcyclohexane or  
25 polybutadienes having molecular weights of 200 to 20 000 g/mol.

Suitability as crosslinkers is possessed, furthermore, by the acrylamides, methacrylamides, and N-allylamines of at least difunctional amines. Examples of such amines are 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane,  
30 1,12-dodecanediamine, piperazine, diethylenetriamine or isophoronediamine. Likewise suitable are the amides of allylamine and unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, or at least dibasic carboxylic acids, of the kind described above.

35 Further suitable as crosslinkers are triallylamine and triallylmonoalkylammonium salts, such as triallylmethylammonium chloride or triallylmethylammonium methyl sulfate, for example.

Also suitable are N-vinyl compounds of urea derivatives, at least difunctional amides, cyanurates or urethanes, such as of urea, ethyleneurea, propyleneurea or tartaramide,  
40 e.g., N,N'-divinylethyleneurea or N,N'-divinylpropyleneurea.

Further suitable crosslinkers are divinylidioxane, tetraallylsilane or tetravinylsilane. It will be appreciated that mixtures of the aforementioned compounds can also be used.

The crosslinking monomers also, moreover, include those which as well as an ethylenically unsaturated double bond contain a reactive functional group, an aldehyde, keto or oxirane group, for example, which are able to react with an added crosslinker. The functional groups are preferably keto groups or aldehyde groups. The keto or aldehyde groups are preferably attached to the polymer through copolymerization of copolymerizable, ethylenically unsaturated compounds containing keto groups or aldehyde groups. Suitable such compounds are acrolein, methacrolein, vinyl alkyl ketones having 1 to 20, preferably 1 to 10, carbon atoms in the alkyl radical, formylstyrene, (meth)acrylic acid alkyl esters having one or two keto or aldehyde groups, or one aldehyde group and one keto group, in the alkyl radical, said alkyl radical comprising preferably a total of 3 to 10 carbon atoms, examples being methacryloyloxyalkylpropanals, as described in DE-A-2722097. Also suitable, furthermore, are N-oxoalkyl(meth)acrylamides of the kind known, for example, from US-A-4226007, DE-A-2061213 or DE-A-2207209. Particularly preferred are acetoacetyl (meth)acrylate, acetoacetoxylethyl (meth)acrylate, and, in particular, diacetoneacrylamide. The crosslinkers preferably comprise a compound having at least two functional groups, more particularly two to five functional groups, which are able to enter into a crosslinking reaction with the functional groups of the polymer, especially the keto groups or aldehyde groups. For this purpose, for example, hydrazide, hydroxylamine or oxime ether or amino groups are included as functional groups for the crosslinking of the keto or aldehyde groups. Suitable compounds with hydrazide groups are, for example, polycarboxylic hydrazides having a molar weight of up to 500 g/mol. Particularly preferred hydrazide compounds are dicarboxylic dihydrazides having preferably 2 to 10 C atoms. These include, for example, oxalic dihydrazide, malonic dihydrazide, succinic dihydrazide, glutaric dihydrazide, adipic dihydrazide, sebacic dihydrazide, maleic dihydrazide, fumaric dihydrazide, itaconic dihydrazide and/or isophthalic dihydrazide. Of particular interest are the following: adipic dihydrazide, sebacic dihydrazide, and isophthalic dihydrazide. Suitable compounds with hydroxylamine or oxime ether groups are specified for example in WO 93/25588.

Surface crosslinking can additionally be generated by means, as well, of appropriate additization of the aqueous polymer dispersion (PD). This includes, for example, addition of a photoinitiator or siccatives. Suitable photoinitiators are those which are excited by sunlight, such as benzophenone or derivatives of benzophenone, for example. Suitable siccatives are the metal compounds recommended for aqueous alkyd resins, based for example on Co or Mn (overview in U. Poth, Polyester und Alkydharze, Vincentz Network 2005, p. 183 f).



The crosslinking component is used preferably in an amount of 0.0005% to 5%, more preferably 0.001% to 2.5%, more particularly 0.01% to 1.5%, by weight, based on the overall weight of the monomers used for the polymerization (including the crosslinker).

- 5 Polymer dispersions (PD) comprising no crosslinker in copolymerized form constitute one special embodiment.

- 10 The free-radical polymerization of the monomer mixture M may take place in the presence of at least one regulator. Regulators are used preferably in an amount of 0.0005% to 5%, more preferably of 0.001% to 2.5%, and more particularly of 0.01% to 1.5% by weight, based on the overall weight of the monomers used for the polymerization.

- 15 The term "regulators" (polymerization regulators) is applied generally to compounds having high transfer constants. Regulators accelerate chain transfer reactions and so bring about a reduction in the degree of polymerization of the resulting polymers without influencing the overall reaction rate. Among the regulators a distinction may be made between monofunctional, difunctional, and polyfunctional regulators, according to the number of functional groups in the molecule that are able to lead to one or more chain transfer reactions. Suitable regulators are, for example, described comprehensively by K. C. Berger and G. Brandrup in J. Brandrup, E. H. Immergut, Polymer Handbook, 3rd edn., John Wiley & Sons, New York, 1989, pp. II/81 - II/141.
- 20

- 25 Examples of suitable regulators include aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, and isobutyraldehyde.

- As regulators it is also possible, furthermore, to use the following: formic acid, its salts or esters, such as ammonium formate, 2,5-diphenyl-1-hexene, hydroxylammonium sulfate, and hydroxylammonium phosphate.

- 30 Further suitable regulators are halogen compounds, examples being alkyl halides such as tetrachloromethane, chloroform, bromotrichloromethane, bromoform, allyl bromide, and benzyl compounds such as benzyl chloride or benzyl bromide.

- 35 Further suitable regulators are allyl compounds, such as allyl alcohol, functionalized allyl ethers, such as allyl ethoxylates, alkyl allyl ethers or glycerol monoallyl ethers.

- 40 Further suitable regulators are inorganic hydrogen sulfites, disulfites, and dithionites or organic sulfides, disulfides, polysulfides, sulfoxides, and sulfones. They include di-n-butyl sulfide, di-n-octyl sulfide, diphenyl sulfide, thiodiglycol, ethylthioethanol, diisopropyl disulfide, di-n-butyl disulfide, di-n-hexyl disulfide, diacetyl disulfide, diethanol sulfide, di-t-butyl trisulfide, dimethyl sulfoxide, dialkyl sulfide, dialkyl disulfide and/or diaryl sulfide.

Additionally suitable as polymerization regulators are thiols (compounds which maintain sulfur in the form of SH groups, also referred to as mercaptans). Preferred regulators are mono-, di-, and polyfunctional mercaptans, mercapto alcohols and/or mercapto-

5 carboxylic acids. Examples of these compounds are allyl thioglycolates, ethyl thioglycolate, cysteine, 2-mercaptoethanol, 1,3-mercaptopropanol, 3-mercaptopropane-1,2-diol, 1,4-mercaptobutanol, mercaptoacetic acid, 3-mercaptopropionic acid, mercaptosuccinic acid, thioglycerol, thioacetic acid, thiourea, and alkyl mercaptans such as n-butyl mercaptan, n-hexyl mercaptan or n-dodecyl mer-

10 captan.

Examples of difunctional regulators which comprise two sulfur atoms in bonded form are difunctional thiols such as dimercaptopropanesulfonic acid (sodium salt), dimercaptosuccinic acid, dimercapto-1-propanol, dimercaptoethane, dimercaptopropane, dimer-

15 captobutane, dimercaptopentane, dimercaptohexane, ethylene glycol bithioglycolates, and butanediol bithioglycolate, for example. Examples of polyfunctional regulators are compounds which comprise more than two sulfur atoms in bonded form. Examples thereof are trifunctional and/or tetrafunctional mercaptans.

20 Mercaptosilane chain transfer agents are preferably utilized to place crosslink sites at one end of the copolymer molecule in order to improve the cohesive strength of the cured composition.

Preferred mercaptosilane chain transfer agents for use with the invention have the

25 general formula:



where RS is a divalent alkylene group, R6 is an alkyl group, x is 1, 2 or 3, and Z is a

30 hydrolyzable group. The alkylene groups, alkyl groups, and hydrolyzable groups are generally the same or similar to those set forth with respect to the silane functionalized addition monomers.

Suitable mercaptosilane chain transfer agents include  $\gamma$ -mercapto propyl triethoxysi-

35 lane,  $\gamma$ -mercaptopropyl, trimethoxy silane, mercaptomethyl methyl dimethoxysilane, and the like, with  $\gamma$ -mercaptopropyl trimethoxy silane being preferred. The quantities of chain transfer agents used are similar to those disclosed in the prior art. I will try to get more mercapto silanes when we do the second draft. Are there still coming more?

40

All of the stated regulators may be used individually or in combination with one another. One specific embodiment relates to polymer dispersions PD which are prepared by free-radical emulsion polymerization without addition of a regulator.

- 5 For the preparation of the polymers, the monomers can be polymerized with the aid of initiators which form free radicals.

As initiators for the free-radical polymerization it is possible to use the peroxy compounds and/or azo compounds that are typical for these purposes, examples being  
10 alkali metal or ammonium peroxydisulfates, diacetyl peroxide, dibenzoyl peroxide, succinyl peroxide, di-tert-butyl peroxide, tert-butyl perbenzoate, tert-butyl perpivalate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl permaleate, cumene hydroperoxide, diisopropyl peroxydicarbamate, bis(o-toluoxy) peroxide, didecanoyl peroxide, dioctanoyl peroxide, dilauroyl peroxide, tert-butyl perisobutyrate, tert-butyl peracetate, di-tert-amyl  
15 peroxide, tert-butyl hydroperoxide, azobisisobutyronitrile, 2,2'-azobis(2-amidinopropane) dihydrochloride or 2,2'-azobis(2-methylbutyronitrile). Mixtures of these initiators, too, are suitable.

Further initiators which can be used are reduction/oxidation (= redox) initiator systems.  
20 The redox initiator systems are composed of at least one, usually inorganic, reducing agent and one organic or inorganic oxidizing agent. The oxidation component is, for example, one of the emulsion polymerization initiators already specified above. The reduction component comprises, for example, alkali metal salts of sulfurous acid, such as sodium sulfite, sodium hydrogen sulfite, alkali metal salts of disulfurous acid such as  
25 sodium disulfite, bisulfite addition compounds of aliphatic aldehydes and ketones, such as acetone bisulfite, or reducing agents such as hydroxymethanesulfonic acid and its salts, or ascorbic acid. The redox initiator systems may be used in conjunction with soluble metal compounds whose metallic component is able to occur in a plurality of valence states. Examples of typical redox initiator systems include ascorbic acid/iron(II)  
30 sulfate/sodium peroxydisulfate, tert-butyl hydroperoxide/sodium disulfite, tert-butyl hydroperoxide/Na hydroxymethanesulfonic acid. The individual components, the reduction component for example, may also be mixtures: an example is a mixture of the sodium salt of hydroxymethanesulfonic acid and sodium disulfite.

- 35 The amount of the initiators is generally 0.1% to 10%, preferably 0.1% to 5%, by weight, based on all of the monomers to be polymerized. It is also possible for two or more different initiators to be used in the emulsion polymerization.

40 The polymer dispersion (PD) is prepared typically in the presence of at least one surface-active compound. A comprehensive description of suitable protective colloids is found in Houben-Weyl, Methoden der organischen Chemie, volume XIV/1, Makromolekulare Stoffe, Georg Thieme Verlag, Stuttgart, 1961, pp. 411 to 420. Suitable emulsifi-

ers are also found in Houben-Weyl, Methoden der organischen Chemie, volume 14/1, Makromolekulare Stoffe, Georg Thieme Verlag, Stuttgart, 1961, pages 192 to 208.

5 Suitable emulsifiers include anionic, cationic, and nonionic emulsifiers. As surface-active substances it is preferred to use emulsifiers, whose relative molecular weights are typically below those of protective colloids.

Useful nonionic emulsifiers are araliphatic or aliphatic nonionic emulsifiers, examples being ethoxylated mono-, di-, and trialkylphenols (EO degree: 3 to 50, alkyl radical: C<sub>4</sub>-C<sub>10</sub>), ethoxylates of long-chain alcohols (EO degree: 3 to 100, alkyl radical: C<sub>8</sub>-C<sub>36</sub>), and polyethylene oxide/polypropylene oxide homopolymers and copolymers. These may comprise the alkylene oxide units copolymerized in random distribution or in the form of blocks. Highly suitable, for example, are EO/PO block copolymers. Preference is given to using ethoxylates of long-chain alkanols (alkyl radical C<sub>1</sub>-C<sub>30</sub>, average degree of ethoxylation 5 to 100) and, of these, particular preference to those having a linear C<sub>12</sub>-C<sub>20</sub> alkyl radical and an average degree of ethoxylation of 10 to 50, and also ethoxylated monoalkylphenols.

20 Examples of suitable anionic emulsifiers are alkali metal salts and ammonium salts of alkyl sulfates (alkyl radical: C<sub>8</sub>-C<sub>22</sub>), of sulfuric monoesters with ethoxylated alkanols (EO degree: 2 to 50, alkyl radical: C<sub>12</sub>-C<sub>18</sub>) and with ethoxylated alkylphenols (EO degree: 3 to 50, alkyl radical: C<sub>4</sub>-C<sub>9</sub>), of alkylsulfonic acids (alkyl radical: C<sub>12</sub>-C<sub>18</sub>), and of alkylarylsulfonic acids (alkyl radical: C<sub>9</sub>-C<sub>18</sub>). Further suitable emulsifiers are found in Houben-Weyl, Methoden der organischen Chemie, volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pp. 192-208. Likewise suitable as anionic emulsifiers are bis(phenylsulfonic acid) ethers and their alkali metal or ammonium salts, carrying a C<sub>4</sub>-C<sub>24</sub> alkyl group on one or both aromatic rings. These compounds are general knowledge, from US-A-4,269,749, for example, and are available commercially, in the form for example of Dowfax® 2A1 (Dow Chemical Company).

30 Suitable cationic emulsifiers are preferably quaternary ammonium halides, e.g., trimethylcetylammmonium chloride, methyltrioctylammmonium chloride, benzyltriethylammmonium chloride, or quaternary compounds of N-C<sub>6</sub>-C<sub>20</sub> alkylpyridines, -morpholines or -imidazoles, e.g. N-laurylpyridinium chloride.

35 The amount of emulsifier is generally about 0.01% to 10% by weight, preferably 0.1% to 5% by weight, based on the amount of monomers to be polymerized.

40 It is further possible to add typical auxiliaries and additives to the polymer dispersions (PD). These include, for example, pH modifiers, reducing agents, and bleaches, such as the alkali metal salts of hydroxymethanesulfinic acid (e.g., Rongalit® C from BASF Aktiengesellschaft), complexing agents, deodorants, flavors, odorants, and viscosity

modifiers, such as alcohols, e.g., glycerol, methanol, ethanol, tert-butanol, glycol, etc. These auxiliaries and additives may be added to the polymer dispersions in the initial charge, in one of the feeds, or after the end of the polymerization.

- 5 The polymerization takes place in general at temperatures in a range from 0 to 150°C, preferably 20 to 100°C, more preferably 30 to 95°C. The polymerization takes place preferably at atmospheric pressure, although polymerization at an elevated pressure is also possible, an example being the autogenous pressure of the components used for the polymerization. In one suitable embodiment the polymerization takes place in the  
10 presence of at least one inert gas, such as nitrogen or argon, for example.

- However, because the acrylic copolymer of the invention includes organosilane monomers having hydrolyzable groups which serve as cross-linking sites upon exposure to moisture, it is important that the polymerization be performed in the absence of any  
15 significant quantity of water which would cause premature hydrolysis of the organosilanes and subsequent reaction with one another to form siloxane linkages. The polymerization medium should be substantially unreactive with the monomers and not significantly affect the polymerization such as by contributing a significant chain transfer effect. Accordingly, solvent levels are preferably kept relatively low such as to constitute  
20 less than about 50 percent by weight of the reaction solution. Suitable solvents for the polymerization of the acrylic copolymers incorporating polymerizable monomers containing hydrolyzable groups bonded to a silicon atom are well known to the art and literature and include benzene, toluene, xylene, chloroform, carbon tetrachloride, methyl acetate, ethyl acetate, ethylene dichloride, acetone, dioxane, tertiary butyl alcohol and  
25 others, with the aromatic hydrocarbons, and aliphatic hydrocarbons.

- The emulsion polymerization may be conducted either as a batch operation or else in the form of a feed process, including staged or gradient procedures. Preference is given to the feed process in which a portion of the polymerization batch, or else a  
30 polymer seed, is introduced as an initial charge, heated to the polymerization temperature, and its polymerization commenced, after which the remainder of the polymerization batch, typically by way of two or more spatially separate feeds, of which one or more comprise the monomers in pure form or in emulsified form, is supplied to the polymerization zone continuously, in stages or under a concentration gradient, during  
35 which the polymerization is maintained.

- The manner in which the initiator is added to the polymerization vessel in the course of the free-radical aqueous emulsion polymerization is known to a person of ordinary skill in the art. It may either be included in its entirety in the initial charge to the polymeriza-  
40 tion vessel, or else introduced continuously or in stages at the rate at which it is consumed in the course of the free-radical aqueous emulsion polymerization. In each case this will depend, in a manner known to one of ordinary skill in the art, both on the

chemical nature of the initiator system and on the polymerization temperature. It is preferred to include a portion in the initial charge and to supply the remainder to the polymerization zone at the rate at which it is consumed.

- 5 As well as the seed-free preparation of the polymer dispersion (PD) it is possible, according to a further embodiment, to prepare polymer dispersions (PD) having a defined particle size by means of an emulsion polymerization by the seed latex process, or in the presence of a seed latex prepared in situ. Polymerization processes of this kind are known and described, for example, in EP-B 40419, EP-A-614 922, 10 EP-A-567 812, and the literature cited therein, and also in "Encyclopedia of Polymer Science and Technology", vol. 5, John Wiley & Sons Inc., New York 1966, p. 847. The polymerization is preferably carried out in the presence of 0.01% to 3%, preferably 0.02% to 1.5% by weight of a seed latex (the solids content of the seed latex, based on the amount of overall monomer). The seed latex is preferably added at the beginning. 15 Furthermore, the seed latex may also be prepared in situ from a small amount of the monomers intended for the polymerization, in aqueous emulsion, together with a surface-active substance, by the heating of this emulsion to the polymerization temperature and the addition of a portion of the initiator.
- 20 The dispersions formed in the polymerization may be subject, following the polymerization procedure, to a physical or chemical aftertreatment. Examples of such processes are the known processes for residual monomer reduction, such as aftertreatment by addition of polymerization initiators or mixtures of two or more polymerization initiators at suitable temperatures, aftertreatment of the polymer solution by means of steam or 25 ammonia vapor, or stripping with inert gas, or treatment of the reaction mixture with oxidizing or reducing reagents, adsorption processes such as the adsorption of impurities on selected media such as activated carbon, for example, or an ultrafiltration.

- The polymer P which is obtainable by emulsion polymerization of at least one ethylenically unsaturated monomer M preferably has a glass transition temperature  $T_g$  of less 30 than 50°C, more preferably less than 40°C, in particular less than 35°C.

The aqueous polymer dispersion (PD) typically has a solids content of 20% to 65% by weight, preferably 35% to 60% by weight.

35

#### Alkoxysilane (B2)

- 40 According to the invention alkoxysilanes (B2) are alkoxysilyl-group monomers selected from the group of monomers listed for the polymer dispersion (PD) under group (v) or mercaptosilanes like those listed as mercaptosilane chain transfer agents.

The alkoxysilanes (B2) can be used individually, in the form of mixtures within one class of alkoxysilanes, or in the form of mixtures from different classes of alkoxysilanes.

- 5 The alkoxysilane compound (B2) is preferably present in a range of from 0.01 to 5 wt % by weight relative to the total weight of component B. It is particularly preferred if the alkoxysilane compound (B2) is present in an amount of from 0.01 to 3 % by weight relative to the total weight of component B, very particularly preferred from 0.01 to 0.5 % by weight.

10

#### Step (b)

15

Pursuant to step (b) of the present invention the prepolymer obtained in step (a) is hydrolyzed and polycondensed in the presence of

- water and
- at least one antimicrobial agent (Z) comprising at least one antimicrobial active (Z1) and optionally a particulate carrier substance (Z2),

20

wherein the at least one antimicrobial active (Z1) is unreactive during step (b).

The term "antimicrobial active" refers to a compound with antimicrobial activity wherein the compound may be an organic molecule, an inorganic or organic ionic substance or

25

Step (b) may be carried out by many different means. The presence of water can be achieved by using water-containing solvents for solving components (A) and/or (B) such as for instance acetone which is preferred as a solvent. By this means water required for carrying out the hydrolysis and initiating the polycondensation is inherently present in the system. Water can also be added separately prior to step (b).

30

Step (b) can be carried out at room temperature or at increased temperature of from 30 to 100 °C, in particular of from 30 to 60°C. Step (b) can be carried out at normal pressure or under vacuum of from 0,1 to 300 mbar, in particular of from 1 to 100 mbar at the same time. Step (b) can also be referred to as a drying process wherein the hydrolysis and polycondensation takes place inherently. It is preferred to conduct step (b) such that a coating is formed. In other words, the forming of the inventive composition and a coating on a substrate take place synchronously.

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The hydrolysis and polycondensation according to step (b) can optionally be catalyzed by a catalyst. Suitable catalysts such as acids and bases are known to the person skilled in the art.

- 5 Step (b) leads to a polymeric network containing the antimicrobial active (Z1). The antimicrobial active (Z1) is not covalently bound to the silica network obtained during step (b) and in specific embodiments can be released automatically or upon triggering. Step (b) comprises condensing the hydrolyzed siloxy groups resulting in the formation of a silica network covalently linked to a polymer and containing the antimicrobial active
- 10 (Z1) in an embedded but not covalently linked form. Preferably, the inventive composition retains the antimicrobial active (Z1), preferably releasing it in the presence of water.

Antimicrobial agent (Z)

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The antimicrobial agent (Z) may consist of a single antimicrobial active compound (Z1), a mixture of two or more different antimicrobial active compounds (Z1) or of one or more than one antimicrobial active compound (Z1) in or on a carrier substance (Z2) which is present in particulate form.

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- According to the invention it is a prerequisite that the at least one antimicrobial active (Z1) is unreactive during step (b). The term "unreactive" means that the antimicrobial active (Z1) is incapable of reacting during step (b), i.e., incapable of co-reacting with the prepolymer during the hydrolysis and polycondensation reaction in the presence of
- 25 water. The terms "reactive" and "reacting" refer to a chemical reaction, i.e., the formation of chemical bonds in contrast to a physical interaction such as an entrapment. In other words, "unreactive during step (b)" means that substantially no chemical bonds to the antimicrobial active (Z1) are formed during step (b).

- 30 Step (b) comprises the further polymerization of the prepolymer preferably by means of hydrolyzing and polycondensing component (B2) which is covalently bound to the prepolymer.

- Preferably the antimicrobial active (Z1) does not contain any functional groups capable of reacting with Si-OH groups which are preferably present as intermediates in step (b). In other words, the antimicrobial active is not covalently bound to the inorganic part of the hybrid network formed during step (b).
- 35

- In principle any antimicrobial agent (Z) can be used under the above-defined conditions.
- 40



In a preferred embodiment the antimicrobial agent (Z) not only contains an antimicrobial active (Z1) but also a particulate carrier substance (Z2). The carrier substance (Z2) in a specific embodiment may contain reactive groups on the surface capable of reacting during step (b).

5

According to a first preferred embodiment, in the following referred to as "PE-1", the antimicrobial agent (Z) comprises silver ions as antimicrobial active (Z1) and one selected from the group of zeolites and polymer hydrogels as the particulate carrier substance (Z2).

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According to a second preferred embodiment, in the following referred to as "PE-2", the antimicrobial agent (Z) comprises a particulate antimicrobial active (Z1) with number average particle size of from 1 to 500 nm selected from (i) zinc oxide and (ii) titanium dioxide containing AgBr and apatite.

15

Titanium dioxide encapsulated with AgBr and apatite is known to the person skilled in the art. AgBr is known to increase the photocatalytic properties and/or the antimicrobial efficiency of titanium dioxide. An apatite encapsulation is known to help prevent degrading the organic polymer around.

20

According to a third preferred embodiment, in the following referred to as "PE-3", the antimicrobial agent (Z1) is selected from at least one of the group consisting of quaternary ammonium salts and 2-bromo-2-nitropropane-1,3-diol.

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In the following, the preferred embodiments PE-1, PE-2 and PE-3 are discussed in detail.

According to the preferred embodiment PE-1 the antimicrobial agent (Z) comprises silver ions as antimicrobial active (Z1) and one selected from the group of zeolites and polymer hydrogels as the particulate carrier substance (Z2).

30

In principle any zeolite capable of retaining silver ions is suitable as particulate carrier substance (Z2) for the present invention. Zeolite particles retaining silver ions having antimicrobial properties are known from the prior art. For instance silver zeolites which can be used for the purpose of the present invention are described in US-P 4911898, US-P 4911899, US-P 4938955, US-P4906464, US-P4775585 and WO 03/055314.

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These zeolites could be modified with organosilicon comonomers like tris(2-acetoxyethyltrimethylsiloxy)silylpropyl acrylate and methacrylate tris(2-carboxyethyltrimethylsiloxy)silylpropyl acrylate and methacrylate tris(3-hydroxypropyltrimethylsiloxy)silylpropyl acrylate and methacrylate acrylate and methacrylate functional, fluorosubstituted alkyl/aryl siloxanes such as:

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tris(3,3,3 trifluoropropyl dimethylsiloxy) silyl propyl acrylate and methacrylate  
 tris[3-heptafluoroisopropoxy propyl] dimethylsiloxy silylpropyl acrylate and methacrylate  
 tris(pentafluorophenyl dimethylsiloxy)silyl propyl acrylate and methacrylate and other or  
 silane containing chain transfer reagents. Preferred mercaptosilane chain transfer  
 5 agents for use with the invention have the general formula:



where RS is a divalent alkylene group, R6 is an alkyl group, x is 1, 2 or 3, and Z is a  
 10 hydrolyzable group. The alkylene groups, alkyl groups, and hydrolyzable groups are  
 generally the same or similar to those set forth with respect to the silane functionalized  
 addition monomers.

Suitable mercaptosilane chain transfer agents include  $\gamma$ -mercapto propyl triethoxysi-  
 15 lane,  $\gamma$ -mercaptopropyl, trimethoxy silane, mercaptomethyl methyl dimethoxysilane,  
 and the like, with  $\gamma$ -mercaptopropyl trimethoxy silane being preferred. The quantities of  
 chain transfer agents used are similar to those disclosed in the prior art.

Polymer hydrogels retaining silver ions are known from the prior art as well. In principle  
 20 any polymer hydrogel capable of retaining silver ions can be used as particulate carrier  
 substance (Z2) for the present invention.

The term "gel" refers to materials whose containing a liquid phase and a solid phase  
 consisting of polymeric, i.e. long chain, molecules linked together to form a three-  
 25 dimensional network. The polymeric network is embedded in a liquid medium. A gel  
 preferably has a bicontinuous phase. A hydrogel refers to a gel where the liquid phase  
 is water.

The polymer backbone of hydrogels is typically formed by hydrophilic monomer units  
 30 and may be neutral or ionic. Examples of neutral and hydrophilic monomer units are  
 ethylene oxide, vinyl alcohol, (meth)acrylamide, N-alkylated (meth)acrylamides, N-  
 methylol(meth)acrylamide, N-vinylamides, N-vinylformamide, N-vinylacetamide, N-  
 vinyl-N-methylacetamide, N-vinyl-N-methylformamide, hydroxyalkyl (meth)acrylates  
 such as hydroxyethylmethacrylate, vinylpyrrolidone, (meth)acrylic esters of polyethyl-  
 35 ene glycol monoallyl ethers, allyl ethers, of polyethylene glycols, sugar units such as  
 glucose or galactose. Examples of cationic hydrophilic monomer units are ethyle-  
 neimine (in the protonated form), diallyldimethylammonium chloride and trimethylam-  
 monium propylmethacrylamide chloride. Examples of anionic monomer units are  
 (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, 2-acrylamido-  
 40 2-methylpropanesulfonic acid, vinylsulfonic acid, vinylphosphonic acid, 2-  
 methacryloyloxyethanesulfonic acid, 4-vinylbenzenesulfonic acid, allylsulfonic acid,

vinyltoluenesulfonic acid and vinylbenzenephosphonic acid (every one of the recited compounds in the deprotonated form).

- Hydrogels suitable as particulate carrier substance (Z2) are furthermore obtainable by
- 5 polymerization of unsaturated acids, for example acrylic acid, methacrylic acid and acrylamidopropanesulfonic acid, in the presence of small amounts of multiply olefinically unsaturated compounds containing Specific organosilicon comonomers like
- tris(2-acetoxyethyl dimethylsiloxy)silylpropyl acrylate and methacrylate
- tris(2-carboxyethyl dimethylsiloxy)silylpropyl acrylate and methacrylate
- 10 tris(3-hydroxypropyl dimethylsiloxy)silylpropyl acrylate and methacrylate acrylate and methacrylate functional, fluorosubstituted alkyl/aryl siloxanes such as: tris(3,3,3 trifluoropropyl dimethylsiloxy) silyl propyl acrylate and methacrylate tris[3-heptafluoroisopropoxy propyl] dimethylsiloxy silylpropyl acrylate and methacrylate tris(pentafluorophenyl dimethylsiloxy)silyl propyl acrylate and methacrylate and other
- 15 that are already known as superabsorbent polymers. In a preferred embodiment the antimicrobial agent (Z) not only contains an antimicrobial active (Z1) but also a particulate carrier substance (Z2). The carrier substance (Z2) in a specific embodiment may contain reactive groups on the surface capable of reacting during step (b). Such hydrogels are for example described in US-P 4,057,521, US-P 4,062,817, US-P 4,525,527, US-P 4,286,082, US-P 4,340,706 and US-P 4,295,987.
- 20

- Hydrogels that are obtainable by graft copolymerization of olefinically unsaturated acids onto different matrices, for example polysaccharides, polyalkylene oxides and also derivatives thereof, are suitable as particulate carrier substance (Z2), too. Such graft copolymers are known for example from US-P 5,011,892, US-P 4,076,663 and US-P 4,931,497.
- 25

- Hydrogels are generally dried, following their comminution, using known contact or
- 30 convective drying processes. Examples of contact dryers are hotplate, thin film, can, contact belt, sieve drum, screw, tumble or contact disk dryers. Examples of convection dryers are tray, chamber, channel, flat web, plate, rotary drum, free fall shaft, sieve belt, stream, atomization, fluidized bed, moving bed, paddle or spherical bed dryers (Kirk-Othmer 7, 326-398; (3rd) 1, 598-624; 8, 75-130, 311-339; 5, 104-112; Ullmann 1, 529-609; 11, 642 ff.; (4th) 2, 698-721; vt Industrielle Praxis: "Fortschritte auf dem Gebiet der Einbandtrockner, Teil 1: Auslegungsverfahren, E. Tittmann; Research Disclosure 96-38363: "Drying of Pasty Materials using a Continuous Through-Circulation Belt Dryer").
- 35
- 40 Hydrogels used in the present invention are preferably slightly crosslinked. As crosslinkers, vinyl, non-vinyl, or dimodal crosslinkers can be employed, either alone, as

mixtures, or in various combinations. Polyvinyl crosslinkers commonly known in the art for use in superabsorbent polymers advantageously are employed. Preferred compounds having at least two polymerizable double bonds include: di- or polyvinyl compounds such as divinyl benzene, divinyl toluene, divinyl xylene, divinyl ether, divinyl ketone and trivinyl benzene; di- or polyesters of unsaturated mono- or polycarboxylic acids with polyols, such as di- or tri-(meth)acrylic acid esters of polyols such as ethylene glycol, diethylene glycol, triethylene glycol, tetra ethylene glycol, propylene glycol, dipropylene glycol, tri propylene glycol, tetra propylene glycol, trimethylol propane, glycerin, polyoxyethylene glycols and polyoxypropylene glycols; unsaturated polyesters that can be obtained by reacting any of the above-mentioned polyols with an unsaturated acid such as maleic acid; di- or polyesters of unsaturated mono- or polycarboxylic acids with polyols derived from reaction of C<sub>2</sub>-C<sub>10</sub> polyhydric alcohols with 2 to 8 C<sub>2</sub>-C<sub>4</sub> alkylene oxide units per hydroxyl group, such as trimethylol propane hexaethoxyl triacrylate; di- or tri-(meth)acrylic acid esters that can be obtained by reacting polyepoxide with (meth)acrylic acid; bis(meth) acrylamides such as N,N-methylene-bisacrylamide; carbamyl esters that can be obtained by reacting polyisocyanates such as tolylene diisocyanate, hexamethylene diisocyanate, 4,4'-diphenyl methane diisocyanate and NCO-containing prepolymers obtained by reacting such diisocyanates with active hydrogen atom-containing compounds with hydroxyl group-containing monomers, such as di-(meth)acrylic acid carbamyl esters obtainable by reacting the above-mentioned diisocyanates with hydroxyethyl(meth)acrylate; di- or poly(meth)allyl ethers of polyols such as alkylene glycols, glycerol, polyalkylene glycols, polyoxyalkylene polyols and carbohydrates such as polyethylene glycol diallyl ether, allylated starch, and allylated cellulose; di- or poly-allyl esters of polycarboxylic acids, such as diallyl phthalate and diallyl adipate; and esters of unsaturated mono- or polycarboxylic acids with mono(meth)allyl ester of polyols, such as allyl methacrylate or (meth)acrylic acid ester of polyethylene glycol monoallyl ether.

The preferred classes of crosslinkers include, for example, bis(meth)acrylamides; allyl(meth)acrylates; di- or poly-esters of (meth)acrylic acid with polyols such as diethylene glycol diacrylate, trimethylol propane triacrylate, and polyethylene glycol diacrylate; and di- or polyesters of unsaturated mono- or polycarboxylic acids with polyols derived from the reaction of C<sub>1</sub>-C<sub>10</sub> polyhydric alcohols with 2 to 8 C<sub>2</sub>-C<sub>4</sub> alkylene oxide units per hydroxyl group, such as ethoxylated trimethylol propane triacrylate.

The antimicrobial agents (Z) according to the preferred embodiment PE-1 contain silver ions as antimicrobial active (Z1). The antimicrobial active (Z1) is preferably present as a silver salt.

Examples of silver salts include, for example silver acetate, silver acetylacetonate, silver azide, silver acetylide, silver arsenate, silver benzoate, silver bifluoride, silver monofluoride, silver fluoride, silver borfluoride, silver bromate, silver bromide, silver carbon-

ate, silver chloride, silver chlorate, silver chromate, silver citrate, silver cyanate, silver cyanide, silver-(cis,cis- 1,5-cyclooctadiene)-1,1,1,5,5,5,-hexafluoroacetylacetonate, silver dichromate tetrakis-(pyridine)-complex, silver diethyldithiocarbamate, silver(I) fluoride, silver(II) fluoride, silver-7,7-dimethyl -1,1,1,2,2,3,3 ,-heptafluor4,6-octandionate, silver hexafluoroantimonate, silver hexafluoroarsenate, silver hexafluorophosphate, silver iodate, silver iodide, silver isothiocyanate, silver potassium cyanide, silver lactate, silver molybdate, silver nitrate, silver nitrite, silver(I) oxide, silver(II) oxide, silver oxalate, silver perchlorate, silver perfluorobutyrate, silver perfluoropropionate, silver permanganate, silver perrhenate, silver phosphate, silver picrate monohydrate, silver propionate, silver selenate, silver selenide, silver selenite, silver sulfadiazine, silver sulfate, silver sulfide, silver sulfite, silver telluride, silver tetrafluoroborate, silver tetraiodomecurate, silver tetratungstenate, silver thiocyanate, silver-p-toluensulfonate, trifluoromethanesulfonic acid silver salt, trifluoroacetic acid silver salt, and silver vanadate. Mixtures of various silver salts can also be used. The preferred silver salts are silver acetate, silver benzoate, silver bromate, silver chlorate, silver lactate, silver molybdate, silver nitrate, silver nitrite, silver(I) oxide, silver perchlorate, silver permanganate, silver selenate, silver selenite, silver sulfadiazine, and silver sulfate. The most preferred silver salts are silver acetate and silver nitrate. Mixtures of silver salts can be employed, too.

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The preferred content of silver in the hydrogel is from 0.07 to 0.7 % by weight with respect to the total dry weight of the hydrogel.

25

According to the preferred embodiment PE-2, the antimicrobial agent (Z) comprises a particulate antimicrobial active (Z1) with number average particle size of from 1 to 500 nm selected from zinc oxide and titanium dioxide containing AgBr and Apatite.

30

The number average particle size refers to the value as determined by TEM measurements combined with image analysis.

35

The number average particle size of the particulate antimicrobial active as component (Z1) is preferably in the range of from 5 to 100 nm, in particular of from 10 to 50 nm, particularly preferred of from 15 to 45 nm, very particularly preferred from 20 to 40 nm.

40

It is preferred to use stabilized particles of the antimicrobial active (Z1). If Z1 is zinc oxide then stabilization by means of acrylic polymers is preferred.

It is furthermore preferred to use zinc oxide which is doped with a doping agent as described in US-A 2005/0048010.

40

The doping agent can be added to the zinc oxide dispersion by means known to the person skilled in the art. Suitable doping agents for zinc oxide are, in particular, metal

ions with one electron more or one electron less on the external shell. Main group metals and sub-group metals in oxidation state +III are particularly suitable. Boron(III), aluminum(III), gallium(III) and indium(III) are very particularly preferred. These metals can be added to the dispersion in the form of soluble salts, the choice of metal salt being dependent on whether it dissolves in the dispersant in the desired concentration. In the case of aqueous dispersions, many inorganic salts or else complexes are suitable, such as carbonates, halides, salts with EDTA, nitrates, salts with EDTA, acetyl acetate etc. Doping with precious metals, such as palladium, platinum, gold, etc. is likewise possible.

It is particularly preferred to use surface-modified zinc oxide nanoparticles as antimicrobial active (Z1). Surface modification of ZnO nanoparticles is known to the person skilled in the art and for instance described in US-A 2006/0210495 which is herewith incorporated by reference. Surface modification preferably is obtained by means of applying a surface-modifying agent to the ZnO nanoparticles, in particular to a dispersion containing the nanoparticles. In particular, suitable surface-modifying agent are disclosed in paragraphs 89 (page 5) to 183 (page 6) of US-A 2006/0210495.

It is also possible to modify the surface of ZnO nanoparticles using polymers as described in US-A 2007/0243145 the content of which is herewith incorporated by reference.

Said polymers used for modifying the surface of ZnO nanoparticles for the purpose of the present invention are preferably selected from copolymers as described in paragraphs 18 (page 2) to 35 (page 3).

Suitable titanium dioxide containing AgBr and apatite is known from M. R. Elahifard, S. Rahimnejad, S. Haghighi, M. R. Gholami, J. Am. Chem. Soc 2007; 129(31); 9552-9553

Preferably, the TiO<sub>2</sub> used in the present invention is surface modified, in particular by means of silanes as surface-modifying agent.

Different suitable silanes as surface-modifying agents are listed in documents the whole content of which is herewith incorporated by reference, in particular:

- US-P 6,013,372, column 13 (line 54) to column 14 (line 54),
- US-P 6,663,851, column 2 (line 9) to column 2 (line 54), and
- US-A 2006/0159637, paragraph 44 (page 2) to paragraph 83 (page 3).

A mixture of two or more of the above-described silanes can be used for the surface modification.

It is also preferred to use a photocatalyst with an antibacterial enhancer as described in US-P 6,013,372 the content of which is herewith incorporated by reference, in particular page 15.

- 5 It is furthermore preferred to use a doped photocatalyst as described in US-P 6013372, on page 15 lines 25-30.

US Patents 6627173, 7175911, and 5597515 describe the doping of titanium dioxide with nitrogen, fluorine, and carbon which is also suitable.

- 10 In a preferred embodiment the  $\text{TiO}_2$  is coated with calcium apatite as described in US-A 2007/0154378, the content of which is herewith incorporated by reference, in particular paragraphs 15 and 16 (page 2).

- According to the third preferred embodiment "PE-3", the antimicrobial agent (Z1) is  
15 selected from at least one of the group consisting of quaternary ammonium salts and 2-bromo-2-nitropropane-1,3-diol.

- Preferred quaternary ammonium salts are benzyl-alkyldimethyl ammonium chloride, [2-  
20 [[2-[(2-Carboxyethyl)(2-hydroxyethyl)amino]ethyl]amino]-2-oxo-ethyl]coco alkyldimethyl ammonium hydroxide, benzyl- $\text{C}_{12-14}$ -alkyldimethyl ammonium chloride, benzyl- $\text{C}_{12-16}$ -alkyldimethyl ammonium chloride, benzyl- $\text{C}_{12-18}$ -alkyl-dimethyl ammonium chloride,  $\text{C}_{12-14}$ -alkyl[(ethylphenyl)methyl]dimethyl ammonium chloride, reaction products of  $n\text{-C}_{10-16}$ -alkyltrimethylenediamines with chloroacetic acid, di- $\text{C}_{8-10}$ -alkyldimethyl ammonium chloride, dialkyl( $\text{C}_{8-18}$ )dimethyl ammonium compounds, didecyldimethylammonium  
25 chloride, cetylpyridinium chloride, biphenyl-2-ol, bronopol, cetylpyridinium chloride, chlorocresol, chloroxylonol, compound of D-gluconic acid with N,N'-bis(4-chlorophenyl)-3,12-diimino-2,4,11,13 tetraazatetradecanediamidine (2:1), ethanol, formaldehyde, formic acid, glutaraldehyde, hexa-2,4-dienoic acid, 1-phenoxypropan-2-ol and 2-phenoxypropanol, oligo-(2-(2-ethoxy)ethoxyethyl guanidinium chloride), pentapotas-  
30 sium bis(peroxymonosulphate) bis(sulphate), 2-phenoxyethanol, ortho-phthalaldehyde, 6-(phthalimido)peroxyhexanoic acid, poly(hexamethylenediamine guanidinium chloride), potassium (E,E)-hexa-2,4-dienoate, propan-1-ol, propan-2-ol, tetrakis(hydroxymethyl)-phosphonium salts, ortho-phenylphenol and salts of ortho-phenylphenol, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane salts, (5-chloro-2,4-dichlorophenoxy)-  
35 phenol, 3,4,4'-trichlorocarbanilide (triclocarban), o-benzo-p-chlorophenol, p-hydroxybenzoates, 2-(thiocyanomethylthio) benzothiazole, 3,5-dimethyl-1,3,5-thiadiazinane-2-thione, 2,4-dichlorobenzyl alcohol.

- 2-bromo-2-nitropropane-1,3-diol is particularly preferred as antimicrobial active (Z1).  
40

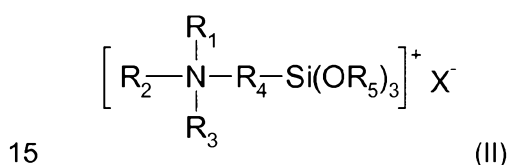
The following preferred embodiments refer to preferred embodiments PE-1, PE-2 and PE-3 as outlined above.

Preferably the antimicrobial agent Z is present in an amount of from 1 to 10 weight % based on the total dry weight of the composition.

- 5 The total dry weight refers to the weight of the composition after removal of the solvent.

In a preferred embodiment, the composition according to the present invention further contains an antimicrobial component (Z') being capable of reacting with components (A) and/or (B) in the presence of water. As a consequence, antimicrobial component  
 10 (Z') is covalently bound to the resulting hybrid network.

Preferred antimicrobial agents (Z') comprise a alkoxyasilane moiety and are represented by the following formula (II)



wherein

- R<sub>1</sub> is an C<sub>1</sub>-C<sub>30</sub> alkyl group, preferably C<sub>8</sub>-C<sub>30</sub> alkyl group,
- R<sub>2</sub> and R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> each independently are an C<sub>1</sub>-C<sub>30</sub> alkyl group or hydrogen,  
 and
- 20 - X is a counter ion, such as Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup>

Examples of organosilicon quaternary ammonium salt compounds for use according to the invention are 3-(triethoxysilyl)-propyl-dimethyloctadecylammonium chloride, 3-(trimethoxysilyl)propyl-methyl-dioctyl ammoniumchloride, 3-(trimethoxysilyl)propyl-  
 25 dimethylcecyl ammonium chloride, 3-(trimethoxysilyl)-propyl-methyldidecyl ammonium chloride, 3-(trimethoxy-silyl)propyldimethyldodecyl ammonium chloride, 3-(trimethoxysilyl)-propyl-methyldidodecyl ammonium chloride, 3-(trimethoxysilyl) propyl-dimethyltetradecyl ammonium chloride, 3-(trimethoxy-silyl)propyl-methyldihexadecyl ammonium chloride, and 3-(trimethoxysilyl)propyl-dimethyloctadecyl ammoniumchloride.  
 30

The antimicrobial agent (Z') is advantageously present in the composition in amounts from about 0.1% to about 50% with respect to the dry weight of the composition. Preferred amounts of the agent are 1% to 10% of the composition based upon the dry  
 35 weight of the composition.

Further components



Preferably, a composition according to the invention further comprises a solvent (D).

Examples of solvents (D) are alcohols, esters, ester alcohols, ethers, ether alcohols, aromatic and/or (cyclo)aliphatic hydrocarbons and their mixtures and halogenated hydrocarbons. Via the amino resins it is also possible to introduce alcohol as well into the mixtures.

Preference is given to alkanoic acid alkyl esters, alkanoic acid alkyl ester alcohols, alkoxyalkanoic acid alkyl esters and mixtures thereof.

Examples of esters include n-butyl acetate, ethyl acetate, 1-methoxyprop-2-yl acetate and 2-methoxyethyl acetate, and also the monoacetyl and diacetyl esters of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol or tripropylene glycol, such as butyl glycol acetate, for example. Further examples are carbonates, as well, such as preferably 1,2-ethylene carbonate, 1,2-propylene carbonate or 1,3-propylene carbonate.

Ethers are, for example, tetrahydrofuran (THF), dioxane, and the dimethyl, diethyl or di-n butyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol or tripropylene glycol.

Alcohols are for example methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol, sec-butanol, n-hexanol, n-heptanol, n-octanol, n-decanol, n-dodecanol (lauryl alcohol), 2-ethylhexanol, cyclopentanol or cyclohexanol.

Alkanoic ester alcohols are for example poly(C<sub>2</sub> to C<sub>3</sub>) alkylene glycol (C<sub>1</sub> to C<sub>4</sub>) monoalkyl ether acetates. Ether alcohols are for example poly(C<sub>2</sub> to C<sub>3</sub>) alkylene glycol di(C<sub>1</sub> to C<sub>4</sub>) alkyl ethers, dipropylene glycol dimethyl ether, preferably butyl glycol.

Aromatic hydrocarbon mixtures are those comprising predominantly aromatic C<sub>7</sub> to C<sub>14</sub> hydrocarbons and being able to comprise a boiling range from 110 to 300°C, particular preference being given to toluene, o-, m- or p-xylene, trimethylbenzene isomers, tetramethylbenzene isomers, ethylbenzene, cumene, tetrahydronaphthalene and mixtures comprising them.

Examples thereof are the Solvesso® grades from ExxonMobil Chemical, especially Solvesso® 100 (CAS no. 64742-95-6, predominantly C<sub>9</sub> and C<sub>10</sub> aromatics, boiling range about 154 – 178°C), 150 (boiling range about 182 – 207°C) and 200 (CAS no. 64742-94-5), and also the Shellsol® grades from Shell, Caromax® grades from Petrochem Carless, Caromax® 18, for example, or products from DHC, Hydrosol® A/170, for example. Hydrocarbon mixtures comprising paraffins, cycloparaffins and aromatics are also available commercially under the names Kristalloel (for example, Kristalloel

30, boiling range about 158 - 198°C or Kristalloel 60: CAS no. 64742-82-1), white spirit (likewise, for example CAS no. 64742-82-1) or solvent naphtha (light: boiling range about 155 - 180°C, heavy: boiling range about 225 - 300°C). The aromatics content of such hydrocarbon mixtures is generally more than 90%, preferably more than 95%,  
5 more preferably more than 98% and very preferably more than 99% by weight. It may be advisable to use hydrocarbon mixtures having a particularly reduced naphthalene content.

The density at 20°C to DIN 51757 of the hydrocarbons may be less than 1 g/cm<sup>3</sup>, preferably less than 0.95 and more preferably less than 0.9 g/cm<sup>3</sup>.  
10

The aliphatic hydrocarbon content is generally less than 5%, preferably less than 2.5% and more preferably less than 1% by weight.

15 Halogenated hydrocarbons are, for example chlorobenzene and dichlorobenzene or its isomer mixtures.

(Cyclo)aliphatic hydrocarbons are for example decalin, alkylated decalin, and isomer mixtures of linear or branched alkanes and/or cycloalkanes.

20

Preference is given to n-butyl acetate, ethyl acetate, 1-methoxyprop-2-yl acetate, 2-methoxyethyl acetate, and mixtures thereof.

Mixtures of this kind can be produced in a volume ratio 10:1 to 1:10, preferably in a volume ratio of 5:1 to 1:5 and more preferably in a volume ratio of 1:1.  
25

Preferred examples are butyl acetate/xylene, 1:1 methoxypropyl acetate/xylene, 1:1 butyl acetate/solvent naphtha 100, 1:2 butyl acetate/Solvesso® 100, and 3:1 Kristalloel 30/Shellisol® A.

30 Alcohols are for example methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, pentanol isomer mixtures, hexanol isomer mixtures, 2-ethylhexanol or octanol.

Examples of further, typical coatings additives (E) that can be used include antioxidants, stabilizers, activators (accelerants), fillers, pigments, dyes, antistats, flame retardants, thickeners, thixotropic agents, surface-active agents, viscosity modifiers, plasticizers or chelating agents.  
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Suitable thickeners, besides free-radically (co)polymerized (co)polymers, include typical organic and inorganic thickeners such as hydroxymethylcellulose or bentonite.  
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Examples of chelating agents that can be used include ethylenediamineacetic acid and its salts, and  $\beta$ -diketones.

- 5     Suitable fillers comprise silicates, examples being silicates obtainable by silicon tetrachloride hydrolysis, such as Aerosil® from Degussa, siliceous earth, talc, aluminum silicates, magnesium silicates, calcium carbonates, etc.

- 10    Suitable stabilizers comprise typical UV absorbers such as oxanilides, triazines and benzotriazole (the latter available as Tinuvin® grades from Ciba-Spezialitätenchemie) and benzophenones. They can be used alone or together with suitable free-radical scavengers, examples being sterically hindered amines such as 2,2,6,6-tetramethylpiperidine, 2,6-di-tert-butylpiperidine or derivatives thereof, e.g., bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate. Stabilizers are used typically in amounts of 0.1% to 5.0% by weight, based on the solid components comprised in the preparation.

- 15    Pigments may likewise be comprised. Pigments, according to CD Römpp Chemie Lexikon – Version 1.0, Stuttgart/New York: Georg Thieme Verlag 1995, with reference to DIN 55943, are particulate, organic or inorganic chromatic or achromatic colorants which are virtually insoluble in the application medium.

- 20    Virtually insoluble here means a solubility at 25°C of below 1 g/1000 g of application medium, preferably below 0.5, more preferably below 0.25, very preferably below 0.1 and in particular below 0.05 g/1000 g of application medium.

- 25    Examples of pigments comprise any desired systems of absorption pigments and/or effect pigments, preferably absorption pigments. There are no restrictions concerning the number and selection of the pigment components. They can be adapted as desired to the particular requirements, such as the desired color impression, for example.

- 30    By effect pigments are meant all pigments which exhibit a platelet-shaped construction and impart specific decorative color effects to a surface coating. The effect pigments comprise, for example, all of the effect-imparting pigments which can be employed commonly in vehicle finishing and industrial coating. Examples of effect pigments of this kind are pure metal pigments, such as aluminum, iron or copper pigments; interference pigments, such as titanium dioxide-coated mica, iron oxide-coated mica, mixed oxide-coated mica (e.g., with titanium dioxide and  $\text{Fe}_2\text{O}_3$  or titanium dioxide and  $\text{Cr}_2\text{O}_3$ ), metal oxide-coated aluminum, or liquid-crystal pigments.

- 40    The color-imparting absorption pigments are, for example, typical organic or inorganic absorption pigments which can be used in the coatings industry. Examples of organic absorption pigments are azo pigments, phthalocyanine pigments, quinacridone pig-

ments and pyrrolopyrrole pigments. Examples of inorganic absorption pigments are iron oxide pigments, titanium dioxide and carbon black.

## 5 Applications

The compositions of this invention are useful as coatings and may in particular be utilized as primers, topcoats or as clearcoats and/or basecoats in clearcoat/basecoat compositions. They are also useful in spray applications.

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### Coating materials

The invention further provides a coating material in the form of an aqueous composition comprising:

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- at least one binder component (B), comprising at least one alkoxysilane (B2) and a polymer dispersion (PD), as defined above
- at least one antimicrobial agent (Z), as defined above
- up to 70% by weight, preferably 10% to 70% by weight, of inorganic fillers and/or
- 20 inorganic pigments,
- 0.1% to 20% by weight of typical auxiliaries, and
- water to 100% by weight.

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An aqueous coating material for the purposes of this specification means that the continuous phase of the coating material is composed to an extent of more than 80% by weight, preferably 90% by weight, and in particular exclusively, of water. Additionally it is possible for water-miscible liquids such as water-soluble monoalcohols, isooctanol for example, diol such as diglyme and polyols to be part of the continuous phase.

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The binder compositions of the invention are employed preferably in aqueous coating materials. These coating materials take the form, for example, of an unpigmented system (clear varnish) or of a pigmented system (emulsion paint or emulsion varnish paint). The fraction of the pigments can be described by the pigment volume concentration (PVC). The PVC describes the ratio of the volume of pigments ( $V_P$ ) and fillers ( $V_F$ ) to the total volume, composed of the volumes of binder ( $V_B$ ), pigments, and fillers of a dried coating film, in percent:  $PVC = (V_P + V_F) \times 100 / (V_P + V_F + V_B)$ . Coating materials can be divided on the basis of the PVC, for example, as follows:

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highly filled interior paint, wash resistant, white/matt	about 85
interior paint, scrub resistant, white/matt	65-80
semigloss paint, silk-matt	about 35

semigloss paint, silk-gloss	about 25
high-gloss paint	12-30
exterior masonry paint, white	30-65
clear varnish	0

5

Elucidated in the text below is the composition of a typical emulsion paint. Emulsion paints comprise generally 30% to 75% and preferably 40% to 65% by weight of non-volatile constituents. By these are meant all constituents of the preparation which are not water, but at least the total weight of binder, filler, pigment, low-volatility solvents (boiling point above 220°C), plasticizers for example, and polymeric auxiliaries. This figure is accounted for to the extent of about

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- a) 3% to 90%, more particularly 10% to 60%, by weight, by the polymer dispersion (PD),
- 15 b) 5% to 85%, preferably 5% to 60%, more particularly 10% to 50%, by weight, by at least one inorganic pigment,
- c) 0% to 85%, more particularly 5% to 60%, by weight, by inorganic fillers, and
- d) 0.1% to 40%, more particularly 0.5% to 20%, by weight, by typical auxiliaries.

20

The term "pigment" is used in the context of this invention comprehensively to identify all pigments and fillers, examples being color pigments, white pigments, and inorganic fillers. These include inorganic white pigments such as titanium dioxide, preferably in the rutile form, barium sulfate, zinc oxide, zinc sulfide, basic lead carbonate, antimony trioxide, lithopones (zinc sulfide + barium sulfate), or colored pigments, examples being iron oxides, carbon black, graphite, zinc yellow, zinc green, ultramarine, manganese black, antimony black, manganese violet, Paris blue or Schweinfurt green. Besides the inorganic pigments the emulsion paints of the invention may also comprise organic color pigments, examples being sepia, gamboge, Cassel brown, toluidine red, para red, 25 Hansa yellow, indigo, azo dyes, anthraquinoid and indigoid dyes, and also dioxazine, quinacridone, phthalocyanine, isoindolinone, and metal complex pigments. Also suitable are synthetic white pigments with air inclusions to increase the light scattering, such as the Rhopaque® dispersions.

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Suitable fillers are, for example, aluminosilicates, such as feldspars, silicates, such as kaolin, talc, mica, magnesite, alkaline earth metal carbonates, such as calcium carbonate, in the form for example of calcite or chalk, magnesium carbonate, dolomite, alkaline earth metal sulfates, such as calcium sulfate, silicon dioxide, etc. Finely divided fillers are of course preferred in coating materials. The fillers can be used as individual components. In actual practice, however, filler mixtures have proven particularly appropriate, examples being calcium carbonate/kaolin and calcium carbonate/talc. Glossy 40

coating materials generally include only small amounts of very finely divided fillers, or comprise no fillers.

5 Finely divided fillers may also be used to increase the hiding power and/or to save on the use of white pigments. In order to adjust the hiding power, the hue, and the depth of color, it is preferred to use blends of color pigments and fillers.

10 The coating material of the invention (aqueous coating material) may comprise - in addition to the binder component (B) and the antimicrobial (Z), the , pigment and, if appropriate, additional film-forming polymers - further auxiliaries.

15 The typical auxiliaries, in addition to the emulsifiers used in the polymerization, include wetting agents or dispersants, such as sodium, potassium or ammonium polyphosphates, alkali metal salts and ammonium salts of acrylic acid copolymers or maleic anhydride copolymers, polyphosphonates, such as sodium 1-hydroxyethane-1,1-diphosphonate, and salts of naphthalenesulfonic acids, more particularly their sodium salts.

20 Further suitable auxiliaries are flow control agents, defoamers, biocides, and thickeners. Suitable thickeners are, for example, associative thickeners, such as polyurethane thickeners. The amount of the thickener is preferably less than 1% by weight, more preferably less than 0.6% by weight, of thickener, based on solids content of the coating material.

25 Additionally suitable auxiliaries are film-forming auxiliaries or coalescence auxiliaries. Preference is given to using, for example, white spirit, ethylene glycol, propylene glycol, glycerol, ethanol, methanol, water-miscible glycol ethers and their acetates such as diethylene glycol, 1-methoxy-2-propanol, 2-amino-2-methyl-1-propanol, isooctanol, butyl glycol, butyl diglycol, diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether or dipropylene glycol monobutyl ether, dipropylene glycol methyl ether, dipropylene glycol propyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, butyl glycol acetate, butyl diglycol acetate, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, diisobutyl esters of long-chain dicarboxylic acids such as Lusolvan® FBH or tripropylene glycol monoisobutyrate.

35 The coating materials of the invention are produced in a known way by blending the components in mixing apparatus customary for the purpose. It has been found appropriate to prepare an aqueous paste or dispersion from the pigments, water, and, if appropriate, the auxiliaries, and only then to mix the polymeric binder, i.e., in general, the aqueous dispersion of the polymer, with the pigment paste or pigment dispersion.

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The coating materials of the invention comprise generally 30% to 75% and preferably 40% to 65% by weight of nonvolatile constituents. By these are meant all constituents of the preparation which are not water, but at least the total amount of binder, pigment, and auxiliary, based on the solids content of the coating material. The volatile constituents are primarily water.

The coating material of the invention may be applied to substrates in a typical way, as for example by spreading, spraying, dipping, rolling, knife coating, etc.

The inventive compositions lead to fast reacting, durable coatings having extended pot-life and excellent cure. The curable compositions of the present invention provide a clearcoat having improved scratch resistance. The compositions of this invention can in principle also be utilized as adhesives, elastomers and plastics.

The coating materials of the invention are suitable for coating substrates including wood, paper, textile, leather, non-wovens, plastics surfaces, glass, ceramic, mineral building materials such as cement moldings and fiber-cement slabs, coated or uncoated metals. Preference is given to the use of the curable compositions for the coating of plastics or metals, particularly in the form of sheets, more preferably to the coating of surfaces made of metal.

The antimicrobial compositions and coatings comprising said antimicrobial compositions are particularly suitable for hospital environments, medical devices, water treatment plants, food service & packaging areas, pharmaceutical labs, childcare facilities and other areas that need extra protection against microbes. The antimicrobial compositions and coatings comprising said antimicrobial composition can advantageously be used in food equipment such as mixing bowls, serving trays, salad bars, sinks, walk-ins, coolers, display cases, and serving counters, home appliances such as refrigerators, washers, dryers, disposals, and trash compactors, food processing such grinders, trays, conveyors, storage bins, slicers, and food processing equipment, medical devices such as instrument trays, racks, sterilization equipment, bedpans, counter tops, examination tables, carts, beds, and lighting fixtures, hospital as well public and private interior equipment such as pushplates, kickplates, towel dispensers, doors, escalators, elevators, and restroom equipment, and as part of transportation means such as vehicle interior parts and surfaces, aircraft interior parts and surfaces, and train interior parts and surfaces.

The substrates are coated with the coating materials of the invention in accordance with conventional techniques which are known to the skilled worker, and which involve applying at least one coating material or coating formulation of the invention to the target substrate in the desired thickness, and removing the volatile constituents of the coating material with heating if appropriate (drying). This operation may, if desired, be

repeated one or more times. Application to the substrate may be made in a known way, for example by spraying, troweling, knife coating, brushing, rolling, roller-coating or pouring. The coating thickness is generally in a range from about 3 to 1000 g/m<sup>2</sup> and preferably 10 to 200 g/m<sup>2</sup>. Curing may then be carried out.

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Curing is generally accomplished by drying the coatings - following application of the coating material to the substrates - at a temperature if appropriate below 80°C, preferably room temperature to 60°C and more preferably room temperature to 40°C, over a period of up to 72 hours, preferably up to 48 hours, more preferably up to 24 hours, very preferably up to 12 hours and in particular up to 6 hours, and subjecting the applied coatings to thermal treatment (curing) under an oxygen-containing atmosphere, preferably air or under inert gas, at temperatures between 80 and 270, preferably between 100 and 240 and, more preferably between 120 and 180°C. Curing of the coating material takes place as a function of the amount of coating material applied and of the crosslinking energy introduced via high-energy radiation, heat transfer from heated surfaces, or via convection of gaseous media, over a period of seconds, for example, in the case of coil coating in combination with NIR drying, up to 5 hours, for example, high-build systems on temperature sensitive materials, usually not less than 10 minutes, preferably not less than 15, more preferably not less than 30, and very preferably not less than 45 minutes. Drying essentially comprises removal of existing solvent, and in addition there may also, even at this stage, be reaction with the binder, whereas curing essentially comprises reaction with the binder.

In addition to or instead of thermal curing, the curing may also take place by means of IR and NIR radiation, with NIR radiation here denoting electromagnetic radiation in the wavelength range from 760 nm to 2.5 µm, preferably from 900 to 1500 nm.

Curing takes place in a time of 1 second to 60 minutes, preferably of 1 minute to 45 minutes.

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Examples of suitable substrates for the coating materials of the invention include thermoplastic polymers, especially polymethyl methacrylates, polybutyl methacrylates, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, acrylonitrile-ethylenepropylene-diene-styrene copolymers (A-EPDM), polyetherimides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

Mention may further be made of polyethylene, polypropylene, polystyrene, polybutadiene, polyesters, polyamides, polyethers, polycarbonate, polyvinylacetal, polyacrylonitrile, polyacetal, polyvinyl alcohol, polyvinyl acetate, phenolic resins, urea resins, melamine resins, alkyd resins, epoxy resins or polyurethanes, block or graft copolymers thereof, and blends of these.

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Mention may preferably be made of ABS, AES, AMMA, ASA, EP, EPS, EVA, EVAL, HDPE, LDPE, MABS, MBS, MF, PA, PA6, PA66, PAN, PB, PBT, PBTP, PC, PE, PEC, PEEK, PEI, PEK, PEP, PES, PET, PETP, PF, PI, PIB, PMMA, POM, PP, PPS, PS, 5 PSU, PUR, PVAC, PVAL, PVC, PVDC, PVP, SAN, SB, SMS, UF, UP plastics (abbreviated names in accordance with DIN 7728) and aliphatic polyketones.

Particularly preferred substrates are polyolefins, such as PP (polypropylene), which optionally may be isotactic, syndiotactic or atactic and optionally may be unoriented or 10 may have been oriented by uniaxial or biaxial stretching, SAN (styrene-acrylonitrile-copolymers), PC (polycarbonates), PVC (polyvinyl chlorides), PMMA (polymethyl methacrylates), PBT (poly(butylene terephthalate)s), PA (polyamides), ASA (acrylonitrile-styrene-acrylate copolymers) and ABS (acrylonitrile-butadiene-styrene-copolymers), and also their physical mixtures (blends). Particular preferably is given to 15 PP, SAN, ABS, ASA and blends of ABS or ASA with PA or PBT or PC. Especially preferred are polyolefins, PMMA and PVC.

Especially preferred is ASA, particularly in accordance with DE 196 51 350 and the ASA/PC blend. Preference is likewise given to polymethyl methacrylate (PMMA) or 20 impact-modified PMMA.

A further-preferred substrate for coating with the coating materials of the invention are metals. The metals in question are especially those which have already been coated with another coating film, such as with an electrocoat, surfacer, primer or basecoat. 25 These coating films may be solvent-based, water-based or powder coating-based, may be crosslinked, part-crosslinked or thermoplastic, may have been cured through their volume or may have been applied wet-on-wet.

As far as the type of metal is concerned, suitable metals may in principle be any desired metals. In particular, however, they are metals or alloys which are typically employed as metallic materials of construction and require protection against corrosion. 30

The surfaces in question are in particular those of iron, steel, Zn, Zn alloys, Al or Al alloys. These may be the surfaces of structures composed entirely of the metals or 35 alloys in question. Alternatively the structures may have been only coated with these metals and may themselves be composed of materials of other kinds, such as of other metals, alloys, polymers or composite materials, for example. They may be surfaces of castings made from galvanized iron or steel. In one preferred embodiment of the present invention the surfaces are steel surfaces.

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Zn alloys or Al alloys are known to the skilled worker. The skilled worker selects the nature and amount of alloying constituents in accordance with the desired end-use

application. Typical constituents of zinc alloys comprise, in particular, Al, Pb, Si, Mg, Sn, Cu or Cd. Typical constituents of aluminum alloys comprise, in particular, Mg, Mn, Si, Zn, Cr, Zr, Cu or Ti. The alloys may also be Al/Zn alloys in which Al and Zn are present in an approximately equal amount. Steel coated with alloys of these kinds is available commercially. The steel may comprise the typical alloying components known to the skilled worker.

Also conceivable is the use of the coating compositions of the invention for treating tin-plated iron/steel (tinplate).

The coatings obtainable from the curable compositions according to the invention exhibit excellent antimicrobial properties.

It is known to the person skilled in the art that under suitable conditions, in particular in the presence of suitable catalysts and water the polyurethane-based polymer obtained according to the present invention is a polyurethane-polyurea-silica polymer.

Another subject of the present invention is a kit comprising a curable composition containing as separate parts

- a) at least one binder component (B) comprising at least one alkoxysilane (B2) and a polymer dispersion (PD), as defined above and
- b) at least one antimicrobial agent (Z) as defined above.

Another subject-matter of the present invention is a hybrid network of a polymer dispersion PD and silica chemically linked via Si-containing groups comprising an antimicrobial agent not covalently linked to said network.

Furthermore, the present invention provides a hybrid network of a polyurethane and silica chemically linked via Si-containing groups comprising an antimicrobial agent covalently linked to said network.

### Examples

In the following examples the following abbreviations are used:

- AMSI: 3-[Bis(2-hydroxyethyl)amino] propyl triethoxysilane
- HDI: Hexamethylene diisocyanate
- BNP: 2-bromo-2-nitro-1,3-propanediol (Bronopol)
- PPG: polypropyleneglycol
- PD: 1,5-pentanediol
- NIPAM: N-isopropylacrylamide

- TEMED: N,N,N',N'-tetramethylenediamine  
MBA: N'N-methylenebisacrylamide  
AP: Ammonium persulfate  
Quat: Dimethyloctadecyl [3-(trimethoxysilyl)propyl] ammonium chloride purchased  
5 from Sigma Aldrich

Hygate 4000 Antimicrobial sample was provided by Ciba Specialty chemicals  
AJ 100 D Sample purchased from AgION Technologies USA

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### Synthesis of Polymer Dispersions

#### Example 1

- 15 To a 4 l glass vessel with anchor stirrer (125 rpm) at 95 C, 87 g of Seed T 6772 and  
560 g of deionized water was charged at 95 C. By lowering the internal temperature to  
70 C, Feed 1 and part of feed 2 were added continuously over the course of 3 h and  
the remainder of feed stream 2 was supplied continuously over the course of 3.5 h, the  
two feed streams being kept spatially separate at a slow rate. Feed 5 was then added  
20 over a period of 15 min with constant stirring. After completion of feed 5, the reactor  
was charged with feed 3 over a period of 30 min followed by feed 4 over a period of 45  
min. The reactor was then cooled down to room temperature and at 40 C; the polym-  
erization was completed by adding the contents of feed 6. The solid content of this dis-  
persion is 51.5 % and the viscosity of the resulting composition was 7 mpas.
- 25 Initial charge  
Deminn Water pH 609.00 g  
Seed T6772 20.60 g  
Part from Feed 6.75g  
Feed 1:
- 30 Deminn Water 419.00 g  
Emulphor NPS 25 110.70g  
Ammonia 5.40g  
AA 38.50g  
Styrene 644.00g
- 35 BA 644.00g  
MTMO 6.60g  
Deminn Water for rinse (thereafter) 20.00 g  
Feed 2:
- 40 Sodium persulfate 116.10g  
Feed 3:  
t-BHP 14.00g  
Deminn Water for rinse (thereafter) 8.00 g

Feed 4 :

Deminn Water 20.00g

Sodium metabisulfite 5.30g

Deminn Water for rinse (thereafter) 5.00 g

5 Feed 5:

Ammonia 16.20g

Feed 6:

Acticide MV 3.00g

Deminn Water for rinse (thereafter)

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Example 2

To a 4 l glass vessel with anchor stirrer (125 rpm) at 95 C, 87 g of Seed T 6772 and 560 g of deionized water was charged at 95 C. By lowering the internal temperature to 70° C, Feed 1 and part of feed 2 were added continuously over the course of 3 h and the remainder of feed stream 2 was supplied continuously over the course of 3.5 h, the two feed streams being kept spatially separate at a slow rate. Feed 5 was then added over a period of 15 min with constant stirring. After completion of feed 5, the reactor was charged with feed 3 over a period of 30 min followed by feed 4 over a period of 45 min. The reactor was then cooled down to room temperature and at 40 C; the polymerization was completed by adding the contents of feed 6. The solid content of this dispersion is 51.5 % and the viscosity of the resulting composition was 7 mPas.

20 Initial charge

Deminn Water pH 609.00 g

25 Seed T6772 20.60 g

Part from Feed 6.75g

Feed 1:

Deminn Water 419.00 g

Emulphor NPS 25 110.70g

30 Ammonia 5.40g

AA 38.50g

Styrene 644.00g

BA 644.00g

MTMO 6.60g

35 Deminn Water for rinse (thereafter) 20.00 g

Feed 2:

Sodium persulfate 116.10g

Feed 3:

t-BHP 14.00g

40 Deminn Water for rinse (thereafter) 8.00 g

Feed 4 :

Deminn Water 20.00g

Sodium metabisulfite 5.30g  
Deminn Water for rinse (thereafter) 5.00 g

Feed 5:

Ammonia 16.20g

5 Feed 6:

Acticide MV 3.00g

Deminn Water for rinse (thereafter)

Paint formulation using the Acronal dispersion

10 These silane containing polymers prepared by the above procedure were mixed with three silane functionalized biocides to generate antibacterial dispersions. The modified dispersions were then formulated into paint. Formulation of paint can be done as described in the patents.

15 Synthesis of Antimicrobial dispersions

Example 3: To 750 g of dispersion obtained using the procedure indicated in example 1, 30 g of antimicrobial agent Quat and 300 g of deionized water were added. After homogenization by shaking, the resulting dispersion was formulated into paint. The obtained paint was then transferred to a polycarbonate slide in the form of a coating and dried at room temperature for 3 days. The samples were submitted for antibacterial tests.

Example 4: To 500 g of dispersion in example 1, 0.5 g of Hygate 4000 powder was added. After homogenization by shaking, the resulting dispersion was formulated into paint. The obtained paint was then transferred to a polycarbonate slide in the form of a coating and dried at room temperature for 3 days. The samples were submitted for antibacterial tests.

Example 5: To 500 g of dispersion in example 1, 5 g of AJ100D powder was added. After homogenization by shaking, the resulting dispersion was formulated into paint. The obtained paint was then transferred to a polycarbonate slide in the form of a coating and dried at room temperature for 3 days. The samples were submitted for antibacterial tests.

Example 6: To 750 g of dispersion obtained using the procedure indicated in example 2, 30 g of antimicrobial agent Quat and 300 g of deionized water were added. After homogenization by shaking, the resulting dispersion was formulated into paint. The obtained paint was then transferred to a polycarbonate slide in the form of a coating and dried at room temperature for 3 days. The samples were submitted for antibacterial tests.

- Example 7: To 500 g of dispersion in example 2, 5 g of AJ100D powder was added. After homogenization by shaking, the resulting dispersion was formulated into paint. The obtained paint was then transferred to a polycarbonate slide in the form of a coating and dried at room temperature for 3 days. The samples were submitted for anti-
- 5 bacterial tests.

#### Antimicrobial activity measurements

- The tests for antimicrobial activity were performed according to Japanese standard
- 10 JIS Z 2801:2000 – Test for antimicrobial activity and efficacy. The following bacteria were used: Escherichia coli (E. coli), Staphylococcus aureus (S. aureus) and Methicillin Resistant Staphylococcus aureus (MRSA). Table 1 collates the antimicrobial activity of the Acronal paints with differing amounts of various antimicrobial components.

#### 15 Zone of Inhibition Test

To find out whether an antimicrobial incorporated in the paint leaches out of the coating, zone of inhibition test was carried out. The procedure for these tests is elaborated here.

#### 20 1. Sample Preparation

The antimicrobial paint obtained from the above examples was coated on both sides of the filter paper of 5 cm diameter. The paint was allowed to dry under ambient conditions for 1 week. The coated filter paper was then cut into 3cm by 3cm individual pieces. Three replicates were used for testing against one type of test organism.

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#### 2. Test method

The zone of inhibition tests were carried out as per the test method JIS L 1902 : 2002 (Halo Method) "Testing for antibacterial activity and efficacy on textile products.

#### 30 3. Results of zone of Inhibition

All the test samples from examples 3-7 did not show any zone of inhibition, clearly indicating the presence of covalent linking of antimicrobials to the polymer backbone.

Table 1: Antimicrobial activity of antimicrobial paints

Example	Dispersion type	Antimicrobial (type)	Antimicrobial load (% by weight)	Antimicrobial Activity, R		
				<i>S. aureus</i>	<i>E. coli</i>	MRSA
3-5	Example 1	Control	0	0.3	0	0
		Quat	2.8	0.2	0	0
		Hygate 4000	0.1	0	0	0
		AJ-100D	1	5.5	5.9	5.1
6-7	Example 2	Control	0	2.2	2.9	1.5
		Quat	2.8	3.3	3.9	3.6
		AglON	1	5.5	5.4	5.1

- Comprises/comprising and grammatical variations thereof when used in this
- 5 specification are to be taken to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Method of preparing a composition comprising:
  - (a) reacting
    - a binder component (B) comprising at least one alkoxysilane (B2), and a polymer dispersion (PD)thus obtaining a prepolymer and subsequently
  - (b) hydrolyzing and polycondensing said prepolymer in the presence of
    - water and
    - at least one antimicrobial agent (Z) comprising at least one antimicrobial active (Z1) and a particulate carrier substance (Z2), which is selected from the group consisting of zeolites and polymer hydrogels,wherein the at least one antimicrobial agent (Z) is unreactive during step (b) and comprises silver ions as antimicrobial active (Z1).
2. Method according to claim 1, wherein the antimicrobial agent (Z) comprises a particulate antimicrobial active (Z1) with number average particle size of from 1 to 500 nm selected from (i) zinc oxide and (ii) particles containing titanium dioxide, AgBr and apatite.
3. Method according to claim 1, wherein the antimicrobial agent (Z) comprises an antimicrobial active (Z1) which is selected from at least one of the group consisting of quaternary ammonium salts and 2-bromo-2-nitropropane-1,3-diol.
4. Method according to any one of claims 1 to 3, wherein the monomers M of the polymer dispersion (PD) are selected from esters of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with C<sub>1</sub>-C<sub>20</sub> alkanols and



C<sub>5</sub>-C<sub>10</sub> cycloalkanols, vinylaromatics, esters of vinyl alcohol with C<sub>1</sub>-C<sub>30</sub> monocarboxylic acids, ethylenically unsaturated nitriles, vinyl halides, vinylidene halides, monoethylenically unsaturated carboxylic and sulfonic acids, phosphorus monomers, esters of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with C<sub>2</sub>-C<sub>30</sub> alkanediols, amides of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with C<sub>2</sub>-C<sub>30</sub> amino alcohols containing a primary or secondary amino group, primary amides of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic acids and their N-alkyl and N,N-dialkyl derivatives, N-vinyl lactams, open-chain N-vinylamide compounds, esters of allyl alcohol with C<sub>1</sub>-C<sub>30</sub> monocarboxylic acids, esters of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids of amino alcohols, amides of  $\alpha,\beta$ -ethylenically unsaturated monocarboxylic and dicarboxylic acids with diamines which contain at least one primary or secondary amino group, N,N-diallyl amines, N,N-diallyl-N-alkyl amines, vinyl- and allyl-substituted nitrogen heterocycles, vinyl ethers, C<sub>2</sub>-C<sub>8</sub> monoolefins, nonaromatic hydrocarbons having at least two conjugated double bonds, polyether (meth)acrylates, monomers containing urea groups, and mixtures thereof.

5. Method according to any one of claims 1 to 4, wherein the polymer P, comprising at least two monomers M has a glass transition temperature in the range from -20 to +60°C.
6. Method according to any one of claims 1 to 5, wherein the principal monomers M1 are selected from methyl(meth)acrylate, ethyl(meth)acrylate, n-propyl(meth)acrylate, isopropyl(meth)acrylate, n-butyl(meth)acrylate, sec-butyl(meth)acrylate, tert-butyl(meth)acrylate, n-pentyl(meth)acrylate, n-hexyl(meth)acrylate, n-heptyl(meth)acrylate, n-octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, styrene, 2-methylstyrene, and mixtures thereof.
7. Method according to any one of claims 1 to 6, wherein the combination of the principal monomers M1 are selected from n-butyl acrylate and methyl methacrylate;

n-butyl acrylate, methyl methacrylate, and styrene;

n-butyl acrylate and styrene;

n-butyl acrylate and ethylhexyl acrylate;

n-butyl acrylate, ethylhexyl acrylate, and styrene.

8. Method according to any one of claims 1 to 7, wherein the alkoxysilane (B2) is selected from alkoxysilyl group-containing monomers such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriisopropoxysilane, vinyltris(0-methoxyethoxy)silane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinyl dimethylmethoxysilane, vinyl dimethylethoxysilane, 3-methacryloypropyltrimethoxysilane, 3-methacryloypropyltriethoxysilane, 3-methacryloypropylmethyldimethoxysilane, 3-methacryloypropylmethyldiethoxysilane, tris(2-acetoxyethyl dimethylsiloxy)silylpropyl acrylate, methacrylate, tris(2-carboxyethyl dimethylsiloxy)silylpropyl acrylate and methacrylate, tris(3-hydroxypropyl dimethylsiloxy)silylpropyl acrylate and methacrylate, acrylate and methacrylate functional, fluorosubstituted alkyl/aryl siloxanes such as tris(3,3,3 trifluoropropyl dimethylsiloxy) silyl propyl acrylate and methacrylate, tris[3-heptafluoroisopropoxy propyl)] dimethylsiloxy silylpropyl acrylate and methacrylate, tris(pentafluorophenyl dimethylsiloxy)silyl propyl acrylate and methacrylate, or have the general formula:



where RS is a divalent alkylene group, R6 is an alkyl group, x is 1, 2 or 3, and Z is a hydrolyzable group, or mixtures thereof.

9. Method according to any one of claims 1 to 8, wherein the alkoxysilane (B2) is present in a range of from 0.01 to 5 wt % by weight relative to the total weight of component B.

10. Method according to any one of claims 1 to 9, wherein the antimicrobial agent (Z) is present in an amount of 1 to 10 % by weight based on the total dry weight of the resulting composition.
11. Composition obtained from the method according to any one of claims 1 to 10.
12. Aqueous coating comprising a composition according to claim 11.
13. Aqueous composition comprising:
  - at least one binder component (B), comprising at least one alkoxysilane (B2) and a polymer dispersion (PD),
  - at least one antimicrobial agent (Z), wherein the at least one antimicrobial agent (2) is as defined in the method according to any one of claims 1 to 10,
  - up to 70% by weight of inorganic fillers and/or inorganic pigments,
  - 0.1% to 20% by weight of typical auxiliaries, and
  - water to 100% by weight.
14. Aqueous composition of claim 13, comprising 10% to 70% by weight of inorganic fillers and/or inorganic pigments.
15. A kit comprising a curable composition containing as separate parts for joint application
  - a) a binder component (B) comprising at least one alkoxysilane (B2) and a polymer dispersion (PD),
  - b) at least one antimicrobial agent (Z),each of the parts a) and b) being as defined in the method according to any one of claims 1 to 10.

16. Hybrid network of acrylate copolymers as defined for polymer dispersion (PD) and silica chemically linked to each other via Si-containing groups comprising an antimicrobial agent not covalently linked to said network.
17. Use of a composition according to claim 11 for preparing antimicrobial coatings.

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