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(54) Titre : DISPERSIONS AQUEUSES DE COPOLYMERES AUTORETICULABLES, UN PROCEDE POUR LEUR
PREPARATION ET LEUR UTILISATION DANS DES LIANTS POUR MATERIAUX DE REVETEMENT

(54) Title: AQUEOUS SELF-CROSSLINKING COPOLYMER DISPERSIONS, A PROCESS FOR PREPARING THEM
AND THEIR USE IN BINDERS FOR COATING MATERIALS

(57) **Abrégé/Abstract:**

Aqueous self-crosslinking copolymer dispersions ABC obtainable by free-radically initiated copolymerization in the first stage of a monomer mixture A comprising olefinically unsaturated monomers A1 having carbonyl groups, unsaturated carboxylic acids or monoesters of unsaturated dicarboxylic acids A2, monomers A3 selected from vinylaromatic compounds, n-butyl methacrylate and also alkyl esters of unsaturated carboxylic acids or dialkyl esters of unsaturated dicarboxylic acids, esters A4 selected from alkyl esters of unsaturated carboxylic acids of dialkyl esters of unsaturated dicarboxylic acids, and other free-radically polymerizable monomers A5, and subsequent addition of a second monomer mixture B and further polymerization in the second stage, the mixture B comprising olefinically unsaturated monomers B1 corresponding to A1, esters B2 corresponding to A4, and monomers B3 corresponding to A5, and subsequently adding compounds C having hydrazine or hydrazide groups.



Abstract

Aqueous self-crosslinking copolymer dispersions **ABC** obtainable by free-radically initiated copolymerization in the first stage of a monomer mixture **A** comprising olefinically unsaturated monomers **A1** having carbonyl groups, unsaturated carboxylic acids or monoesters of unsaturated dicarboxylic acids **A2**, monomers **A3** selected from vinylaromatic compounds, n-butyl methacrylate and also alkyl esters of unsaturated carboxylic acids or dialkyl esters of unsaturated dicarboxylic acids, esters **A4** selected from alkyl esters of unsaturated carboxylic acids of dialkyl esters of unsaturated dicarboxylic acids, and other free-radically polymerizable monomers **A5**, and subsequent addition of a second monomer mixture **B** and further polymerization in the second stage, the mixture **B** comprising olefinically unsaturated monomers **B1** corresponding to **A1**, esters **B2** corresponding to **A4**, and monomers **B3** corresponding to **A5**, and subsequently adding compounds **C** having hydrazine or hydrazide groups.

Aqueous self-crosslinking copolymer dispersions, a process for preparing them and their use in binders for coating materials

5 The invention relates to aqueous self-crosslinking copolymer dispersions having a core-shell structure, at least some of the monomers forming the copolymer in the core having carbonyl groups and carboxyl groups as well as free-radically polymerizable olefinically unsaturated
10 groups, and comprising dicarboxylic dihydrazides or bishydrazine compounds. The invention additionally relates to a two-stage process for preparing these aqueous self-crosslinking copolymer dispersions and to their use as binders for storage-stable one-component
15 coating materials which crosslink at room temperature or at elevated temperature.

EP-A 0 649 865 discloses self-crosslinking carbonyl-containing polyurethane-vinyl hybrid dispersions which
20 crosslink by way of hydrazine compounds but do not have a core-shell structure.

EP-A 0 555 774 discloses copolymer dispersions formed by copolymerizing monomers having carbonyl groups and
25 carboxyl groups. These dispersions also have no core-shell structure, being prepared in a single-stage polymerization with no change in the composition of the monomer mixture. The binders prepared with these dispersions are crosslinked by reaction with the
30 polyamines employed as neutralizing agents. With these products, first a high proportion of carbonyl groups is required to achieve sufficient crosslinking density of the coating films and second this high proportion of corresponding monomers results, during the
35 copolymerization, in the formation of gel specks and coagulum whose removal can only be accomplished at great expense in terms of time and apparatus. In addition, the

polyamine employed as crosslinking component leads to severe yellowing of the coating film and so to problems in numerous applications.

5 AT-B 402 504 describes self-crosslinking aqueous polymer dispersions which are prepared in a two-stage process. In this process, the composition of the monomer mixture for the second stage of the polymerization differs from that of the first stage. These copolymer dispersions have
10 small fractions of carbonyl groups and permit high crosslinking densities without forming the coagulum or gel specks that are difficult to remove. However, the polyamines employed as crosslinking component likewise occasion severe yellowing of the resulting coating films.

15 European Patent Application EP-A 0 795 568 describes aqueous polymer dispersions having a core-shell structure in the core of which at least 50% of the monomers which are employed are those whose homopolymers have a glass
20 temperature of below 0°C while the proportion of such monomers employed in the shell is less than 45%. Difunctional acid hydrazides can also be added to the dispersion. Where such hydrazides are added in the examples, the monomer mixture for the shell of the
25 polymer particles also includes a monomer that contains ketone groups. In this case, the monomer composition is selected in accordance with the desired minimum film-forming temperatures.

30 In AT-B 403 478, the dispersions known from AT-B 402 504 are combined with polyfunctional isocyanates of low molar mass to form two-component binders. Although it is possible in this way to provide coating materials having reduced tendency to yellow and improved resistance to
35 water, chemicals and light exposure, disadvantages include the complex preparation of the coating material,

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the limited pot life, prolonged drying time, and relatively low film hardness.

It has surprisingly now been found that aqueous copolymer
5 dispersions prepared in accordance with AT-B 402 504 by
a two-stage process in which monomers having in each case
carbonyl and carboxyl groups are employed only in the
first stage (which leads to the core of the particles)
can be crosslinked, following neutralization of the
10 carboxyl groups by adding small amounts of ammonia,
amines or aqueous alkalis, with polyfunctional hydrazides
and lead simply to binders having a sufficient pot life
which can be processed to give coating materials having
high film hardness, good resistance to mechanical and
15 chemical exposure, rapid drying, and little or no
tendency to yellow.

The invention accordingly provides aqueous self-
crosslinking copolymer dispersions **ABC** obtainable by
20 free-radically initiated copolymerization in the first
stage of a monomer mixture **A** comprising mass fractions in
the mixture of

A1 from 2 to 55%, preferably from 4 to 45% and, with
25 particular preference, from 6 to 40% of olefinically
unsaturated monomers having in each case at least
one carbonyl group per molecule,

A2 from 0.5 to 20%, preferably from 1 to 15% and, with
30 particular preference, from 3 to 12% of
 α,β -olefinically unsaturated carboxylic acids or
monoesters of α,β -olefinically unsaturated
dicarboxylic acids with linear, branched or cyclic
alcohols having 1 to 15 carbon atoms,

35

A3 from 20 to 70%, preferably from 22 to 60% and, with

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particular preference, from 24 to 50% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate and also alkyl esters of α,β -olefinically unsaturated carboxylic acids or dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group,

A4 from 10 to 60%, preferably from 15 to 50% and, with particular preference, from 20 to 45% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids or dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl methacrylate, and

A5 from 0 to 25%, preferably from 2 to 20% and, with particular preference, from 5 to 15% of other free-radically polymerizable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids,

the sum of the mass fractions of components **A1** to **A5** necessarily being 100%, and by subsequent addition of a second monomer mixture **B** and further free-radically initiated polymerization of this monomer mixture in the second stage, the mixture **B** comprising mass fractions of

B1 from 30 to 90%, preferably from 40 to 80% and, with

- particular preference, from 50 to 75% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate and also alkyl esters of α,β -olefinically unsaturated carboxylic acids or dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group,
- B2** from 10 to 60%, preferably from 20 to 50% and, with particular preference, from 25 to 40% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids or dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl methacrylate, and
- B3** from 0 to 40%, preferably from 5 to 30% and, with particular preference, from 10 to 25% of other free-radically polymerizable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids,
- the sum of the mass fractions of components **B1** to **B3** necessarily being 100%, and the ratio of the mass of the monomer mixture **A** to the mass of the monomer mixture **B** is from 50:50 to 95:5, preferably from 60:40 to 90:10.
- The copolymers **AB** obtainable in this way preferably contain, based on the mass of the solids of the

dispersion, from 0.2 to 1.7 mol/kg of carbonyl groups and from 0.15 to 1.6 mol/kg of carboxyl groups. The molar amount of the carboxyl groups here is always lower than the molar amount of the carbonyl groups; preferably, the
5 ratio of the molar amount of the carboxyl groups $n(-COOH)$ to the molar amount of the carbonyl groups $n(>CO)$ is from 0.5 to 0.95 mol/mol, with particular preference from 0.75 to 0.9 mol/mol.

10 The resulting dispersions of the copolymers **AB** are neutralized following the polymerization by adding ammonia, amines or aqueous alkalis, the amount in which the neutralizing agents are added being such that it is sufficient to neutralize from 0 to 120% of the carboxyl
15 groups present.

To the dispersion neutralized in this way there are subsequently added compounds **C** having at least two hydrazine or hydrazide groups per molecule, in an amount
20 such that the ratio r of the sum of the molar amount of hydrazine groups $n(-NH-NH_2)$ and the molar amount of hydrazide groups $n(-CO-NH-NH_2)$ to the molar amount of the carbonyl groups $n(>CO)$ is from 0.5 to 1.1 mol/mol, preferably between 0.8 and 1.0 mol/mol.

25 The invention additionally provides a process for preparing the copolymer dispersions of the invention, in which water with or without emulsifiers is introduced as initial charge and heated to the desired reaction
30 temperature, a mixture comprising water, emulsifiers if desired, the monomer mixture **A**, and a free-radical polymerization initiator is metered in to this initial charge, the polymerization is continued until at least 95% of the monomers have reacted, then a second mixture
35 comprising water, emulsifiers if desired, and also the monomer mixture **B** and a further free-radically acting

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polymerization initiator is metered in and the polymerization is subsequently continued until the residual monomer content has fallen below 1%. The resulting dispersion is cooled and admixed, with stirring, with the neutralizing agent, preferably in the form of an aqueous solution. Subsequently, the hydrazine compound or hydrazide compound **C** is added with stirring to the neutralized dispersion of the copolymer **AB** to form the self-crosslinking dispersion **ABC**.

10 Finally, the invention also provides for the use of these dispersions as binders for storage-stable one-component coating materials which crosslink at room temperature or at elevated temperature.

The amines or alkalis used if desired for neutralization improve the stability of the aqueous copolymer dispersions.

In one aspect, the invention provides an aqueous self-crosslinking copolymer dispersion **ABC** having a core-shell structure, obtained by: in a first stage, conducting a free-radically initiated copolymerization of a monomer mixture **A** which leads to the core of resultant particles and comprises mass fractions in the mixture of: **A1** from 2 to 55% of olefinically unsaturated monomers having in each case at least one ketone carbonyl group per molecule, **A2** from 0.5 to 20% of α,β -olefinically unsaturated carboxylic acids or monoesters of α,β -olefinically unsaturated dicarboxylic acids with linear, branched or cyclic alcohols having 1 to 15 carbon atoms, **A3** from 20 to 70% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate, alkyl esters of α,β -olefinically unsaturated carboxylic acids or dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl

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groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group, **A4** from 10 to 60% of esters selected from

5 alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl

10 methacrylate, and **A5** from 0 to 25% of other free-radically polymerizable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids, the sum of the mass

15 fractions of components **A1** to **A5** necessarily being 100%, and by subsequent addition of a second monomer mixture **B** and further free-radically initiated polymerization of this monomer mixture in a second stage, the mixture **B** comprising mass fractions of: **B1** from 30 to 90% of olefinically

20 unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate and also alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl

25 groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group, **B2** from 10 to 60% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically

30 unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl methacrylate, and **B3** from 0 to 40% of other free-radically polymerizable monomers selected from vinyl esters

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of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids, the sum of the mass fractions of components **B1** to **B3** necessarily being 100%, and
5 the ratio of the mass of the monomer mixture **A** to the mass of the monomer mixture **B** is from 50:50 to 95:5, and wherein the ratio of the amount of substance of the carboxyl groups in copolymer **AB** to that of the ketone carbonyl groups in said copolymer is from 0.5 mol/mol to 0.95 mol/mol, the
10 mixture **B** being free from compounds having carboxyl or ketone carbonyl groups; and adding compounds **C** having at least two hydrazine or hydrazide groups per molecule in an amount such that the ratio r of the sum of the amount of substance of the hydrazine groups $n(-NH-NH_2)$ and the amount
15 of substance of hydrazide groups $n(-CO-NH-NH_2)$ to the amount of substance of the ketone carbonyl groups $n(>CO)$ is from 0.5 mol/mol to 1.1 mol/mol.

In a further aspect, the invention provides a process for the preparation of an aqueous self-crosslinking
20 copolymer dispersion **ABC** having a core-shell structure, comprising the steps of: in a first stage, conducting a free-radically initiated copolymerisation of a monomer mixture **A** which leads to the core and comprises mass fractions in the mixture of: **A1** from 2% to 55% of
25 olefinically unsaturated monomers having in each case at least one ketone carbonyl group per molecule, **A2** from 0.5% to 20% of α,β -olefinically unsaturated carboxylic acids or monoesters of α,β -olefinically unsaturated dicarboxylic acids with linear, branched or cyclic alcohols having 1 to
30 15 carbon atoms, **A3** from 20% to 70% of olefinically unsaturated monomers selected from vinylaromatic compounds, *n*-butyl methacrylate, alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -

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olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group, **A4** from 10% to 60% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl methacrylate, and **A5** from 0% to 25% of other free-radically polymerisable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids, the sum of the mass fractions of components **A1** to **A5** necessarily being 100%; adding a second monomer mixture **B** with further polymerisation initiator, and further free-radically initiated polymerisation of this monomer mixture in a second stage, the mixture **B** comprising mass fractions in the mixture of: **B1** from 30% to 90% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate, and also alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group, **B2** from 10% to 60% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl

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methacrylate, and **B3** from 0% to 40% of other free-radically polymerisable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of

5 α,β -unsaturated carboxylic acids, the sum of the mass fractions of components **B1** to **B3** necessarily being 100% and the ratio of the mass of monomer mixture **A** to monomer mixture **B** is from 50:50 to about 95:5, and wherein the ratio of the amount of substance of the carboxyl groups in

10 copolymer **AB** to that of the ketone carbonyl groups in the said copolymer is from 0.5 mol/mol to 0.95 mol/mol, the mixture **B** being free from compounds having carboxyl or ketone carbonyl groups; neutralising the carboxyl groups at least partially with ammonia, amines or aqueous alkali; and

15 adding compounds **C** having at least two hydrazine or hydrazide groups per molecule in an amount such that the ratio r of the sum of the amount of substance of hydrazine groups $n(-NH-NH_2)$ and the amount of substance of hydrazide groups $n(-CO-NH-NH_2)$ to the amount of substance of the ketone

20 carbonyl groups $n(>CO)$ is from 0.5 mol/mol to 1.1 mol/mol.

Olefinically unsaturated monomers containing carbonyl groups are employed as monomer component **A1**. Preference is given to the use of linear, branched and cyclic aliphatic compounds having 4 to 20 carbon atoms and

25 each containing at least one carbonyl group and one ethylenic double bond. To a minor extent (up to 10% of the mass of the monomers **A1**) it is also possible to employ compounds having two or more polymerizable double bonds, which leads to crosslinking of the copolymer. Particular

30 preference is given to the use of α,β -olefinically unsaturated monomers such as N-diacetone(meth)acrylamide and (meth)acrylic acid acetoacetoxyalkyl esters whose alkylene group is selected from 1,2-ethylene, 1,2- and 1,3-propylene,

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1,4-butylene and 1,6-hexylene and also 1,5-(3-oxa)pentylene and 1,8-(3,6-dioxa)octylene groups, especially the ethyl esters.

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The monomers **A2** are preferably α,β -unsaturated carboxylic acids having 3 to 4 carbon atoms, such as acrylic acid, methacrylic acid, crotonic and isocrotonic acid and also vinylacetic acid. Monoesters of α,β -unsaturated carboxylic acids with linear, branched or cyclic alcohols having 1 to 15 carbon atoms can also be employed, the dicarboxylic acids preferably having 4 to 6 carbon atoms. Preference is given to monomethyl and monoethyl esters of maleic acid, fumaric acid, and also citraconic, mesaconic, itaconic and glutaconic acid.

Of the monomers **A3**, preference is given to the esters of methanol, ethanol, n- and isopropanol with acrylic and methacrylic acid and to the diesters of said alcohols with the dicarboxylic acids specified under **A2**, and also to n-butyl methacrylate and, of the vinylaromatic compounds, especially styrene, p-methylstyrene and the isomer mixture known as "vinyltoluene". Particular preference is given to methyl and ethyl (meth)acrylate, n-butyl methacrylate, styrene, and dimethyl maleate.

As monomers **A4** it is preferred to employ the esters of n-, sec- and tert-butanol, the isomeric pentanols and the higher alcohols such as n-hexanol and 2-ethylhexyl alcohol with α,β -unsaturated carboxylic acids selected from acrylic and methacrylic acid, vinylacetic acid, maleic acid and fumaric acid; in the case of the dicarboxylic acids referred to, the diesters are used, and n-butyl methacrylate is excluded.

As examples of the hydroxyalkyl esters of olefinically unsaturated carboxylic acids as monomer component **A5** mention may be made of hydroxyethyl and 2-hydroxypropyl (meth)acrylate, (meth)acrylonitrile, (meth)acrylamide and, for the vinyl esters, of vinyl acetate.

In the second stage a polymer having a different chemical structure is produced by adding the monomer mixture **B** alone or together with new initiators.

5 The monomers **B1** correspond to those specified under **A3**,
the monomers **B2** to those specified under **A4**, and the
monomers **B3**, finally, to those specified under **A5**. The
monomer mixture **B** is therefore free from compounds having
functional groups selected from carbonyl and carboxyl
10 groups.

The compounds **C** with hydrazine or hydrazide functionality
comprise two or more hydrazine or hydrazide groups and
preferably have an average molar mass (M_n) of less than
15 1000 g/mol. Examples of such compounds are bishydrazides
of dicarboxylic acids having 2 to 12 carbon atoms such as
the bishydrazides of oxalic acid, malonic acid, succinic
acid, glutaric acid, adipic acid, pinalic acid, suberic
acid, azelic acid, sebacic acid or the isomeric phthalic
20 acids; carbonic bishydrazide, alkylene- or cycloalkylene-
bissemicarbazides, N,N'-diaminoguanidine, alkylene-
bishydrazines such as N,N'-diaminopiperazine,
arylenebishydrazines such as phenylene- or
naphthylenebishydrazine, and alkylenebissemicarbazides.
25 Compounds **C** of higher functionality are, for example, the
hydrazides of nitrilotriacetic acid or of ethyl-
enediaminetetracetic acid.

The copolymer dispersions of the invention have excellent
30 stability on storage and produce films having good
resistance properties. They can be employed as binders
for industrial coatings and primers. In addition, they
can be used to formulate transparent coating materials
which can be used in turn to coat wood, plastic, leather
35 or paper.

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The crosslinking of the copolymer dispersions takes place by reaction of the hydrazine or hydrazide groups of the compounds C with the carbonyl groups of the copolymer dispersions AB at temperatures as low as room temperature following the evaporation of a substantial proportion of water.

The formulation of water-dilutable coating materials using the binders prepared in accordance with the invention, and the application of such coating materials, are known to the skilled worker.

The examples which follow illustrate the invention without restricting it in its scope. In the examples below, as in the text which precedes them, all figures with the unit "%" are mass fractions unless specified otherwise. "Parts" are always parts by mass. Concentration figures in "%" are mass fractions of the dissolved substance in the solution (in g/100 g)).

20

Examples

Example 1

In a reactor suitable for emulsion copolymerization with reflux condenser, thermometer and two feed vessels a mixture of 360 parts of demineralized water, 24 parts of @Triton X 200 (sodium alkylaryl polyether sulfonate, manufacturer: Rohm & Haas, USA) and 5.4 parts of @Triton X 165 (octylphenol ethoxylate, manufacturer: Rohm & Haas, USA) was homogenized with stirring.

The feed vessel A was charged with a homogeneous emulsion consisting of 1150 parts of demineralized water, 24 parts of Triton X 200, 10 parts of Triton X 165, 3.2 parts of ammonium peroxodisulfate, 165 parts of n-butyl

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methacrylate, 280 parts of n-butyl acrylate, 275 parts of styrene, 140 parts of acetoacetoxyethyl methacrylate and 40 parts of methacrylic acid. 5% of this initial emulsion was run into the reactor. The contents of the reactor
5 were heated to 85°C with stirring and held at this temperature for 10 minutes. Then the remaining contents of the feed vessel A were metered into the reactor at a uniform rate over 120 minutes at 85°C.

10 Subsequently, a homogeneous emulsion of 100 parts of demineralized water, 3.1 parts of Triton X 200, 2.4 parts of Triton X 165, 30 parts of butyl acrylate, 70 parts of styrene and 0.8 part of ammonium peroxodisulfate were metered in over 30 minutes at 85°C from the feed vessel
15 B. Following the end of the addition, the contents of the reactor were heated to 88°C and held at this temperature for 120 minutes. Finally, the reaction mixture was cooled to 25°C and adjusted to a pH of 5.5 by adding 10% aqueous ammonia solution. Thereafter, 51.2 parts of adipic
20 dihydrazide were added over the course of 30 minutes. This gave an opalescent dispersion having a mass fraction of solids of 38.8% and an average particle size of 105 nm. The pH was 5.5.

Examples 2 to 7

The procedure of Example 1 is repeated. The compositions of the initial charges to the reactor and of the feeds, plus altered polymerization parameters, can be taken from Table 1, in which the following abbreviations are used:

	ADH	Adipic dihydrazide	HBA	4-Hydroxybutyl acrylate
	ODH	Oxalic dihydrazide	HEMA	2-Hydroxyethyl methacrylate
10	AAEMA	Acetoacetoxyethyl methacrylate	MA	Methacrylic acid
	APS	Ammonium peroxodisulphate	pMST	p-Methylstyrene
	AA	Acrylic acid	NH ₃	Ammonia
	BA	Butyl acrylate	ST	Styrene
	BMA	Butyl methacrylate	X 165	®Triton X 200 (Rohm & Haas, USA)
15	BV	®Hostapal BV conc. (Clariant GmbH, DE)	X 200	®Triton X 200 (Rohm & Haas, USA)
	DAA	Diacetoneacrylamide		®Triton X 305 (Rohm & Haas, USA)
	DBF	Dibutyl fumarate	X 305	
20	DMEA	Dimethylethanolamine		
	DW	Demineralized water		(alkylaryl polyether alcohol)
25	EHA	2-Ethylhexyl acrylate		

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Table 1:

Example	1	2	3	4
Initial charge	360 24 5.4 DW X 200 X 165	420 25 7 DW X 200 X 165	325 25 7 DW X 200 X 165	325 10 7 DW BV X 165
Feed A	1150 24 10 3.2 165 280 275 140 40 DW X 200 X 165 APS BMA BA ST AAEMA MA	1210 25 5.6 5 195 200 320 85 DW X 200 X 165 APS MMA BA AAEMA AA	1100 25 5.6 5 185 420 100 70 25 DW X 200 X 165 APS EHA BMA BA DAA AA	1000 10 5.6 5 250 285 120 45 DW BV X 165 APS ST BA DAA MA
Fraction of feed A in the initial charge (%)	5	7.5	7.5	10
Feed time A (min)	120	100	100	90
Feed B	100 3.1 2.4 0.8 30 70 DW X 200 X 165 APS BA ST	200 6 1.4 0.8 150 50 DW X 200 X 165 APS BMA BA	200 6 1.4 0.8 150 50 DW X 200 X 165 APS ST EHA	250 5 2 1 100 150 50 DW BV X 165 APS pMST BA BMA

Table 1 (continued):

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Example	1	2	3	4
Feed time B (min)	30	45	45	60
Neutralizing agent	55 NH ₃ (10%)	87 DMEA (10%)	24 NH ₃ (10%)	47 NH ₃ (10%)
Crosslinker	51.2 ADH	110.6 ADH	24.4 ODH	58.7 ADH
pH (as 10% strength solution in water)	5.5	6.2	6.4	5.8

Table 1 (continued):

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Example	5	6	7
Initial charge	280 10 7	DW BV X 305	325 10 7
Feed A	1100 8 5 5 150 205 180 65	DW BV X 305 APS MMA DBF DAA MS	DW BV X 165 APS ST BA AAEMA HEMA MS
Fraction of feed A in the initial charge (%)	10	7.5	10
Feed time A (min)	90	100	90
Feed B	300 7 3 1.2 200 100 100	DW BV X 305 APS ST BA BMA	DW BV X 165 APS PMST BA BMA
Feed time B (min)	60	45	60

Table 1 (continued): - 16 -

Example	5	6	7
Neutralizing agent	69 DMEA (10%)	27 NH ₃ (10%)	38 NH ₃ (10%)
Crosslinker	92.7 ADH	31.4 ODH	41.5 ADH
pH (as 10% strength solution in water)	6.0	6.5	5.8

Table 2:

Example	1	2	3	4	5	6	7	V1
Solids content	38.7	37.5	38.3	40.0	39.1	38.5	38.5	38.8
pH	5.5	6.2	6.4	5.8	6.0	6.5	5.8	7.9
Average particle size	105	100	115	100	95	105	100	90
$n(>CO)/m^{(1)}$	0.65	1.5	0.41	0.71	1.07	0.59	0.56	0.65
$n(-COOH)/m^{(2)}$	0.47	1.18	0.35	0.52	0.76	0.49	0.52	0.47
$n(-COOH)/n(>CO)^{(3)}$	0.72	0.79	0.85	0.73	0.71	0.83	0.93	0.72
$r^{(4)}$	0.90	0.85	1.00	0.95	1.00	0.90	0.85	0.95

(1) specific carbonyl group content in mol/kg
(2) specific carboxyl group content in mol/kg
(3) molar ratio $n(-COOH)/n(>CO)$ in mol/mol
(4) molar ratio $r = (n-(NH-NH_2) + n(-CO-NH-NH_2)) / n(>CO)$ in mol/mol
V1 Example from AT-B 402 504

Performance testing in transparent coating materials

The transparent coating materials 1 to 5 and V1 were prepared by mixing an amount of the hydrazide-containing copolymer dispersion such that the mass of solids present therein was 100 g, 0.8 g of a commercially customary defoamer, 0.2 g of a commercially customary leveling agent, and deionized water sufficient to give an efflux time of 25 seconds at 23°C in accordance with DIN 53 211. The results of the performance tests are summarized in Table 3:

Table 3

Transparent coating material	1	2	3	4	5	V1	V2
Tack-free time in minutes	15	15	15	15	15	15	50
Sandability	0	0	0	0	0	0	MIN
Pendulum hardness in s	72	75	82	73	68	80	50
Acetone resistance in s	>60	>60	>60	>60	>60	>60	>60
Ethanol resistance in h	5	4	4	5	4	5	>8
Water resistance in h	>48	>36	>48	>36	>36	>24	>48
Yellowing	1	1-2	1	1	1-2	4	1-2
Pot life (storage stability)	> 3 mths	> 3 mths	> 3 mths	> 3 mths	> 3 mths	> 3 mths	20 hrs

V1 Example 1 from AT-B 402 504, see above

V2 Clearcoat of AT-B 403 478

Tack-free time: Drying recorder, glass strips, application of a coating film with a wet-film thickness of 150 µm, at 20°C (statement of time in minutes until a tack-free surface is obtained)

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Sandability: Veneered wood, application of a coating film with a wet-film thickness of 150 µm; the parameter tested was the clogging of abrasive paper (320 grade) after 10 strokes following a drying time of 60 minutes at room temperature.

10

The clogging of the abrasive paper is a practical test for the user (parquet layer, furniture maker). It refers to the attachment of freshly applied coating films to the abrasive paper in the case of sanding prior to the application of a further coating film.

15

The optimum value is 0 (no clogging) although the value MIN (attachments to less than 10% of the area of the abrasive paper) is also accepted.

20 KÖNIG pendulum hardness (DIN 53157): Glass plates, application of a coating film with a wet-film thickness of 120 µm, drying time of 24 hours at 20°C.

Resistance to acetone, ethanol and water: Glass plates, application of a coating film with a wet-film thickness of 120 µm, drying time of 24 hours at 20°C; a cotton pad soaked with the solvent was placed on the coating film and covered with a glass beaker. The time taken for the film to soften was measured.

25
30

Pot life: The two-component coating material is stirred at hourly intervals. This operation is repeated until the onset of gelling.

35 Yellowing: 200 µm wet-film thickness on maple (veneered). The assessment is made during storage at room temperature

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for 4 weeks (1 = no discernible discoloration 5 = very severe discoloration).

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CLAIMS:

1. An aqueous self-crosslinking copolymer dispersion **ABC** having a core-shell structure, obtained by:

in a first stage, conducting a free-radically
5 initiated copolymerization of a monomer mixture **A** which leads to the core of resultant particles and comprises mass fractions in the mixture of:

A1 from 2 to 55% of olefinically unsaturated monomers having in each case at least one ketone carbonyl
10 group per molecule,

A2 from 0.5 to 20% of α,β -olefinically unsaturated carboxylic acids or monoesters of α,β -olefinically unsaturated dicarboxylic acids with linear, branched or cyclic alcohols having 1 to 15 carbon atoms,

15 **A3** from 20 to 70% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate, alkyl esters of α,β -olefinically unsaturated carboxylic acids or dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being
20 selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group,

A4 from 10 to 60% of esters selected from alkyl
25 esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl methacrylate,
30 and

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A5 from 0 to 25% of other free-radically polymerizable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of
5 α,β -unsaturated carboxylic acids,

the sum of the mass fractions of components A1 to A5 necessarily being 100%, and by subsequent addition of a second monomer mixture B and further free-radically initiated polymerization of this monomer mixture in a second
10 stage, the mixture B comprising mass fractions of:

B1 from 30 to 90% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate and also alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of
15 α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group,

20 B2 from 10 to 60% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the
25 alkyl radical, with the exception of n-butyl methacrylate, and

B3 from 0 to 40% of other free-radically polymerizable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon
30 atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids,

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the sum of the mass fractions of components **B1** to **B3** necessarily being 100%, and the ratio of the mass of the monomer mixture **A** to the mass of the monomer mixture **B** is from 50:50 to 95:5, and wherein the ratio of the amount of substance of the carboxyl groups in copolymer **AB** to that of the ketone carbonyl groups in said copolymer is from 0.5 mol/mol to 0.95 mol/mol, the mixture **B** being free from compounds having carboxyl or ketone carbonyl groups; and

adding compounds **C** having at least two hydrazine or hydrazide groups per molecule in an amount such that the ratio r of the sum of the amount of substance of the hydrazine groups $n(-NH-NH_2)$ and the amount of substance of hydrazide groups $n(-CO-NH-NH_2)$ to the amount of substance of the ketone carbonyl groups $n(>CO)$ is from 0.5 mol/mol to 1.1 mol/mol.

2. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in claim 1, wherein the carbonyl group content is from 0.2 to 1.7 mol/g and the carboxyl group content is from 0.15 to 1.6 mol/kg, based in each case on the mass of the solids of the dispersion.

3. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in claim 1 or 2, wherein up to 10% of the mass of the monomers of **A1** have 2 or more polymerizable double bonds.

4. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in claim 1 or 2, wherein the monomers of **A1** are selected from diacetone(meth)acrylamide and (meth)acrylic acid acetoacetoxyalkyl esters whose alkylene group is selected from 1,2-ethylene, 1,2- and 1,3-propylene, 1,4-butylene and 1,6-hexylene and also 1,5-(3-oxa)pentylene and 1,8-(3,5-dioxa)octylene groups.

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5. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in any one of claims 1 to 4, wherein the monomers of **A2** are selected from acrylic acid and methacrylic acid.

5 6. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in any one of claims 1 to 5, wherein the monomers of **A3** and **B1** independently of one another are selected from methyl and ethyl (meth)acrylate and dimethyl maleate.

10 7. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in any one of claims 1 to 6, wherein the monomers of **A4** and of **B2** independently of one another are selected from the acrylic and methacrylic esters of n-, sec- and isobutanol, n-hexanol and 2-ethylhexanol.

15 8. An aqueous self-crosslinking copolymer dispersion **ABC** as claimed in any one of claims 1 to 7, wherein the monomers of **A5** and of **B3** independently of one another are vinyl acetate.

9. An aqueous self-crosslinking copolymer dispersion
20 **ABC** as claimed in any one of claims 1 to 8, wherein the compounds **C** are selected from oxalic and adipic dihydrazide and diaminopiperazine.

10. A process for the preparation of an aqueous self-crosslinking copolymer dispersion **ABC** having a core-shell
25 structure, comprising the steps of:

in a first stage, conducting a free-radically initiated copolymerisation of a monomer mixture **A** which leads to the core and comprises mass fractions in the mixture of:

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A1 from 2% to 55% of olefinically unsaturated monomers having in each case at least one ketone carbonyl group per molecule,

A2 from 0.5% to 20% of α,β -olefinically unsaturated carboxylic acids or monoesters of α,β -olefinically unsaturated dicarboxylic acids with linear, branched or cyclic alcohols having 1 to 15 carbon atoms,

A3 from 20% to 70% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate, alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group,

A4 from 10% to 60% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the alkyl radical, with the exception of n-butyl methacrylate, and

A5 from 0% to 25% of other free-radically polymerisable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of α,β -unsaturated carboxylic acids,

the sum of the mass fractions of components **A1** to **A5** necessarily being 100%;

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adding a second monomer mixture **B** with further polymerisation initiator, and further free-radically initiated polymerisation of this monomer mixture in a second stage, the mixture **B** comprising mass fractions in the
5 mixture of:

B1 from 30% to 90% of olefinically unsaturated monomers selected from vinylaromatic compounds, n-butyl methacrylate, and also alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of
10 α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having up to 3 carbon atoms in the alkyl radical and cyclic and polycyclic alkyl groups having 5 to 15 carbon atoms in the alkyl group,

15 **B2** from 10% to 60% of esters selected from alkyl esters of α,β -olefinically unsaturated carboxylic acids and dialkyl esters of α,β -olefinically unsaturated dicarboxylic acids, the alkyl groups being selected from linear and branched alkyl groups having more than 3 carbon atoms in the
20 alkyl radical, with the exception of n-butyl methacrylate, and

B3 from 0% to 40% of other free-radically polymerisable monomers selected from vinyl esters of aliphatic saturated carboxylic acids having 2 to 18 carbon atoms, hydroxyalkyl esters, nitriles and amides of
25 α,β -unsaturated carboxylic acids,

the sum of the mass fractions of components **B1** to **B3** necessarily being 100% and the ratio of the mass of monomer mixture **A** to monomer mixture **B** is from 50:50 to about 95:5, and wherein the ratio of the amount of substance of the
30 carboxyl groups in copolymer **AB** to that of the ketone carbonyl groups in the said copolymer is from 0.5 mol/mol

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to 0.95 mol/mol, the mixture **B** being free from compounds having carboxyl or ketone carbonyl groups;

neutralising the carboxyl groups at least partially with ammonia, amines or aqueous alkali; and

5 adding compounds **C** having at least two hydrazine or hydrazide groups per molecule in an amount such that the ratio **r** of the sum of the amount of substance of hydrazine groups **n**(-NH-NH₂) and the amount of substance of hydrazide groups **n**(-CO-NH-NH₂) to the amount of substance of the ketone
10 carbonyl groups **n**(>CO) is from 0.5 mol/mol to 1.1 mol/mol.

11. A binder for coating materials, comprising a copolymer dispersion as claimed in any one of claims 1 to 9.

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