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- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

(54) Title: AQUEOUS BINDER COMPOSITION

(57) Abstract: An aqueous binder composition comprising at least one polymer P, at least one saccharide compound S and at least one metal compound M selected from the group comprising magnesium, calcium and zinc, in the form of an oxide, hydroxide, carbonate or bicarbonate.



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Aqueous binder composition

Description

5 The present invention relates to an aqueous binder composition comprising

a) at least one polymer P constructed from

- 10 ≥ 5 and ≤ 25 wt% of at least one acid-functional ethylenically unsaturated monomer (monomers A)
 ≥ 75 and ≤ 95 wt% of at least one other ethylenically unsaturated monomer (monomers B)

15 in polymerized form, wherein the amounts of monomers A and B sum to 100 wt%,

b) at least one saccharide compound S, the amount of which is determined such that it is ≥ 1 and ≤ 100 parts by weight per 100 parts by weight of polymer P, and

20 c) at least one metal compound M selected from the group comprising magnesium, calcium and zinc, in the form of an oxide, hydroxide, carbonate or bicarbonate, the amount of which is determined such that it is ≥ 10 and ≤ 50 mol% based on amount of monomers A in polymer P.

25 The present invention further relates to the use of the aforementioned aqueous binder composition as binder for granular and/or fibrous substrates, processes for production of shaped articles by using the aqueous binder composition and also to the shaped articles thus obtained, more particularly bonded fiber webs which in turn are used for producing bituminized roofing membranes.

30 Polysaccharide-containing aqueous binder compositions must be viewed in light of the following prior art:

EP-A 649 870 discloses mixtures of polycarboxylic acids and saccharide compounds in a weight ratio ranging from 95:5 to 20:80 for production of gas barrier films.

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EP-A 911 361 discloses aqueous binder systems for granular and/or fibrous substrates, comprising a polycarboxy polymer having a weight average molecular weight of at least

1000 g/mol and a polysaccharide having a weight average molecular weight of at least 10 000 g/mol, the amounts of which are determined such that the equivalence ratio of carboxyl groups to hydroxyl groups is in the range from 3:1 to 1:20.

5 EP-A 1 578 879 discloses aqueous binder compositions for coating glass fibers, comprising a polycarboxy polymer, a polyalcohol having at least two hydroxyl groups and also a so-called water-soluble extender, wherein polysaccharides having an average molecular weight below 10 000 g/mol are proposed as water-soluble extender.

10 WO 2008/150647 discloses aqueous binder systems for production of fiber mats, comprising a urea-formaldehyde resin and an aqueous copolymer dispersion whose copolymer is constructed essentially of styrene, alkyl acrylates and/or methacrylates, acrylonitrile and an optionally substituted acrylamide. Optionally, the aqueous copolymer dispersion may further comprise starch.

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US-A 2009/170978 discloses aqueous binder systems for fiber webs, comprising an aqueous copolymer dispersion whose copolymer comprises between 5 and 40 wt% of at least one carboxyl-containing monomer in polymerized form, and a natural binder component selected from the group comprising polysaccharides, vegetable proteins, lignins and/or lignosulfonates.

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A textile fabric being solidified by a binder system comprising an aqueous dispersion of starch and an emulsion polymer is disclosed in US-A 2018/119337.

25 WO 2012/117017 discloses aqueous binder systems, comprising a specific dispersion polymer whose dispersion polymer comprises between 0.1 and 2.5 wt% of at least one carboxyl-containing monomer in polymerized form, and a saccharide compound.

30 WO 2012/136605 discloses aqueous binder systems, comprising a specific dispersion polymer whose dispersion polymer which contains between 0.1 and 15 wt% of at least one carboxyl-containing monomer and between 8 and 30 wt% of at least one nitrile group containing monomer in polymerized form, and a saccharide compound.

35 WO 2013/024084 discloses aqueous binder systems, comprising a dispersion polymer being polymerized in the presence of a saccharide compound, and an alkanol amine comprising at least two hydroxy groups.

Aqueous binder compositions comprising a dispersion polymer and a magnesium, calcium or a zinc metal compound must be viewed in light of the following prior art:

DE-A 29 26 230 discloses a composition for a sizing treatment of staple fibre yarns, comprising
5 a water-soluble alkaline earth salt of a polymer based on (meth)acrylic acid and (meth)acrylonitrile and a water-soluble starch. Following the sizing treatment the composition is removed from the yarns.

DE-A 40 04 915 discloses a binder composition, comprising a specific dispersion polymer
10 whose dispersion polymer comprises between 3 and 45 wt% of at least one carboxyl-containing monomer in polymerized form, and a magnesium, calcium or zinc compound, in the form of an oxide, hydroxide, carbonate or bicarbonate. This binder composition is especially suitable for manufacturing of non-woven fabrics being used as the basis for bituminized roofing membranes.

DE-A 101 28 894 discloses a composition for soil release treatment of surfaces, comprising
15 acidic group containing crosslinked dispersion polymer particles and at least one polyvalent metal ion, especially water-soluble salts of magnesium, calcium, zinc or aluminium.

The non-published European priority patent application with the EP-application number
20 18161901.6 filed at the European Patent Office on March 15, 2018, discloses a binder composition for varnishes and other coatings, comprising a specific polymer P being prepared in the presence of an acidic group containing polymer A having a low molecular weight and a high glass transition temperature, and a magnesium, calcium or zinc compound, in the form of
25 an oxide, hydroxide, carbonate or bicarbonate.

Prior art binder systems are disadvantageous in that they, in the production of shaped articles from granular and/or fibrous substrates, are not always fully satisfactory especially with regard to mechanical properties thereof.

30 The problem addressed by the present invention was therefore that of providing aqueous binder compositions whereby the disadvantages of prior art aqueous binder compositions can be overcome and whereby shaped articles having improved longitudinal transverse breaking strength at room temperature and/or reduced extension at elevated temperature can be made
35 available.

The problem was solved by the aqueous binder composition mentioned at the beginning.

One essential constituent of the aqueous binder composition is a polymer P which in polymerized form is constructed from

- 5 ≥ 5 and ≤ 25 wt% of at least one acid-functional ethylenically unsaturated monomer (monomers A), and
 ≥ 75 and ≤ 95 wt% of at least one other ethylenically unsaturated monomer (monomers B).

As monomers A there come into consideration all ethylenically unsaturated compounds which include at least one acid group [proton donor], for example a sulfonic acid, phosphonic acid or carboxylic acid group, such as vinylsulfonic acid, allylsulfonic acid, styrenesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, vinylphosphonic acid, allylphosphonic acid, styrenephosphonic acid and 2-acrylamido-2-methylpropanephosphonic acid. Advantageously, however, the monomers A are α,β -monoethylenically unsaturated, especially C_3 to C_6 and preferably C_3 or C_4 mono- or dicarboxylic acids such as, for example acrylic acid, methacrylic acid, ethylacrylic acid, itaconic acid, allylacetic acid, crotonic acid, vinylacetic acid, fumaric acid, maleic acid, 2-methylmaleic acid. But the monomers A also comprise the anhydrides of appropriate α,β -monoethylenically unsaturated dicarboxylic acids, for example maleic anhydride or 2-methylmaleic anhydride. The monomer A is preferably selected from the group comprising acrylic acid, methacrylic acid, crotonic acid, fumaric acid, maleic acid, maleic anhydride, 2-methylmaleic acid, itaconic acid and vinylsulfonic acid, of which acrylic acid, methacrylic acid, fumaric acid, maleic acid and/or vinylsulfonic acid are advantageously preferred. However, methacrylic acid is particularly preferred. It will be appreciated that the monomers A also comprise the fully or partially neutralized water-soluble salts, especially the alkali metal or ammonium salts, of the aforementioned acids. However, the non-neutralized monomers A are preferred

The amount of monomers A polymerized into polymer P is ≥ 5 and ≤ 25 wt%, preferably ≥ 7.5 and ≤ 22.5 wt% and more preferably ≥ 10 and ≤ 20 wt%.

As monomers B there come into consideration all ethylenically unsaturated compounds which differ from monomers A. For example, as monomers B there come into consideration all ethylenically unsaturated monomers whose homopolymer have a glass transition temperature $\leq 30^\circ\text{C}$, such as conjugated aliphatic C_4 to C_9 diene compounds, esters of vinyl alcohol and a C_1 to C_{10} monocarboxylic acid, C_1 to C_{10} alkyl acrylate, C_5 to C_{10} alkyl methacrylate, C_5 to C_{10} cycloalkyl acrylate, C_5 to C_{10} cycloalkyl methacrylate, C_1 to C_{10} dialkyl maleate and/or C_1 to C_{10} dialkyl fumarate, vinyl ethers of C_3 to C_{10} alkanols, branched and unbranched C_3 to C_{10} olefins.

From this group it is advantageous for vinyl acetate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, di-n-butyl maleate, di-n-butyl fumarate to be used as monomers B.

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C₁ to C₁₀ Alkyl groups herein are linear or branched alkyl radicals of 1 to 10 carbon atoms, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, tert-pentyl n-hexyl, 2-ethylhexyl, n-nonyl or n-decyl. C₅ to C₁₀ cycloalkyl groups are preferably cyclopentyl or cyclohexyl groups, which may optionally be substituted by 1, 2 or 3 C₁ to C₄ alkyl groups.

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As another group of monomers B which come into consideration are all ethylenically unsaturated monomers whose homopolymer have a glass transition temperature $\geq 50^{\circ}\text{C}$, such as vinylaromatic monomers, nitrile monomers and C₁ to C₄ alkyl methacrylates. Vinylaromatic monomers are more particularly derivatives of styrene or of α -methylstyrene in each of which the phenyl nuclei are optionally substituted by 1, 2 or 3 C₁ to C₄ alkyl groups, halogen, especially bromine or chlorine and/or methoxy groups. Advantageous nitriles monomers are derived from the aforementioned α,β -monoethylenically unsaturated C₃ to C₆ and preferably C₃ or C₄, mono- or dicarboxylic acids, for example acrylonitrile, methacrylonitrile, maleonitrile and/or fumaronitrile, of which acrylonitrile and/or methacrylonitrile are particularly preferred. Preference is given to such monomers whose homopolymers have a glass transition temperature $\geq 80^{\circ}\text{C}$. Particularly preferred monomers are styrene, α -methylstyrene, o-vinyltoluene, p-vinyltoluene, p-acetoxystyrene, p-bromostyrene, p-tert-butylstyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, methyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, ethylmethacrylate, isobutyl methacrylate, n-hexyl acrylate, cyclohexyl methacrylate, but also for example tert-butyl vinyl ether or cyclohexyl vinyl ether, although acrylonitrile, methacrylonitrile, methyl methacrylate and/or styrene are particularly preferred from this monomer group.

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As auxiliary monomers B there come also into consideration all compounds which include at least two nonconjugated ethylenically unsaturated groups. Examples thereof are monomers including two vinyl radicals, monomers including two vinylidene radicals and also monomers including two alkenyl radicals. Of particular advantage here are the diesters of dihydric alcohols with α,β -monoethylenically unsaturated monocarboxylic acids, among which acrylic acid and methacrylic acid are preferred. Examples of such monomers including two nonconjugated ethylenically unsaturated double bonds are alkylene glycol diacrylates and alkylene glycol dimethacrylates, such as ethylene glycol diacrylate, 1,2-propylene glycol diacrylate, 1,3-propylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate and

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ethylene glycol dimethacrylate, 1,2-propylene glycol dimethacrylate, 1,3-propylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, 1,4-butylene glycol dimethacrylate, triesters of trihydric alcohols with α,β -monoethylenically unsaturated monocarboxylic acids, for example glycerol triacrylate, glycerol trimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, and also divinylbenzene, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, methylenebisacrylamide, cyclopentadienyl acrylate, triallyl cyanurate or triallyl isocyanurate. 1,4-Butylene glycol diacrylate, allyl methacrylate and/or divinylbenzene are particularly preferred.

- 10 The amount of these auxiliary monomers B optionally polymerized into polymer P is ≥ 0 and ≤ 2.0 wt%, preferably ≥ 0 and ≤ 1.5 wt% and more preferably ≥ 0 and ≤ 1.0 wt%, based on the total amount of all monomers B.

As auxiliary monomers B there come further into consideration all α,β -monoethylenically unsaturated C_3 to C_6 mono- or dicarboxamides. These monomers B likewise include the
 15 aforementioned compounds whose carboxamide group is substituted with an alkyl group or with a methylol group. Examples of these monomers B are the amides or diamides of α,β -monoethylenically unsaturated C_3 to C_6 and preferably C_3 or C_4 mono- or dicarboxylic acids such as, for example, acrylamide, methacrylamide, ethylacrylamide, itaconic acid monoamide, itaconic acid diamide, allylacetamide, crotonic acid monoamide, crotonic acid diamide,
 20 vinylacetamide, fumaric acid monoamide, fumaric acid diamide, maleic acid monoamide, maleic acid diamide, 2-methylmaleic acid monoamide and 2-methylmaleic acid diamide. Examples of α,β -monoethylenically unsaturated C_3 to C_6 mono- or dicarboxamides whose carboxamide group are substituted with an alkyl group or with a methylol group are N-alkylacrylamides and
 25 N-alkylmethacrylamides, e.g., N-tert-butylacrylamide and N-tert-butylmethacrylamide, N-methylacrylamide and N-methylmethacrylamide, and N-methylolacrylamide and N-methylolmethacrylamide. Preferred monomers B are acrylamide, methacrylamide, N-methylolacrylamide and/or N-methylolmethacrylamide, of which methylolacrylamide and/or N-methylolmethacrylamide are particularly preferred.

- 30 The amount of these auxiliary monomers B optionally polymerized into polymer P is ≥ 0 and ≤ 10 wt%, preferably ≥ 0 and ≤ 4 wt% and more preferably 0 wt%, based on the total amount of all monomers B.

- 35 From the aforementioned groups it is advantageous for n-butyl acrylate, 2-ethylhexylacrylate, acrylonitrile, methacrylonitrile, methyl methacrylate and styrene to be used as monomers B.

The total amount of monomers B polymerized into polymer P is ≥ 75 and ≤ 95 wt%, preferably ≥ 77.5 and ≤ 92.5 wt% and more preferably ≥ 80 and ≤ 90 wt%.

5 The polymer P principally shows a glass transition temperature T_g^P in the range ≥ -60 and $\leq 200^\circ\text{C}$, preferred ≥ -20 and $\leq 50^\circ\text{C}$ and advantageously preferred ≥ -10 and $\leq 10^\circ\text{C}$, determined by the DSC method according to DIN EN ISO 11357-2 (2013-05).

The reference to a glass transition temperature T_g is to be understood as meaning the glass transition temperature limit which the glass transition temperature approaches with increasing
 10 molecular weight, according to G. Kanig (Kolloid-Zeitschrift & Zeitschrift für Polymere, volume 190, page 1, equation 1). The T_g values for the homopolymers of most monomers are known and are listed for example in Ullmann's Encyclopedia of Industrial Chemistry, VCH Weinheim, 1992, Volume 5, Vol. A21, p. 169; further sources for glass transition temperatures of
 homopolymers include for example J. Brandrup, E.H. Immergut, Polymer Handbook, 1st Ed., J.
 15 Wiley, New York 1966, 2nd Ed. J. Wiley, New York 1975, and 3rd Ed. J. Wiley, New York 1989).

According to the present invention it is advantageously preferred that the at least one monomer A is selected from the group comprising acrylic acid, methacrylic acid, fumaric acid, maleic acid and vinylsulfonic acid and the at least one monomer B is selected from the group comprising n-
 20 butyl acrylate, 2-ethylhexylacrylate, acrylonitrile, methacrylonitrile, methyl methacrylate and styrene.

In one preferred embodiment, the aqueous binder composition comprises a polymer P constructed from

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≥ 7.5 and ≤ 22.5 wt%	of at least one monomer A, and
≥ 77.5 and ≤ 92.5 wt%	of at least one monomer B.

In another preferred embodiment, the aqueous binder composition comprises a polymer P constructed from

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≥ 10 and ≤ 20 wt%	of acrylic acid and/or methacrylic acid
≥ 70 and ≤ 90 wt%	of n-butyl acrylate and/or 2-ethylhexylacrylate, and
≥ 0 and ≤ 10 wt%	of vinylsulfonic acid, acrylonitrile, methacrylonitrile, methyl 35 methacrylate and/or styrene.

In advantageously preferred embodiment, the aqueous binder composition comprises a polymer P constructed from

- ≥ 10 and ≤ 20 wt% of methacrylic acid
- 5 ≥ 70 and ≤ 80 wt% of n-butyl acrylate,
- ≥ 5 and ≤ 9.5 wt% acrylonitrile, and
- ≥ 0.05 and ≤ 0.5 wt% of vinylsulfonic acid.

The preparation of polymers P will in principle be familiar to a person skilled in the art and is
 10 effected for example through free-radical polymerization of monomers A and B by the method of substance, emulsion, solution, precipitation or suspension polymerization, although free-radically initiated aqueous emulsion polymerization is particularly preferred. It is therefore advantageous according to the present invention for the polymer P to be dispersed in an aqueous medium, i.e., used in the form of an aqueous polymer dispersion.

15 The performance of free-radically initiated emulsion polymerizations of ethylenically unsaturated monomers in an aqueous medium has been extensively described and therefore is sufficiently familiar to a person skilled in the art [cf. Emulsion polymerization in Encyclopedia of Polymer Science and Engineering, Vol. 8, pages 659 ff. (1987); D.C. Blackley, in High Polymer Latices, Vol. 1, pages 35 ff. (1966); H. Warson, The Applications of Synthetic Resin Emulsions, chapter
 20 5, pages 246 ff. (1972); D. Diederich, Chemie in unserer Zeit 24, pages 135 to 142 (1990); Emulsion Polymerisation, Interscience Publishers, New York (1965); DE-A 40 03 422 and Dispersionen synthetischer Hochpolymerer, F. Hölscher, Springer-Verlag, Berlin (1969)]. A free-radically initiated aqueous emulsion polymerization is typically carried out by the ethylenically
 25 unsaturated monomers being dispersed in an aqueous medium, generally by co-use of dispersing assistants, such as emulsifiers and/or protective colloids, and polymerized using at least one water-soluble free-radical polymerization initiator. Frequently, in the aqueous polymer dispersions obtained, the residual contents of unconverted ethylenically unsaturated monomers are reduced by chemical and/or physical methods likewise known to a person skilled in the art
 30 [see for example EP-A 771328, DE-A 19624299, DE-A 19621027, DE-A 19741184, DE-A 19741187, DE-A 19805122, DE-A 19828183, DE-A 19839199, DE-A 19840586 and 19847115], the polymer solids content is adjusted to a desired value by thinning or concentrating, or the aqueous polymer dispersion is mixed with further customary addition agents, for example bactericidal, foam- or viscosity-modifying additives. From this general
 35 procedure, the production of an aqueous dispersion of polymer P merely differs by the specific use of the aforementioned monomers A and B. It will be appreciated in this connection that

producing polymer P herein shall also comprise the seed, staged and gradient modes of operation which are familiar to a person skilled in the art.

Therefore, according to the present invention, the aqueous binder compositions are advantageously obtained using aqueous dispersions of a polymer P constructed from

≥ 5 and ≤ 25 wt% of at least one monomer A, and
 ≥ 75 and ≤ 95 wt% of at least one monomer B,

advantageously from

≥ 7.5 and ≤ 22.5 wt% of at least one monomer A, and
 ≥ 77.5 and ≤ 92.5 wt% of at least one monomer B,

more advantageously from

≥ 10 and ≤ 20 wt% of acrylic acid and/or methacrylic acid
 ≥ 70 and ≤ 90 wt% of n-butyl acrylate and/or 2-ethylhexylacrylate, and
 ≥ 0 and ≤ 10 wt% of vinylsulfonic acid, acrylonitrile, methacrylonitrile, methyl
methacrylate and/or styrene,

and even more advantageously from

≥ 10 and ≤ 20 wt% of methacrylic acid
 ≥ 70 and ≤ 80 wt% of n-butyl acrylate,
 ≥ 5 and ≤ 9.5 wt% acrylonitrile, and
 ≥ 0.05 and ≤ 0.5 wt% of vinylsulfonic acid

in polymerized form.

The polymers P used according to the present invention are obtainable in the form of their aqueous polymer dispersion by initially charging the overall amount of monomers A and B in the aqueous reaction medium before initiating the polymerization reaction. However, it is also possible to optionally merely initially charge a portion of monomers A and B in the aqueous reaction medium before initiating the polymerization reaction and then, after initiating the polymerization, to add the overall amount or, as may be, the remaining quantity under polymerization conditions during the free-radical emulsion polymerization at the rate of

consumption, continuously with constant or varying flow rates, or discontinuously. The monomers A and B can be dosed as separate individual streams, as homogeneous or inhomogeneous (partial) mixtures, or as monomer emulsion. Advantageously, the monomers A and B are dosed in the form of a monomer mixture and more particularly in the form of an aqueous monomer emulsion.

The polymers P used according to the present invention are obtained in the form of their aqueous polymer dispersion by co-using dispersing assistants which keep both the monomer droplets and the produced polymer particles in a state of dispersion in the aqueous medium and so ensure the stability of the aqueous polymer dispersion produced. As dispersing assistants there come into consideration the protective colloids typically used for performance of free-radical aqueous emulsion polymerizations as well as emulsifiers.

Suitable protective colloids are for example polyvinyl alcohols, polyalkylene glycols, alkali metal salts of polyacrylic acids and polymethacrylic acids, gelatin derivatives or acrylic acid, methacrylic acid, maleic anhydride, 2-acrylamido-2-methylpropanesulfonic acid and/or 4-styrenesulfonic acid-containing copolymers and their alkali metal salts but also N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylcarbazole, 1-vinylimidazole, 2-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, acrylamide, methacrylamide, amino-bearing acrylates, methacrylates, acrylamides and/or methacrylamides-containing homo- and copolymers. An extensive description of further suitable protective colloids is given in Houben-Weyl, Methoden der organischen Chemie, volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 411 to 420.

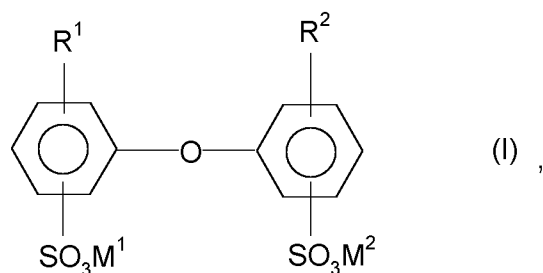
It will be appreciated that mixtures of protective colloids and/or emulsifiers can also be used. Frequently, the dispersing agents used are exclusively emulsifiers whose relative molecular weights are typically below 1000, unlike protective colloids. They can be anionic, cationic or nonionic in nature. It will be appreciated that, when the mixtures of surface-active substances are used, the individual components have to be compatible with each or one another, which in the case of doubt can be verified in a few preliminary tests. In general, anionic emulsifiers are compatible with other anionic emulsifiers and with nonionic emulsifiers. The same applies to cationic emulsifiers, while anionic and cationic emulsifiers are usually not compatible with one another. An overview of suitable emulsifiers is given in Houben-Weyl, Methoden der organischen Chemie, volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 192 to 208.

However, especially emulsifiers are used as dispersing assistants.

Customary nonionic emulsifiers are for example ethoxylated mono-, di- and tri-alkylphenols (EO degree: 3 to 50, alkyl radical: C₄ to C₁₂) and also ethoxylated fatty alcohols (EO degree: 3 to 80, alkyl radical: C₈ to C₃₆). Examples thereof are the Lutensol® A brands (C₁₂C₁₄ fatty alcohol ethoxylates, EO degree: 3 to 8), Lutensol® AO brands (C₁₃C₁₅ oxo process alcohol ethoxylates, EO degree: 3 to 30), Lutensol® AT brands (C₁₆C₁₈ fatty alcohol ethoxylates, EO degree: 11 to 80), Lutensol® ON brands (C₁₀-oxo process alcohol ethoxylates, EO degree: 3 to 11) and the Lutensol® TO brands (C₁₃ oxo process alcohol ethoxylates, EO degree: 3 to 20) from BASF SE.

Customary anionic emulsifiers are for example alkali metal and ammonium salts of alkyl sulfates (alkyl radical: C₈ to C₁₂), of sulfuric monoesters of ethoxylated alkanols (EO degree: 4 to 30, alkyl radical: C₁₂ to C₁₈) and ethoxylated alkylphenols (EO degree: 3 to 50, alkyl radical: C₄ to C₁₂), of alkylsulfonic acids (alkyl radical: C₁₂ to C₁₈) and of alkylarylsulfonic acids (alkyl radical: C₉ to C₁₈).

Suitable anionic emulsifiers further include compounds of the general formula (I)



where R¹ and R² are H atoms or C₄ to C₂₄ alkyl that are not H atoms at the same time, and M¹ and M² can be alkali metal ions and/or ammonium ions. In the general formula (I), R¹ and R² are preferably linear or branched alkyl radicals of 6 to 18 carbon atoms and more particularly of 6, 12 and 16 carbon atoms, or hydrogen, with the proviso that R¹ and R² are not both an H atom at the same time. M¹ and M² are each preferably sodium, potassium or ammonium, of which sodium is particularly preferred. Particularly advantageous are compounds (I) in which M¹ and M² are both sodium, R¹ is a branched alkyl radical of 12 carbon atoms and R² an H atom or R¹. Technical grade mixtures are frequently used that include a 50 to 90 wt% fraction of monoalkylated product, for example Dowfax® 2A1 (trademark of Dow Chemical Company). Compounds (I) are common knowledge, for example from US-A 4269749, and commercially available.

Suitable cation-active emulsifiers are generally C₆-C₁₈-alkyl-, -alkylaryl- or heterocyclyl-containing primary, secondary, tertiary or quaternary ammonium salts, alkanolammonium salts, pyridinium salts, imidazolinium salts, oxazolinium salts, morpholinium salts, thiazolinium salts and also salts of amine oxides, quinolinium salts, isoquinolinium salts, tropylium salts, sulfonium salts and phosphonium salts. Examples which may be mentioned are dodecylammonium acetate and the corresponding sulfate, the sulfates or acetates of the various 2-(N,N,N-trimethylammonium)ethyl paraffinic acid esters, N-cetylpyridinium sulfate, N-laurylpyridinium sulfate and also N-cetyl-N,N,N-trimethylammonium sulfate, N-dodecyl-N,N,N-trimethylammonium sulfate, N-octyl-N,N,N-trimethylammonium sulfate, N,N-distearyl-N,N-dimethylammonium sulfate and also the Gemini surfactant N,N'-(lauryldimethyl)ethylenediamine disulfate, ethoxylated tallowalkyl N-methylammonium sulfate and ethoxylated oleylamine (for example Uniperol® AC from BASF SE, about 11 ethylene oxide units). Numerous further examples are given in H. Stache, Tensid-Taschenbuch, Carl-Hanser-Verlag, Munich, Vienna, 1981 and in McCutcheon's, Emulsifiers & Detergents, MC Publishing Company, Glen Rock, 1989. It is beneficial when the anionic counter-groups have very low nucleophilicity, for example perchlorate, sulfate, phosphate, nitrate and carboxylates, for example acetate, trifluoroacetate, trichloroacetate, propionate, oxalate, citrate, benzoate, and also conjugated anions of organosulfonic acids, for example methylsulfonate, trifluoromethylsulfonate and para-toluenesulfonate, further tetrafluoroborate, tetraphenylborate, tetrakis(pentafluorophenyl)borate, tetrakis[bis(3,5-trifluoromethyl)phenyl]borate, hexafluorophosphate, hexafluoroarsenate or hexafluoroantimonate.

The emulsifiers preferred for use as dispersing assistants are advantageously used in an overall amount ≥ 0.005 and ≤ 10 wt%, preferably ≥ 0.01 and ≤ 5 wt% and more particularly ≥ 0.1 and ≤ 3 wt%, all based on the overall amount of monomers A and B (total monomer quantity).

The overall amount of the protective colloids used as dispersing assistants in addition to or in lieu of emulsifiers is often ≥ 0.1 and ≤ 40 wt% and frequently ≥ 0.2 and ≤ 25 wt%, all based on the total monomer quantity.

Preferably, however, it is anionic and/or nonionic emulsifiers and more preferably anionic emulsifiers that are used as dispersing assistants.

The polymers P used according to the present invention are obtainable in the form of their aqueous polymer dispersion by initially charging the overall amount of dispersing assistant in the aqueous reaction medium before initiating the polymerization reaction. However, it is also possible to optionally merely initially charge a portion of the dispersing assistant in the aqueous

reaction medium before initiating the polymerization reaction and then to add the overall amount or as the case may be any remaining quantity of dispersing assistant under polymerization conditions during the free-radical emulsion polymerization, continuously or batchwise.

Preferably, the main or overall quantity of dispersing assistant is added in the form of an aqueous monomer emulsion.

The free-radically initiated aqueous emulsion polymerization is triggered using a free-radical polymerization initiator. In principle, not only peroxides but also azo compounds can be concerned here. Redox initiator systems also come into consideration, as will be appreciated.

As peroxides there can be used in principle inorganic peroxides, such as hydrogen peroxide or peroxodisulfates, such as the mono- or di-alkali metal or ammonium salts of peroxodisulfuric acid, for example its mono- and di-sodium, potassium or ammonium salts or organic peroxides, such as alkyl hydroperoxides, for example tert-butyl hydroperoxide, p-mentyl hydroperoxide or cumyl hydroperoxide, and also dialkyl or diaryl peroxides, such as di-tert-butyl or dicumyl peroxide. As azo compound it is essentially 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile) and 2,2'-azobis(amidinopropyl) dihydrochloride (AIBA, corresponds to V-50 from Wako Chemicals) which are used. As oxidizing agents for redox initiator systems it is essentially the abovementioned peroxides which come into consideration. As corresponding reducing agents there can be used sulfur compounds of low oxidation state, such as alkali metal sulfites, for example potassium and/or sodium sulfite, alkali metal hydrogensulfites, for example potassium and/or sodium hydrogensulfite, alkali metal metabisulfites, for example potassium and/or sodium metabisulfite, formaldehydesulfoxylates, for example potassium and/or sodium formaldehydesulfoxylate, alkali metal salts, specifically potassium and/or sodium salts of aliphatic sulfinic acids and alkali metal hydrogensulfides, for example potassium and/or sodium hydrogensulfide, salts of multivalent metals, such as iron(II) sulfate, iron(II) ammonium sulfate, iron(II) phosphate, enediols, such as dihydroxymaleic acid, benzoin and/or ascorbic acid and also reducing saccharides, such as sorbose, glucose, fructose and/or dihydroxyacetone. In general, the amount of free-radical initiator used is from 0.01 to 5 wt%, preferably 0.1 to 3 wt% and more preferably 0.2 to 1.5 wt%, based on the total monomer quantity.

The polymers P used according to the present invention are obtainable in the form of their aqueous polymer dispersion by initially charging the overall amount of free-radical initiator in the aqueous reaction medium before initiating the polymerization reaction. However, it is also possible to optionally initially charge merely a portion of the free-radical initiator in the aqueous reaction medium before initiating the polymerization reaction and then to add the overall amount or as the case may be any remaining quantity under polymerization conditions during the free-radical emulsion polymerization at the rate of consumption, continuously or discontinuously.

Initiating the polymerization reaction refers to starting the polymerization reaction of the monomers in the polymerization vessel after free-radical formation on the part of the free-radical initiator. The polymerization reaction can be initiated by addition of free-radical initiator to the aqueous polymerization mixture in the polymerization vessel under polymerization conditions. However, it is also possible for the addition of some or all of the free-radical initiator to the aqueous polymerization mixture comprising the initially charged monomers, in the polymerization vessel, to take place under conditions which are not suitable for triggering a polymerization reaction, for example at low temperature, and for polymerization conditions to be established in the aqueous polymerization mixture thereafter. Polymerization conditions are generally those temperatures and pressures under which the free-radically initiated aqueous emulsion polymerization proceeds at a sufficient polymerization rate. They are more particularly dependent on the free-radical initiator used. Advantageously, free-radical initiator type and quantity, the polymerization temperature and the polymerization pressure are selected such that the free-radical initiator has a half-life < 3 hours, more advantageously < 1 hour and even more advantageously < 30 minutes, while sufficient starting free-radicals are available at all times in order that the polymerization reaction may be initiated and maintained.

The entire range from 0 to 170°C comes into consideration as reaction temperature for the free-radical aqueous emulsion polymerization. Temperatures employed are generally in the range from 50 to 120°C, preferably in the range from 60 to 110°C and more preferably in the range from 70 to 100°C. The free-radical aqueous emulsion polymerization can be carried out at a pressure below, equal to or above 1 atm [1.013 bar (absolute), atmospheric pressure], so that the polymerization temperature can exceed 100°C and range up to 170°C. In the presence of monomers A and B having a low boiling point, the emulsion polymerization is preferably performed under elevated pressure. This pressure can assume values of 1.2, 1.5, 2, 5, 10, 15 bar (absolute) or even higher. When the emulsion polymerization is carried out under reduced pressure, pressures of 950 mbar, frequently of 900 mbar and often 850 mbar (absolute) are set. Advantageously, the free-radical aqueous emulsion polymerization is carried out at 1 atm or at elevated pressures in the absence of oxygen, more particularly under an inert gas, for example under nitrogen or argon.

The aqueous reaction medium can in principle also comprise minor amounts (< 5 wt%) of water-soluble organic solvents, for example methanol, ethanol, isopropanol, butanols, pentanols, but also acetone etc. Preferably, however, the process of the present invention is carried out in the absence of such solvents.

In addition to the aforementioned components, chain transfer agents can optionally also be used during the emulsion polymerization to reduce/police the molecular weight of the polymers P obtainable by the polymerization. Here it is essentially aliphatic and/or araliphatic halogen compounds, for example n-butyl chloride, n-butyl bromide, n-butyl iodide, methylene chloride, ethylene dichloride, chloroform, bromoform, bromotrichloromethane, dibromodichloromethane, carbon tetrachloride, carbon tetrabromide, benzyl chloride, benzyl bromide, organic thio compounds, such as primary, secondary or tertiary aliphatic thiols, for example ethanethiol, n-propanethiol, 2-propanethiol, n-butanethiol, 2-butanethiol, 2-methyl-2-propanethiol, n-pentanethiol, 2-pentanethiol, 3-pentanethiol, 2-methyl-2-butanethiol, 3-methyl-2-butanethiol, n-hexanethiol, 2-hexanethiol, 3-hexanethiol, 2-methyl-2-pentanethiol, 3-methyl-2-pentanethiol, 4-methyl-2-pentanethiol, 2-methyl-3-pentanethiol, 3-methyl-3-pentanethiol, 2-ethylbutanethiol, 2-ethyl-2-butanethiol, n-heptanethiol and its isomeric compounds, n-octanethiol and its isomeric compounds, n-nonanethiol and its isomeric compounds, n-decanethiol and its isomeric compounds, n-undecanethiol and its isomeric compounds, n-dodecanethiol and its isomeric compounds, n-tridecanethiol and its isomeric compounds, substituted thiols, for example 2-hydroxyethanethiol, aromatic thiols, such as benzenethiol, ortho-benzenethiol, meta-methylbenzenethiol or para-methylbenzenethiol, and also all further sulfur compounds described in Polymerhandbook 3rd edition, 1989, J. Brandrup and E.H. Immergut, John Wiley & Sons, section II, pages 133 to 141, but also aliphatic and/or aromatic aldehydes, such as acetaldehyde, propionaldehyde and/or benzaldehyde, unsaturated fatty acids, such as oleic acid, dienes with nonconjugated double bonds, such as divinylmethane or vinylcyclohexane or hydrocarbons having readily extractable hydrogen atoms, such as toluene for example, which are used. But it is also possible to use mixtures of aforementioned chain transfer agents that are noninterfering.

The total amount of chain transfer agents optionally used during the emulsion polymerization is generally ≤ 5 wt%, often ≤ 3 wt% and frequently ≤ 1 wt%, based on the total monomer quantity.

It is beneficial when all or some of the optional chain transfer agent is added to the aqueous reaction medium prior to initiating the free-radical polymerization. In addition, all or some of the chain transfer agent can advantageously be added to the aqueous reaction medium together with the monomers A and B during the polymerization.

The polymer P principally shows a glass transition temperature $T_g^P \geq -60$ and $\leq 200^\circ\text{C}$, preferably ≥ -20 and $\leq 50^\circ\text{C}$ and advantageously preferred ≥ -10 and $\leq 10^\circ\text{C}$, determined by the DSC method according to DIN EN ISO 11357-2 (2013-05).

Therefore, the monomers A and B are chosen in terms of type and amount such that the polymers P formed merely therefrom have a glass transition temperature $T_g^P \geq -60$ and $\leq 200^\circ\text{C}$, preferably ≥ -20 and $\leq 50^\circ\text{C}$ and advantageously ≥ -10 and $\leq 10^\circ\text{C}$.

- 5 According to Fox (T.G. Fox, Bull. Am. Phys. Soc. 1956 [Ser. II] 1, page 123 and as per Ullmann's Encyclopädie der technischen Chemie, volume 19, page 18, 4th edition, Verlag Chemie, Weinheim, 1980) the glass transition temperature of at most lightly crosslinked copolymers is given to good approximation by:

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$$1/T_g = x_1/T_g^1 + x_2/T_g^2 + \dots x_n/T_g^n,$$

where $x_1, x_2, \dots x_n$ are the mass fractions of monomers 1, 2, ..., n and $T_g^1, T_g^2, \dots T_g^n$ are the glass transition temperatures in degrees kelvin of the polymers each constructed of just one of the monomers 1, 2, ..., n. The glass transition temperatures of these homopolymers of most ethylenically unsaturated monomers are known (or are simple to determine experimentally in a conventional manner) and are listed for example in J. Brandrup, E.H. Immergut, Polymer Handbook 1st Ed. J. Wiley, New York, 1966, 2nd Ed. J. Wiley, New York, 1975 and 3rd Ed. J. Wiley, New York, 1989, and also in Ullmann's Encyclopedia of Industrial Chemistry, page 169, Verlag Chemie, Weinheim, 1992.

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It is essential that the free-radically initiated aqueous emulsion polymerization can also be carried out in the presence of a polymer seed, for example in the presence of 0.01 to 3 wt%, frequently of 0.02 to 2 wt% and often of 0.04 to 1.5 wt% of a polymer seed, all based on the total monomer quantity.

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A polymer seed is used in particular when the particle size of the polymer particles to be obtained by free-radical aqueous emulsion polymerization is to be set to a specific value (see for example US-A 2520959 and US-A 3397165).

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One polymer seed used in particular has polymer seed particles with a narrow particle size distribution and weight average diameter $D_w \leq 100$ nm, often ≥ 5 nm to ≤ 50 nm and frequent ≥ 15 nm to ≤ 35 nm. Weight average particle diameter determination is known to a person skilled in the art and is done via the analytical ultracentrifuge method for example. Weight average particle diameter herein is to be understood as being the weight average D_{w50} value

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determined by the analytical ultracentrifuge method (cf. S.E. Harding et al., Analytical Ultracentrifugation in Biochemistry and Polymer Science, Royal Society of Chemistry, Cambridge, Great Britain 1992, Chapter 10, Analysis of Polymer Dispersions with an Eight-Cell-

AUC-Multiplexer: High Resolution Particle Size Distribution and Density Gradient Techniques, W. Mächtle, pages 147 to 175).

Narrow particle size distribution herein is to be understood as meaning that the ratio of the analytical ultracentrifuge method weight average particle diameters D_{w50} and number average particle diameters D_{N50} [D_{w50}/D_{N50}] is < 2.0 , preferably < 1.5 and more preferably < 1.2 or < 1.1 .

The polymer seed is typically used in the form of an aqueous polymer dispersion. The aforementioned amount recitations are based on the polymer solids content of the aqueous polymer seed dispersion.

When a polymer seed is used it is advantageous to employ an exogenous polymer seed. Unlike an in situ polymer seed, which is prepared in the reaction vessel before the actual emulsion polymerization is commenced, and which generally has the same monomeric composition as the polymer prepared by the ensuing free-radically initiated aqueous emulsion polymerization, an exogenous polymer seed is a polymer seed which has been prepared in a separate reaction step and whose monomeric composition differs from the polymer prepared by the free-radically initiated aqueous emulsion polymerization, although this means nothing more than that different monomers, or monomer mixtures with a different composition, are used for preparing the exogenous polymer seed and for preparing the aqueous polymer dispersion. Preparing an exogenous polymer seed is familiar to a person skilled in the art and is typically accomplished by the introduction as initial charge to a reaction vessel of a relatively small amount of monomers and also a relatively large amount of emulsifiers, and by the addition at reaction temperature of a sufficient amount of polymerization initiator.

In case a polymer seed is used, it is preferred in accordance with the present invention to use an exogenous polymer seed having a glass transition temperature $\geq 50^{\circ}\text{C}$, frequently $\geq 60^{\circ}\text{C}$ or $\geq 70^{\circ}\text{C}$ and often $\geq 80^{\circ}\text{C}$ or $\geq 90^{\circ}\text{C}$. A polystyrene or polymethyl methacrylate polymer seed is preferred in particular.

The total amount of exogenous polymer seed can be initially charged to the polymerization vessel. But it is also possible to merely include a portion of the exogenous polymer seed in the initial charge to the polymerization vessel and to add the remainder during the polymerization together with monomers A and B. If necessary, however, the total polymer seed quantity can also be added during the polymerization. Preferably, the total amount of exogenous polymer seed is initially charged to the polymerization vessel before initiating the polymerization reaction.

The aqueous polymer P dispersions obtainable by emulsion polymerization typically have a polymer solids content of ≥ 10 and ≤ 70 wt%, frequently ≥ 20 and ≤ 65 wt% and often ≥ 25 and ≤ 60 wt%, all based on the aqueous polymer dispersion. The number average particle diameter as determined by quasi-elastic light scattering (ISO standard 13 321) (cumulant z-average) is generally in the range ≥ 10 and ≤ 2000 nm, frequently in the range ≥ 10 and ≤ 700 nm and often in the range ≥ 50 to ≤ 400 nm.

It will be appreciated that aqueous polymer P dispersions are also obtainable in principle in the form of so-called secondary polymer dispersions (concerning in-principle preparation of secondary polymer dispersions see for example Eckersley et al., Am. Chem. Soc., Div. Polymer Chemistry, 1977, 38(2), pages 630, 631, US-A 3360599, US-A 3238173, US-A 3726824, US-A 3734686 or US-A 6207756). Secondary aqueous polymer P dispersions are generally obtained when polymers P obtained by the method of substance or solution polymerization are dissolved in a suitable organic solvent and dispersed in an aqueous medium to form aqueous polymer/solvent (mini)emulsions. Subsequent solvent removal yields the corresponding aqueous polymer P dispersions.

Accordingly, the aqueous binder compositions of the present invention comprise aqueous dispersions of polymers P whose number average particle diameter is in the range ≥ 10 and ≤ 2000 nm, advantageously in the range ≥ 10 and ≤ 700 nm and more advantageously in the range ≥ 50 to ≤ 400 nm.

The inventive aqueous binder compositions typically have a polymer P solids content ≥ 0.1 and ≤ 60 wt%, preferably ≥ 1 and ≤ 40 wt% and advantageously ≥ 5 and ≤ 20 wt%, all based on the aqueous binder composition.

At least one saccharide compound S is an essential constituent of the aqueous binder composition as well as at least one polymer P.

A saccharide compound S herein is to be understood as meaning monosaccharides, oligosaccharides, polysaccharides, sugar alcohols and also substitution products and derivatives thereof.

Monosaccharides are organic compounds of the generic formula $C_nH_{2n}O_n$, where n is an integer 5, 6, 7, 8 or 9. These monosaccharides are also known as pentoses, hexoses, heptoses, octoses or nonoses, and these compounds can be subdivided into the corresponding aldoses,

which include an aldehyde group, and ketoses, which include a keto group. Accordingly, monosaccharides comprise aldo- or ketopentoses, aldo- or ketohexoses, aldo- or ketoheptoses, aldo- or keto-octoses or aldo- or ketononoses. Monosaccharide compounds which are preferred according to the present invention are the pentoses and hexoses which also occur in nature, of which glucose, mannose, galactose and/or xylose are particularly preferred. It will be appreciated that the present invention also comprehends all stereoisomers of all aforementioned monosaccharides.

Sugar alcohols are the hydrogenation products of the aforementioned aldo- or ketopentoses, aldo- or ketohexoses, aldo- or ketoheptoses, aldo- or keto-octoses or aldo- or ketononoses, which have the general formula $C_nH_{2n+2}O_n$, where n is an integer 5, 6, 7, 8 or 9. Mannitol, lactitol, sorbitol and xylitol are preferred sugar alcohols. It will be appreciated that the present invention shall also comprehend all stereoisomers of all aforementioned sugar alcohols.

It is known that the aforementioned monosaccharides are present in the form of their hemiacetals or -ketals, formed from a hydroxyl group and the aldehyde or keto group, respectively, generally with the formation of a five- or six-membered ring. If, then, a hydroxyl group (from the hemiacetal or hemiketal group or from the carbon scaffold chain) of one monosaccharide molecule reacts with the hemiacetal or hemiketal group of another monosaccharide molecule by water elimination to form an acetal or, respectively, ketal group (such a bond is also called glycosidic bond), disaccharides are obtained (with the general empirical formula $C_nH_{2n-2}O_{n-1}$). Furthermore, such a disaccharide can react with a further monosaccharide by water elimination to form a trisaccharide. Further reactions with monosaccharides give tetrasaccharides, pentasaccharides, hexasaccharides, heptasaccharides, octasaccharides, nonasaccharides or decasaccharides. Compounds constructed of at least two but not more than ten monosaccharide structural units via glycosidic bonds are known as oligosaccharides. Preferred oligosaccharides are disaccharides, among which it is lactose, maltose and/or sucrose which are particularly preferred. It will be appreciated that the present invention shall also comprehend all stereoisomers of all aforementioned oligosaccharides.

Saccharide compounds constructed of more than ten monosaccharide structural units are herein known as polysaccharide compounds. Polysaccharide compounds can in effect be constructed of the structural elements of a monosaccharide (so-called homoglycans) or the structural elements of two or more different monosaccharides (so-called heteroglycans). It is homoglycans which are preferably used according to the present invention.

Among the homoglycans it is the starches, which are constructed of α -D-glucose units, which are particularly preferred. The starches consist of the polysaccharides amylose (D-glucose units linked together α -1,4-glycosidically and amylopectin (D-glucose units linked together α -1,4- and additionally about 4% α -1,6-glycosidically). Naturally occurring starch typically comprises about 20 to 30 wt% of amylose and about 70 to 80 wt% of amylopectin. However, the ratio between amylose and amylopectin can vary as a result of breeding and according to plant species. Useful starches include all native starches, for example starches from maize, wheat, oats, barley, rice, millet, potatoes, peas, tapioca, sorghum or sago. Also of interest are those natural starches that have a high amount of amylopectin content such as waxy maize starch and waxy potato starch. The amylopectin content of these starches is ≥ 90 wt%, often ≥ 95 and ≤ 100 wt%.

It will be appreciated that the term saccharide compound S also comprises the substitution products and derivatives of the aforementioned mono-, oligo- and polysaccharide compounds and also of sugar alcohols.

In substitution products of a saccharide compound S, at least one hydroxyl group of saccharide compound S was functionalized, for example by esterification, etherification, oxidation, etc., with preservation of the saccharide structure. Esterification for example is effected by reacting the saccharide compound S with organic or inorganic acids, their anhydrides or halides. Phosphated and acetylated saccharide compounds are of particular interest. Etherification is generally effected by reacting the saccharide compounds S with organic halogen compounds, epoxides or sulfates in aqueous alkaline solution. Known ethers are alkyl ethers, hydroxyalkyl ethers, carboxyalkyl ethers and allyl ethers. Oxidation of at least one hydroxyl group using an oxidizing agent customary in the organic chemistry of carbohydrates, for example nitric acid, hydrogen peroxide, ammonium persulfate, peroxyacetic acid, sodium hypochlorite and/or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), gives rise to the corresponding keto compound (on oxidation of a secondary hydroxyl group), or carboxyl compound (on oxidation of a primary hydroxyl group).

Derivatives of saccharide compounds S are such reaction products of oligo- and polysaccharides as are obtained by cleaving at least one acetal or ketal group (at least one glycosidic bond) and therefore by degrading the original saccharide structure. Such degradation reactions are familiar to a person skilled in the art and they take place in particular in that an oligo- or polysaccharide compound is exposed to thermal, enzymatic, oxidative and/or hydrolytic conditions.

Preferred is the at least one saccharide compound S selected from the group comprising starch, cellulose, guaran, xanthan, alginate, pectin, chitosan, gum arabic, gellan and substitution products or derivatives thereof.

- 5 Particular preference is given to starches, starch derivatives and/or starch substitution products, advantageously maltodextrines and/or glucose syrup.

DE value is a very common way in commercial practice to characterize the degree of starch degradation. DE is for dextrose equivalent and refers to the percentage fraction of the dry
10 substance which is attributable to reducing sugars. The DE value therefore corresponds to the amount, in grams, of glucose (= dextrose) which would have the same reducing power per 100 g of dry substance. The DE value is a measure of how far polymer degradation has gone. Hence starches of low DE value have a high proportion of polysaccharides and a low content of low molecular weight mono- and oligosaccharides, while starches of high DE consist in the main
15 of low molecular weight mono- or disaccharides. The maltodextrins preferred in the context of the present invention have DE values in the range from 3 to 20 and weight average molecular weights in the range from 10000 to 30000 g/mol. A glucose syrup likewise preferred in the context of the present invention has DE values in the range from 20 to 30 and weight average molecular weights in the range from 3000 to 9000 g/mol. Owing to their method of making,
20 these products are obtained in the form of aqueous solutions and they are therefore generally also commercialized as such. Suitable solutions of maltodextrins have solids contents of 50 to 70 wt%, while suitable solutions of glucose syrup have solids contents of 70 to 95 wt%. Especially maltodextrins, however, are also obtainable in spray-dried form as powders. Preference according to the present invention is also given to modified degraded starches
25 which have DE values of 1 to 3 and weight average molecular weights Mw in the range from 100000 to 1000000 g/mol and are typically obtainable as a solid material.

The saccharide compound S generally has a weight average molecular weight in the range ≥ 1000 and ≤ 5000000 g/mol, advantageously in the range ≥ 1000 and ≤ 500000 g/mol,
30 preferably in the range ≥ 3000 and ≤ 50000 g/mol and more preferably in the range ≥ 5000 and ≤ 25000 g/mol. The weight average molecular weight here is determined using gel permeation chromatography with defined standards which is familiar to a person skilled in the art.

It is preferable when the saccharide compound S used according to the present invention has a
35 solubility of ≥ 10 g, advantageously ≥ 50 g and more advantageously ≥ 100 g per liter of deionized water at 20°C and atmospheric pressure. The present invention, however, also comprehends embodiments where the saccharide compound S has a solubility < 10 g per liter

of deionized water at 20°C and atmospheric pressure. Depending on the amount of these employed saccharide compounds S, these can then also be present in the form of their aqueous suspension. When saccharide compounds S are used according to the present invention in terms of type and amount such that they are present in aqueous suspension, it is advantageous when the saccharide S particles suspended in the aqueous medium have an average particle diameters are $\leq 5 \mu\text{m}$, preferably $\leq 3 \mu\text{m}$ and more preferably $\leq 1 \mu\text{m}$. Average particle diameters are determined as for the aqueous polymer P dispersions via the method of quasi-elastic light scattering (ISO standard 13 321).

It is essential for the present invention that the total amount of saccharide compound S can be added to the aqueous polymerization medium before or during the emulsion polymerization of monomers A and B or to the aqueous dispersion of polymer P on completing the emulsion polymerization. As will be appreciated, it is also possible to add merely a portion of saccharide compound S to the aqueous polymerization medium before or during the emulsion polymerization of monomers A and B and the remainder to the aqueous dispersion of polymer P on completing the emulsion polymerization. When all or some of saccharide compound S is added before or during the emulsion polymerization of monomers A and B, the quantity added can generally perform the protective colloid function, making it possible to reduce the amount of other protective colloids and/or emulsifiers and/or to entirely dispense with them, if appropriate.

In a preferred embodiment the monomers A and B were polymerized in the presence of the at least one saccharide compound S, which means, the polymer P was prepared in the presence of the at least one saccharide compound S.

The at least one saccharide compound S is principally used in an overall amount ≥ 1 and ≤ 100 parts by weight per 100 parts by weight of polymer P.

When – in one preferred embodiment – the at least one saccharide compound S is added before or during the emulsion polymerization of monomers A and B, the amount of saccharide compound S is generally in the range ≥ 5 and ≤ 50 parts by weight, advantageously ≥ 10 and ≤ 40 parts by weight and more advantageously ≥ 15 and ≤ 35 parts by weight of saccharide compound S per 100 parts by weight of polymer P (= total monomer quantity).

When – in one other preferred embodiment – the saccharide compound S is added after the emulsion polymerization, the amount of saccharide compound S is generally also in the range

≥ 5 and ≤ 50 parts by weight, advantageously ≥ 10 and ≤ 40 parts by weight and more advantageously ≥ 15 and ≤ 35 parts by weight of saccharide compound S per 100 parts by weight of polymer P.

5 At least one metal compound M selected from the group comprising magnesium, calcium and zinc, in the form of an oxide, hydroxide, carbonate or bicarbonate is a further essential constituent of the aqueous binder composition as well as the at least one polymer P and the at least one saccharide compound S.

10 In a preferred embodiment calcium oxide [CaO], calcium hydroxide [Ca(OH)₂], calcium carbonate [CaCO₃] and/or calcium bicarbonate [Ca(HCO₃)₂] are used as an at least one metal compound M, especially in the form of an aqueous suspension or solution. In a more preferred embodiment calcium hydroxide, especially in the form of an aqueous suspension, is used as the at least one metal compound M.

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The amount of metal compounds M is generally ≥ 10 and ≤ 50 mol% and preferably ≥ 30 and ≤ 45 mol%, based on amount of monomers A in polymer P.

The aqueous binder composition is prepared as such that in a first step an aqueous dispersion
20 of polymer P is prepared. In case the emulsion polymerization of the monomers A and B has not been carried out in the presence of the saccharide compound S, this compound is added to the aqueous dispersion of polymer P under homogenization at a temperature in the range ≥ 10 and $\leq 50^\circ\text{C}$ in a second step. To this mixture the metal compound M, preferably in the form of an aqueous suspension or solution, is added also under homogenization. To avoid
25 hydrolysis of the polymer P, the solids content of the aqueous suspension or solution of the metal compound M is preferably in the range ≥ 10 and ≤ 50 wt%, advantageously ≥ 20 and ≤ 40 wt% and/or the metal compound M is added slowly (preferably in a time period ≥ 15 and ≤ 120 minutes) to the aqueous mixture comprising polymer P and saccharide compound S.

30 It is essential that the aqueous binder composition of the present invention, in addition to polymer P, saccharide compound S and metal compound M, may additionally comprise still further components familiar to a person skilled in the art in terms of type and quantity, examples being thickeners, pigment dispersers, dispersants, emulsifiers, buffers, neutralizers, biocides, defoamers, polyol compounds having at least 2 hydroxyl groups and having a molecular weight
35 ≤ 200 g/mol, film formation auxiliaries, organic solvents, pigments or fillers etc..

Advantageously, however, the aqueous binder composition comprises ≤ 1 wt%, more advantageously ≤ 0.5 wt% of a polyol compound having at least 2 hydroxyl groups and having a molecular weight ≤ 200 g/mol, especially ≤ 150 g/mol, for example ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2,3-propanetriol, 1,2-butanediol, 1,4-butanediol, 1,2,3,4-butanetetrol, diethanolamine, triethanolamine, etc., based on the summed overall amounts of polymer P and saccharide compound S.

The binder compositions of the present invention are principally useful as binders in the production of adhesives, sealants, polymeric renders, papercoating slips, fiber nonwovens (fiber webs), and paints, and also in sand consolidation, as a component in the production of textile assistants or leather assistants, and impact modifiers, or for modifying mineral binders and plastics.

The aqueous binder compositions of the present invention are particularly suitable for use as binders for granular and/or fibrous substrates. Therefore, the aqueous binder compositions mentioned can be used with advantage in the production of shaped articles from granular and/or fibrous substrates.

Granular and/or fibrous substrates are familiar to a person skilled in the art. They are for example wood chips, wood fibers, cellulose fibers, textile fibers, polymeric fibers, glass fibers, mineral fibers or natural fibers such as jute, flax, hemp or sisal, but also cork chips or sand and also other organic or inorganic natural and/or synthetic granular and/or fibrous compounds whose longest dimension is ≤ 10 mm, preferably ≤ 5 mm and especially ≤ 2 mm in the case of granular substrates. As will be appreciated, the term substrate shall also comprehend the webs obtainable from fibers, for example so-called mechanically consolidated, for example needled or chemically prebonded fiber webs. It is especially advantageous that the aqueous binder composition of the present invention is useful as formaldehyde-free binder system for the aforementioned fibers and mechanically consolidated or chemically prebonded fiber webs.

The process for producing a shaped article from a granular and/or fibrous substrate and the aforementioned aqueous binder composition advantageously comprises applying the aqueous binder composition of the present invention to a granular and/or fibrous substrate (by impregnation), shaping the granular and/or fibrous substrate thus treated and then subjecting the resulting granular and/or fibrous substrate to a thermal treatment step at a temperature $\geq T_g^P$, preferably $T_g^P + \geq 50^\circ\text{C}$ and more preferably at a temperature $\geq 110^\circ\text{C}$, advantageously $\geq 130^\circ\text{C}$ and more advantageously $\geq 150^\circ\text{C}$, wherein the binder composition undergoes filming and curing. However, it is essential that a drying step has to be conducted after applying the

aqueous binder composition of the present invention to the granular and/or fibrous substrate, during the shaping step and/or thereafter and/or during the thermal treatment step.

It should be clear that the essential components of the aqueous binder composition, i.e., the aqueous dispersion of polymer P, the saccharide compound S, especially in the form of its solution or suspension, and the metal compound M, can be mixed homogeneously before the applying to the granular and/or fibrous substrate. But it is also possible to mix these three components only immediately before the applying, for example using a static and/or dynamic mixing device. It is self-evidently also possible first to apply the aqueous dispersion of polymer P premixed with the metal compound M and then the aqueous solution or suspension of saccharide compound S to the granular and/or fibrous substrate, in which case the mixing takes place on the granular and/or fibrous substrate. Similarly, however, it is also possible first to apply the aqueous solution or suspension of the saccharide compound S and then the aqueous dispersion of polymer P premixed with the metal compound M to the granular and/or fibrous substrate. It will be appreciated that hybrid forms of applying the three essential components should also be comprehended according to the present invention.

Impregnating the granular and/or fibrous substrate generally takes the form of the aqueous binder composition being applied uniformly to the surface of the fibrous and/or granular substrate. The amount of aqueous binder composition is chosen such that, per 100 g of granular and/or fibrous substrate, ≥ 1 and ≤ 100 g, preferably ≥ 2 and ≤ 50 g and more preferably ≥ 5 and ≤ 30 g of binder (reckoned as summed overall amounts of polymer P and saccharide compound S, on solids basis) are used. The actual method of impregnating the granular and/or fibrous substrate is familiar to a person skilled in the art and is effected by drenching or spraying the granular and/or fibrous substrate for example.

After impregnation, the granular and/or fibrous substrate is formed into a desired shape, for example by introduction into a press or mold. Thereafter, the shaped impregnated granular and/or fibrous substrate is dried and cured/filmed in a manner familiar to a person skilled in the art.

Drying and/or curing/filming of the shaped impregnated granular and/or fibrous substrate frequently takes place in two temperature stages, with a drying step being carried out at a temperature $< 100^{\circ}\text{C}$, preferably ≥ 20 and $\leq 90^{\circ}\text{C}$ and more preferably ≥ 40 and $\leq 80^{\circ}\text{C}$ and the curing/filming step at a temperature $\geq 110^{\circ}\text{C}$, preferably ≥ 130 and $\leq 150^{\circ}\text{C}$ and more preferably ≥ 180 and $\leq 220^{\circ}\text{C}$.

However, it is self-evidently also possible for the drying step and the curing/filming step of the shaped articles to take place in one operation, for example in a ventilated molding press.

The shaped articles obtainable by the process of the present invention have advantageous properties, more particularly an improved longitudinal breaking strength at room temperature and also distinctly lower extension at 180°C compared with the prior art shaped articles.

The aqueous binder compositions of the present invention are therefore particularly advantageous for production of fiber webs based on polyester and/or glass fiber, which in turn are particularly useful for production of bituminized roofing membranes.

The actual method of producing bituminized roofing membranes is familiar to a person skilled in the art and is more particularly effected by application of liquefied optionally modified bitumen to one and/or both of the sides of a polyester and/or glass fiber web bonded with a binder composition of the present invention.

Accordingly the specification comprise the following embodiments:

1. An aqueous binder composition comprising

a) at least one polymer P constructed from

≥ 5 and ≤ 25 wt% of at least one acid-functional ethylenically unsaturated monomer (monomers A), and

≥ 75 and ≤ 95 wt% of at least one other ethylenically unsaturated monomer (monomers B)

in polymerized form, wherein the amounts of monomers A and B sum to 100 wt%,

b) at least one saccharide compound S, the amount of which is determined such that it is ≥ 1 and ≤ 100 parts by weight per 100 parts by weight of polymer P, and

c) at least one metal compound M selected from the group comprising magnesium, calcium and zinc, in the form of an oxide, hydroxide, carbonate or bicarbonate, the amount of which is determined such that it is ≥ 10 and ≤ 50 mol% based on amount of monomers A in polymer P.

2. The aqueous binder composition according to embodiment 1 wherein the monomer A is selected from the group comprising acrylic acid, methacrylic acid, fumaric acid, maleic acid and vinylsulfonic acid and the monomer B is selected from the group comprising n-butyl acrylate, 2-ethylhexylacrylate, acrylonitrile, methacrylonitrile, methyl methacrylate and styrene.
3. The aqueous binder composition according to any one of embodiments 1 or 2 wherein the polymer P shows a glass transition temperature $T_g^P \geq -20$ and $\leq 50^\circ\text{C}$, determined by the DSC method according to DIN EN ISO 11357-2 (2013-05).
4. The aqueous binder composition according to any one of embodiments 1 to 3 wherein the polymer P is used in the form of an aqueous polymer dispersion.
5. The aqueous binder composition according to any one of embodiments 1 to 4 wherein the

≥ 10 and ≤ 20 wt%	of acrylic acid and/or methacrylic acid
≥ 70 and ≤ 90 wt%	of n-butyl acrylate and/or 2-ethylhexylacrylate, and
≥ 0 and ≤ 10 wt%	of vinylsulfonic acid, acrylonitrile, methacrylonitrile, methyl methacrylate and/or styrene.
6. The aqueous binder composition according to any one of embodiments 1 to 5 wherein the saccharide compound S is selected from a group comprising starch, cellulose, guaran, xanthan, alginate, pectin, chitosan, gum arabic, gellan and substitution products or derivatives thereof.
7. The aqueous binder composition according to any one of embodiments 1 to 6 wherein a starch, a starch derivative and/or a starch substitution product is used as saccharide compound S.
8. The aqueous binder composition according to any one of embodiments 1 to 7 wherein the at least one saccharide compound S has a weight average molecular weight ≥ 5000 and ≤ 25000 g/mol.
9. The aqueous binder composition according to any one of embodiments 1 to 8 wherein the monomers A and B were polymerized in the presence of the at least one saccharide compound S.

10. The aqueous binder composition according to any one of embodiments 1 to 9 wherein calcium hydroxide is used as metal compound M.
- 5 11. The aqueous binder composition according to any one of embodiments 1 to 10 wherein the amount of metal compounds M is ≥ 30 and ≤ 45 mol% based on amount of monomers A in polymer P.
- 10 12. The use of an aqueous binder composition according to any one of embodiments 1 to 11 as a binder in the production of adhesives, sealants, polymeric renders, papercoating slips, fiber nonwovens, and paints, and also in sand consolidation, as a component in the production of textile assistants or leather assistants, and impact modifiers, or for modifying mineral binders and plastics.
- 15 13. A process for producing a shaped article from granular and/or fibrous substrates wherein an aqueous binder composition according to any one of embodiments 1 to 11 is applied to the granular and/or fibrous substrate, the granular and/or fibrous substrate thus treated is shaped and then the granular and/or fibrous substrate thus obtained is subjected to a thermal treatment step at a temperature $\geq T_g^P$.
- 20 14. A shaped article obtainable by a process according to embodiment 13.
15. The use of a shaped article according to embodiment 14 for producing bituminized roofing membranes.

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The examples which follow illustrate the invention and are nonlimiting.

Examples

30 I Preparation of aqueous binder compositions

Comparative binder composition V1

In a 2 l glass flask fitted with a stirrer and 4 metering devices, 105 g of deionized water and
 35 5,5 g of a 33 wt% aqueous polystyrene seed dispersion (average particle diameter 32 nm) were initially charged at 20 to 25°C (room temperature) and under nitrogen and heated to 85°C under agitation. This was followed by the metered addition, commenced at the same time, of feed 1 in

the form of an aqueous emulsion over a period of 3 hours and feed 2 in the form of an aqueous solution over a period of 3 hours and 15 minutes at continuously constant flow rates while maintaining the aforementioned temperature.

5 Feed 1:

90.0 g of methacrylic acid

42.0 g of acrylonitrile

467.4 g of n-butyl acrylate

2.4 g of a 25 wt% aqueous solution of Na vinylsulfonate (Golpanol VS®;

10 sales product of BASF SE)

6.8 g of a 40 wt% aqueous solution of an alkylsulfonate (Emulgator K 30®;
sales product of Lanxess AG)

303.4 g of deionized water

15 Feed 2:

58.3 g of a 7wt% aqueous solution of sodium persulfate

The polymerization mixture was subsequently allowed to undergo secondary polymerization at 85°C for 30 minutes and cooled down to 50°C. Then feed 3 and feed 4 were started and

20 metered within 1 hour.

Feed 3:

12.0 g of a 10 wt% aqueous solution of tert-butylhydroperoxide

25 Feed 4:

15.6 g of a 13.1 wt% aqueous solution of sodium acetone bisulfite

The reaction batch was cooled down to room temperature. The number average particle diameter determined was 180 nm and the glass transition temperature T_g^P measured was
30 +3°C. Then 180 g of a 20 wt% aqueous suspension of calcium hydroxide were added to the batch under stirring. The resulting pH value measured was 7.5. By adding deionized water the solids content was adjusted to 45% by weight based on the total weight of the aqueous composition.

35 Solids contents were generally determined by drying a defined amount of the aqueous polymer dispersion or the aqueous binder composition (about 0.8 g) using the HR73 moisture determinator from Mettler Toledo at a temperature of 130°C to constant weight (about 2 hours).

Two measurements were carried out in each case. The value reported in each case is the average value of these measurements.

Number average particle diameters for the polymer particles were generally determined by dynamic light scattering on a 0.005 to 0.01 weight percent aqueous polymer dispersion at 23°C using an Autosizer IIC from Malvern Instruments, England. The reported value is the (cumulant z average) of the measured autocorrelation function (ISO standard 13321).

Glass transition temperatures were generally determined by the DSC method according to DIN EN ISO 11357-2 (2013-05) using an Differentialkalorimeter Q 2000 from TA Instruments applying a heating rate of 20 K/min.

pH values of the aqueous dispersions or binder compositions were generally determined by using a Portamess 911 pH-meter from Knick Elektronische Messgeräte GmbH & Co.KG.

Comparative binder composition V2

The preparation of comparative binder composition V1 was repeated except that after the polymerization reaction no suspension of calcium hydroxide was added.

The number average particle diameter measured was 178 nm. The resulting pH value measured was 2.5. By adding a 10 wt% aqueous solution of sodium hydroxide the pH was adjusted to 7.5. Thereafter, the solids content of the aqueous polymer dispersion was adjusted to 45% by weight by adding deionized water.

Comparative binder composition V3

The preparation of comparative binder composition V1 was repeated except that after the polymerization reaction 360 g of a 50 wt% aqueous solution of a maltodextrine (Roclys® C1967S; weight average molecular weight of 11.200 g/mol; DE-value: 19) were added instead of the calcium hydroxide suspension.

The number average particle diameter measured was 182 nm. The resulting pH value measured was 3.0. By adding a 10 wt% aqueous solution of sodium hydroxide the pH was adjusted to 7.5. Thereafter, the solids content of the aqueous polymer dispersion was adjusted to 45% by weight by adding deionized water.

Inventive binder composition KM

The preparation of comparative binder composition V1 was repeated except that after the addition of calcium hydroxide further 360 g of a 50 wt% aqueous solution of the aforementioned maltodextrine (Roclys® C1967S) were added before adjusting the solids content of the binder composition to 45% by weight.

Inventive binder composition KG1

10 The preparation of comparative binder composition V1 was repeated except that 120 g of a 50 wt% aqueous solution of the aforementioned maltodextrine (Roclys® C1967S) were additionally charged in the glass flask before heating and carrying out the polymerization reaction.

15 The number average particle diameter measured was 230 nm and the pH value measured was 7.4.

The aqueous binder composition obtained such was also adjusted to a solids content of 45% by weight by adding deionized water.

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Inventive binder composition KG2

The preparation of comparative polymer dispersion V1 was repeated except that 240 g of a 50 wt% aqueous solution of the aforementioned maltodextrine (Roclys® C1967S) were additionally charged in the glass flask before heating and carrying out the polymerization reaction.

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The particle size distribution obtained was very broad (range from 400 to 700 nm). The pH value measured was 7.6.

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The aqueous polymer dispersion obtained such was also adjusted to a solids content of 45% by weight by adding deionized water.

Inventive binder composition KG3

The preparation of comparative polymer dispersion V1 was repeated except that 360 g of a 50 wt% aqueous solution of the aforementioned maltodextrine (Roclys® C1967S) were additionally charged in the glass flask before heating and carrying out the polymerization reaction.

The particle size distribution obtained was very broad (range from 200 to 700 nm). The pH value measured was 7.4.

The aqueous polymer dispersion obtained such was also adjusted to a solids content of 45% by weight by adding deionized water.

Comparative binder composition V4

The preparation of inventive binder composition KG3 was repeated except that after the polymerization reaction no suspension of calcium hydroxide was added.

The particle size distribution obtained was very broad (range from 200 to 700 nm). The resulting pH value measured was 3.0.

By adding a 10 wt% aqueous solution of sodium hydroxide the pH was adjusted to 7.5. Thereafter, the solids content of the aqueous polymer dispersion was adjusted to 45% by weight by adding deionized water.

II Performance testing

Production of impregnating liquors

The impregnating liquors were produced from the inventive binder composition KM, KG1 to KG3 and also the comparative binder composition V1 to V4 by adjusting these compositions to a solids content of 14% by weight by diluting with deionized water.

The corresponding impregnating liquors obtained are signified as impregnating liquors FKM, FKG1 to FKG3 and FV1 to FV4.

Production of bonded fiber webs

Bonded fiber webs were produced using as raw web a needled polyethylene terephthalate spunbonded (40 cm length, 37 cm width) having a density of 165 g/m² from Freudenberg-Politex.

The bonded fiber webs were produced by saturating the raw web with the respective impregnating liquors FKM, FKG1 to FKG3 and FV1 to FV4 in the longitudinal direction in an HVF impregnating rig with pad-mangle from Mathis (rubber roll Shore A = 85° /steel roll). In each case, the wet pick-up was adjusted to 34.9 g of impregnating liquor (corresponding to a solids content of 4.9 g). The impregnated fiber webs obtained were subsequently dried and cured in an LTV laboratory dryer with needle frame from Mathis (in circulating air operation). To this end, the impregnated fiber webs were each placed on an open needle frame, fixed by folding shut and then cured in the laboratory dryer at 200°C for 3 minutes. The bonded fiber webs obtained in the process are signified as fiber webs FKM, FKG1 to FKG3 and FV1 to FV4, depending on the impregnating liquors used.

Determination of breaking strength in longitudinal direction

Breaking strength in longitudinal direction was determined for fiber webs FKM, FKG1 to FKG3 and FV1 to FV4 at room temperature in accordance with DIN 52123 using a breaking machine from Frank (model 71565). To this end, 270 x 50 mm strips (longitudinal direction) were die-cut out of fiber webs FKM, FKG1 to FKG3 and FV1 to FV4 in the longitudinal direction and clamped with a length of 200 mm into the pulling device. In each case, 5 separate measurements were carried out. The measurements in N/50 mm which are reported in table 1 represent the respective averages of these measurements. The higher the measured values obtained, the better the breaking strength in the longitudinal direction.

Determination of heat resistance

The heat resistance of fiber webs FKM, FKG1 to FKG3 and FV1 to FV4 was determined by extension measurements using a breaking machine from Zwick (model Z10) with integrated heating chamber. To this end, 50 x 210 mm strips (longitudinal direction) were die-cut out of fiber webs FKM, FKG1 to FKG3 and FV1 to FV4 in the longitudinal direction and clamped with a length of 100 mm into the pulling device. After introduction to the heating chamber, the test strips were each heated at 180°C for 60 minutes and thereafter extended at this temperature with increasing tensile force at an extension rate of 150 mm/min. The extension of the test strips

in percent was determined on reaching a tensile force of 40 N/ 50 mm. The lower the extension values obtained, the better the heat resistance. In each case, 5 separate measurements were carried out. The values likewise reported in table represent the averages of these measurements.

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Table 1: Results for breaking strength in transverse direction and heat resistance of fiber webs FKM, FKG1 to FKG3 and FV1 to FV4

10	Fiber web	longitudinal breaking strength	Extension at
		at room temperature	40 N/50 mm and 180°C
		[in N/50 mm]	[in %]
	FV1	342	11.3
	FV2	337	14.2
	FV3	339	13.7
15	FKG1	352	9.2
	FKG2	357	8.1
	FKG3	383	8.6
	FKM	363	9.5
	FV4	335	12.8

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It is clearly apparent from the results that the fiber webs produced with the inventive binder compositions have improved longitudinal breaking strength at room temperature and lower extension at 180°C.

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Claims:

1. An aqueous binder composition comprising
 - 5 a) at least one polymer P constructed from

≥ 5 and ≤ 25 wt%	of at least one acid-functional ethylenically unsaturated monomer (monomers A), and
≥ 75 and ≤ 95 wt%	of at least one other ethylenically unsaturated monomer (monomers B)
 - 10 in polymerized form, wherein the amounts of monomers A and B sum to 100 wt%,
 - b) at least one saccharide compound S, the amount of which is determined such that it
 - 15 is ≥ 1 and ≤ 100 parts by weight per 100 parts by weight of polymer P, and
 - c) at least one metal compound M selected from the group comprising magnesium, calcium and zinc, in the form of an oxide, hydroxide, carbonate or bicarbonate, the amount of which is determined such that it is ≥ 10 and ≤ 50 mol% based on amount of
 - 20 monomers A in polymer P.
2. The aqueous binder composition according to claim 1 wherein the monomer A is selected from the group comprising acrylic acid, methacrylic acid, fumaric acid, maleic acid and vinylsulfonic acid and the monomer B is selected from the group comprising n-butyl
 - 25 acrylate, 2-ethylhexylacrylate, acrylonitrile, methacrylonitrile, methyl methacrylate and styrene.
3. The aqueous binder composition according to any one of claims 1 or 2 wherein the polymer P shows a glass transition temperature $T_g^P \geq -20$ and $\leq 50^\circ\text{C}$, determined by the
 - 30 DSC method according to DIN EN ISO 11357-2 (2013-05).
4. The aqueous binder composition according to any one of claims 1 to 3 wherein the polymer P is used in the form of an aqueous polymer dispersion.

5. The aqueous binder composition according to any one of claims 1 to 4 wherein the polymer P is constructed from

≥ 10 and ≤ 20 wt% ≥ 70 and ≤ 90 wt% ≥ 0 and ≤ 10 wt%	of acrylic acid and/or methacrylic acid of n-butyl acrylate and/or 2-ethylhexylacrylate, and of vinylsulfonic acid, acrylonitrile, methacrylonitrile, methyl methacrylate and/or styrene.
--	---
6. The aqueous binder composition according to any one of claims 1 to 5 wherein the saccharide compound S is selected from a group comprising starch, cellulose, guaran, xanthan, alginate, pectin, chitosan, gum arabic, gellan and substitution products or derivatives thereof.
7. The aqueous binder composition according to any one of claims 1 to 6 wherein a starch, a starch derivative and/or a starch substitution product is used as saccharide compound S.
8. The aqueous binder composition according to any one of claims 1 to 7 wherein the at least one saccharide compound S has a weight average molecular weight ≥ 5000 and ≤ 25000 g/mol.
9. The aqueous binder composition according to any one of claims 1 to 8 wherein the monomers A and B were polymerized in the presence of the at least one saccharide compound S.
10. The aqueous binder composition according to any one of claims 1 to 9 wherein calcium hydroxide is used as metal compound M.
11. The aqueous binder composition according to any one of claims 1 to 10 wherein the amount of metal compounds M is ≥ 30 and ≤ 45 mol% based on amount of monomers A in polymer P.
12. The use of an aqueous binder composition according to any one of claims 1 to 11 as a binder in the production of adhesives, sealants, polymeric renders, papercoating slips, fiber nonwovens, and paints, and also in sand consolidation, as a component in the production of textile assistants or leather assistants, and impact modifiers, or for modifying mineral binders and plastics.

13. A process for producing a shaped article from granular and/or fibrous substrates wherein an aqueous binder composition according to any one of claims 1 to 11 is applied to the granular and/or fibrous substrate, the granular and/or fibrous substrate thus treated is shaped and then the granular and/or fibrous substrate thus obtained is subjected to a thermal treatment step at a temperature $\geq T_g^P$.
14. A shaped article obtainable by a process according to claim 13.
15. The use of a shaped article according to claim 14 for producing bituminized roofing membranes.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/060897

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J133/08 B32B5/00 C09J133/00 C09J133/14 D04H1/64
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J C08K B32B D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2017/210895 A1 (CENTNER ALEXANDER [DE] ET AL) 27 July 2017 (2017-07-27) paragraphs [0001], [0027], [0044] - [0058], [0099], [0127], [0134] - [0143], [0198] - [0206] Inventive example 2; paragraphs [0227] - [0234]; tables 1-2	1-15
A	Omya Construction: "Extra -GU Excellent Optics and Dispersibility with ChameleoBoost(TM) Technology Omya Construction", 1 February 2019 (2019-02-01), XP055710837, Retrieved from the Internet: URL:https://www.omya.com/Documents/Constru ction/CON_FLY_Omyacarb.pdf [retrieved on 2020-07-01] page 1	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017210895 A1	27-07-2017	CN 106536572 A	22-03-2017
		EP 3166978 A1	17-05-2017
		ES 2680818 T3	11-09-2018
		PL 3166978 T3	31-10-2018
		US 2017210895 A1	27-07-2017
		WO 2016005468 A1	14-01-2016
