

## Emulsion adhesives

The present invention relates to aqueous, polyvinyl ester-based emulsion adhesives having a practical pot life, films of which have increased water resistance, to  
5 the preparation of these emulsion adhesives, and to their use for bonding porous and semiporous substrates.

Aqueous emulsions of polyvinyl esters, in particular of polyvinyl acetate, are used for gluing wood and other porous substrates. The chemistry of these adhesives,  
10 which are produced in large industrial volumes, has long been the subject-matter of patent publications and has been described in specialist publications, for example in Wood Adhesives - Chemistry and Technology, Volume 1, chapter 7, Marcel Dekker, New York, 1983.

15 A subgroup of polyvinyl ester emulsions is formed by those having increased water resistance of their films. The sensitivity of polyvinyl ester-based adhesive bonds to water is due predominantly to the presence of hydrophilic stabilizers, in particular of polyvinyl alcohol,  
20 which are usually used in the production of the adhesive emulsion. One way of achieving an improvement in the water resistance is therefore, for example, to reduce the hydrophilicity of the adhesive by crosslinking the polyvinyl alcohol by means of reactive compounds.

25 Thus, DE-B 22 61 402 states that a polyvinyl ester emulsion to which a crosslinking-inducing resin, for example a urea-formaldehyde resin, is admixed gives water-resistant adhesive bonds in combination with a free organic or inorganic acid or an acidic metal salt.

30 Another method, which has been known for some time, of reducing the hydrophilicity of the adhesive is to copolymerize vinyl esters in the presence of monomers which can be crosslinked with polyvinyl alcohol, such as

N-methylol(meth)acrylamide. A method of this type is described, for example, in US-A 3,301,809. Combination with acidic curing agents, for example organic acids or acidic ammonium salts, gives water-resistant adhesives.

- 5 As curing agents for crosslinkable, polyvinyl alcohol-stabilized polyvinyl acetate adhesive emulsions, US-A 3,563,851 proposes, in particular, the acidic salts of Al(III) and of Cr(III).

- 10 The specifications DE-C 26 20 738 and DE-A 39 42 628 likewise relate to adhesive systems based on copolymers of vinyl esters with crosslinkable comonomers including N-methylolacrylamide, which crosslink with acidic catalysis. These adhesives likewise require the use of strong water-soluble acids or metal salts thereof, in particular  
15 salts of Cr(III), Al(III), Fe(III) and Zr(IV). According to DE-A 39 42 628, the achievement of adhesive bonds which are resistant to hot water, in accordance with the BS EN 204 test standard, strength group D4 (formerly DIN 68602 B4), additionally requires the copolymerization  
20 of highly branched vinyl carboxylates if acidic aluminum salts are used as curing agents.

- By contrast to these adhesive systems which crosslink catalyzed exclusively by acidic curing agents, it is also known subsequently to add to the emulsions various  
25 additives which increase the water resistance of adhesive bonds produced using these emulsions. The effect of these additives is due to crosslinking reactions involving the polyvinyl alcohol.

- One group of these additives is formed by hydrophobic,  
30 aliphatic or aromatic polyisocyanates. US-A 3,931,088 mentions the addition of polyfunctional isocyanate compounds, for example toluidene diisocyanate, to aqueous adhesive emulsions containing polyvinyl alcohol. These compounds are added in solvents.

As a further development, EP-A 0 206 059 describes a water-dispersible polyisocyanate preparation in which some of the isocyanate groups are masked by emulsifiers. The addition of this product to polyvinyl acetate emulsions gives adhesive bonds which are resistant to hot water and are classified in BS EN 204 strength group D4.

A further group of additives which improve the water resistance of emulsion adhesives is formed by polyfunctional aldehydes.

10 In US-A 3,932,335, polyvinyl ester emulsions which give water-resistant adhesive bonds are obtained by adding glyoxal in combination with water-soluble polyols.

EP-A 0 191 460 describes polyvinyl alcohol-stabilized polyvinyl acetate emulsions which are crosslinked with glutaraldehyde and give films which are resistant to boiling water for at least 30 minutes.

The abovementioned curing agent systems have some disadvantages for the user. The use of acidic curing agents results in a drop in viscosity of the emulsions, in particular when relatively large amounts are used. In addition, relatively large amounts of these additives, in particular in the case of chromium and aluminum salts, cause an undesired increase in the powder point of the emulsions and a drop in the short-term bonding strength.

25 Any acidic salt solution admixed separately can cause corrosion in the application equipment. In addition, the aqueous solutions of the salts represent hazardous materials during application due to their irritant action. The blue-green adhesive joint formed on use of chromium(III) salts, which are furthermore toxic, adversely affects the visual impression of glued articles, in particular in the case of pale wood types.

The use of urea-formaldehyde resins as described in

DE-B 22 61 402 results in gradual liberation of formaldehyde from the adhesive. Use of the crosslinking polyisocyanates as described in EP-A 0 206 059 results in gradual, undesired foaming of the preparations during application caused by released carbon dioxide (comparative examples V1, V2 and V3, Table 1).

Some of the emulsion adhesives prepared as described in EP-A 0 191 460 with addition of polyaldehydes satisfy the existing demands, but, with the systems whose adhesive bonds have high water resistance, cannot simultaneously achieve the requisite practical pot lives of at least 8 hours. In addition, systems of this type form a strong odor nuisance due to the high content of free polyaldehyde (comparative example V4, Table 1).

Accordingly, it is an object of the present invention to provide a polyvinyl ester emulsion for adhesives which has improved adhesive properties and practical pot lives and enables the production of adhesive bonds having increased water resistance over comparable systems without having the disadvantages of known adhesives.

It has now been found that this object can be achieved by an aqueous polyvinyl ester emulsion which, in addition to polymeric protective colloids, contains water-soluble compounds which can be complexed with the protective colloids and contains derivatives of polyaldehydes from which aldehyde groups can be liberated under acidic conditions.

The present invention thus relates to an aqueous emulsion adhesive having a pH of from 2 to 6, comprising homo- or copolymeric polyvinyl esters, polymeric protective colloids, water-soluble compounds which can be complexed with the polymeric protective colloids, and at least partially masked polyaldehydes preferably having at least

three carbon atoms, from which aldehyde groups can be liberated in a controlled manner in acidic media.

Suitable emulsion polymers employed as the polymer base in the novel emulsion adhesives are homo- or copolymeric polyvinyl esters.

Suitable monomers for these homo- or copolymeric polyvinyl esters are vinyl formate, vinyl acetate, vinyl propionate, vinyl isobutyrate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl esters of saturated, branched monocarboxylic acids having 9 to 10 carbon atoms in the acid radical, vinyl esters of relatively long-chain, saturated or unsaturated fatty acids, such as, for example, vinyl laurate, vinyl stearate and vinyl esters of benzoic acid and substituted derivatives of benzoic acid, such as vinyl p-tert-butylbenzoate. Of these, however, vinyl acetate is particularly preferred. Said vinyl esters can also be present alongside one another in the polyvinyl ester. The proportion of these vinyl esters in the polymer is at least 50% by weight, preferably at least 75% by weight.

Other ethylenically unsaturated monomers which can be copolymerized with vinyl esters are  $\alpha,\beta$ -unsaturated acids, for example acrylic acid, methacrylic acid, and esters thereof with primary and secondary, saturated, monohydric alcohols having 1 to 18 carbon atoms, for example methanol, ethanol, propanol, butanol, 2-ethylhexyl alcohol, cycloaliphatic alcohols and relatively long-chain fatty alcohols. It is also possible to use  $\alpha,\beta$ -unsaturated dicarboxylic acids, for example maleic acid, fumaric acid, itaconic acid or citraconic acid, and mono- or diesters thereof with saturated, monohydric, aliphatic alcohols having 1 to 18 carbon atoms. The proportion of these comonomers of the total amount of monomers is up to 25% by weight, preferably 0.1 to 15% by weight.

- Other suitable comonomers are ethylenically unsaturated hydrocarbons, such as ethylene or  $\alpha$ -olefins having 3-18 carbon atoms, for example propylene, butylene, furthermore styrene, vinyltoluene, vinylxylene and halogenated, unsaturated, aliphatic hydrocarbons, for example vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride. The proportion of these comonomers of the total amount of monomers is up to 50% by weight, preferably 1 to 25% by weight.
- 10 The polymer can also contain polyethylenically unsaturated monomers, for example diallyl phthalate, diallyl maleate, triallyl cyanurate, tetraallyloxyethane, divinylbenzene, butanediol 1,4-dimethacrylate, triethylene glycol dimethacrylate, divinyl adipate, allyl (meth)acrylate, vinyl crotonate, methylenebisacrylamide, hexanediol diacrylate, pentaerythritol diacrylate and trimethylolpropane triacrylate. The proportion of these comonomers of the total amount of monomers is up to 10% by weight, preferably 0.01 to 2% by weight.
- 20 Particularly suitable comonomers are those containing N-functional groups, including, in particular, (meth)-arylamide, allyl carbamate, acrylonitrile, N-methylol(meth)acrylamide, N-methylolallyl carbamate and the N-methylol esters, alkyl ethers and Mannich bases of N-methylol(meth)acrylamide and N-methylolallyl carbamate, acrylamidoglycolic acid, methyl acrylamidomethoxyacetate, N-(2,2-dimethoxy-1-hydroxyethyl)acrylamide, N-dimethylaminopropyl(meth)acrylamide, N-methyl(meth)acrylamide, N-butyl(meth)acrylamide, N-cyclohexyl(meth)acrylamide, N-dodecyl(meth)acrylamide, N-benzyl(meth)acrylamide, p-hydroxyphenyl(meth)acrylamide, N-(3-hydroxy-2,2-dimethylpropyl)methacrylamide, ethylimidazolidone methacrylate, N-vinylformamide, N-vinylpyrrolidone. The proportion of these comonomers of the total amount of monomers is up to 15% by weight, preferably 0.1 to 10% by weight.

Other particularly suitable comonomers which, owing to their functional groups, can improve the adhesive properties and the water resistance of the emulsion in combination with derivatives of polyaldehydes are hydroxy-  
5 functional monomers, such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and adducts thereof with ethylene oxide or propylene oxide. The proportion of these comonomers of the total amount of monomers is up to 25% by weight, preferably 0.1 to 15% by weight.

10 Also particularly suitable are comonomers which are crosslinkable or self-crosslinking via carbonyl groups, from the group consisting of diacetoneacrylamide, allyl acetoacetate, vinyl acetoacetate and acetoacetoxyethyl (meth)acrylate. The proportion of these comonomers of the  
15 total amount of monomers is up to 10% by weight, preferably 0.01 to 5% by weight.

The proportion of comonomer units present in the polymer in addition to the vinyl ester units totals up to 50% by weight.

20 In addition to the homo- or copolymeric polyvinyl ester, the novel adhesive emulsions contain polymeric protective colloids. An example of a suitable compound is polyvinyl alcohol, in particular polyvinyl alcohol having a degree of hydrolysis of 60-100 mol%, preferably from 70 to  
25 98 mol%, and a viscosity of from 2 to 70 mPa·s for a 4% strength by weight aqueous solution at 20°C. It is also permissible to use products of the reaction of polyvinyl alcohol with diketene or copolymeric, carboxyl-carrying types of polyvinyl alcohols. The protective colloids can  
30 furthermore be etherified cellulose derivatives, for example hydroxyethylcellulose or carboxymethylcellulose. These can be used either alone or in combination with polyvinyl alcohol. Also suitable are polyvinylpyrrolidone, polycarboxylic acids, such as  
35 polyacrylic acid, and copolymers of maleic acid or of

maleic anhydride with ethylenically unsaturated compounds, such as methyl vinyl ether or styrene. Based on the solids content, the proportion of polymeric protective colloids is preferably from 1 to 20% by weight, in particular from 2 to 10% by weight.

In addition to the polymeric protective colloids, up to 2% by weight, based on the polymer, of nonionic and/or ionic emulsifiers can also be used in the polymerization liquor.

10 The term at least partially masked polyaldehydes, i.e. compounds containing at least two aldehyde groups from which aldehyde groups are liberated in aqueous acidic media, is taken to mean compounds which preferably undergo controlled hydrolysis at a pH of from 2 to 6, in particular from 2.5 to 4, liberating an adjustable amount of aldehyde groups per time unit. In these derivatives of polyaldehydes, at least some of the aldehyde groups, preferably all of the aldehyde groups, are initially blocked. Particularly preferred derivatives of polyaldehydes are their bisulfite adducts. The counterions in these bisulfite adducts are preferably lithium, sodium, potassium, magnesium, calcium, aluminum, ammonium or substituted ammonium ions.

25 Examples of suitable bisulfite adducts are those of malonic dialdehyde, propanonedial (mesoxalic dialdehyde), succinic dialdehyde, butanonedial, glutaric dialdehyde, adipaldehyde,  $\beta$ -methylglutaric dialdehyde, pimelic dialdehyde, suberic dialdehyde, maleic dialdehyde, fumaric dialdehyde, sebacic dialdehyde, malic dialdehyde, 30 phthalic dialdehyde, isophthalic dialdehyde, terephthalic dialdehyde and ring-substituted derivatives of these compounds.

Particularly suitable are bisulfite adducts of aliphatic dialdehydes having at least 3 carbon atoms. Of these,

glutaric dialdehyde/bisalkali metal bisulfites are particularly preferred.

5 Other derivatives of at least bifunctional aldehydes which are suitable according to the invention are open-chain acetals thereof with aliphatic ( $C_1-C_{20}$ )-, preferably ( $C_1-C_{12}$ )-monoalcohols, in particular methanol and ethanol, and cyclic acetals thereof with at least bifunctional alcohols, preferably ethylene glycol, 1,2-propylene glycol and 1,3-propylene glycol.

10 Specific mention may be made by way of example of chloro-malonic dialdehyde bisdiethyl acetal, succinic dialdehyde mono- and bisdimethyl acetal, succinic dialdehyde bisdiethyl acetal, 2-bromosuccinic dialdehyde bisdimethyl acetal, oximinosuccinic dialdehyde bisdimethyl acetal and  
15 the bisdimethyl and bisdiethyl acetals of maleic dialdehyde.

This group furthermore includes the intramolecular cyclic acetals of succinic dialdehyde, maleic dialdehyde and glutaric dialdehyde and more highly ring-substituted  
20 derivatives thereof such as 2,5-dimethoxytetrahydrofuran, 2,5-diethoxytetrahydrofuran, 2,5-dihydro-2,5-dimethoxyfuran, 2,5-dihydro-2,5-diethoxyfuran, 3-formyl-2,5-dimethoxytetrahydrofuran, 2,6-dimethoxytetrahydro-2H-pyran and 2,6-diethoxytetrahydro-2H-pyran. Particularly  
25 suitable compounds in this group are the open-chain bisdimethyl and bisdiethyl acetals of malonic dialdehyde and glutaric dialdehyde and the cyclic acetals of succinic dialdehyde.

Other suitable derivatives of polyaldehydes are the enol  
30 ethers, enol esters, acylates and mixed acylate ethers of polyfunctional aldehydes. These also include compounds containing aldehyde groups which, for constitutional reasons, are predominantly in the enol form, for example oxypyruvic aldehyde (reduction). These, and products of

the reaction of enols, in which the remaining aldehyde groups not in the enol form can furthermore be masked, are likewise suitable derivatives.

Other polyaldehyde derivatives which are suitable according to the invention are the cleavable products of the reaction of the polyaldehydes with nitrogen compounds. These derivatives include the oximes, oxime esters, oxime ethers, imines (Schiff bases), enamines, amins, hydrazones, semicarbazones,  $\alpha,\alpha$ -diurethanes and enamine urethanes of polyfunctional aldehydes.

Specific mention may be made by way of example of glutaric dialdehyde dioxime, phthalic dialdehyde mono- and dioxime, phthalic dialdehyde oxime semicarbazone, isophthalic aldoxime, terephthalic aldoxime, terephthalic aldehyde dihydrazone, and the anils of malonic dialdehyde, succinic dialdehyde and glutaric dialdehyde.

Naturally, mixed forms between the masking possibilities mentioned here are also permissible for the purposes of the invention.

The amount of the polyaldehyde derivatives used is from 0.001 to 10% by weight, based on the solids content of the adhesive emulsion, and depends on the nature of the derivatives employed and on the composition of the emulsion. The preferred range is from 0.01 to 5% by weight, in particular from 0.1 to 2% by weight, based on the solids content of the adhesive emulsion.

The compounds which can be complexed with the polymeric protective colloids are preferably salts, in particular acidic salts with polyvalent complexible cations, as mentioned, for example, in DE-B 22 61 402, DE-C 26 20 738 and DE-A 39 42 628. Preference is given to the water-soluble metal salts of Al(III) or Zr(IV), in particular aluminum chloride, aluminum nitrate and zirconium

oxychloride. Other compounds which are suitable for complexing with the polymeric protective colloids are acids and salts with oxo anions, preferably oxo anions which are capable of binding polyanions, for example borates and phosphates. Free boric acid and phosphoric acid are particularly suitable. The proportion of compounds which can be complexed with the protective colloids preferably amounts to 0.1 to 20% by weight, in particular to 0.5 to 10% by weight, relative to the weight of the adhesive emulsion.

The adhesive emulsion may contain further conventional additives, for example film-formation aids for reducing the MFT, plasticizers, antifoams, fillers and preservatives.

The solids content of the novel adhesive emulsion is preferably from 20 to 65% by weight, in particular from 30 to 60% by weight.

The adhesive emulsion has an acidic pH in a range in which the novel polyaldehyde derivatives are slowly hydrolyzed and the aldehyde groups are liberated in a controlled manner. This pH range is preferably from 2 to 6, in particular from 2.5 to 4. A suitable pH can already be achieved after emulsion polymerization of the homo- or copolymeric vinyl esters or can be established subsequently by addition of acidic compounds.

In order to establish the pH in the desired acidic range, organic or inorganic Lewis and Brønsted acids are suitable. Preferred Brønsted acids have a  $pK_a$  value of  $<2.5$ , for example hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, p-toluenesulfonic acid, in particular phosphoric acid. Particularly suitable Lewis acids are the acidic salts of complexible metal ions, in particular aluminum chloride, aluminum nitrate and zirconium oxychloride.

The present invention also relates to a process for the preparation of the novel emulsion adhesive. To this end, a homo- or copolymeric polyvinyl ester emulsion containing the polymeric protective colloids and, if  
5 desired, emulsifiers is preferably first prepared.

The polyvinyl ester emulsion is prepared by the conventional continuous or batch procedure of free-radical emulsion polymerization, using water-soluble and/or oil-soluble initiator systems, such as peroxodisulfates, azo  
10 compounds, hydrogen peroxide, organic hydroperoxides or dibenzoyl peroxide. These can be used either alone or in combination with reducing compounds, such as Fe(II) salts, sodium pyrosulfite, sodium bisulfite, sodium sulfite, sodium dithionite, sodium formaldehyde  
15 sulfoxylate, or ascorbic acid as redox catalyst system.

The polymeric protective colloids and emulsifiers can be added before, during or after the polymerization. The compounds which can be complexed with the polymeric protective colloids and the polyaldehyde derivatives are  
20 then added to this emulsion and, if necessary, the pH is adjusted to the requisite range by addition of Lewis or Brønsted acid.

It is particularly preferred that the polyvinyl ester emulsion containing the polymeric protective colloids is  
25 first preformulated with the complexible compounds, preferably acidic metal salts or salts or acids of oxo anions, in particular aluminum chloride, aluminum nitrate or zirconium oxychloride, or phosphoric acid or boric acid and only finally, as a two-component system, mixed  
30 with the polyaldehyde derivatives.

These components can be added to the polyester emulsion either by dissolving the pure compounds in the emulsion or by adding a solution in a suitable solvent, for example aliphatic alcohols, or an aqueous solution. The

addition is preferably carried out in the form of a concentrated aqueous solution in order to minimize the drop in viscosity of the adhesive emulsion. The compounds glutaric dialdehyde bis-sodium bisulfite and glutaric  
5 dialdehyde bis-potassium bisulfite which are particularly preferred as polyaldehyde derivatives can, for example, be added in the form of an approximately 20% strength by weight aqueous solution.

An undesired drop in viscosity of the emulsion after  
10 addition of an aqueous solution of the polyaldehyde derivatives can advantageously be prevented by first mixing the aqueous solution with additives which increase the viscosity of this solution. These can be, in particular, polymeric protective colloids, preferably polyvinyl  
15 alcohol, polyvinylpyrrolidone or etherified cellulose derivatives, for example hydroxyethyl cellulose or carboxymethyl cellulose. The solution is incorporated into the emulsion using conventional equipment, for example paddle or anchor stirrers.

20 In the process according to the invention, it is also permissible to preformulate the polyvinyl ester emulsion with the polyaldehyde derivatives. To this end, a homo- or copolymeric polyvinyl ester emulsion is first prepared in the presence of polymeric protective colloids, and  
25 first at least partially masked polyaldehydes and subsequently complexible metal salts or acids are added thereto at a pH above 4. In this case, the emulsion should as far as possible have a neutral pH, preferably above 5, in particular above 6, at which the polyaldehyde  
30 derivatives remain stable. For this purpose, the pH of the emulsion can also subsequently be increased to the required value by addition of conventional neutralizers. The system is then preferably activated in a two-component system by addition of suitable amounts of an acidic  
35 complexible compound, in particular an aqueous solution

of aluminum chloride, aluminum nitrate, zirconium oxychloride or phosphoric acid.

A further embodiment of this process in which the polyvinyl ester emulsion is preformulated with the polyaldehyde derivatives comprises forming the polyfunctional aldehyde bisulfite adducts which are particularly preferred in accordance with the invention in situ in the adhesive emulsion. To this end, first a homo- or copolymeric polyvinyl ester emulsion is prepared in the presence of polymeric protective colloids, and polyfunctional aldehydes and compounds which supply bisulfite ions in aqueous systems, and subsequently complexible metal salts or acids are added at a pH above 5.

The emulsion has a pH range which is suitable for the formation of bisulfite adducts, established either before or after addition of the salts supplying bisulfite ions by means of conventional neutralizers, for example dilute sodium hydroxide solution. In this case, the pH should be above 5, in particular above 6. Suitable compounds which supply bisulfite ions in aqueous systems are salts such as alkali metal bisulfites, alkali metal sulfites and alkali metal pyrosulfites. The corresponding sodium salts are particularly preferred. The polyfunctional aldehyde is then added to this emulsion either as such or in the form of a preferably aqueous solution and is distributed uniformly in the emulsion by means of conventional stirrers. The degree of masking of the polyfunctional aldehyde can be adjusted by selection of the ratio between the amounts of bisulfite and the aldehyde groups present. An at least stoichiometric ratio between bisulfite ions on the one hand and the aldehyde groups present on the other hand should preferably be established. The amount of added salt is advantageously such that a small excess of at least 0.1 equivalent of bisulfite per aldehyde group is present.

Also permissible is a variant of the above-described procedure in which first the polyfunctional aldehyde is introduced into the emulsion, whose pH can already have been increased to a pH above 5, and converted in the aqueous phase of the emulsion into the products masked in accordance with the invention by addition of the above-described salts which supply bisulfite ions after dissociation.

In both cases, the system is activated by means of the above-described acidic, complexible compounds.

The novel adhesive emulsions have pot lives of at least 8 hours, preferably at least 16 hours, in particular at least 24 hours. Adhesive bonds made from the novel emulsion adhesives have better water resistance than comparable systems. Thus, they satisfy at least strength group D2, preferably D3, in particular D4, of the BS EN 204 test standard.

The invention furthermore relates to the use of the novel emulsion adhesive for bonding porous and semiporous substrates.

The specific suitability of the novel adhesive preparations is in their use as boiling-water-resistant adhesive, in particular for cellulosic substrates, such as wood. The adhesives are suitable for manual or machine application and, in particular, also applications in which the adhesive bonds are cured by high-frequency alternating currents.

Further general illustrative applications are water-resistant adhesive bonds of paper, board, cardboard, foam, cement, leather, textile or laminates.

Other applications are in the construction sector as

floor, wall or ceiling adhesives or as adhesive for furniture sheeting or carpet backings.

Other areas of suitability are in water-resistant binders for fiberboard or fibrous leather, and binders for  
5 insulation materials made from paper or plastic fibers, furthermore in water-resistant building material emulsions as binders for plaster or cement. Furthermore, in building material emulsions, the barrier action to solvents in concrete and mortar can be improved by the  
10 novel crosslinking agents.

Another application is the textiles sector, where the novel adhesive emulsions can be employed as binders for textiles and nonwovens and for textile printing and as textile finishes.

15 It should be emphasized that the novel emulsion adhesives are advantageously systems which are free from isocyanates and also substantially free from formaldehyde. In particular in emulsions containing formaldehyde-releasing constituents, the particularly preferred  
20 polyaldehyde/bisulfite adducts additionally offer the further advantage that the bisulfite liberated on acid cleavage and subsequent crosslinking also functions as a formaldehyde scavenger and thus significantly reduces the concentration of free formaldehyde in the adhesives or  
25 binders.

The examples below serve to illustrate the invention. In the examples, parts and percentages are by weight, unless otherwise stated.

#### Base emulsion A1

30 A solution of 6 parts of ®Mowiol 18-88 (Hoechst AG, partly hydrolyzed polyvinyl alcohol having a degree of hydrolysis of 88 mol%) in 92 parts by weight of deminer-

alized water is prepared in a stirred glass reactor fitted with anchor stirrer, feed means, reflux condenser, mantle heating and mantle cooling. After 0.1 part of ®Agitan 280 (Münzing-Chemie) antifoam and 0.006 part of Rongalit C have been added, 5 of a total of 100 parts of vinyl acetate are emulsified in. The internal temperature is raised to 50°C and the polymerization is initiated after addition of a solution of 0.03 part of ®Trigonox AW 70 (tert-butyl hydroperoxide, 70%, Akzo-Chemie) in 0.5 part of water.

After the reaction has commenced, two feeds comprising firstly 95 parts of vinyl acetate with 0.09 part of tert-butyl hydroperoxide (70%) and secondly 0.03 part of Rongalit C in 10 parts by weight of water are metered in parallel over the course of 3 hours. The mantle temperature is controlled so that the polymerization proceeds without reflux at a slowly rising internal temperature from 68°C at the beginning to about 80°C. The polymerization is then continued with subsequent addition of aqueous solutions of 0.014 part of tert-butyl hydroperoxide (70%) and 0.004 part of Rongalit C. After cooling, 4 parts of butyldiglycol acetate are slowly stirred into the emulsion.

Solids content: 50.8%

Viscosity, Brookfield RVT, spindel 6, 20 rpm:  
23,600 mPa·s

#### Base emulsions A2 to A4

The preparation is carried out as described above, with the difference that only 80 parts of water are used in the polymerization liquor and, as third feed, in each case a solution of 0.5 part (in the case of A2), 1 part (in the case of A3) and 2 parts (in the case of A4) of N-methylolacrylamide in 12 parts of water are metered in. The solutions are prepared by diluting the commercially available 48% strength solution of N-methylolacrylamide.

The amount of vinyl acetate metered in is in each case reduced by the amount of N-methylolacrylamide metered in, to 94.5, 94 and 93 parts respectively.

**Emulsion A2**

- 5    Solids content: 50.1%  
Viscosity, Brookfield RVT, 6/20: 17,800 mPa·s

**Emulsion A3**

Solids content: 50.0%  
Viscosity, Brookfield RVT, 6/20: 20,200 mPa·s

10   **Emulsion A4**

Solids content: 49.9%  
Viscosity, Brookfield RVT, 6/20: 29,400 mPa·s

**Examples 1 to 15 and Comparative Examples V1 to V4**

- 15    The base emulsions A1 to A4 are (apart from Example 8)  
initially mixed with a 10% strength aqueous solution of  
aluminum chloride. The corresponding amounts of solid  
AlCl<sub>3</sub>, based on the solids content of the emulsion, are  
shown in Table 1 with the resultant pH values of the mix-  
tures. After a ripening time of at least one day, the  
20    curing agent is admixed. The amounts of curing agent are  
likewise shown in Table 1.

**Determination of the tear strengths of beechwood test  
specimens after treatment with boiling water in accord-  
ance with BS EN 204/D4 test standard.**

- 25    The test specimens are produced as described in BS EN  
205. The gluing and testing are carried out with the  
following parameters:

- Ripening time after  
addition of curing agent: 2 hours  
Glue application rate:  $150 \pm 20 \text{ g/m}^2$ , application  
to both sides
- 5 Open waiting time: 3 minutes  
Closed waiting time: 3 minutes  
Pressing time: 2 hours  
Pressing pressure:  $0.7 \pm 0.1 \text{ N/mm}^2$   
Number of test specimens
- 10 per test sequence: 20  
Testing after 7 days, standard climatic  
conditions\*)
- Storage sequence in  
accordance with 6 hours in boiling water
- 15 BS EN 204, D4/5: 2 hours in cold water  
Test temperature:  $23^\circ\text{C} \pm 2^\circ\text{C}$   
Feed rate: 50 mm/min.

Classification in strength group D4/5 is carried out at  
a tear strength of  $\geq 4 \text{ N/mm}^2$ .

- 20 \*)  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  relative atmospheric humidity

**Pot life:**

- This is taken to mean the time for which the adhesive  
emulsion remains reliably flowable after addition of  
curing agent with a viscosity of  $\leq 40,000 \text{ mPa}\cdot\text{s}$ , measured
- 25 in accordance with Brookfield RVT, 6/20.

Table 1

| Example | Base emulsion | Comonomer | % of AlCl <sub>3</sub> , based on the solids content of each emulsion | pH  | Amount of curing agent added, in %, based on the emulsion | Tear strength, in accordance with BS EN 204, D4/5 |      | Pot life, hours   |
|---------|---------------|-----------|-----------------------------------------------------------------------|-----|-----------------------------------------------------------|---------------------------------------------------|------|-------------------|
|         |               |           |                                                                       |     |                                                           | N/mm <sup>2</sup>                                 | WT % |                   |
| 1       | A1            | -         | 1.7                                                                   | 2.8 | 2.50% GABNA 20%                                           | 5.9                                               | 82   | > 48              |
| V1      | A1            | -         | 1.7                                                                   | 2.8 | 5.00% Desmodur DA                                         | 3.2                                               | 0    | 24 <sup>1)</sup>  |
| 2       | A2            | 0.5% NMA  | 1.7                                                                   | 2.9 | 1.25% GABNA 20%                                           | 6.6                                               | 77   | > 24              |
| 3       | A2            | 0.5% NMA  | 1.7                                                                   | 2.9 | 2.50% GABNA 20%                                           | 6.7                                               | 22   | > 24              |
| V2      | A2            | 0.5% NMA  | 1.7                                                                   | 2.9 | 5.00% Desmodur DA                                         | 3.6                                               | 0    | 24 <sup>1)</sup>  |
| 4       | A3            | 1.0% NMA  | 1.7                                                                   | 2.9 | 0.25% GABNA 20%                                           | 6                                                 | 2    | > 8               |
| 5       | A3            | 1.0% NMA  | 1.7                                                                   | 2.9 | 1.25% GABNA 20%                                           | 7.4                                               | 60   | > 8               |
| 6       | A3            | 1.0% NMA  | 1.7                                                                   | 2.9 | 2.50% GABNA 20%                                           | 7.1                                               | 67   | > 8               |
| V3      | A3            | 1.0% NMA  | 1.7                                                                   | 2.9 | 5.00% Desmodur DA                                         | 5                                                 | 53   | 24 <sup>1)</sup>  |
| 7*      | A4            | 2.0% NMA  | -                                                                     | 4   | 2.50% GABNA 20%                                           | 0.8                                               | -    | > 24              |
| 8*      | A4            | 2.0% NMA  | 0.6                                                                   | 3   | -                                                         | 1.5                                               | -    | > 24              |
| 9*      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | -                                                         | 3.2                                               | -    | > 24              |
| 10      | A4            | 2.0% NMA  | 0.6                                                                   | 3   | 1.25% GABNA 20%                                           | 3                                                 | -    | > 8               |
| 11      | A4            | 2.0% NMA  | 0.6                                                                   | 3   | 2.50% GABNA 20%                                           | 2.9                                               | -    | > 8               |
| 12      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | 0.25% GABNA 20%                                           | 4.7                                               | -    | > 8               |
| 13      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | 1.25% GABNA 20%                                           | 6.2                                               | -    | > 8               |
| 14      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | 2.50% GABNA 20%                                           | 6.7                                               | 27   | > 8               |
| V4      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | 0.41% glutaric dialdehyde 40%                             | 6.6                                               | 28   | < 8 <sup>2)</sup> |
| 15      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | 1% MABDEA                                                 | 5.2                                               | 7    | > 8               |
| 16      | A4            | 2.0% NMA  | 1.7                                                                   | 2.8 | 3% MABDEA                                                 | 6.0                                               | 23   | < 8               |

Key to Table 1:

GABNA 20% = 20% strength solution of, glutaric dialdehyde bissodium bisulfite in water

NMA = N-methylolacrylamide

5 MABDEA = Malonic dialdehyde bisdiethyl acetal

WT % = Percentage wood tear at the bonded surface

1) Foam development > 50% by vol. after 24 hours

2) Strong odor nuisance

\*) not in accordance with this invention

- 10 Comparative Examples V1, V2 and V3, which do not conform to the invention, relate to an adhesive containing the commercially available polyisocyanate crosslinking-agent ®Desmodur DA (Bayer AG) in accordance with the prior art. Compared with this, the corresponding examples according to the invention containing GABNA have significantly better tear strengths with significantly lower amounts used. Example 1 also has a pot life of 2 days.

- 20 Comparative Example V4 shows that although comparably high boiling-water resistances are achieved when the same molar amount of glutaric dialdehyde is used as the amount of GABNA employed in Example 14, the pot life of the mixture is, however, less than 8 hours and the processing properties of this system are impaired by a strong odor nuisance.

- 25 Examples 7, 8 and 9, which are not in accordance with this invention, clearly show that GABNA has no effect in the absence of acidic aluminum chloride and conversely the use of only aluminum chloride produces no boiling-water resistance, even in the presence of 2% of NMA in the copolymer.
- 30

Only a combination of the two components produces a significant effect with respect to the water resistance, as shown in Examples 10 to 14.

### Determination of the short-term binding strengths

The setting rate is determined on single-overlapped beechwood test specimens produced and tested by gluing two beechwood panels, each with a thickness of 3 mm, a length of 85 mm and a width of 20 mm, under the following technical conditions:

Ripening time after  
addition of curing agent: 2 hours  
Pressing time: 2.5 or 5 minutes  
10 Pressing pressure:  $0.7 \pm 0.1 \text{ N/mm}^2$   
Number of test specimens  
per test sequence: 10  
Bonded area:  $300 \text{ mm}^2$   
Test temperature:  $23^\circ\text{C} \pm 2^\circ\text{C}$   
15 Feed rate: 50 mm/min.

The binding strength results after pressing times of 2.5 and 5 minutes are shown in Table 2:

Table 2

| Example | Base emulsion | Amount of curing agent added | Tear strength $\text{N/mm}^2$ after |        |
|---------|---------------|------------------------------|-------------------------------------|--------|
|         |               |                              | 2.5 min.                            | 5 min. |
|         |               | %, based on the emulsion     |                                     |        |
| 4       | A3            | 0.25% GABNA 20%              | 1.1                                 | 2.5    |
| 5       | A3            | 1.25% GABNA 20%              | 0.9                                 | 2.3    |
| 6       | A3            | 2.50% GABNA 20%              | 1.3                                 | 2.8    |
| V3      | A3            | 5.00% Desmodur DA            | 0.7                                 | 1.9    |

Examples 4-6 according to the invention show higher short-term binding strengths than Comparative Example V3 both after a pressing time of 2.5 minutes and after a pressing time of 5 minutes.

### Determination of free formaldehyde

The determination of free formaldehyde in the emulsions is carried out by UV/VIS spectrometry in the ultra-centrifuge serum of the diluted emulsion by a modified acetylacetone method.

The acetylacetone method is described in the literature (H. Petersen and N. Petri, Melliand Textilberichte 66, 363 (1985)).

The measurement is carried out after a ripening time of 8 hours from admixture of the curing agent. The measurement results are shown in Table 3.

Table 3

| Example | Base emulsion | Amount of curing agent added | Free HCHO |
|---------|---------------|------------------------------|-----------|
|         |               | %, based on the emulsion     | ppm       |
| 9       | A4            | none                         | 347       |
| 12      | A4            | 0.25% GABNA 20%              | 227       |
| 13      | A4            | 1.25% GABNA 20%              | 144       |
| 14      | A4            | 2.50% GABNA 20%              | 91        |

# Claims

1. An aqueous emulsion adhesive having a pH of from 2 to 6, comprising homo- or copolymeric polyvinyl esters, polymeric protective colloids, water-soluble compounds which can be complexed with the polymeric protective colloids, and at least partially masked polyaldehydes having at least three carbon atoms, from which aldehyde groups can be liberated in a controlled manner in acidic media.
2. An emulsion adhesive as claimed in claim 1, wherein the polyvinyl ester comprises at least 50% by weight of vinyl acetate monomer units.
3. An emulsion adhesive as claimed in claim 1, wherein the polyvinyl ester comprises monomer units from the group consisting of polyethylenically unsaturated monomers and monomers which are subsequently cross-linkable or self-crosslinking via hydroxyl, carboxyl, N-functional groups or carbonyl groups.
4. An emulsion adhesive as claimed in claim 1, wherein the polymeric protective colloid is polyvinyl alcohol.
5. An emulsion adhesive as claimed in claim 1, wherein the compounds which can be complexed with the polymeric protective colloids are water-soluble metal salts containing polyvalent cations.
6. An emulsion adhesive as claimed in claim 5, wherein the polyvalent cations in the complexible metal salts are Al(III) or Zr(IV).



7. An emulsion adhesive as claimed in claim 1, wherein the compounds which can be complexed with polymeric protective colloids are acids or salts containing oxo anions.
- 5 8. An emulsion adhesive as claimed in claim 7, wherein the oxo anions are phosphate or borate.
9. An emulsion adhesive as claimed in claim 1, wherein the at least partially masked polyaldehydes are present in an amount of from 0.01 to 5% by weight,  
10 based on the solids content of the emulsion adhesive.
10. An emulsion adhesive as claimed in claim 1, wherein the masked polyaldehydes are partially or fully masked bisaldehydes.
- 15 11. An emulsion adhesive as claimed in claim 10, wherein the masked bisaldehydes are derivatives of glutaric dialdehyde.
12. An emulsion adhesive as claimed in claim 1, wherein the masked polyaldehydes are their bisulfite  
20 adducts.
13. An emulsion adhesive as claimed in claim 1, wherein the pH of the aqueous adhesive emulsion is from 2.5 to 4.
14. An emulsion adhesive as claimed in claim 1, wherein  
25 the pot life during which the viscosity of the adhesive does not exceed 40,000 mPa·s is at least 8 hours.



- 5 15. A process for the preparation of an emulsion adhesive as claimed in claim 1 which comprises first preparing a homo- or copolymeric polyvinyl ester emulsion in the presence of polymeric protective colloids, and subsequently adding complexible metal salts or acids and finally adding at least partially masked polyaldehydes thereto.
- 10 16. A process for the preparation of an emulsion adhesive as claimed in claim 1, which comprises preparing a homo- or copolymeric polyvinyl ester emulsion in the presence of polymeric protective colloids, and then, at a pH above 4, firstly adding at least partially masked polyaldehydes and subsequently complexible metal salts or acids.
- 15 17. A process for the preparation of an emulsion adhesive as claimed in claim 1, which comprises first preparing a homo- or copolymeric polyvinyl ester emulsion in the presence of polymeric protective colloids, and then adding, at a pH above 5, polyfunctional aldehydes and compounds which supply bisulfite ions in aqueous systems and subsequently adding complexible metal salts or acids.
- 20
- 25 18. A method of using an emulsion adhesive as claimed in claim 1, for bonding porous or semiporous substrates.
19. A method of using an emulsion adhesive as claimed in claim 1 as a water-resistant adhesive for cellulosic substrates.

