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(54) Titre : AGENTS DE REVETEMENT AQUEUX A BASE DE EPOXYBUTENE-POLYETHERS

(54) Title: AQUEOUS COATING AGENT BASED ON EPOXYBUTENE POLYETHERS

(57) **Abrégé/Abstract:**

The invention relates to water-dilutable polyurethanes comprising structural units derived from 3,4-epoxy-1-butene, and aqueous dispersions containing said polyurethanes. The invention also relates to a method for producing said polyurethanes and to the use of the same as aqueous, oxidatively drying and/or UV-crosslinking coating agents.

ABSTRACT

The invention relates to water-dilutable polyurethanes comprising structural units derived from 3,4-epoxy-1-butene, and aqueous dispersions containing said polyurethanes. The invention also relates to a method for producing said polyurethanes and to the use of the same as aqueous, oxidatively drying and/or UV-crosslinking coating agents.

LeA 35732

Aqueous coating compositions based on epoxybutene polyethers

The invention relates to water-dilutable polyurethanes which contain structural units derived from 3,4-epoxy-1-butene, and to aqueous dispersions which comprise these polyurethanes, a process for their preparation and their use as aqueous oxidation-drying and/or UV-crosslinking coating compositions.

Polymeric compounds which can contain the structural units of 3,4-epoxy-1-butene are known in principle. For example, EP-A 0 217 660 describes the preparation of poly(α -hydroxycarboxylic acid) copolymers using ethylenically unsaturated epoxides.

US-A 5,393,867 discloses hydroxy-functional polyethers which are obtained by polymerization of 3,4-epoxy-1-butene with palladium catalysts.

EP-A 0 859 021 describes compounds with lateral vinyl groups which are prepared by reaction of (a) compounds which contain at least one vinyl group and at least one epoxide group, (b) a polybasic compound or anhydride thereof and optionally (c) a CH-acid compound, and epoxidized derivatives thereof.

WO 00/66646 discloses oil-free, oxidation-drying polyester resins which are obtained by derivatization of carboxyl-functional polyesters with 3,4-epoxy-1-butene, and the use of these resins in combination with an organic solvent and a drying catalyst in coatings which dry at room temperature.

Finally, WO 00/66649 discloses coating compositions based on polyether-alcohols which are prepared by ring-opening polymerization of 3,4-epoxybutene with water or alcohols. The polyether-alcohols prepared in this way can be used as reactive thinners or binders in oxidation-drying coatings and as a building unit for such binders.

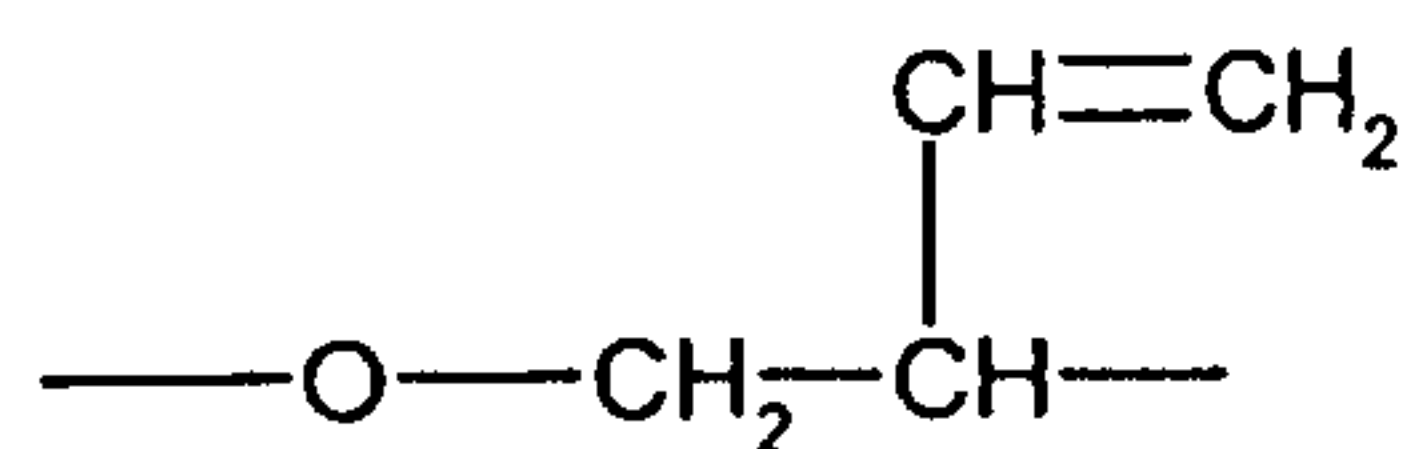
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A disadvantage of aqueous one-component paints known hitherto in paint technology is that, for example, the drying of oxidation-crosslinking water-based paints at room temperature often proceeds only slowly even if siccatives are added as drying accelerators, and only moderate film hardnesses are achieved. On the other hand, UV-curing water-based one-component paints show an inadequate crosslinking on areas which have been irradiated with a lower dose of UV radiation or not at all (shadow regions). The paint films have a lower level of properties on these areas.

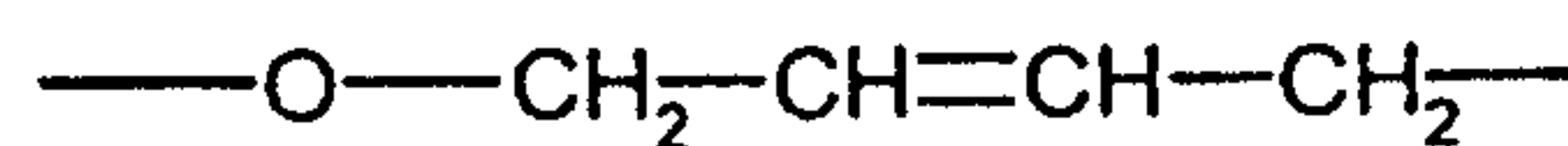
The object of the present invention was thus to provide water-based dispersions which are capable of oxidation drying and/or crosslinking with UV light and can be processed to one-component paints with a high level of properties, in particular in respect of the visual properties of the film, hardness, resistance to solvents and weathering and fast drying.

It has been possible to achieve this object by providing a water-dilutable polymer which contains urethane groups and the structural units of 3,4-epoxy-1-butene and can be employed as the basis for a one-component aqueous dispersion.

The present invention thus provides a water-dilutable polymer which contains urethane groups and has ionic and/or potentially ionic groups, characterized in that the polymer contains the recurring units (A1) of the formula (I) and/or (A2) of the formula (II)

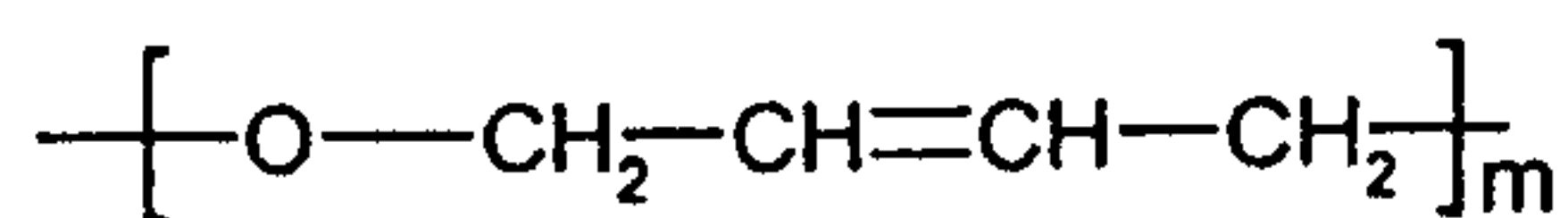
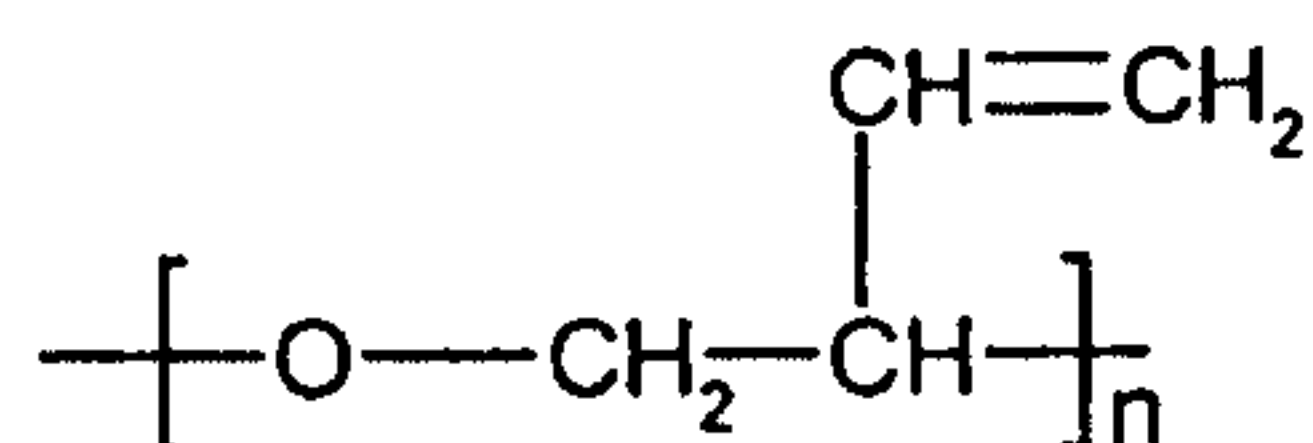


(I)



(II)

The recurring units A1, A2 or mixtures A1/A2 are present in the polymer in blocks



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or in mixed blocks of both structural units with p recurring units, wherein n, m and p each represent integers from 3 to 100.

5 It is also possible for the A1 or A2 recurring units to be distributed differently in the copolymer.

The content of A1 and/or A2 units in the polymer according to the invention is 2 to 80 wt.%, preferably 5 to 50 wt.%, particularly preferably 8 to 35 wt.%.

10 The structural units A1 and/or A2 contained in the polymers according to the invention can be obtained by ring-opening of the epoxide ring of 3,4-epoxy-1-butene. There is the possibility here of adding 3,4-epoxy-1-butene (once or several times) on to nucleophilic centres of a polymer or oligomeric chain by ring-opening of the epoxide ring, such as e.g. an addition on to COOH-, OH- or NH-functional
15 chain ends. On the other hand, it is also possible to employ a polyether-alcohol oligomer or polymer with one or more OH groups prepared by ring-opening polymerization of 3,4-epoxy-1-butene as units for building up the polyurethane chain, optionally in the presence of further monomers which can be polymerized under these conditions, such as e.g. ethylene oxide, propylene oxide or butylene
20 oxide. The structural units A1 and/or A2 are preferably introduced into the polyurethanes by incorporation of hydroxy-functional polyether-polyols.

The polyether-polyols can be built up entirely from recurring units A1 and/or A2 (homopolymers), apart from initiator constituents incorporated into the chain, or can
25 also be present as copolymers with other monomers which can be polymerized under these conditions, e.g. with ethylene oxide, propylene oxide or butylene oxide. A macroinitiator containing recurring units of the abovementioned comonomers can be employed for the preparation of polyether-alcohols by homopolymerization of 3,4-epoxy-1-butene. Suitable catalysts for the preparation of the polyether-alcohols
30 are e.g. KOH, trifluoromethanesulfonic acid or salts thereof with yttrium or other lanthanide metals, palladium(0) compounds corresponding to US-A 5,393,867, such as e.g. tetrakis(triphenylphosphine)-palladium(0)

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It is preferable to use double metal cyanide catalysis (DMC catalysis) in the ring-opening polymerization of 3,4-epoxybutene with alcohols as starter molecules to give polyether alcohols. DMC catalysts and the polymerization of epoxides with such catalysts are described e.g. in EP-A 0 700 949.

The polymer according to the invention contains 1 to 40 wt.% of urethane groups [NHCOO], preferably 2 to 30 wt.% of urethane groups, particularly preferably 5 to 25 wt.%, and very particularly preferably 15 to 25 wt.% of urethane groups.

The polymers according to the invention furthermore contain 9 to 100 meq/100 g in total of ionic and/or potentially ionic groups in order to achieve dispersibility or solubility in an aqueous medium. The content of ionic and/or potentially ionic groups is preferably 20 to 60 meq/100 g in total, particularly preferably 25 to 50 meq/100 g in total.

The water-dilutable polymer according to the invention is preferably a reaction product A) comprising the components

- (a1) 5 to 80 wt.%, preferably 10 to 60 wt.% of polyisocyanates,
- (a2) 10 to 80 wt.%, preferably 40 to 70 wt.% of polyols and/or polyamines with an average molecular weight M_n of at least 400,
- (a3) 2 to 15 wt.%, preferably 3 to 10 wt.% of compounds which contain at least one group which is reactive towards isocyanate groups and at least one ionic and/or potentially ionic group,
- (a4) 0 to 20 wt.%, preferably 1 to 10 wt.% of low molecular weight polyols and/or secondary polyamines,
- (a5) 0 to 20 wt.% of chain stoppers,
- (a6) 0 to 20 wt.% of chain lengtheners which contain at least two groups which are reactive towards isocyanate groups and differ from (a2), (a3) and (a4).

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The water-dilutable polymers according to the invention have an average molecular weight M_n of 1,000 to 50,000, preferably 1,600 to 10,000.

5 The polyisocyanates, preferably diisocyanates, (a1) are the compounds known in the field of polyurethanes and paints, such as aliphatic, cycloaliphatic or aromatic diisocyanates.

Compounds of the general formula $Q(NCO)_2$, wherein Q represents a hydrocarbon radical having 4 to 40 C atoms, preferably 4 to 20 C atoms, are suitable. Q is
10 preferably an aliphatic C_4-C_{12} radical, a cycloaliphatic C_6-C_{15} radical, an aromatic C_6-C_{15} radical or an araliphatic C_7-C_{15} radical.

Particularly preferred diisocyanates are, for example, tetramethylene-diisocyanate, hexamethylene-diisocyanate, dodecamethylene-diisocyanate, 1,4-diisocyanato-
15 cyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate (isophorone-diisocyanate), 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanato-2,2-dicyclohexylpropane, 1,4-diisocyanatobenzene, 2,4- or 2,6-diisocyanatotoluene and mixtures of these isomers, 4,4'- or 2,4'-diisocyanatodiphenylmethane, 4,4'-diisocyanato-2,2-diphenylpropane, p-xylylene-diisocyanate and $\alpha,\alpha,\alpha',\alpha'$ -
20 tetramethyl-m- or -p-xylylene-diisocyanate and mixtures consisting of these compounds.

In addition to these simple polyisocyanates, those which contain heteroatoms in the radical linking the isocyanate groups and/or have a functionality of greater than or
25 equal to 2 NCO groups per molecule are also suitable. Examples of these are polyisocyanates which contain carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups, acylated urea groups, iminooxadiazine-dione groups, uretdione groups or biuret groups, and 4-isocyanato-methyl-1,8-octane-diisocyanate (nonane-triisocyanate).

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In respect of further suitable polyisocyanates, reference is made, for example, to DE-A 29 28 552, p. 14 - 16. Mixtures of these compounds are also suitable.

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Component (a2) preferably has an average molecular weight M_n of 400 to 5,000, particularly preferably 800 to 2,000. The hydroxyl number or amine number is in general 22 to 400, preferably 50 to 200, and particularly preferably 80 to 160 mg KOH/g.

5

Suitable polyols (a2) are the compounds known from polyurethane chemistry, such as e.g. polyether-polyols, polyester-polyols, polycarbonate-polyols, polyester-amide-polyols, polyamide-polyols, epoxy resin-polyols and reaction products thereof with CO_2 , polyacrylate-polyols and similar compounds. Such polyols, which can also be employed as a mixture, are described, for example, in DE-A 20 20 905, DE-A 23 14 513 and DE-A 31 24 784 and in EP-A 0 120 466.

10

Instead of OH groups, the compounds of component (a2) can also contain primary or secondary amino groups (as a proportion or entirely) as NCO-reactive groups.

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Aspartic acid esters of the abovementioned molecular weight, such as are mentioned, for example, in EP-A 0 403 921, p. 4 - 5, are also suitable as component (a2). Such secondary amines can also be employed as a mixture with the polyols.

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Preferred polyols are the polyether- and polyester-polyols, and those which have only terminal OH groups and have a functionality of less than 3, preferably 2.8 to 2, are particularly preferred.

25

Preferred polyester-polyols are the known polycondensates of di- and optionally poly(tri, tetra)ols and mono-, di- and optionally poly(tri,tetra)carboxylic acids or hydroxycarboxylic acids or lactones. Instead of the free polycarboxylic acids, it is also possible to use the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols for the preparation of the polyesters. Examples of suitable diols are ethylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyalkylene glycols, such as polyethylene glycol, and furthermore propanediol, butane-1,4-diol, hexane-1,6-diol, neopentylglycol or hydroxypivalic acid neopentylglycol ester. Hexane-1,6-diol,

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neopentylglycol or hydroxypivalic acid neopentylglycol ester are preferred compounds. Trimethylolpropane, glycerol, erythritol, pentaerythritol, trimethylolbenzene or trishydroxyethyl isocyanurate, for example, are to be mentioned here as polyols which are optionally to be co-employed.

5

Suitable di- or polycarboxylic acids are, for example, phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexanedicarboxylic acid, adipic acid, azelaic acid, sebacic acid, glutaric acid, tetrachlorophthalic acid, maleic acid, fumaric acid, itaconic acid, malonic acid, 10 suberic acid, 2-methylsuccinic acid, 3,3-diethylglutaric acid, 2,2-dimethylsuccinic acid, trimellitic acid or pyromellitic acid. Anhydrides of these acids can also be employed, where these exist. For the purposes of the present invention, the anhydrides are consequently included in the term "acid". Monocarboxylic acids can also be used provided that the average functionality of the polyol is greater than or 15 equal to 2.

Suitable hydroxycarboxylic acids for the preparation of a polyester-polyol with a terminal hydroxyl are, for example, hydroxycaproic acid, hydroxybutyric acid, hydroxydecanoic acid, hydroxystearic acid and the like. Suitable lactones are e.g. 20 caprolactone, butyrolactone and the like.

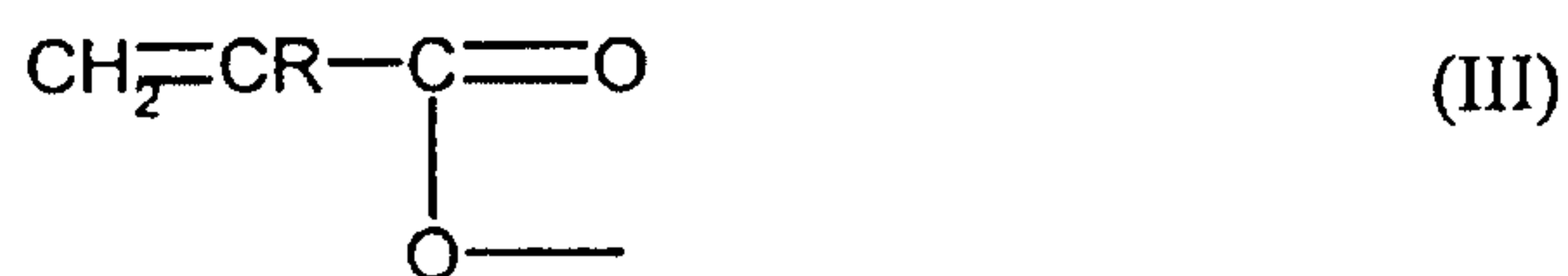
Polyether-polyols which contain entirely or a proportion of A1 and/or A2 recurring units and polyoxyethylene-polyols, polyoxypropylene-polyols, polyoxybutylene-polyols or polytetrahydrofurans with terminal OH groups are very particularly 25 preferred.

The polymers according to the invention can furthermore comprise polyoxyalkylene ethers which are free from A1 and/or A2 recurring units but carry at least one hydroxyl or amino group per molecule, such as can be prepared e.g. from an alcohol 30 and from polyethylene oxide/polypropylene oxide blocks with a molecular weight of 400 to 4,000.

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In a preferred embodiment of the present invention, component (a2) comprises at least a proportion of an oligoester or polyester which contains mono- and/or polyunsaturated fatty acids. Suitable fatty acids are e.g. coconut oil fatty acid, soya oil fatty acid, safflower oil fatty acid, castor oil fatty acid, ricinene acid, groundnut oil fatty acid, tall oil fatty acid or conjugene fatty acid. Suitable further monocarboxylic acids are e.g. benzoic acid, tert-butylbenzoic acid, hexahydrobenzoic acid, 2-ethylhexanoic acid, isononanoic acid, decanoic acid or octadecanoic acid. Soya oil fatty acid or a mixture of 70 to 100 wt.% soya oil fatty acid and 0 to 30 wt.% benzoic acid is preferably employed as the monocarboxylic acid. The polymer according to the invention thus preferably additionally contains C=C double bonds of mono- or polyunsaturated fatty acids in addition to the allylic double bonds present in the structural units A1 and/or A2.

In another preferred embodiment, component (a2) comprises at least a proportion of a polyol which additionally contains C=C double bonds in acrylic acid ester and/or methacrylic acid ester units A3) of the formula (III).



Polyester-acrylates which contain hydroxyl groups and have an OH number of 30 to 300 mg KOH/g are preferably employed. A total of 7 groups of monomer constituents can be used for the preparation of the hydroxy-functional polyester-acrylates:

1. (Cyclo)alkanediols, e.g. dihydric alcohols with (cyclo)aliphatically bonded hydroxyl groups of the molecular weight range from 62 to 286, such as ethanediol, 1,2- and 1,3-propanediol, 1,2-, 1,3- and 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, cyclohexane-1,4-dimethanol, 1,2- and 1,4-cyclohexanediol, 2-ethyl-2-butylpropanediol and diols containing ether-oxygen, such as e.g. diethylene glycol, triethylene glycol,

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5 tetraethylene glycol, dipropylene glycol, tripropylene glycol or polyethylene, polypropylene or polybutylene glycols with a maximum molecular weight of 2,000, preferably 1,000, and particularly preferably 500. Reaction products of the abovementioned diols with ϵ -caprolactone or other lactones can also be employed as diols.

10 2. Tri- and higher than tri-hydric alcohols of the molecular weight range from 92 to 254, such as e.g. glycerol, trimethylolpropane, pentaerythritol, dipentaerythritol and sorbitol or polyethers started on these alcohols, such as e.g. the reaction product of 1 mol of trimethylolpropane with 4 mol of ethylene oxide.

15 3. Monoalcohols, such as e.g. ethanol, 1- and 2-propanol, 1- and 2-butanol, 1-hexanol, 2-ethylhexanol, cyclohexanol and benzyl alcohol.

20 4. Dicarboxylic acids of the molecular weight range from 104 to 600 and/or anhydrides thereof, such as e.g. phthalic acid, phthalic anhydride, isophthalic acid, tetrahydrophthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic acid, hexahydrophthalic anhydride, cyclohexanedicarboxylic acid, maleic anhydride, fumaric acid, malonic acid, succinic acid, succinic anhydride, glutaric acid, adipic acid, pimelic acid, suberic acid, sebacic acid, dodecanedioic acid and hydrogenated dimer fatty acids.

25 5. Carboxylic acids of higher functionality and anhydrides thereof, such as e.g. trimellitic acid and trimellitic anhydride.

30 6. Monocarboxylic acids, such as e.g. benzoic acid, cyclohexanecarboxylic acid, 2-ethylhexanoic acid, caproic acid, caprylic acid, capric acid, lauric acid and naturally occurring and synthetic fatty acids.

7. Acrylic acid, methacrylic acid and dimeric acrylic acid.

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Particularly preferred polyester-acrylates containing hydroxyl groups comprise the reaction product of at least one constituent from group 1 or 2 with at least one constituent from group 4 or 5 and at least one constituent from group 7.

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It is also possible to also incorporate into the polyester-acrylates to be employed according to the invention groups which have a dispersing action and are generally known from the prior art, thus, for example, described in Progress in Organic Coatings, 9 (1981), 291 - 296. Thus, for example, a proportion of polyethylene glycols and/or methoxypolyethylene glycols can be incorporated as the alcohol component. Compounds which may be mentioned are e.g. polyethylene glycols and polypropylene glycols started on alcohols and block copolymers thereof, as well as the monomethyl ethers of these polyglycols. Polyethylene glycol 1500 and/or polyethylene glycol 500 monomethyl ether is preferred.

15

It is furthermore possible to react some of the (excess) carboxyl groups, in particular those of (meth)acrylic acid, with mono-, di- or polyepoxides. Preferred epoxides are epoxides (glycidyl ethers) of monomeric, oligomeric or polymeric bisphenol A, bisphenol F, hexanediol and/or butanediol. This reaction can be used, in particular, to increase the OH number of the polyester-acrylate, since an OH group is in each case formed in the epoxide-acid reaction.

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The preparation of polyester-acrylates in the context of the present invention is described, for example, in DE-A-4 040 290, DE-A-3 316 592 and P. K. T. Oldring (ed.), Chemistry & Technology of UV & EB Formulations for Coatings, Inks & Paints, vol. 2, 1991, SITA Technology, London, p. 123 - 135.

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The acid number of the polyester-acrylates is less than 20 mg KOH/g, preferably less than 10 mg KOH/g, and particularly preferably less than 5 mg KOH/g.

Alternatively, epoxyacrylates containing hydroxyl groups, polyether-acrylates containing hydroxyl groups or polyurethane-acrylates containing hydroxyl groups,

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which are known per se and have OH numbers of 20 to 300 mg KOH/g, can also be employed, as well as mixtures thereof with one another and mixtures with unsaturated polyesters containing hydroxyl groups as well as mixtures with polyester-acrylates or mixtures of unsaturated polyesters containing hydroxyl groups with polyester-acrylates.

The polymer according to the invention thus preferably additionally contains (meth)acrylate double bonds, in addition to the allylic double bonds present from the structural units in A1 and/or A2.

Compounds which are suitable as component (a3) are those which contain at least one group which is reactive towards isocyanate groups and at least one ionic and/or potentially ionic group. Those groups which are capable of the formation of an ionic group are to be understood as potentially ionic. Ionic or potentially ionic groups are, for example, carboxyl, sulfonic acids, phosphoric acid or phosphonic acid groups or their corresponding anions. Carboxyl/carboxylate and/or sulfone/sulfonate groups are preferred. Suitable components (a3) are described, for example, in US-A 3,412,054, columns 1 and 2, US-A 3,640,924, column 3 and in DE-A 26 24 442, pages 25 to 26, to which reference is made here.

Compounds (a3) containing amino groups, such as, for example, α,δ -diaminovaleric acid or 2,4-diamino-toluene-5-sulfonic acid, are also suitable. Mixtures of these compounds (a3) can also be employed.

Particularly preferred compounds (a3) are alcohols which contain at least one carboxyl group, preferably 1 to 3 carboxyl groups per molecule. Examples of these are hydroxypivalic acid, dihydroxycarboxylic acids, such as α,α -dialkylolalkanoic acids, in particular α,α -dimethylolalkanoic acids, such as 2,2-dimethylolacetic acid, 2,2-dimethylolpropionic acid, 2,2-dimethylolbutyric acid and 2,2-dimethylolpentanoic acid, and dihydroxysuccinic acid, and furthermore polyhydroxy acids, such as gluconic acid. 2,2-Dimethylolpropionic acid is very particularly preferred.

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5 The low molecular weight polyols and/or secondary polyamines (a4) optionally employed for building up the polymers according to the invention as a rule have the effect of stiffening of the polymer chain. They have a molecular weight of 62 to 400, preferably 62 to 200, and can contain aliphatic, alicyclic or aromatic groups.

10 Suitable components (a4) which are to be mentioned are low molecular weight polyols having up to about 20 carbon atoms per molecule, such as e.g. ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,3-butylene glycol, cyclohexanediol, 1,4-cyclohexanedimethanol, 1,6-hexanediol, bisphenol A (2,2-bis(4-hydroxyphenyl)-propane), hydrogenated bisphenol A (2,2-bis(4-hydroxycyclohexyl)propane) and aspartic acid esters, such as are described in EP-A 0 403 924, and mixtures thereof. Triols, such as trimethylolpropane and/or glycerol, can also be co-used. Polyols which contain a maximum of 5 epoxybutene units (A1/A2) started on water, short-chain polyols or polyamines and have an average molecular weight of less than 400 are also suitable.

20 The polymer according to the invention can optionally also comprise units (a5), which are in each case at the chain ends and close these off, so-called chain stoppers.

Suitable components (a5) are derived from monofunctional compounds which are reactive with NCO groups, such as e.g. monoamines, preferably mono-secondary amines, or monoalcohols. Examples which may be mentioned here are methylamine, ethylamine, propylamine, butylamine, octylamine, laurylamine, stearylamine, isononyloxypropylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, N-methyl-aminopropylamine, diethyl(methyl)aminopropylamine, morpholine, piperidine or substituted derivatives thereof, amidoamines from diprimary amines and monocarboxylic acids, monoketimines from diprimary amines and primary/tertiary amines, such as N,N-dimethylaminopropylamine.

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Monohydroxy-functional esters of acrylic and/or methacrylic acid, so-called (meth)acrylates, are also suitable components (a5). Examples of such compounds are the mono(meth)acrylates of dihydric alcohols, such as e.g. ethanediol, the isomeric propanediols and butanediols, or (meth)acrylates of polyhydric alcohols, such as e.g. trimethylolpropane, glycerol and pentaerythritol, which contain on average one free hydroxyl group.

Preferred compounds (a5) are those which contain active hydrogen of varying reactivity with respect to NCO groups. These are, for example, compounds which, in addition to a primary amino group, also contain secondary amino groups or, in addition to an OH group, also contain COOH groups or, in addition to an amino group (primary or secondary), also contain OH groups, the latter being preferred. Examples of these are primary/secondary amines, such as 3-amino-1-methylaminopropane, 3-amino-1-ethylaminopropane, 3-amino-1-cyclohexylaminopropane, 3-amino-1-methylaminobutane, mono-hydroxycarboxylic acids, such as hydroxyacetic acid, lactic acid or malic acid, and furthermore alkanolamines, such as N-aminoethylethanolamine, ethanolamine, 3-aminopropanol, neopentanolamine and, particularly preferably, diethanolamine. Aspartic acid esters based on the amino alcohols mentioned, such as are mentioned in EP-A 0 743 333, are also suitable.

The polymer according to the invention can optionally also contain units (a6) which are derived from so-called chain lengtheners. Possible chain lengtheners here are the known compounds which are reactive with NCO groups and are preferably difunctional, are not identical to (a2), (a3), (a4) and (a5) and usually have average molecular weights of less than 400. Examples which may be mentioned here are water, hydrazine, adipic acid dihydrazide, poly(di)amines, such as ethylenediamine, diethylenetriamine, dimethylethylenediamine, diaminopropane, hexamethylenediamine, isophoronediamine and 4,4'-diaminodicyclohexylmethane, which can also carry substituents, such as OH groups, and mixtures of the components mentioned. Such polyamines are disclosed, for example, in DE-A 36 44 371.

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The preparation of the polymers according to the invention is described in the prior art, e.g. in EP-A 0 355 682, EP-A 0 427 028 or DE-A 39 01 190.

5 For example, the preparation can be carried out by a procedure in which an isocyanate-functional prepolymer is first prepared and an OH- and/or NH-functional compound is obtained in a second reaction step by reaction with compounds (a5) and/or (a6), as disclosed e.g. in EP-A 0 355 682. However, the preparation can also be carried out such that the polyurethane resin containing OH groups is formed directly by reaction of components (a1) to (a6), as described e.g. in EP-A 0 427 028.

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The polymer A) according to the invention is preferably prepared by a procedure in which a polyurethane prepolymer which contains on average at least 1.7, preferably 2 to 2.5 free isocyanate groups per molecule is first prepared from components (a1, polyisocyanates), (a2, polyols) and optionally component (a4, low molecular weight polyols) and components (a3), and this prepolymer is then reacted completely or
15 partly with components (a5) and/or (a6) in a non-aqueous system.

The polyisocyanate is employed in an excess with respect to the polyols (a2) to (a4) in the process according to the invention, so that a product with free isocyanate
20 groups results. These isocyanate groups are terminal and/or lateral, preferably terminal. The amount of polyisocyanate here is expediently high enough for the equivalent ratio of isocyanate groups to the total number of OH groups in the polyols (a2) to (a4) to be 1.05 to 2.0, preferably 1.1 to 1.6.

25 The preparation of the prepolymer is usually carried out at temperatures from 40° to 140°C, depending on the reactivity of the isocyanate employed. Suitable catalysts such as are known to the expert for accelerating the NCO-OH reaction can be employed to accelerate the urethanation reaction. Examples are tertiary amines, such as e.g. triethylamine, organotin compounds, such as e.g. dibutyltin oxide,
30 dibutyltin dilaurate or tin bis(2-ethylhexanoate), or other organometallic compounds.

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The urethanation reaction is preferably carried out in the presence of solvents which are inactive towards isocyanates. Those solvents which are compatible with water, such as, for example, ethers, ketones and esters, as well as N-methylpyrrolidone, are possible in particular for this. The amount of this solvent expediently does not exceed 25 wt.% and is preferably in the range from 5 to 15 wt.%, in each case based on the total of polyurethane resin and solvent. The polyisocyanate can be added here swiftly to the solution of the other components.

The prepolymer or solution thereof is then reacted with the compound according to (a5) and/or (a6), the temperature expediently being in the range from 0° to 90°C, preferably 20° to 60°C, until the NCO content in the prepolymer has fallen practically to zero. For this, the compound (a5) is employed in less than the stoichiometric amount or in a slight excess, the amounts usually being 40 to 110 wt.%, preferably 60 to 105 wt.% of the required stoichiometric amount. If less reactive diisocyanates are used for the preparation of the prepolymer, this reaction can also be carried out in water simultaneously with the neutralization. Some of the (non-neutralized) COOH groups, preferably 5 to 30 wt.%, can optionally be reacted with difunctional compounds which are reactive with COOH groups, such as diepoxides.

Alternatively, before the dispersing operation, a proportion (based on the isocyanate content) of the prepolymer can also be reacted with (a5), before all or a proportion of the remaining isocyanate groups are reacted with component (a6) after the dispersing operation. The neutralization of the carboxyl groups can be carried out here either before the dispersing step, by adding the neutralizing agent to the prepolymer, or during the dispersing operation, by adding the neutralizing amine to the dispersing water.

The polymer A) according to the invention can also be prepared by a procedure in which components (a1) to (a6) are reacted in a direct reaction to give an OH-functional resin. The reaction conditions here correspond to the conditions

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described for the preparation of the prepolymer containing NCO groups. Such a process is described e.g. in EP-A 0 427 028.

5 Another possibility for the preparation of the polyurethane prepolymer according to the invention comprises reacting resins which contain COOH and/or SO₃H groups and which additionally contain one or more isocyanate-reactive groups via di- and/or polyisocyanates with polyether-alcohols which contain at least a proportion of recurring units A1 and/or A2. Resins which are suitable for this are e.g. vinyl
10 polymers, polyesters, epoxides or hybrid resins (e.g. acrylate-grafted polyesters or polyurethanes), such as are known from the prior art.

Tertiary amines, e.g. trialkylamines having 1 to 12, preferably 1 to 6 C atoms in each alkyl radical, are suitable in particular for neutralization of the resulting product containing COOH and/or SO₃H groups. Examples are trimethylamine,
15 triethylamine, methyldiethylamine, tripropylamine and diisopropylethylamine. The alkyl radicals can also carry, for example, hydroxyl groups, such as in the case of the dialkylmonoalkanol-, alkylodialkanol- and trialkanolamines, such as e.g. dimethylethanolamine, which is preferably used as the neutralizing agent. Inorganic bases, such as ammonia or sodium hydroxide or potassium hydroxide, can
20 optionally also be employed as the neutralizing agent. The neutralizing agent is usually employed in a molar ratio to the acid groups of the prepolymer of 0.3:1 to 1.3:1, preferably 0.5:1 to 1:1.

The neutralization of the COOH or SO₃H groups can be carried out before, during or
25 after the urethanation reaction. The neutralization is as a rule carried out at between room temperature and 100°C, preferably from 40 to 80°C. It can be carried out in any desired manner here, e.g. by adding the water-containing neutralizing agent to the polyurethane resin or vice versa. However, it is also possible first to add the neutralizing agent to the polyurethane resin and only then to add the water. In
30 general, solids contents of 20 to 70 wt.%, preferably 30 to 50 wt.%, are obtained in this manner.

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The present invention also provides aqueous dispersions comprising

- (A) 20 to 70 wt.%, preferably 25 to 50 wt.% of at least one water-dilutable polymer according to the invention containing urethane groups,
- 5 (B) 0 to 20 wt.%, preferably 0 - 10 wt.% of organic co-solvents and
- (C) 10 to 70 wt.%, preferably 30 to 60 wt.% of water.

A mixture of several polymers (A) according to the invention can also be employed.

10 Suitable organic co-solvents (B) are the conventional paint solvents known per se, such as e.g. ethyl acetate, butyl acetate, ethylene glycol monomethyl or -ethyl ether-acetate, 1-methoxypropyl 2-acetate, 3-methoxy-n-butyl acetate, acetone, 2-butanone, 4-methyl-2-pentanone, cyclohexanone, toluene, xylene, chlorobenzene, white spirit, mixtures which comprise above all more highly substitute aromatics, such as are
15 commercially available, for example, under the names solvent naphtha, Solvesso[®] (Exxon Mobil Chem. Comp., Houston), Cypar[®] (Shell Chemicals, UK), Cyclo Sol[®] (Shell Chem.), Tolu Sol[®] (Shell Chem.) and Shellsol[®] (Shell Chem.), carbonic acid esters, such as dimethyl carbonate, diethyl carbonate, 1,2-ethylene carbonate and 1,2-propylene carbonate, lactones, such as β -propiolactone, γ -butyrolactone, ϵ -caprolactone and ϵ -methylcaprolactone, and also solvents such as propylene glycol diacetate, diethylene glycol dimethyl ether, dipropylene glycol dimethyl ether, diethylene glycol ethyl and butyl ether-acetate, N-methylpyrrolidone and N-methylcaprolactam, or any desired mixtures of such solvents.

25 The organic co-solvents (B) can be added to the water-dilutable polymer according to the invention containing urethane groups or the dispersion thereof subsequently or during the preparation. At least some of the organic solvent is conventionally added during the preparation or dispersing of the polymer according to the invention. For the preparation of dispersions which have a low co-solvent content or are free from
30 co-solvent it is also possible to use auxiliary solvents during the preparation process, which are removed again in a later step.

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In the use as coating compositions, the dispersions comprising the water-dilutable polymers according to the invention containing urethane groups are employed either by themselves or in combination with other aqueous binders. Such aqueous binders can be built up e.g. from polyester, polyacrylate, polyepoxide or polyurethane polymers. Combination with radiation-curable binders, such as are described e.g. in EP-A-0 753 531, is also possible. The dispersions comprising the polymers according to the invention can be employed as such as or in combination with the auxiliary substances and additives known from paint technology, such as e.g. pigments, fillers and paint auxiliaries, e.g. anti-sedimentation agents, defoamers and/or wetting agents, flow control agents, reactive thinners, plasticizers, catalysts, auxiliary solvents or thickeners, for the production of coatings.

The present invention also provides coating compositions comprising the water-dilutable polymers according to the invention containing urethane groups.

The dispersions comprising the polymers according to the invention are used as binders for the production of coatings. Such coatings can be applied to any desired substrates, e.g. wood, metal, plastic, paper, leather, textiles, felt, glass or mineral substrates.

The production of oxidation-drying water-based coatings, characterized in that the coating composition comprises the water-dilutable polymers (A) according to the invention containing urethane groups as binders, is preferred.

Siccatives can be added to accelerate the oxidation crosslinking.

An advantage of the dispersions which comprise the polymers (A) according to the invention is that the production of fast-drying coatings without the addition of siccatives becomes possible.

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The production of UV-curing coatings, characterized in that the coating composition comprises the water-dilutable polymers (A) according to the invention containing urethane groups as binders and one or more photoinitiators, is also preferred.

5 The UV-curing coatings produced in this way are distinguished by a particularly good shadow curing compared with the UV-curing paints of the prior art. In the coating of shaped structures in particular, in contrast to sheet-like structures, the problem frequently arises that UV-curing coatings are soft, tacky and/or not resistant on areas exposed to no or only a low dose of UV light. After-curing via a second
10 mechanism which does not depend on UV light is advantageous here.

Suitable photoinitiators are e.g. aromatic ketone compounds, such as benzophenones, alkylbenzophenones, 4,4'-bis(dimethylamino)benzophenone (Michler's ketone), anthrone and halogenated benzophenones. Acylphosphine
15 oxides, such as e.g. 2,4,6-trimethyl-benzoyl-diphenylphosphine oxide, phenylglyoxylic acid esters, anthraquinone and its derivatives, benzil ketals and hydroxyalkylphenones are also suitable. Mixtures of these compounds may also be employed.

20 The coating compositions comprising the polymers (A) according to the invention can be applied in known manners, e.g. by brushing, pouring, knife-coating, spraying, atomizing, whirler-coating, rolling or dipping. Drying of the paint film can take place at room temperature or elevated temperature, and also by stoving at up to 200°C. Drying preferably takes place at room temperature or only slightly above.
25 If the dispersions according to the invention comprise UV-curing constituents, the drying process can additionally also include irradiation with UV light.

During drying of the coatings, water and, where appropriate, further solvents are preferably first removed from the coating by known processes, irradiation with UV
30 light is then carried out, and finally the oxidation drying.

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The present invention also relates to substrates coated with coating compositions comprising the water-dilutable polymers (A) according to the invention containing urethane groups.

Examples

All the percentage data are percentages by weight.

5 **Example 1** (according to the invention)

1,022 g isophthalic acid, 6,900 g soya oil fatty acid, 1,278 g benzoic acid, 3,353 g pentaerythritol and 911 g phthalic anhydride are weighed into a 15 l reaction vessel with a stirrer, heating device and water separator with a cooling device, and are
10 heated up to 140°C under nitrogen in the course of one hour. The mixture is heated up to 220°C in the course of a further 8 hours and the condensation reaction is carried out at this temperature until an acid number of less than 3 is reached. The polyester resin obtained in this way has a viscosity (determined as the flow time of a 75% solution of the polyester in xylene in a DIN 4 cup at 23°C) of 105 seconds and
15 an OH number of 175 mg KOH/g.

607 g of the polyester described above are initially introduced into a 4 l reaction vessel with a cooling, heating and stirring device, and are heated up to 80°C together with 58 g dimethylolpropionic acid, 150 g of a linear polyether-diol with an OH
20 number of 75 mg KOH/g, which has been prepared by ring-opening polymerization of 3,4-epoxy-1-butene with 3,4-dihydroxy-1-butene as the starter molecule, 75 g N-methylpyrrolidone, 75 g dipropylene glycol dimethyl ether and 22 g triethylamine, and the mixture is homogenized for 30 min. 185 g 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) are then added, with vigorous stirring, and the
25 mixture is heated up to 100°C (utilizing the exothermicity of the reaction) and is kept at this temperature until NCO groups can no longer be detected.

The linear polyether-diol was prepared at 120°C by adding a solution of 37g (0.42 mole) of 3,4-dihydroxy-1-butene, 600g of 3,4-epoxy-1-butene and 1 ml of trimethyl
30 orthobenzoate to 52g of a DMC catalyst according to EP-A 0 700 049, dissolved in 5 ml of toluene. The rate of addition was chosen so that the reaction temperature does not exceed 155°C. The reaction temperature is then maintained at 150°C until the

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3,4-epoxy-1-butene has fully reacted. The product has a molecular weight, determined by means of GPC, of 2074 and a polydispersity of $M_w/M_n = 1.15$.

5 The product is then dispersed with 1,000 g dist. water at 95°C and adjusted to a viscosity of 930 mPas ($D = 40 \text{ s}^{-1}$, 23°C) with water and triethylamine.

The aqueous urethane-modified polyester resin obtained in this way has an acid number of 26 mg KOH/g, an average particle size of 150 nm and a solids content of 45.6%.

10

Example 2 (according to the invention)

607 g of the polyester from ex. 1 are initially introduced into a 4 l reaction vessel with a cooling, heating and stirring device, and are heated up to 80°C together with
15 58 g dimethylolpropionic acid, 150 g of a linear polyether-diol with an OH number of 73 mg KOH/g and a number-average molecular weight of 1,300, which has been prepared by ring-opening polymerization of a mixture of 3,4-epoxy-1-butene and propylene oxide (molar ratio 50:50) with tripropylene glycol as the starter molecule, 150 g N-methylpyrrolidone and 22 g triethylamine, and the mixture is homogenized
20 for 30 min. 185 g 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) are then added, with vigorous stirring, and the mixture is heated up to 100°C (utilizing the exothermicity of the reaction) and is kept at this temperature until NCO groups can no longer be detected.

25 The linear polyether-diol was prepared corresponding to Example 1, except that the reaction of the catalyst, starter, propylene oxide and 3,4-epoxy-1-butene was carried out in an autoclave.

The product is then dispersed with 1,000 g dist. water at 95°C and adjusted to a
30 viscosity of 640 mPas ($D = 40 \text{ s}^{-1}$, 23°C) with water and triethylamine.

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The aqueous urethane-modified polyester resin obtained in this way has an acid number of 26 mg KOH/g, an average particle size of 170 nm and a solids content of 45.8%.

5 **Example 3** (according to the invention)

612 g of the polyester from ex. 1 are initially introduced into a 4 l reaction vessel with a cooling, heating and stirring device, and are heated up to 80°C together with 58 g dimethylolpropionic acid, 150 g of a polyether-triol with an OH number of 10 56 mg KOH/g and a number-average molecular weight of 4,200, which has been prepared by ring-opening polymerization of a mixture of 3,4-epoxy-1-butene and propylene oxide (molar ratio 50:50) with a propylene oxide polyether, which has been started on glycerol, of OH number 238 as the starter molecule, 150 g N-methylpyrrolidone and 22 g triethylamine, and the mixture is homogenized for 30 15 min. 180 g 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) are then added, with vigorous stirring, and the mixture is heated up to 100°C (utilizing the exothermicity of the reaction) and is kept at this temperature until NCO groups can no longer be detected.

20 The linear polyether-diol was prepared corresponding to Example 1, except that the reaction of the catalyst, starter, propylene oxide and 3,4-epoxy-1-butene was carried out in an autoclave.

25 The product is then dispersed with 1,000 g dist. water at 95°C and adjusted to a viscosity of 1,070 mPas ($D = 40 \text{ s}^{-1}$, 23°C) with water and triethylamine.

The aqueous urethane-modified polyester resin obtained in this way has an acid number of 27 mg KOH/g, an average particle size of 200 nm and a solids content of 46.1%.

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Example 4 (according to the invention)

602 g of the polyester from ex. 1 are initially introduced into a 4 l reaction vessel with a cooling, heating and stirring device, and are heated up to 80°C together with
5 58 g dimethylolpropionic acid, 150 g of the linear polyether-diol of OH number 75 mg KOH/g used in ex. 1, 150 g N-methylpyrrolidone and 22 g triethylamine, and the mixture is homogenized for 30 min. 190 g 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) are then added, with vigorous stirring, and the mixture is heated up to 100°C (utilizing the exothermicity of the reaction) and is
10 kept at this temperature until NCO groups can no longer be detected.

The product is then dispersed with 1,000 g dist. water at 95°C and adjusted to a viscosity of 620 mPas ($D = 40 \text{ s}^{-1}$, 23°C) with water and triethylamine.

15 The aqueous urethane-modified polyester resin obtained in this way has an acid number of 26 mg KOH/g, an average particle size of 240 nm and a solids content of 45.7%.

Example 5 (according to the invention):

20

1,347 g trimethylolpropane, 5,631 g soya oil fatty acid, 3,722 g phthalic anhydride and 2,614 g neopentylglycol are weighed into a 15 l reaction vessel with a stirrer, heating device and water separator with a cooling device, and the mixture is heated up to 140°C under nitrogen in the course of one hour. The mixture is heated up to
25 220°C in the course of a further 8 hours and the condensation reaction is carried out at this temperature until an acid number of less than 3 is reached. The polyester resin obtained in this way has a viscosity (determined as the flow time of an 80% solution of the polyester in xylene in a DIN 4 cup at 23°C) of 59 seconds and an OH number of 46 mg KOH/g.

30

1,410 g of the polyester precursor described above are initially introduced into a 4 l reaction vessel with a cooling, heating and stirring device and are heated up to

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100°C together with 151 g dimethylolpropionic acid, 390 g of the linear polyether-
diol of OH number 75 mg KOH/g described in ex. 1 and 650 g
N-methylpyrrolidone, and the mixture is homogenized for 30 min. It is then cooled
to 70°C and 650 g 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane
5 (IPDI) are added, with vigorous stirring. The reaction mixture is kept at this
temperature, while stirring, until an NCO content of 2.5% is reached (approx. 10 -
15 h). 114 g triethylamine are then stirred in homogeneously.

2,080 g of the NCO prepolymer obtained in this way, which is heated at 55°C, is
10 then introduced with stirring into 1,395 g dist. water pre-heated to 30°C in a 6 l
reaction vessel with a cooling, heating and stirring device in the course of
5 - 10 min. A mixing temperature of approx. 40°C is established. The crude
dispersion is cooled to approx. 30°C and a solution of 36.4 g ethylenediamine
in 815 g dist. water is then added, while stirring. The mixture is subsequently stirred
15 at 35 - 40°C for a further 2 h and is then adjusted to a viscosity of 2,300 mPas ($D = 40 \text{ s}^{-1}$, 23°C) with water and triethylamine.

The polyurethane dispersion prepared in this way has an acid number (100%) of
25 mg KOH/g, an average particle size of 42 nm and a solids content of 37.2%.

20

Example 6 (comparison example):

Preparation of a fatty acid-based urethane-modified polyester dispersion

1,126 g of the polyester precursor from ex. 1 are initially introduced into a 4 l
25 reaction vessel with a cooling, heating and stirring device, and are heated up to 80°C
together with 87.5 g dimethylolpropionic acid, 244 g N-methylpyrrolidone and 33 g
triethylamine, and the mixture is homogenized for 30 min. 286.5 g 1-isocyanato-
3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) are then added, with
vigorous stirring, and the mixture is heated up to 100°C (utilizing the exothermicity
30 of the reaction) and kept at this temperature until NCO groups can no longer be
detected.

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14.4 g ethoxylated nonylphenol are then added and the mixture is dispersed in approx. 1,400 g water, homogenized and adjusted with water and triethylamine to a viscosity of 1,100 mPas ($D = 40 \text{ s}^{-1}$, 23°C). The aqueous urethane-modified polyester resin obtained has an acid number of 27 mg KOH/g and a solids content of 45%.

Use example 1 (oxidation-drying top paints):

Octasoligen[®] Co 7 aqua (cobalt siccative, 50% in water, Borchers GmbH), corresponding to a concentration of 0.06% Co metal, based on the solids resin (binder 100%), is added to the dispersions of examples 1 - 5 and comparison example 6 and the mixture is diluted with water to a flow time of approx. 30 seconds (DIN 4 cup, 23°C) and applied with a doctor blade to degreased glass plates or degreased steel sheets (dry film layer thickness 50 µm). After drying at room temperature, defect-free paint films with a good level of properties are obtained.

Use properties of oxidation-drying paints according to use example 1 based on the dispersions from ex. 1 - 6:

Dispersion from example	Gloss 20°	Complete drying	Xylene resistance *	Pendulum hardness after 2d/14d RT	Water-res. wrinkling (8 / 24 h)	Water-res. loss of gloss* (3 / 8 / 24 h)
1	80	7 h	2	24 / 76 s	OK/OK	0 / 2 / 4
2	77	8 h	2	18 / 46 s	OK/OK	0 / 2-3 / 5
3	74	8 h	2	16 / 54 s	OK/OK	0 / 3 / 5
4	71	7 h	2	31 / 95 s	OK/OK	0 / 0 / 3
5	75	7 h	2	21 / 35 s	OK/OK	0 / 1 / 4
6 (comparison)	78	8 h	2	26 / 59 s	wrinkled/ severely wrinkled	2 / 4 / 5

20 *: Ratings of 0 - 5 possible; 0 = film undamaged, 5 = film very severely damaged

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Table 1 shows that the dispersions prepared according to examples 1 - 5 according to the invention have an improved resistance to water. In the case of comparison example 6, both a significant loss of gloss after only 3 h and a slight wrinkling after 8 h and a severe wrinkling of the film after 24 h, which is also no longer reversible, are found. The paints based on examples 1 to 5, on the other hand, show significantly better results.

Example 7 (according to the invention):

10

163.8 g of the linear polyether-diol of OH number 75 mg KOH/g described in ex. 1, 181 g of a polytetramethylene ether glycol with an OH number of 56 mg KOH/g, 37.2 g dimethylolpropionic acid, 18.3 g 1,6-hexanediol and 97.4 g N-methylpyrrolidone are mixed with one another in a 2 l four-necked flask with a stirring device, reflux condenser and internal thermometer and the mixture is heated up to 70°C, before 275.5 g Desmodur® W (product from Bayer AG, Leverkusen) are added swiftly. The temperature is kept at 80°C, before it is lowered to 70°C, when an NCO content of the prepolymer of 4.4% is reached, and 19.6 g triethylamine are added. After 10 min 500 g of the prepolymer are transferred in the course of 5 minutes into a second 2 l flask fitted with a stirrer and filled with 670 g water (20°C). After stirring intensively for 10 minutes, a mixture of 5.2 g hydrazine hydrate, 8.4 g ethylenediamine and 74.4 g water is added in the course of 5 min. Thereafter, the mixture is stirred at 40°C until NCO is no longer detectable in the dispersion. The polyurethane dispersion has an average particle size of 69 nm and a solids content of 35.3%.

25

A clear paint comprising 87.9% of this polyurethane dispersion, 3.0% butyl glycol, 1.0% Byk® 028 (defoamer, Byk Chemie, Wesel), 0.2% Byk® 024 (defoamer, Byk), 0.2% Byk® 346 (substrate wetting additive, Byk), 0.5% Byk® 381 (flow additive, Byk), 0.2% TS® 100 (matting agent, Degussa AG, Frankfurt), 2.0% Aquamat® 263 (wax/slip additive, Byk) and 2.0% Acrysol® RM 8 (5%, thickener, Rohm and Haas, Philadelphia) is knife-coated with a doctor blade with a gap width of 200 µm on to a

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glass plate and dried for 7 d at room temperature. A clear, glossy film with a pendulum hardness (drying for 14 days at RT) of 115 seconds is obtained.

Example 8 (according to the invention)

5

163.8 g of the linear polyether-diol of OH number 73 mg KOH/g described in ex. 2, 181 g of a polytetramethylene ether glycol with an OH number of 56 mg KOH/g, 37.2 g dimethylolpropionic acid, 18.3 g 1,6-hexanediol and 97.4 g N-methylpyrrolidone are mixed with one another in a 2 l four-necked flask with a stirring device, reflux condenser and internal thermometer and the mixture is heated up to 70°C, before 275.5 g Desmodur® W (product from Bayer AG, Leverkusen) are added swiftly. The temperature is kept at 80°C, before it is lowered to 70°C, when an NCO content of the prepolymer of 4.4% is reached, and 19.6 g triethylamine are added. After 10 min 500 g of the prepolymer are transferred in the course of 5 minutes into a second 2 l flask fitted with a stirrer and filled with 670 g water (20°C). After stirring intensively for 10 minutes, a mixture of 5.2 g hydrazine hydrate, 8.4 g ethylenediamine and 74.4 g water is added in the course of 5 min. Thereafter, the mixture is stirred at 40°C until NCO is no longer detectable in the dispersion. The polyurethane dispersion obtained in this way has an average particle size of 70 nm and a solids content of 35.3%.

20

A clear paint comprising 87.9% of this polyurethane dispersion, 3.0% butyl glycol, 1.0% Byk® 028 (defoamer, Byk), 0.2% Byk® 024 (defoamer, Byk), 0.2% Byk® 346 (substrate wetting additive, Byk), 0.5% Byk® 381 (flow additive, Byk), 0.2% TS® 100 (matting agent, Degussa), 2.0% Aquamat® 263 (wax/slip additive, Byk) and 2.0% Acrysol® RM 8 (5%, thickener, Rohm and Haas) is knife-coated with a doctor blade with a gap width of 200 µm on to a glass plate and dried for 7 d at room temperature. A clear, glossy film with a pendulum hardness (drying for 14 days at RT) of 80 seconds is obtained.

25
30

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Example 9*Oligomer precursor for ex. 10*

5 3,200 g castor oil and 1,600 g soya oil as well as 2.4 g dibutyltin oxide are weighed into a 5 l reactor with a distillation attachment. A stream of nitrogen (5 l/h) is passed through the reactants. The mixture is heated up to 240°C in the course of 140 min. After 7 h at 240°C, the mixture is cooled. The OH number is 109 mg KOH/g and the acid number is 2.5 mg KOH/g.

10 **Example 10** (comparison example):

Preparation of a fatty acid-based polyurethane dispersion

15 339 g polytetramethylene ether glycol with an OH number of 56 mg KOH/g, 248 g of the polyester oligomer precursor, 70 g dimethylolpropionic acid, 34 g 1,6-hexanediol and 34 g N-methylpyrrolidone are heated up to 70°C and the mixture is stirred until a clear solution has formed. 516 g Desmodur[®] W (Bayer AG, Leverkusen) are then added and the mixture is heated up to 100°C. It is stirred at this temperature until the NCO content is 4.1%. It is then cooled to 70°C and 52.6 g triethylamine are added.

20

650 g of this solution are dispersed with vigorous stirring in 601 g water, which is initially introduced at a temperature of 30°C. After the dispersing operation, the mixture is subsequently stirred for 5 min. A solution of 3.9 g hydrazine hydrate and 10.2 g ethylenediamine in 200 g water is then added in the course of 5 min. For
25 complete reaction of the isocyanate groups, the mixture is stirred at 45°C until NCO groups are no longer detectable.

The polyurethane dispersion prepared in this way has an average particle size of 60 nm and a solids content of 35%.

30

A clear paint comprising 87.9% of this polyurethane dispersion, 3.0% butyl glycol, 1.0% Byk[®] 028 (defoamer, Byk), 0.2% Byk[®] 024 (defoamer, Byk), 0.2% Byk[®] 346

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(substrate wetting additive, Byk), 0.5% Byk[®] 381 (flow additive, Byk), 0.2% TS[®] 100 (matting agent, Degussa), 2.0% Aquamat[®] 263 (wax/slip additive, Byk) and 2.0% Acrysol[®] RM 8 (5%, thickener, Rohm and Haas) is knife-coated with a doctor blade with a gap width of 200 µm on to a glass plate and dried for 7 d at room temperature. A clear, glossy film with a pendulum hardness (drying for 14 days at RT) of 75 seconds is obtained.

Example 11 (according to the invention):

UV-curing and oxidation-drying dispersion

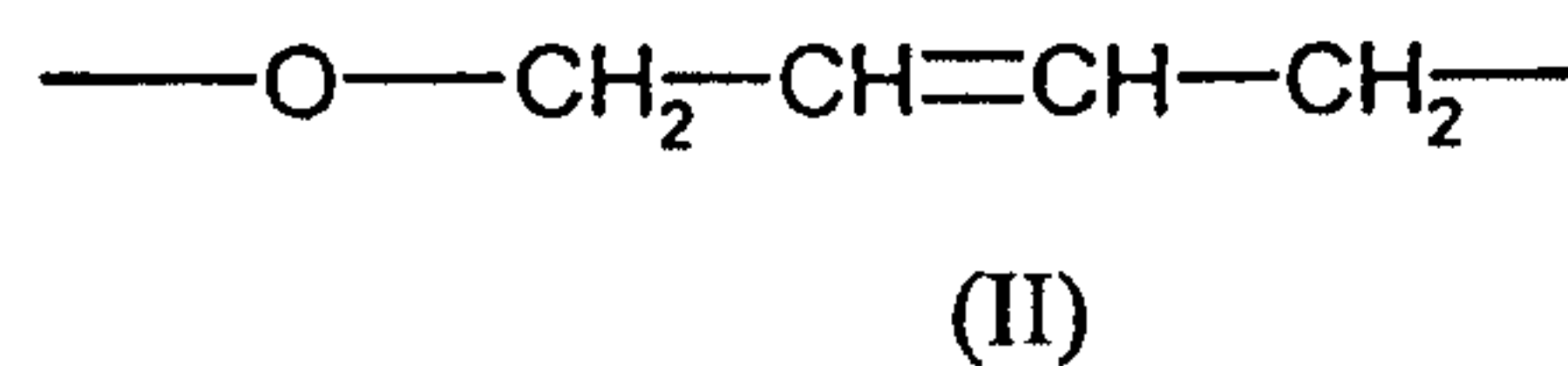
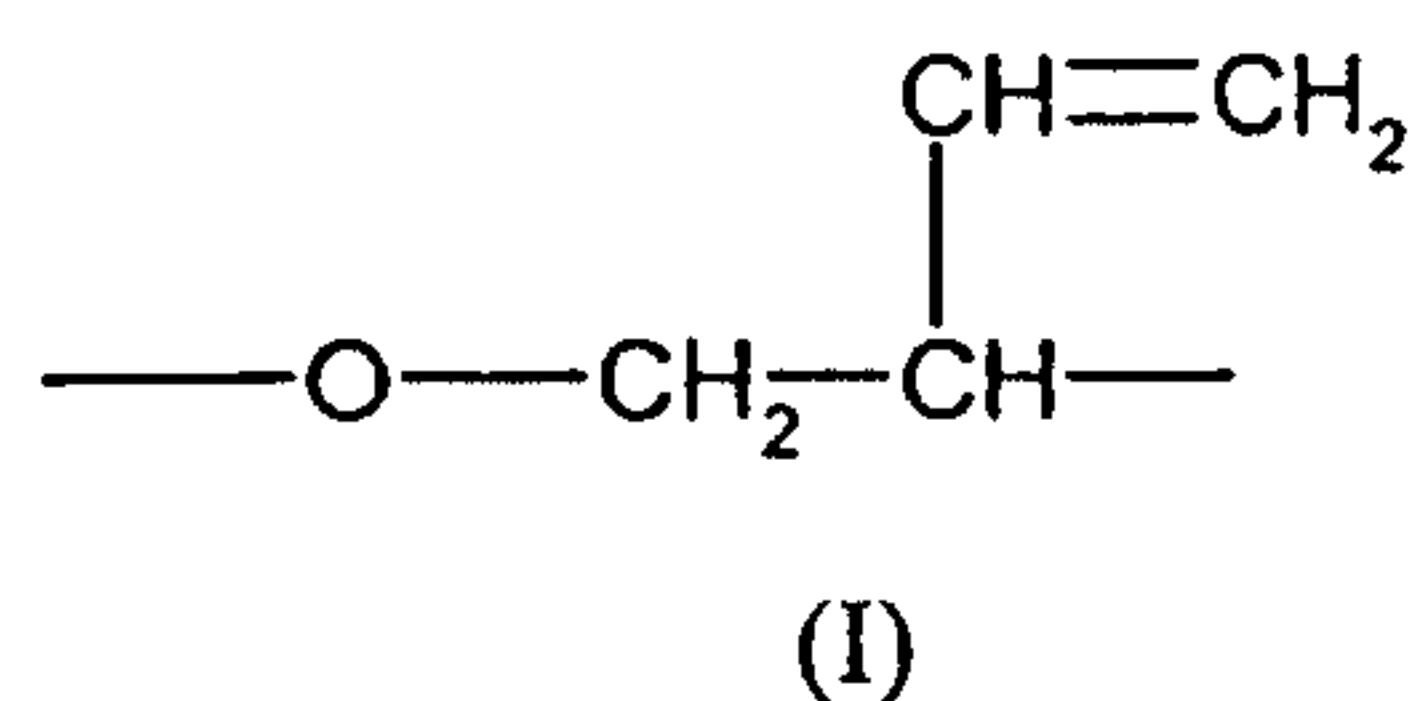
313.0 g of the polyester-acrylate Laromer[®] PE 44F (polyester-acrylate; BASF AG, Ludwigshafen, DE), OH content approx. 80 mg KOH/g, and 87.7 g of the polyether-diol from example 1, 21.0 g dimethylolpropionic acid, 0.5 g dibutyltin dilaurate and 172.2 g acetone are initially introduced into a 2 l reaction vessel with a stirrer, internal thermometer and gas inlet (stream of air of 2 to 3 l/h), 79.9 g Desmodur[®] I (isophorone-diisocyanate; Bayer AG, Leverkusen, DE) and 39.4 g Desmodur[®] H (hexamethylene-diisocyanate; Bayer AG, Leverkusen, DE) are added and the mixture is heated up such that a constant acetone reflux prevails. It is stirred at this temperature until the reaction mixture contains an NCO content of 1.6 wt.%. It is then cooled to 40°C and 15.8 g triethylamine are added rapidly. After 10 min the reaction mixture is poured into 938.1 g water of 18°C with rapid stirring. When the dispersion has formed, 8.0 g ethylenediamine in 23.5 g water are added. After the mixture has been subsequently stirred without heating or cooling for 30 min, the product is distilled in vacuo (50 mbar, max. 50°C) until a solids content of 38.6 wt.% is reached. The viscosity of the dispersion was a flow time of 24.7 s in a DIN 4 cup, the pH was determined as 8.6 and the average particle size according to laser correlation spectroscopy measurement (Zetasizer 1000, Malvern Instruments, Malvern, UK) was 60.0 nm.

Use example 12

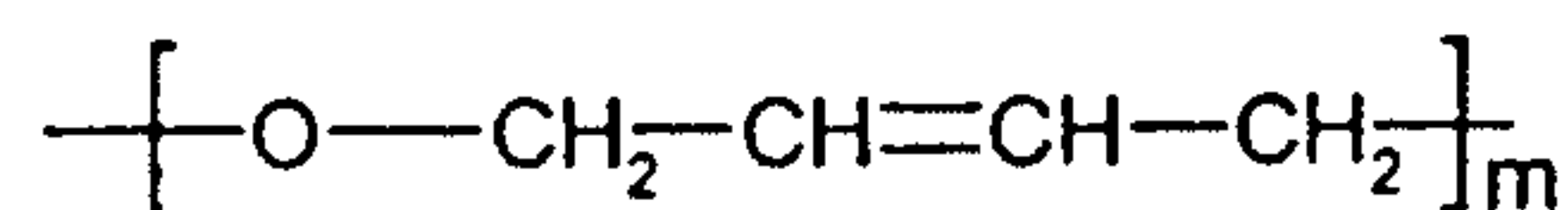
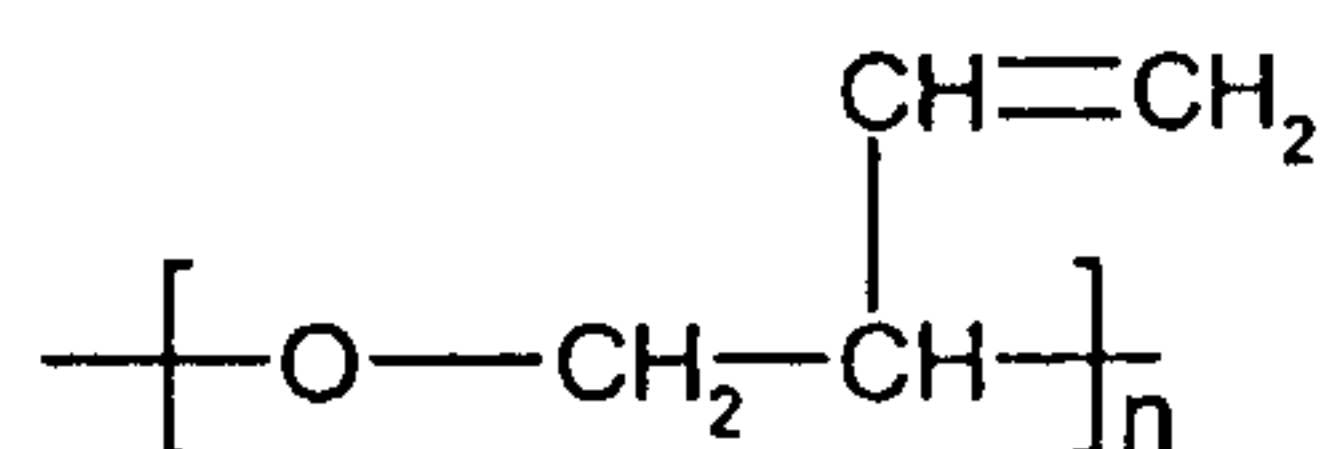
1.5 wt.% Irgacure[®] 500 (photoinitiator, Ciba Spezialitätenchemie, Lampertheim, DE), calculated with respect to the solids content of the dispersions, are stirred into a
5 portion of the dispersion according to the invention of example 11. After the dispersion has been left to stand overnight, it is drawn on to a glass plate by means of a 150 µm bone doctor-blade. The coated glass plate is kept at room temperature for 40 min. A clear, transparent and touch-dry film is formed. Thereafter, the coated glass plate is moved at a speed of 5 m/min under a medium pressure mercury
10 lamp (output 80 W/cm lamp length). The film UV-cured in this way shows a König pendulum hardness of 59 30 min after the irradiation. The pendulum hardness rises to 82 in the course of storage at room temperature for 36 hours.

Patent claims

1. Water-dilutable polymer which contains urethane groups and has ionic and/or potentially ionic groups, characterized in that the polymer comprises the recurring units (A1) of the formula (I) and/or (A2) of the formula (II)



2. Water-dilutable polymer according to claim 1, characterized in that the recurring units A1, A2 or mixtures of A1/A2 are present in the polymer in blocks



- or in mixed blocks of both structural units with p recurring units, wherein n, m and p each represent integers from 3 to 100.

3. Water-dilutable polymer according to claims 1 or 2, characterized in that the polymer is a reaction product comprising the components

- (a1) 5 to 80 wt.% of polyisocyanates,
- (a2) 10 to 80 wt.% of polyols and/or polyamines with an average molecular weight M_n of at least 400,
- (a3) 2 to 15 wt.% of compounds which contain at least one group which is reactive towards isocyanate groups and at least one ionic and/or potentially ionic group,

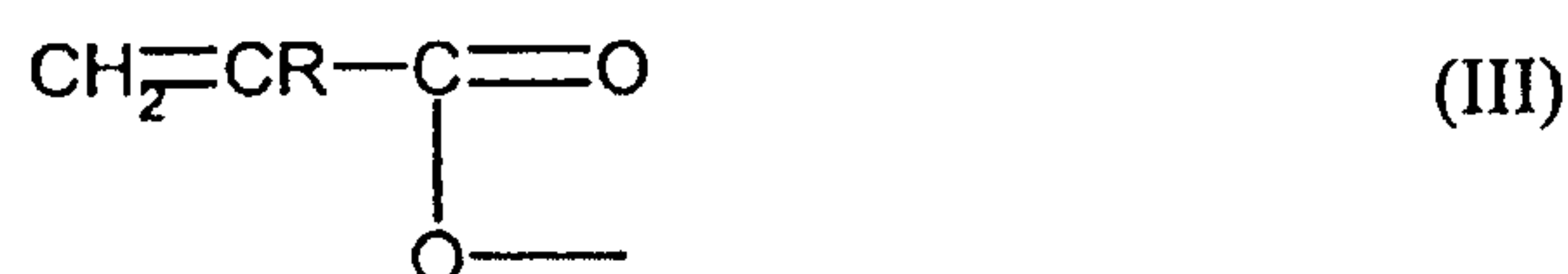
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- (a4) 0 to 20 wt.% of low molecular weight polyols and/or secondary polyamines,
(a5) 0 to 20 wt.% of chain stoppers,
(a6) 0 to 20 wt.% of chain lengtheners which contain at least two groups which are reactive towards isocyanate groups and differ from (a2), (a3) and (a4).

4. Water-dilutable polymer according to claim 1, characterized in that it additionally contains C=C double bonds in structural units of mono- or polyunsaturated fatty acids.

5. Water-dilutable polymer according to claim 1, characterized in that it additionally contains C=C double bonds in acrylic acid and/or methacrylic acid ester units A3 of the formula (III)

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6. Water-dilutable polymer according to one or more of claims 1 to 5, characterized in that the polymer has a content of ionic and/or potentially ionic groups of 9 to 100 meq/100 g.

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7. Water-dilutable polymer according to one or more of claims 1 to 6, characterized in that the ionic and/or potentially ionic groups are carboxyl and/or sulfonic acid groups.

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8. Water-dilutable polymer according to one or more of claims 1 to 7, characterized in that the polymer has a content of urethane groups [NHCOO] of 1 to 40 wt.%.

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9. Water-dilutable polymer according to one or more of claims 1 to 8, characterized in that the polymer has a content of structural units A1 and/or A2 of 2 to 80 wt.%.
- 5 10. Aqueous dispersion comprising
- (A) 20 to 70 wt.% of at least one water-dilutable polymer containing urethane groups according to claim 1,
- (B) 0 to 20 wt.% of organic co-solvents and
- (C) 10 to 70 wt.% of water.
- 10 11. Coating compositions comprising a water-dilutable polymer containing urethane groups according to claim 1.
- 15 12. Process for the production of oxidation-drying coatings, characterized in that the coating composition comprises water-dilutable polymers containing urethane groups according to claim 1 as binders.
- 20 13. Process for the production of UV-curing coatings, characterized in that the coating composition comprises water-dilutable polymers containing urethane groups according to claim 1 as binders and one or more photoinitiators.
14. Use of the water-dilutable polymers containing urethane groups according to claim 1 for the production or oxidation-drying coatings.
- 25 15. Use of the water-dilutable polymers containing urethane groups according to claim 1 for the production of UV-curing coatings.
16. Substrates coated with coating compositions comprising water-dilutable polymers containing urethane groups according to claim 1.