Proposed is an aqueous polymer dispersion for use in coating compositions to obtain high gloss topcoats, use being made in the preparation of monomer compositions A and B, one of which has a Tg in the polymerised state of at least 40 °C, as well as at least 60 °C higher than the Tg of the other monomer composition in the polymerised state, with the overall monomer composition being formed by ethylenically unsaturated compounds composed of: 1) at least 80 wt.% of one or more compounds selected from the group of alkenyl aromatic monomer, acrylonitrile, an alkyl, (hetero)cycloalkyl or aralkyl ester of acrylic acid and methacrylic acid having 4-22 C-atoms, acrylamide and methacyrylamide, acrylamide and methacrylamide N-substituted with an alkyl, cycloalkyl or aralkyl group having 1 to 18 carbon atoms, vinyl acetate, and vinyl versatate, with up to 25 wt.% of these compounds optionally containing a second functional group capable of reacting with an appropriate curing agent; 2) 0.1 to 5 wt.% of an ethylenically unsaturated carboxylic acid; and 3) 0.1 to 5 wt.% of a nitrogenous, adhesion promoting, copolymerisable monomer, with the proviso that at least 60 wt.% of the carboxylic acid is incorporated into the monomer composition holding less than 40 wt.% of the adhesion promoting comonomer, with the mass flow to the reactor of monomers of the composition containing monomer composition A, which is larger by a factor of 1.1 to 11, proceeding simultaneously with the mass flow of monomers of monomer composition B to the composition containing monomer composition A.
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AQUEOUS POLYMER DISPERSION FOR USE IN WATER BASED GLOSSY LACQUERS

The invention pertains to an aqueous polymer dispersion which can be obtained by the emulsion polymerisation of \( \alpha, \beta \)-ethylenically unsaturated monomers comprising a monomer composition A and a monomer composition B, with the reactor being fed the monomer composition A continually being replenished with the monomer composition B, to a process for preparing such dispersions, to aqueous coating compositions incorporating these dispersions, and to high gloss topcoats obtained using these coating compositions.

The preparation of polymer dispersions of the aforesaid type is disclosed, int. al., in US-A-3,804,881. The monomer flow charged to the reactor is continually varying in compositional content through the supply of one or more monomer flows of a different composition to the vessel from which the monomer flow is fed to the reactor. In this way particles continually varying in compositional content are obtained. A key advantage of the process described in this document is indicated to be that the thus obtained polymer dispersions are characterised by a very broad glass transition temperature range. As a result, the topcoats obtained using coating compositions prepared with these dispersions are more flexible at room temperature and have less tendency to exhibit surface tack. The adhesion of the topcoats can be improved still further by a gradual and continuous increase in the concentration of adhesion promoting monomers in monomer composition A prior to the conclusion of the polymerisation reaction, which will cause a layer of adhesion promoting functional groups to form on the surface of the disperse particles.

Although coating compositions which contain dispersions prepared in this manner have very good adhesion as compared with coating compositions
which do not incorporate adhesion promoting monomers, it was found that the
gloss of the topcoats obtained using coating compositions containing these
dispersions shows greater similarity to that of topcoats obtained using coating
compositions incorporating dispersions of the core/shell type. It was further
found that the simultaneous presence of adhesion promoting monomers and
carboxylic groups-containing monomers required for the stability of the
dispersions is attended with substantial contamination of the reactor.
The invention now provides polymer dispersions with markedly enhanced
properties, notably as regards the adhesion and gloss of topcoats obtained
using coating compositions containing these dispersions, without any problems
being experienced during the preparation of these dispersions as a result of
contamination of the reactor.
The invention consists in that in the preparation of a polymer dispersion of the
known type mentioned in the opening paragraph use is made of the monomer
compositions A and B, one of which has a Tg in the polymerised state of at
least 40°C, as well as at least 60°C higher than that of the other monomer
composition in the polymerised state, and the overall monomer composition is
formed by ethylenically unsaturated compounds composed of:

1) at least 80 wt.% of one or more compounds selected from the group of
alkenyl aromatic monomer, acrylonitrile, an alkyl, (hetero)cycloalkyl or aralkyl
ester of acrylic acid and methacrylic acid having 4-22 C-atoms, acrylamide
and methacrylamide, acrylamide and methacrylamide N-substituted with an
alkyl, cycloalkyl or aralkyl group having 1 to 18 carbon atoms, vinyl acetate,
and vinyl versatate, with up to 25 wt.% of these compounds optionally
containing a second functional group capable of reacting with an appropriate
curing agent,

2) 0.1 to 5 wt.% of an ethylenically unsaturated carboxylic acid, and

3) 0.1 to 5 wt.% of a nitrogenous, adhesion promoting copolymerisable
monomer, with the proviso that at least 60 wt.% of the carboxylic acid is
incorporated into the monomer composition holding less than 40 wt.% of the
adhesion promoting comonomer, with the mass flow to the reactor of monomers of the composition containing monomer composition A, which is larger by a factor of 1.1 to 11, proceeding simultaneously with the mass flow of monomers of monomer composition B to the composition containing monomer composition A.

By “mass flow to the reactor of monomers of the composition containing monomer composition A” is meant according to the invention the amount of mass (A + B) fed to the reactor per unit of time. By “mass flow of monomers of monomer composition B to the composition containing monomer composition A” is meant the amount of mass of monomer composition B introduced into the tank holding the composition containing monomer composition A per unit of time. Monomer composition B can be charged from a single tank into the one holding monomer composition A. Alternatively, the monomers of composition B can be charged into the tank holding monomer composition A from tanks holding different compositions rather than from a single tank. In that case, composition B is first formed in situ in the tank holding monomer composition A. The mass flow of the monomer composition charged to the reactor is up to 11 times higher than the mass flow of monomer composition B to the tank in which monomer composition A is present. In this process, preference is given to a mass flow of up to 5 times higher than the mass flow of monomer composition B to the tank. Optimum results were obtained with a mass flow to the reactor twice as high as the mass flow of monomer composition B to the tank holding the composition containing monomer composition A.

It should be noted that polymer dispersions with which coating compositions for topcoats having high gloss and good adhesion can be obtained were recently proposed in US-A-5,021,469. Unlike the presently proposed polymer dispersions, the known polymer dispersions are made up of particles having a core and a shell, the core consisting of a material having a glass transition
temperature (Tg) of at least 40°C and the shell consisting of a material having a
Tg of less than 70°C and at least 20°C below the Tg of the core material. The
shell contains, int. al., ethylenically unsaturated carboxylic acids and
nitrogenous, adhesion promoting monomers. Unlike with the preparation of the
presently proposed polymer dispersions, there is substantial contamination of
the reactor during the preparation. Moreover, when using the presently
proposed dispersions topcoats of higher gloss and better adhesion can be
obtained.

US-A-5,326,814 proposes a more specific process for preparing polymer
dispersions for the aforesaid use. To improve adhesion up to 5 wt.% of an
ethylenureido group-containing monomer and 1 to 3 wt.% of an ethylenically
unsaturated carboxylic acid are added. The preparative process involves first
making a pre-emulsion of all the monomers except for those having an
ethylenureido group. Next, the pre-emulsion is slowly added to the reactor,
with an emulsion of the ethylenureido group-containing monomer also being
introduced into the reactor during the first part of the addition process.
The topcoats obtained using these dispersions likewise are in need of
improvement when it comes to gloss and tack. Moreover, the process
described in this document also has substantial contamination of the reactor.
Where the text refers to glass transition temperature, Tg, what is meant is Tg as
calculated in accordance with a method described by T.G. Fox in the Bulletin of
the American Physical Society, Volume 1, Issue 3, p. 123 (1956). This
calculation employs the constants as specified by J. Brandup and E.H. Imergut
(1975). (Meth)acrylate in the text stands for acrylate as well as methacrylate.
(Hetero)cycloalkyl in the text stands for heterocycloalkyl as well as cycloalkyl.
The monomer composition having a Tg in the polymerised state of at least 40°C
is essentially composed of monomers where the Tg of the homopolymers is at
least 80°C, such as styrene, α-methyl styrene, acrylonitrile, and methacrylo-
nitrile, methyl, isopropyl, tert. butyl, and cyclohexyl methacrylate or vinyl chloride.

Examples of comparatively soft monomers where the Tg of the homopolymers generally is below 80°C and preferably below 40°C are acrylate esters of the

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formula \( \text{CH}_2=\text{C}(\text{R}^1)-\text{C}(\text{O})-\text{OR}^2 \), wherein \( \text{R}^1 \) stands for a hydrogen atom or a methyl group and \( \text{R}^2 \) stands for an alkyl or cycloalkyl group having at least 2 and not more than 18 carbon atoms. Examples include n-butyl acrylate, sec. butyl methacrylate, 2-ethylhexyl methacrylate, iso-octyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, nonyl acrylate, dicyclopentenyl oxyethyl methacrylate, isodecyl acrylate, lauryl methacrylate, and stearyl methacrylate. Examples of aralkyl esters are 2-phenylethyl methacrylate and 3-phenylpropyl methacrylate. Examples of heterocyclic alkyl esters of acrylic and methacrylic acid, respectively, are furfuryl methacrylate and tetrahydrofurfuryl acrylate.

Examples of other suitable monomers are N-substituted compounds of acrylamide and methacrylamide such as N-tert.butyl acrylamide, N-tert.hexyl acrylamide, N-tert.octyl acrylamide, N-(1,5-dimethyl-1-ethyl)hexyl acrylamide, N-(1,1-dimethyl-2-phenyl)ethyl acrylamide, N-cyclohexyl acrylamide, N-(1-methylbutyl)acrylamide, N-ethyl acrylamide, N-ethylhexyl acrylamide, N-butyl methacrylamide, and N-cyclohexyl methacrylamide.

20 Also, functional groups such as hydroxyl, amino, epoxy, and carbonyl may be present, or ethylenically unsaturated groups such as are present in the reaction product of an unsaturated fatty acid with glycidyl methacrylate and dicyclopentadienyl acrylate.

Examples of hydroxy-functional monomers are 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, and hydroxybutyl acrylate.

The hydroxy-functional monomers can be cross-linked with polyisocyanates which may be blocked or not, melamines, and urea resins.
Examples of amino-functional monomers are N,N-dimethyl aminoethyl methacrylate, N,N-dimethyl aminoethyl acrylate, and N-tert.butyl aminoethyl methacrylate.

The amino-functional monomers can be cross-linked with epoxy-functional compounds, polyisocyanates which may be blocked or not, and polycarboxylic acids.

One example of an epoxy-functional monomer is glycidyl methacrylate. This monomer can be cross-linked with di- and multifunctional compounds having a carboxyl, hydroxyl and/or amino function.

Examples of carbonyl-functional monomers are diacetone acrylamide and acetoacetoxyethyl methacrylate. They can be cross-linked with hydrazides and amines.

Examples of compounds where the Tg of the homopolymers is at least 80°C are alkenyl aromatic monomers such as styrene, o-methyl styrene, p-methyl styrene, o,p-dimethyl styrene, o,p-diethyl styrene, p-chlorostyrene, isopropyl styrene, t-butyl styrene, o-methyl-p-isopropyl styrene, o,p-dichlorostyrene, and mixtures thereof.

Also, cross-linking agents having two or more, say, two to six, ethylenically unsaturated groups per molecule may be present, such as triallyl cyanurate, vinyl or allyl acrylate or methacrylate, diol diacrylates and diol dimethacrylates, and methylene bisacrylamide or methylene bismethacrylamide. The quantity of these cross-linking agents used generally ranges from 0.01 to 5 wt.%. The presence of a small quantity of cross-linking agent can have a beneficial effect on the film's hardness and the adhesion properties.

The weight ratio of monomer composition A to monomer composition B can vary within a wide range, but is generally selected in the range of 1:10 to 10:1. As a rule, preference is given to a composition where the monomer composition which has the highest Tg in the polymerised state makes up 10 to 50 wt.% of the polymer dispersion, calculated on the weight of the polymer.
The ethylenically unsaturated carboxylic acid makes up at least 0.1 to 5 wt.% of the overall monomer composition. Preferably, at least 60 wt.% thereof is incorporated into monomer composition A. Of the adhesion promoting monomer preferably at least 60 wt.% is present in monomer composition B.

Examples of suitable ethylenically unsaturated carboxylic acids are acrylic acid, methacrylic acid, maleic acid, fumaric acid, and itaconic acid.

The monomer composition incorporating more than 60 wt.% of the present carboxylic acid preferably contains 65 to 100 wt.% of the overall quantity of carboxylic acid. To enhance the stability of the obtained dispersions during the polymerisation process it may be advantageous for up to 20% of the carboxylic acid to be present in the salt form through neutralisation with ammonia, inorganic bases such as alkali hydroxides, e.g., lithium hydroxide, potassium hydroxide or sodium hydroxide, or organic amines, such as N,N-dimethyl ethanolamine, N,N-diethyl ethanolamine, triethyl amine, and morpholine.

Optionally, in addition to the ethylenically unsaturated carboxylic acids other acid, non-carboxylic groups-containing monomers polymerisable under the influence of radicals may be present. As examples may be mentioned 2-acrylamido-2-methylpropene sulphonic acid or the alkali, ammonia or amine salt thereof and the sodium salt of the adduct of allylglucidyl ether to sodium bisulphite.

The monomer composition incorporating more than 60 wt.% of the adhesion promoting monomer preferably contains over 65 wt.% thereof, with optimum results being obtainable at a percentage in the range of 80 to 100 wt.%.

Suitable adhesion promoting monomers generally are monomers polymerisable under the influence of radicals and containing amino, ureido or N-heterocyclic groups. Examples of such monomers are dimethyl aminoethyl(meth)acrylate, diethyl aminoethyl(meth)acrylate, 3-dimethylamino-2,2-dimethylprop-1-(meth)-acrylate, N-dimethylenaminomethyl(meth)acrylamide, N-(4-morpholinomethyl) (meth)acrylamide, vinyl imidazole, and vinyl pyrrolidone. Further mention may be made of compounds having a pyrrolidine, piperidine, morpholine, piperazine,
imidazole, pyrrolidin-(2)-one or imidazolidin-2-one (ethylene urea) ring. In this case preference is given to ureido-functional monomers such as N-(2-methacryloyloxyethyl)ethylene urea, 1-(2-(3-allyloxy-2-hydroxypropylamino) ethyl)-imidazolidin-2-one, and 2-ethylenureido-ethyl methacrylate.

To promote film forming at lower temperatures also compounds may be incorporated which enter into a chemical combination with other monomeric, difunctional compounds at low temperature, resulting in the polymer being cross-linked.

Examples of such monomers are acrolein, methacrolein, diacetone acrylamide, diacetone methacrylamide, and vinyl acetoacetate. These compounds generally make up 1 to 4 wt.% of the overall monomer composition. At low temperature and in an aqueous medium they react with hydrazides of aliphatic dicarboxylic acids of which 0,3 to 1, preferably 0,4 to 0,8 mole is present per mole of the difunctional compound. Examples of suitable dihydrazides are oxalic dihydrazide, glutaric dihydrazide, adipic dihydrazide, sebacic dihydrazide, maleic dihydrazide, fumaric dihydrazide and/or itaconic dihydrazide.

Within the framework of the invention preference is given to compositions at least 80 wt.% of which is made up of styrene, methyl methacrylate, 2-ethylhexyl acrylate and/or butyl acrylate.

Optimum results are generally obtained when the composition of the monomers forming the polymer dispersion is such that the Tg of the copolymer thereof is in the range of 10 to 40°C. Further, preference is given to a polymer dispersion where the concentration of ethylenically unsaturated carboxylic acid in composition A is at least twice as high as in composition B.

The invention also pertains to a process for preparing aqueous polymer dispersions of the aforesaid composition by subjecting a monomer composition A which is continually replenished with a monomer composition B to an emulsion polymerisation, with the Tg of one of the monomer compositions in the polymerised state being at least 40°C, as well as at least 60°C higher than the Tg of the other monomer composition in the polymerised state, with the
overall monomer composition being formed by ethylenically unsaturated compounds composed of:

1) at least 80 wt.% of one or more compounds selected from the group of alkenyl aromatic monomer, acrylonitrile, an alkyl, (hetero)cycloalkyl or aralkyl ester of acrylic acid and methacrylic acid having 4 to 22 C-atoms, acrylamide and methacrylamide, acrylamide and methacrylamide N-substituted with an alkyl, cycloalkyl or aralkyl group having 1 to 18 carbon atoms, vinyl acetate, and vinyl versatate, with up to 25 wt.% of these compounds optionally containing a second functional group capable of reacting with an appropriate curing agent,

2) 0,1 to 5 wt.% of an ethylenically unsaturated carboxylic acid, and

3) 0,1 to 5 wt.% of a nitrogenous, adhesion promoting, copolymerisable monomer, with the proviso that at least 60 wt.% of the carboxylic acid is incorporated into the monomer composition holding less than 40 wt.% of the adhesion promoting comonomer, with the mass flow to the reactor of monomers of the composition containing monomer composition A, which is larger by a factor of 1,1 to 11, proceeding simultaneously with the mass flow of monomers of monomer composition B to the composition containing monomer composition A.

In actual practice, the preparation of the polymer dispersions according to the present invention will generally proceed as follows. In a first process step the use of batchwise emulsion polymerisation results in so-called seed particles being formed. The number of formed seed particles is determined essentially by the temperature during polymerisation and by the quantity of emulsifier and initiator used in this process. In a subsequent process step more monomer mixture is added, and the seed particles grow to become the final particles of the dispersion. The size of these particles usually does not exceed 250 nm, but preferably is < 150 nm.
The emulsion polymerisation is carried out using a radical initiator such as alkali or ammonium persulphate, bis(2-ethylhexyl) peroxydicarbonate, di-n-butyl peroxydicarbonate, t-butyl perpivalate, t-butyl hydroperoxide, cumene hydroperoxide, dibenzoyl peroxide, dilauroyl peroxide, 2,2'-azobis iso-butyronitrile, and 2,2'-azobis-2-methyl butyronitrile. Suitable reducing agents which are used in combination with, e.g., a persulphate or a hydroperoxide include: ascorbic acid, sodium formaldehyde sulfoxylate, thiosulphates, disulphates, hydrosulphates, water-soluble amines, such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, N,N'-dimethyl ethanolamine, N,N-diethyl ethanolamine, and reducing salts, such as cobalt, iron, nickel, and copper sulphate. If so desired, a chain-length regulator, e.g., mercaptoethanol, n-octyl mercaptan, dodecyl mercaptan or 3-mercaptopropionic acid may be employed.

The copolymerisation of the monomer mixtures is generally carried out under atmospheric pressure at a temperature of 40-100°C, preferably 60-90°C, in an atmosphere of an inert gas, such as nitrogen. If so desired, however, it is also possible to carry out the copolymerisation under elevated pressure and at a temperature of 40-100°C or higher.

As a rule, the monomer concentration of the two monomer compositions is selected such that the solids content of the polymer dispersion is in the range of 25 to 60 wt.%. The monomers can be fed as such, but usually a pre-emulsion is employed.

When preparing the emulsion usually an emulsifier is employed. Preferably, the emulsifiers used in the emulsion polymerisation are of an anionic or non-ionic nature. Examples of anionic emulsifiers are: potassium laurate, potassium stearate, potassium oleate, sodium decyl sulphate, sodium dodecyl sulphate, and sodium rosinate. Examples of non-ionic emulsifiers are: linear and branched alkyl and alkylaryl polyethylene glycol ethers and thioethers and linear and branched alkyl and alkylaryl polypropylene glycol ethers and thioethers, alkylphenoxyprop(ethylenoxy)ethanols such as the adduct of 1 mole
of nonylphenol to 5-50 moles of ethylene oxide, or the alkali salt or ammonium salt of the sulphate or the phosphate of said adduct.

The dispersions according to the invention are pre-eminently suited to be incorporated into an aqueous coating composition. These coating compositions can be hardened by physical drying. Curing can also be carried out in a different manner, when the addition polymer contains hydroxyl groups and the aqueous dispersion contains a curing agent which reacts with hydroxyl groups. Suitable curing agents include N-methylocryl- and/or N-methylocryl ether groups-containing aminoplasts obtained by reacting an aldehyde, e.g., formaldehyde, with an amino groups- or amido groups-containing compound, such as melamine, urea, N,N'-ethylene urea, dicyandiamide, and benzoguanamine. The resulting compounds preferably are wholly or partially etherified with alcohols having 1 to 6 carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, amyl alcohol, hexanol, or mixtures thereof.

Especially favourable results can be obtained when use is made of a methylocryl melamine having 4 to 6 methyl groups per molecule of melamine, with at least 3 methylol groups being etherified with butanol, or a condensation product of formaldehyde and N,N'-ethylene diurea etherified with butanol. Other suitable curing agents are, e.g., water-dispersible polyisocyanates which may be blocked or not, such as a methylcyclohexyl ketoxime-blocked, isocyanate group-containing adduct of a polyisocyanate to a hydroxycarboxylic acid, e.g., dimethylol propionic acid.

The dispersions according to the invention can be applied to a substrate in any manner desired, e.g., by means of rolling, spraying, brushing, sprinkling, flow coating, dipping, (electrostatic) spraying, or coating by electrophoresis. Suitable substrates include those of wood, metal, paper, hardboard and softboard, concrete, stone, masonry, glass, ceramic material, and synthetic material. Curing can be carried out at ambient temperature or, optionally, at an elevated temperature to reduce the curing time. If so desired, the composition can be
baked at higher temperatures, e.g., of between 60 and 160°C, in a drying oven for 10 to 60 minutes.

The invention will be further illustrated below with reference to the following examples, which are submitted for a better understanding of the invention only. They are not to be construed as being limiting in any manner whatsoever. Unless otherwise specified, all parts in the examples and comparative examples are parts by weight.

The viscosity in the examples below was determined using a Brookfield LVT viscometer with No. 3 spindle and 60 revolutions per minute (rpm) at 20°C.

The solids content, SC, was determined in accordance with ISO 3251.

The gloss was determined with the aid of a BYK Haze-gloss 4601 in accordance with ISO 2813.

The particle size was determined by means of dynamic light scattering using a Malvern Autosizer Lo-C. The contamination of the reactor was measured by filtering the dispersion through a 250 mesh (about 60 μm) filter gauze, and drying and weighing the residue. The percentage by weight is calculated on the overall dispersion.

Sticking together (blocking) was measured using a BYK Gardner Blocking Tester (as per Rohm & Haas). This test apparatus was used in a climatisation room to measure, at room temperature and a relative humidity (RH) of 50%, the force required to separate two panels first aged for 6 days and then placed with the paint surfaces face to face. To this end the coating composition to be tested was applied with an automatic film applicator (K Control Coater, RL Print-Coat Instrument, Ltd) under standard conditions (23°C and a relative atmospheric
humidity of 50%) as 125 μm thick films onto a number of white chart forms (Leneta). After 6 days of ageing at 23°C and 50% RH small rectangles of 25x50 mm were cut out. The side of these rectangles not covered with coating composition was then taped to glass slides with double-face adhesive tape. A BYK Gardner centering device was used to stack the slides two by two, with the coating compositions placed face to face, after which a load weight of 1000 g was placed on the slides for 2 hours. Next, the slides were arranged in the Blocking Tester, and measurements were carried out with load weights of 0,2500 g and 5000 g. The tables below list the force required to separate the films for the different coating compositions.

The hardness according to König was determined in accordance with DIN 5157.

Wet adhesion was measured as follows. First, a wooden panel was primed with a filler which gives a very flat surface, after which a dark high-gloss paint based on an alkyd resin was applied. The panel was dried for at least 1 month at 23°C and 50% RH. Half of the panel was sandpapered with 120 grain sandpaper. Next, the coating composition was applied onto the entire panel with a 150 μm applicator blade. The film was dried for 1 week at 23°C and 50% RH. A pad of kleenex tissue soaked with water was applied to the film. Subsequently, a check pattern was made in the two halves using an "ISO-ASTM-DIN-NF crosscut." To this pattern 38 mm wide transparent filament tape (3M, ref. 898F) was stuck, which was quickly pulled loose at a 45° angle without tearing. The result is given on a scale of 0 (no adhesion) to 5 (perfect adhesion without the film coming loose).

**Example I (Preparation of polymer dispersion I)**

A 2,5 l polymerisation reactor equipped with a stirrer, a thermometer, a reflux condenser, and various inlets was filled with:

618,4 g of demineralised water,
29.7 g of emulsifier (sodium salt of nonylphenol ether sulphate having 10 ethylene oxide units (Perlankrol SN ex Akros Chemicals)
Two tanks, A and B, were filled with monomer mixtures of the following composition:

<table>
<thead>
<tr>
<th>Monomer Mixture</th>
<th>B</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demineralised water</td>
<td>177.1</td>
<td>194.9</td>
</tr>
<tr>
<td>Perlankrol SN(^1)</td>
<td>8.7</td>
<td>9.7</td>
</tr>
<tr>
<td>Diacetone acrylamide</td>
<td></td>
<td>31.2</td>
</tr>
<tr>
<td>2-ethylhexyl acrylate</td>
<td>59.3</td>
<td>388.0</td>
</tr>
<tr>
<td>Styrene</td>
<td>197.6</td>
<td>62.4</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>227.3</td>
<td>12.0</td>
</tr>
<tr>
<td>Nourycryl MA 123(^2)</td>
<td>31.2</td>
<td>--</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>9.9</td>
<td>21.3</td>
</tr>
<tr>
<td>Ammonia (25 wt.%)</td>
<td>0.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>

\(^1\) Perlankrol SN (ex Akros Chemicals) = sodium salt of nonylphenol ether sulphate having 10 ethylene oxide units
\(^2\) Nourycryl MA 123 (ex Akzo Nobel Chemicals) = 1-(2-methacroyl oxyethyl) imidazolin-2-one as 50 wt.% solution in methyl methacrylate.

Charged into the reactor were 36 parts of monomer mixture A, after which the contents of the reactor were heated up to a temperature of 72°C under an atmosphere of nitrogen. Next, a solution of 1.1 parts of sodium persulphate in 10.3 parts of demineralised water were added. On conclusion of the exothermic reaction the temperature was increased to 79°C. The monomer mixture of tank B was pumped into tank A, with vigorous stirring, over a period of 2.5 hours. At the same time, the contents of tank A were pumped into the reactor. Simultaneous with the feeding of the contents of tank A an initiator mixture composed of 1.8 parts of sodium persulphate and 168.9 parts of demineralised
water was charged to the reactor. After all additions had ceased the temperature of the reactor was kept at 79°C for a further 30 minutes. The reaction mixture was then cooled to 65°C and neutralised with 9.5 parts of ammonia (25 wt.% solution in water), after which there were added to it 1.4 parts of tert.butyl hydroperoxide in 4.6 parts of demineralised water followed by a solution of 0.6 parts of sodium sulphoxylate formaldehyde in 8 parts of demineralised water. After 30 minutes a solution of 19.2 parts of adipodihydrazide in 75.9 parts of demineralised water was added to the reaction mixture. The mixture was cooled to 30°C, and 3.8 parts of ammonia (25 wt.% solution in water) dissolved in 8.7 parts of demineralised water and 3.6 parts of Acticide SR911 (biocide ex Thor Chemicals) were added. The properties measured on the dispersion were as follows: pH 8.8, SC 44.6%, viscosity 560 mPas, and particle size 90 nm. Reactor contamination was about 0.05 wt.%.

Comparative example IA (Preparation of polymer dispersion IA)

The comparative example below shows that the simultaneous presence of adhesion enhancing agent and ethylenically unsaturated carboxylic acid leads to contamination of the reactor. The preparation proceeded in a manner analogous to that disclosed in Example I, with the proviso that this time the composition of the monomer mixtures was as follows:
Table 2

<table>
<thead>
<tr>
<th>monomer mixture</th>
<th>B</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>demineralised water</td>
<td>177,1</td>
<td>194,9</td>
</tr>
<tr>
<td>Perkrol SN</td>
<td>8,7</td>
<td>9,7</td>
</tr>
<tr>
<td>diacetone acrylamide</td>
<td></td>
<td>31,2</td>
</tr>
<tr>
<td>2-ethylhexyl acrylate</td>
<td>59,3</td>
<td>388</td>
</tr>
<tr>
<td>styrene</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>164,9</td>
<td>74,4</td>
</tr>
<tr>
<td>Nourycryl MA123</td>
<td></td>
<td>31,2</td>
</tr>
<tr>
<td>methacrylic acid</td>
<td>9,9</td>
<td>21,3</td>
</tr>
<tr>
<td>ammonia (25 wt.% solution in water)</td>
<td>0,5</td>
<td>1,3</td>
</tr>
</tbody>
</table>

The properties measured on the dispersion were as follows:

pH 9, SC 44.2%, viscosity 250 mPas, and particle size 95 nm.

Reactor contamination was about 0.1 wt.%.

**Comparative example IB (Preparation of polymer dispersion IB)**

In the comparative example below it is shown that the same monomers as in Example I can be used to obtain a polymer dispersion where the individual particles are composed of a shell and a core. The shell contains both carboxyl groups and more or less basic, adhesion promoting groups. To prevent the carboxyl groups from interfering with the adhesion promoting groups, the shell is applied in two phases.

The preparation proceeded in a manner analogous to that disclosed in Example I, with the proviso that this time use was made of three pre-emulsions instead of two, with these pre-emulsions, unlike in the process adhered to in Example I, being fed to the reactor successively in accordance with the teaching of US-A-5,021,469 discussed above.

The composition of pre-emulsions 1, 2, and 3 is given in the table below.
Table 3

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>demineralised water</td>
<td>194,9</td>
<td>177,1</td>
<td>88,5</td>
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<tr>
<td>Perlankrol SN</td>
<td>9,7</td>
<td>8,7</td>
<td>4,35</td>
</tr>
<tr>
<td>diacetone acrylamide</td>
<td>31,2</td>
<td></td>
<td>29,7</td>
</tr>
<tr>
<td>2-ethylhexyl acrylate</td>
<td>388</td>
<td>59,3</td>
<td>113,7</td>
</tr>
<tr>
<td>styrene</td>
<td>62,4</td>
<td>260</td>
<td>98,8</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>12,0</td>
<td>164,9</td>
<td></td>
</tr>
<tr>
<td>Nourycryl MA 123</td>
<td></td>
<td></td>
<td>31,2</td>
</tr>
<tr>
<td>methacrylic acid</td>
<td>21,3</td>
<td>9,9</td>
<td></td>
</tr>
</tbody>
</table>

Fed to the reactor was a mixture made up of 618,4 parts of demineralised water, 29,7 parts of Perlankrol SN, and 36 parts of pre-emulsion A. The contents of the reactor were then heated to 72°C under a nitrogen atmosphere, after which 1,1 parts of sodium persulphate in 10,3 parts of demineralised water were added. On conclusion of the exothermic reaction the temperature was raised to 79°C. The remaining pre-emulsion A and 50% of the initiator mixture were fed to the reactor in 70 minutes, after which the reactor was kept at said temperature for a further 20 minutes. Next, in 40 minutes, pre-emulsion B was added along with 25% of the initiator mixture, whereupon the reactor was kept at a temperature of 79°C for another 30 minutes. Next, in 40 minutes, pre-emulsion C was added along with the remaining 25% of initiator mixture, after which the temperature of the reaction mixture was kept at 79°C for 30 more minutes. The dispersion was then cooled to room temperature, neutralised with 15,38 parts of ammonia (25 wt.% solution in water) in 50,14 parts of demineralised water, and filtered.

The properties measured on the dispersion were as follows:
pH 8,7, SC 45,0%, viscosity 1060 mPas, and particle size 85 nm.
Reactor contamination was about 6 wt. %.

**Comparative example IC (Preparation of polymer dispersion IC)**

The comparative example below shows that the preparation of the polymer dispersions as described in US-A-5,326,814, which are obtained from the same monomers as the dispersions according to the present invention, also is attended with noticeable reactor contamination.

The composition of the two pre-emulsions, A and B, is given in the table below.

<table>
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<tr>
<th>Pre-emulsion</th>
<th>A</th>
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<td>demineralised water</td>
<td>372</td>
<td>69.9</td>
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<tr>
<td>Perlankrol SN</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td>diacetone acrylamide</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td>2-ethylhexyl acrylate</td>
<td>447.3</td>
<td></td>
</tr>
<tr>
<td>styrene</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>239.3</td>
<td></td>
</tr>
<tr>
<td>Nourycryl MA 123</td>
<td></td>
<td>31.2</td>
</tr>
<tr>
<td>methacrylic acid</td>
<td>32.2</td>
<td></td>
</tr>
</tbody>
</table>

To the reactor was fed a mixture composed of 618.4 parts of demineralised water, 29.7 parts of Perlankrol SN, and 36 parts of pre-emulsion A. The contents of the reactor were then heated to 72°C under a nitrogen atmosphere, after which 1.1 parts of sodium persulphate in 10.2 parts of demineralised water were added. On conclusion of the exothermic reaction the temperature was increased to 79°C. Over a period of 2.5 hours the remaining pre-emulsion A was fed to the reactor along with an initiator solution composed of 3.45 parts of sodium persulphate in 160 parts of demineralised water, with pre-emulsion B being fed to the reactor for the first 30 minutes of the process. After all emulsions had been introduced into the reactor, its temperature was kept at
79°C for a further 30 minutes. Next, the reactor was cooled to room temperature, followed by neutralisation with a 25 wt.% ammonia solution in water until the pH was about 9.

The polymer dispersion was then filtered through an 80 μm perlon filter.

The properties measured on the dispersion were as follows:

pH 9.2, SC 44.3%, viscosity 230 mPas, and particle size 103 nm.

Reactor contamination was about 1.4 wt.%.

Example II (Preparation of polymer dispersion II)

A 3 l polymerisation reactor equipped with a stirrer, a thermometer, a reflux condenser, and various inlets was filled with:

- 833.1 g of demineralised water,
- 45.0 g of emulsifier (sodium salt of alkyl ether sulphate having 10 ethylene oxide units (Perlankrol EP 36 ex Akros Chemicals) and
- 0.2 g of ammonia (25 wt.%).

Two tanks, A and B, were filled with monomer mixtures of the following composition:
Table 5

<table>
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<tr>
<th></th>
<th>B</th>
<th>A</th>
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</thead>
<tbody>
<tr>
<td>demineralised water</td>
<td>238,5</td>
<td>262,5</td>
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<tr>
<td>Perlinkrol EP 36</td>
<td>14,0</td>
<td>15,0</td>
</tr>
<tr>
<td>diacetone acrylamide</td>
<td>-</td>
<td>41,2</td>
</tr>
<tr>
<td>n-butyl acrylate</td>
<td>-</td>
<td>569,0</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>302,0</td>
<td>-</td>
</tr>
<tr>
<td>styrene</td>
<td>197,6</td>
<td>62,4</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>336,0</td>
<td>55,0</td>
</tr>
<tr>
<td>N,N'-dimethyl aminoethyl methacrylate</td>
<td>26,6</td>
<td>--</td>
</tr>
<tr>
<td>methacrylic acid</td>
<td>-</td>
<td>21,0</td>
</tr>
<tr>
<td>ammonia (25 gew.%)</td>
<td>0,7</td>
<td>1,7</td>
</tr>
<tr>
<td>Cylink Triallyl cyanurate</td>
<td>1,0</td>
<td>1,0</td>
</tr>
<tr>
<td>Cylink TAC ex Cytec Industries</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The contents of the reactor were heated to a temperature of 70°C under an atmosphere of nitrogen, after which 48,5 parts of monomer mixture A and an initiator solution made up of 1,5 parts of sodium persulphate in 13,9 parts of demineralised water were added. On conclusion of the exothermic reaction the temperature was increased to 85°C and at the same time the dosing of mixtures A and B was started.

The monomer mixture of tank B was pumped into tank A, with vigorous stirring, over a period of 1,5 hours. At the same time, the contents of tank A were pumped into the reactor. Simultaneous with the feeding of the contents of tank A an initiator mixture composed of 2,5 parts of sodium persulphate and 227,4 parts of demineralised water was added to the reactor. After dosing of the 2 monomer mixtures had ceased the temperature of the reaction mixture was kept at 85°C for a further 30 minutes, after which the pumps of tanks A and B were flushed with 5 parts of demineralised water. Next, the reaction mixture was cooled to 65°C, followed by the incorporation into the reaction mixture over
15 minutes of 1,8 parts of tert.butyl hydroperoxide in 6,3 parts of demineralised water and then of a solution of 0,8 parts of sodium sulphoxylate formaldehyde in 10,8 parts of demineralised water. After 30 minutes a solution of 25,9 parts of adipodihydrazide was added. The mixture was cooled to 30°C, and 4,8 parts of Acticide AS (biocide ex Thor Chemicals) were added.

The properties measured on the dispersion were as follows:

pH 6,8, SC 45,8%, viscosity 20 mPas, and particle size 135 nm.

Reactor contamination was about 0,05 wt.%.

10 Comparative example IIA (Preparation of polymer dispersion IIA)

The comparative example below shows that the simultaneous presence of adhesion enhancing agent and ethylenically unsaturated carboxylic acid leads to contamination of the reactor. The preparation proceeded in a manner analogous to that disclosed in Example II, with the proviso that this time the composition of the monomer mixtures was as follows:

<table>
<thead>
<tr>
<th>monomer mixture</th>
<th>B</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>demineralised water</td>
<td>238,5</td>
<td>262,5</td>
</tr>
<tr>
<td>Peralanrol EP 36</td>
<td>14,0</td>
<td>15,0</td>
</tr>
<tr>
<td>diacetone acrylamide</td>
<td>-</td>
<td>41,2</td>
</tr>
<tr>
<td>n-butyl acrylate</td>
<td>59,3</td>
<td>388</td>
</tr>
<tr>
<td>n-butyl methacrylate</td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>164,9</td>
<td>74,4</td>
</tr>
<tr>
<td>N,N'-dimethyl aminoethyl methacrylate</td>
<td>-</td>
<td>26,6</td>
</tr>
<tr>
<td>methacrylic acid</td>
<td>7,0</td>
<td>14,0</td>
</tr>
<tr>
<td>ammonia (25 wt.% solution in water)</td>
<td>0,7</td>
<td>1,7</td>
</tr>
<tr>
<td>Cylink Trially cyanurate</td>
<td>1,0</td>
<td>1,0</td>
</tr>
<tr>
<td>Cylink TAC ex Cytec Industries</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As the dosing of the monomer mixtures was coming to an end, coagulation occurred.

**Example III**

The example below shows that the use of polymer dispersions according to the present invention in coating compositions leads to topcoats having a higher gloss than are obtained when the polymer dispersion of comparative example I A is employed in comparable coating compositions.

The preparation of the coating compositions was as follows. First, a premix based on 210 parts of titanium dioxide (Finnititan RD3 ex Kemira) was prepared in 19,9 parts of water containing 5,7 parts of a dispersant (Dispex GA40 ex Allied Colloids), 6,6 parts of the biocide Acticide EP Paste (ex Thor Chemicals) and 2 parts of the biocide Proxel XL2 (ex Zeneca), 40 parts of propylene glycol, 2 parts of a 90% solution in water of aminomethyl propanol (AMP-90 ex Angus Chemical), and 1 part antifoaming agent (Dehydran 1293 ex Henkel KGAA).

The premix was homogenised by being mixed for 10 minutes with a high-speed mixer at 500 to 1000 rpm. 287,2 parts of the premix were then mixed with 595,2 parts of the dispersions of Example I and Comparative example IA, respectively. Following the addition of 19,1 parts of 2,2,4-trimethyl-1,3-pentane diol-monoisobutyrate, 5,1 parts of aqueous ammonia (25%), 3,1 parts of antifoaming agent (Dehydran 1293 ex Henkel KGAA), and 57,3 parts of a thickener solution composed of 50% of Acrysol RM5 (ex Rohm & Haas) the solution was diluted with an 8.6% solution of ammonia in water up to a total of 1000 parts, and the pH of the composition was determined to be about 9. Next, the two compositions were applied onto a glass plate as one 200 μm thick film with the aid of a brushing knife, or with a brush as two films onto a wooden panel already coated with a primer (Flexa Universal Primer, ex Akzo Nobel). The gloss of the coats of lacquer (measured at 20°) in all cases was determined
after 24 hours of ageing at room temperature. The outcome of the measurements is listed in the table below.

<table>
<thead>
<tr>
<th>Table 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>gloss (measured at 20°)</td>
</tr>
<tr>
<td>coat of lacquer based on dispersion of Example I</td>
</tr>
<tr>
<td>coat of lacquer based on dispersion of Example IA</td>
</tr>
</tbody>
</table>

The results listed in the table above clearly show not only that the preparation of dispersions according to the present invention produces substantially lower contamination of the reactor, but also that the coating compositions so prepared exhibit substantially improved gloss.

Water resistance was determined by the glass plate onto which the coating composition to be tested was coated being immersed in a water bath containing demineralised water at room temperature. The plate coated with the coating composition of Example I did not show any sign of blistering after 7 hours of immersion, whereas microblisters were already forming on the plate of Comparative example IA after 5 hours.

**Example IV**

In a manner analogous to that disclosed in Example III coating compositions were made of the dispersions of Example I and Comparative examples IB and IC.

First, a premix based on 199,7 parts of titanium dioxide (type Kronos 2190 ex Kronos Titan GmbH), 1,5 parts of a dispersant (Orotan 1124 ex Rohm & Haas), 1,5 parts of ammonia (25%), 0,5 parts of a biocide (Proxel XL2 ex Zeneca), and 1 part of an antifoaming agent (Foamaster 111 ex Henkel) was prepared. The premix was dispersed in a horizontal pearl mill to a fineness of less than 10 μm.
After there had been added to 608.8 parts each of the polymer dispersions of Example I and Comparative examples IB and IC 22 parts of a 25% aqueous solution of a wetting agent (Berol 09 ex Berol Nobel), 2 parts of a antifoaming agent (Dehydran 1293 ex Henkel KGaA), 60 parts of demineralised water, and 0.5 parts of a flow additive (Dow Corning PA 84 ex Dow Corning), the thus obtained polymer dispersions were mixed, with stirring, with 271 parts of the premix. The resulting coating compositions were mixed with 65.2 parts of an aqueous thickener solution (32.6 parts of demineralised water, 4.1 parts of ammonia (25%), and 28.5 parts of Acrysol (ex Rohm & Haas)), after which demineralised water was employed to achieve a spraying viscosity of 25 s. (DIN cup No. 4).

The resulting coating compositions were sprayed onto MDF panels, whereupon after 7 days the gloss was measured at angles of 20° and 60°. Also, a number of properties were determined, such as the minimum film-forming temperature (MFFT) and the König hardness after 1 day and 1 week. To this end the coating compositions were applied onto a glass plate in one 120 µm thick film. Also measured were blocking and wet adhesion. To this end the coating compositions were coated onto a dark, high-gloss alkyd film (black Levislux ex Akzo Nobel). The outcome of the measurements is shown in Table 8.

<table>
<thead>
<tr>
<th>coating composition based on polymer dispersion of Example</th>
<th>I</th>
<th>IB</th>
<th>IC</th>
</tr>
</thead>
<tbody>
<tr>
<td>gloss at 20°</td>
<td>33</td>
<td>22</td>
<td>27</td>
</tr>
<tr>
<td>gloss at 60°</td>
<td>82</td>
<td>72</td>
<td>79</td>
</tr>
<tr>
<td>MFFT (polymer dispersion)</td>
<td>&lt; 0°C</td>
<td>&lt; 0°C</td>
<td>9°C</td>
</tr>
<tr>
<td>König hardness after 1 day</td>
<td>44s</td>
<td>31s</td>
<td>23s</td>
</tr>
<tr>
<td>König hardness after 1 week</td>
<td>59s</td>
<td>32s</td>
<td>39s</td>
</tr>
<tr>
<td>blocking (N/cm²)</td>
<td>&lt; 0.15</td>
<td>0.21</td>
<td>9.6</td>
</tr>
<tr>
<td>wet adhesion</td>
<td>5</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
The results listed in the table above clearly show that the gloss, the film-forming rate, the König hardness, and the blocking of coating compositions based on the dispersions according to the present invention are superior to those of the well-known polymer dispersions based on core/shell particles.
Claims

1. An aqueous polymer dispersion which can be obtained by the emulsion polymerisation of \( \alpha,\beta \)-ethylenically unsaturated monomers comprising a monomer composition A and a monomer composition B, with the reactor being fed the monomer composition A continually being replenished with the monomer composition B, characterised in that the Tg of one of the monomer compositions in the polymerised state is at least 40°C, as well as at least 60°C higher than that of the other monomer composition in the polymerised state, and the overall monomer composition is formed by ethylenically unsaturated compounds composed of:

1) at least 80 wt.% of one or more compounds selected from the group of alkenyl aromatic monomer, acrylonitrile, an alkyl, (hetero)cycloalkyl or aralkyl ester of acrylic acid and methacrylic acid having 4-22 C-atoms, acrylamide and methacrylamide, acrylamide and methacrylamide N-substituted with an alkyl, cycloalkyl or aralkyl group having 1 to 18 carbon atoms, vinyl acetate, and vinyl versatate, with up to 25 wt.% of these compounds optionally containing a second functional group capable of reacting with an appropriate curing agent,

2) 0.1 to 5 wt.% of an ethylenically unsaturated carboxylic acid, and

3) 0.1 to 5 wt.% of a nitrogenous adhesion promoting, copolymerisable monomer, with the proviso that at least 60 wt.% of the carboxylic acid is incorporated into the monomer composition holding less than 40 wt.% of the adhesion promoting comonomer, with the mass flow to the reactor of monomers of the composition containing monomer composition A, which is larger by a factor of 1.1 to 11, proceeding simultaneously with the mass flow of monomers of monomer composition B to the composition containing monomer composition A.
2. A polymer dispersion according to claim 1, characterised, in that the Tg of monomer composition A in the polymerised form is at least 40°C.

3. A polymer dispersion according to claim 1, characterised in that the Tg of the overall monomer composition is in the range of 10 to 40°C.

4. A polymer dispersion according to claim 1, characterised in that the concentration of ethylenically unsaturated carboxylic acid in one composition is at least twice as high as in the other composition.

5. A polymer dispersion according to claim 1, characterised in that the nitrogenous, copolymerisable monomer is a compound having one or more amino, ureido and/or N-heterocyclic groups.

6. A process for the preparation of an aqueous polymer dispersion according to one or more of the preceding claims by the emulsion polymerisation of \( \alpha,\beta \)-unsaturated polymers comprising a monomer composition A and a monomer composition B, with the reactor being fed monomer composition A being continually replenished with monomer composition B, characterised in that the Tg of one of the monomer compositions in the polymerised state is at least 40°C as well as at least 60°C higher than that of the other monomer composition in the polymerised state, and the overall monomer composition is formed by ethylenically unsaturated compounds composed of:

1) at least 80 wt.% of one or more compounds selected from the group of alkenyl aromatic monomer, acrylonitrile, an alkyl, (hetero)cycloalkyl or aralkyl ester of acrylic acid and methacrylic acid having 4-22 C-atoms, acrylamide and methacrylamide, acrylamide and methacrylamide N-substituted with an alkyl, cycloalkyl or aralkyl group having 1 to 18 carbon atoms, vinyl acetate, and vinyl versatate, with up to 25 wt.% of
these compounds optionally containing a second functional group capable of reacting with an appropriate curing agent,

2) 0.1 to 5 wt.% of an ethylenically unsaturated carboxylic acid, and

3) 0.1 to 5 wt.% of a nitrogenous, adhesion promoting copolymerisable monomer, with the proviso that at least 60 wt.% of the carboxylic acid is incorporated into the monomer composition holding less than 40 wt.% of the adhesion promoting comonomer, with the mass flow to the reactor of monomers of the composition containing monomer composition A, which is larger by a factor of 1.1 to 11, proceeding simultaneously with the mass flow of monomers of monomer composition B to the composition containing monomer composition A.

7. An aqueous coating composition incorporating a polymer dispersion according to one or more of claims 1 to 5 and, optionally, a curing agent.

8. Use of an aqueous coating composition according to claim 7 to apply a topcoat which will exhibit high gloss after curing.
A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F2/22

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

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

Electronic database consulted during the international search (name of database and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>A</td>
<td>US 3 804 881 A (D. ROBINSON) 16 April 1974 cited in the application</td>
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<td>A</td>
<td>FR 2 328 721 A (UNION CARBIDE CORP.) 20 May 1977</td>
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<td>A</td>
<td>WO 92 01004 A (NOVACEL) 23 January 1992</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search: 14 January 1998

Date of mailing of the international search report: 22/01/1998

Name and mailing address of the ISA

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Fax: (+31-70) 340-3016

Authorized officer

Cauwenberg, C
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