

Description

This invention relates to selfcrosslinkable aqueous coating compositions containing certain vinyl polymers, and to certain vinyl polymers for use therein.

The provision of polymeric film coatings on a variety of substrates, usually for protective or adhesive purposes, is a well established field of technology. It is well known to improve the performance of such coatings by causing them to become crosslinked during and/or after film-formation from the composition. Aqueous polymer coating compositions for achieving such an objective are well known and a useful refinement has been to employ selfcrosslinkable polymer coating compositions for this purpose.

We have now discovered a new and useful class of selfcrosslinkable coating compositions for providing coatings of excellent properties which comprise certain vinyl polymers having certain functional groups dispersed therein to effect selfcrosslinking, often at ambient or low temperatures, during and/or after film-formation.

According to the present invention there is provided an aqueous selfcrosslinkable coating composition which comprises an aqueous dispersion comprising at least one vinyl polymer, wherein the polymer system constituted by said at least one vinyl polymer has chain-pendant amine functional groups and chain-pendant carbonyl functional groups to provide a selfcrosslinking reaction during and/or after coating formation from the composition, where by an amine functional group is meant an amine group which is bonded to a carbon atom and which can take part in selfcrosslinking with a carbonyl functional group, and by a carbonyl functional group is meant the carbonyl functionality of a ketone or aldehyde group.

For the purposes of this invention an "aqueous dispersion" means a dispersion of the at least one vinyl polymer in an aqueous medium of which water is the principal component.

Preferably the aqueous dispersion is an aqueous latex of said at least one vinyl polymer. Minor amounts of organic liquids may optionally be present.

By an amine functional group is meant, as defined above, an amine group which is bonded to a carbon atom and which can take part in selfcrosslinking with a carbonyl functional group. Preferably the amine group is bonded to a carbon atom of an aliphatic or aromatic grouping such as an alkylene or arylene group; the amine group is particularly a primary ($-NH_2$) aliphatic or aromatic amine group. It is particularly preferred that the pendant amine groups are incorporated by being part of chain-pendant aminoalkyl carboxylate groups of formula $-C(O)-O-R_1-NH_2$ where R_1 is an alkylene group, preferably of up to 20 carbon atoms, more preferably 2 or 3 carbon atoms.

By a carbonyl functional group in this specification (unless otherwise specified) is meant, as defined above, the carbonyl functionality of a ketone or aldehyde group. Such groups are derived from at least one carbonyl-functional olefinically unsaturated monomer used in the preparation of the vinyl polymer(s).

It may be mentioned here that US-A-3929743 discloses compositions comprising a water-soluble polymer having pendant carbonyl groups provided by carboxylic acid groups and pendant carbon-bound amine groups provided by pendant carboxylic amino ester groups. Such compositions, while not selfcrosslinkable, may be made crosslinkable by the addition of a compound which can form complexes or salts with the acid and/or amine groups, particularly a polyvalent metal ion. Such crosslinks may, however, be subsequently broken with ammonia or acid.

There are two basic possibilities embraced by the scope of the present invention. These are as follows:

A. The composition comprises at least one vinyl polymer bearing both chain-pendant amine functional groups and chain-pendant carbonyl functional groups in the same vinyl polymer molecules. This is the preferred possibility for the present invention. The compositions of this embodiment can optionally include additional vinyl polymer(s) bearing chain-pendant amine and/or carbonyl functional groups in different polymer molecules, although this is not preferred.

B. The at least one vinyl polymer of the composition consists of two or more vinyl polymers which bear chain-pendant amine functional groups and chain-pendant carbonyl functional groups in different vinyl polymer molecules.

The selfcrosslinking reaction afforded by the compositions of the invention probably occurs via the formation of azomethine groups



from the amine and carbonyl functionalities.

It is preferred that the composition of the invention contains amine functional and carbonyl functional groups in a ratio of 1:20 to 20:1, more preferably 1:10 to 10:1.

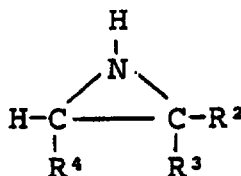
By a "vinyl polymer" in this specification is meant any addition polymer derived from one or more olefinically unsaturated monomers, ie the term is intended to be used in a general sense (and is not merely directed to polymers derived from monomers having the vinyl grouping) and eg embraces acrylic polymers and polymers comprising a high proportion of polymerised vinylidene chloride units.

It is believed that a vinyl polymer bearing both chain-pendant amine functional groups and chain-pendant carbonyl functional groups, as employed in the preferred composition of the invention (possibility A), is novel and inventive in its own right. Accordingly, the present invention is further directed to such a polymer.

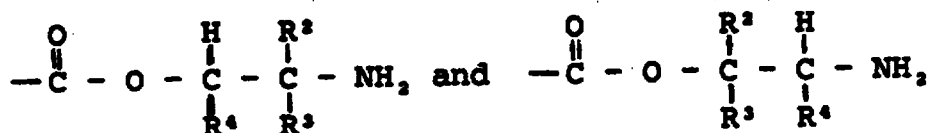
A vinyl polymer bearing both chain-pendant amine functionality and chain pendant carbonyl functionality is preferably a copolymer formed by first preparing, using a free-radical polymerisation process, a precursor copolymer comprising polymerised units of at least one olefinically unsaturated monomer having an amine precursor group(s) (i.e. a group which may be subsequently reacted to provide a pendant amine functional group, at least one carbonyl-containing olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer (i.e. monomer providing neither amine groups, amine precursor groups nor carbonyl functionality), and subsequently reacting at least a proportion of the amine precursor groups to provide chain-pendant amine functional groups.

The chain-pendant precursor group is particularly a carboxylic acid group $-\text{CO}_2\text{H}$ (or its carboxylate salt). Accordingly, the preferred vinyl polymer comprises a free radical addition polymer comprising polymerised units of at least one olefinically unsaturated monomer providing chain-pendant carboxyl groups at least a proportion of which have been subsequently reacted to provide chain-pendant amine functional groups, at least one carbonyl-containing olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer (providing neither amine groups, carboxyl groups nor carbonyl functionality).

It is particularly preferred that the chain-pendant amine functionality is introduced into the vinyl polymer by an imination reaction involving the carboxyl (or carboxylate salt) groups of the precursor polymer and an added aziridine compound. The aziridine compound is commonly referred to as an alkylene imine and preferably has the formula



where R^2 and R^3 which may be the same or different are selected from hydrogen, benzyl, aryl, and alkyl of 1 to 5 carbon atoms; and where R^4 is hydrogen or alkyl of 1 to 5 carbon atoms. More preferably R^2 is hydrogen, R^3 is hydrogen or alkyl of 1 to 5 carbon atoms (particularly methyl) and R^4 is hydrogen. Ethylene imine ($\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$) and propylene imine ($\text{R}^2 = \text{R}^4 = \text{H}$; $\text{R}^3 = \text{methyl}$) are particularly preferred aziridines because of their relatively low cost and ready availability. The corresponding chain-pendant amino ester groups (providing chain-pendant amine functional groups) formed by the imination reaction have the formulae



where R^2 , R^3 and R^4 are as defined above (in the case of using ethylene imine, these two formulae will be the same).

The amount of alkylene imine used should be sufficient to iminate the desired proportion of the carboxyl groups to aminoalkyl ester groups. Preferably the amount used should be sufficient to iminate about 5% to 95%, preferably 20% to 80%, of the carboxyl groups on the precursor polymer. The imination technique is in itself well-known and may be performed by techniques known to the art.

Monomers which can be used to provide carboxyl groups in the precursor polymer are particularly α,β -monoolefinically unsaturated monocarboxylic acids and/or dicarboxylic acids, usually of 3 to 6 carbon atoms, especially acrylic acid, methacrylic acid, beta-carboxyethylacrylate, fumaric acid and itaconic acid.

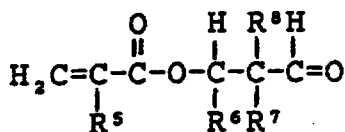
The chain-pendant amine functionality may also be introduced into the vinyl polymer by techniques other than imination.

In one such other method the amine precursor groups are oxazoline groups derived from the polymerisation of an olefinically unsaturated oxazoline monomer (i.e. an oxazoline having an unsaturated substituent in the 2-position). An example of such a monomer would be 2-isopropenyl oxazoline. Hydrolysis of oxazoline groups in the precursor polymer will yield aminoalkyl ester groups and hence provide chain-pendant amine groups.

In another such method, the amine precursor groups are ketimine groups derived from the polymerisation of a ketimine unsaturated monomer. Such monomers can e.g. be produced by first reacting a ketone or aldehyde with an aliphatic amino compound (selected from primary amines, secondary amines, and ethanolamines) to produce a ketimine, and further reacting the ketimine with an ethylenic derivative containing an ethylenically unsaturated group. A ketimine monomer can also be prepared by reacting an amino-containing olefinically unsaturated monomer with ketones or aldehydes (see US 4328144). Hydrolysis of ketimine groups in the precursor polymer will generate chain-pendant amine functional groups.

In another such method, there may be employed hindered amine monomers, i.e. olefinically unsaturated monomers bearing amine groups which are in a sterically hindered environment (e.g. by being bonded to a tertiary or perhaps secondary carbon atom).

Examples of olefinically unsaturated monomers which provide chain-pendant carbonyl functionality in the vinyl polymer (and in the precursor polymer to the vinyl polymer if precursor groups are used for the provision of amines functionality as described above) include acrolein, methacrolein, diacetone acrylamide, crotonaldehyde, 4-vinylbenzaldehyde, vinyl alkyl ketones of 4 to 7 carbon atoms such as vinyl methyl ketone, and acryloxy- and methacryloxy-alkyl propanals of formula



where R^5 is H or methyl, R^6 is H or alkyl of 1 to 3 carbon atoms, R^7 is alkyl of 1 to 3 carbon atoms, and R^8 is alkyl of 1 to 4 carbon atoms. Other examples include acrylamidopivalaldehyde, methacrylamidopivalaldehyde, 3-acrylamidomethyl-anisaldehyde, diacetone acrylate, acetonyl acrylate, diacetone methacrylate, acetoacetoxyethyl methacrylate, 2-hydroxypropylacrylate-acetylacetate, and butanediolacrylate acetylacetate.

The carbonyl-containing monomer(s) is preferably selected from acrolein, diacetone acrylamide, acetoacetoxyethyl methacrylate and methyl vinyl ketone.

The at least one vinyl polymer will normally also comprise a high proportion of polymerised units derived from one or more olefinically unsaturated monomers which provide neither amine functional groups, amine precursor groups, nor carbonyl functional groups. Examples of such monomers which may be mentioned include 1,3-butadiene, isoprene, styrene, divinyl benzene, acrylonitrile methacrylonitrile, vinyl halides such as vinylidene chloride (in particular) and vinyl chloride, vinyl esters such as vinyl acetate, vinyl propionate and vinyl laurate), heterocyclic vinyl compounds, alkyl esters of monoolefinically unsaturated dicarboxylic acids (such as di-n-butyl maleate and di-n-butyl fumarate) and, in particular, esters of acrylic acid and methacrylic acid of formula



where R^9 is H or methyl and R^{10} is alkyl or cycloalkyl of 1 to 20 carbon atoms (more preferably 1 to 8 carbon atoms) examples of which are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-propyl acrylate and n-propyl methacrylate.

Particularly preferred vinyl polymers according to the invention comprise at least the following polymerised units:

(a) units having pendant amine functional groups which are present in groups of formula $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}_2\text{NH}_2$, or $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ and $-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$, derived from precursor car-

boxyl groups in a corresponding precursor polymer by imination thereof with ethylene imine or propylene imine respectively;

(b) units derived from at least one carbonyl-containing monomer selected from acrolein, diacetone acrylamide, acetoacetoxyethyl methacrylate, and methyl vinyl ketone; and

5 (c) units derived from at least one olefinically unsaturated monomer other than one for providing chain-pendant amine and carbonyl functional groups, and particularly at least one monomer selected from those of formula $\text{CH}_2 = \text{CR}^9 \text{COOR}^{10}$ (as defined above) and vinylidene chloride.

The polymerised units of a precursor polymer having precursor carboxyl groups for conversion into units (a) (by imination) is preferably derived from at least one of acrylic acid, methacrylic acid, beta-
10 carboxyethylacrylate, fumaric acid, and itaconic acid.

Vinyl polymers having chain-pendant amine functional groups but not chain-pendant carbonyl functional groups, or having chain-pendant carbonyl functional groups but not chain-pendant amine functional groups (as might be used in possibility B) are known to the art and may be prepared as such. For example, a vinyl polymer having chain-pendant amine functionality (but not chain-pendant carbonyl functionality) could be
15 prepared as already described above for preparing the novel vinyl monomers of the invention with the omission of the use of any carbonyl-containing monomer (although the amine functionality could of course be achieved more simply by the direct polymerisation of an amine-containing olefinically unsaturated monomer such as an aminoalkyl ester of an olefinically unsaturated carboxylic acid). Similarly a vinyl polymer having chain-pendant carbonyl functionality (but not chain-pendant amine functionality) could be
20 prepared as already described above for preparing the novel vinyl polymers of the invention with either the omission of the use of any monomer which can provide (directly, or indirectly by means of a precursor group) chain-pendant amine functionality, or if such a monomer (of the precursor type) is in fact used, not performing any subsequent conversion to an amino function.

A vinyl polymer (or a precursor polymer thereof) for use in the composition of the present invention
25 (whether of the novel type used in possibility A or of the known type used in possibility B) may be prepared by any suitable free-radical initiated polymerisation technique, a free-radical initiator and (usually) appropriate heating being employed. The polymerisation is normally effected in an aqueous medium, and in particular aqueous emulsion polymerisation is used to prepare the polymer with conventional dispersants being used (e.g. anionic and/or non-ionic emulsifiers such as Na salts of dialkylsulphosuccinates, Na salts of
30 sulphated oils, Na salts of alkyl sulphonic acids, Na, K and ammonium alkyl sulphates, C_{22-24} fatty alcohols, ethoxylated fatty acids and/or fatty amides, and Na salts of fatty acids such as Na stearate and Na oleate; the amount used is usually 0.1 to 3% by weight on the weight of total monomer(s) charged) and conventional free radical initiators being used (e.g. hydrogen peroxide, persulphates such as ammonium persulphate, K persulphate and Na persulphate; redox systems may be used; the amount is generally 0.05
35 to 3% based on the weight of total monomers charged).

In one advantageous embodiments of the invention, a sequential polymerisation process is adopted whereby monomers of the core region (i.e. fed early) will provide a "soft" polymeric phase (e.g. glass transition temperature $T_g \leq 20^\circ\text{C}$, more preferably -45 to 15°C) while monomers for the shell region (i.e. late fed) will provide a "hard" polymeric phase (e.g. $T_g \geq 50^\circ\text{C}$, more preferably 60 to 95°C). The partition
40 of monomers between the first (early) and second (late) monomer feed can vary between wide limits. The early fed monomers are preferably used in an amount of 45 to 95% by weight based on total monomer feed, more preferably 60 to 90% by weight. The late fed monomers are preferably used in an amount of 5 to 55% by weight based on total monomer feed, more preferably 10 to 40% by weight.

Examples of "soft" core monomers include 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, n-butylacrylate, n-butyl methacrylate, n-octylacrylate, n-decyl acrylate, n-lauryl acrylate, n-lauryl methacrylate, ethyl acrylate; and examples of "hard" shell monomers include methyl methacrylate, isobutyl methacrylate, styrene, ethyl methacrylate, n-butyl methacrylate, and acrylonitrile. It should be appreciated that monomers which if they were polymerised alone would provide homopolymers of high T_g (e.g. $\geq 50^\circ\text{C}$) may optionally be used in the "soft" phase, and monomers providing homopolymers of low T_g (e.g. $< 10^\circ\text{C}$) may
50 optionally be used in the "hard" phase, so long as the T_g 's of both phases remain essentially soft and hard as discussed above and preferably within the above mentioned limits.

The said at least one vinyl polymer for use in the composition of the invention preferably has a weight average molecular weight within the range 5000 to 6,000,000 (more preferably 30,000 to 2,000,000).

The polymer system constituted by said at least one vinyl polymer and having chain-pendant amine and carbonyl functional groups as defined preferably contains a proportion of amine groups within the range
55 5 to 120 millimoles per 100g of (solid) polymer (more preferably 10 to 100 millimoles per 100g of solid polymer) and a proportion of carbonyl groups within the range 5 to 120 millimoles per 100g of solid polymer (more preferably 10 to 100 millimoles per 100g of solid polymers). As described already, such

groups may be present on different vinyl polymer chains or (more preferably) on the same vinyl polymer chain.

In the preferred vinyl polymers, which have both chain-pendant amine groups and chain-pendant carbonyl groups (being novel and claimed herein), the proportion of polymerised units bearing pendant amine groups is preferably in the range 1 to 20 mole% (more preferably 2 to 14 mole%), the proportion of polymerised units bearing pendant carbonyl groups is preferably in the range 1 to 20 mole % (more preferably 2 to 14 mole%), and the proportion of polymerised units bearing neither pendant amine nor pendant carbonyl groups is preferably in the range 60 to 90 mole % (more preferably 72 to 96 mole %).

In a further embodiment of the invention, the aqueous coating composition includes at least one polyhydrazine (or polyhydrazone) compound, i.e a compound having 2 or more hydrazine (or hydrazone) groups. This may further enhance the selfcrosslinking capacity of the composition and hence may further improve the properties of the resulting crosslinked coating.

Where the composition of the invention does incorporate a polyhydrazine (or polyhydrazone) compound, the level of such polyhydrazine (or polyhydrazone) compounds(s) is preferably that to provide a range 0.02 to 1.8 moles hydrazine (or hydrazone) groups per mole of carbonyl groups present in the vinyl polymer(s), more preferably 0.1 to 1.0 moles. Examples of such suitable polyhydrazine (or polyhydrazone) compounds include dicarboxylic acid bishydrazides of formula



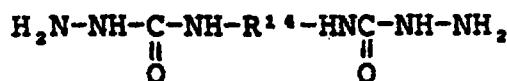
and dicarboxylic acid bis-hydrazones of formula.



wherein R^{11} is a covalent bond or a polyalkylene (preferably polymethylene) or alicyclic group having from 1 to 34 carbon atoms or a divalent aromatic ring, and R^{12} and R^{13} are selected from the group consisting of H and (C_1 to C_6) alkyl and alicyclic groups. Examples of suitable dihydrazides includes oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, cyclohexane dicarboxylic acid bis-hydrazide, azelaic acid bis-hydrazide, and sebacic acid dihydrazide. Other suitable compounds are polyhydrazides of carbonic acid, eg. carbonic acid dihydrazide and compounds of the general formula



where x is from 1 to 5, preferably from 1 to 3, and bis-semicarbazides, especially aliphatic and cycloaliphatic bis-semicarbazides of the general formula:



where $-\text{R}^{14}-$ is a straight or branched aliphatic radical of 2 to 7 carbon atoms or a carbocyclic radical of 6 to 10 carbon atoms, eg. o-, m- or p-phenylene or toluylene or cyclohexylidene or methylcyclohexylidene. Polyhydrazides of aromatic polycarboxylic acids, eg. the dihydrazides of phthalic acid, terephthalic acid and isophthalic acid, and the dihydrazides, the trihydrazide and the tetrahydrazide of pyromellitic acid, are other examples. Examples of other suitable compounds are polyhydrazides of polyacrylic acids which contain 2 or more hydrazide groups, in most cases from 20 to 100 hydrazide groups, per molecule, trihydrazides, eg. nitrilotriacetic acid trihydrazide, and tetrahydrazides, e.g. ethylenediaminetetraacetic acid tetrahydrazide. Further possible hydrazides are dihydrazino- and trihydrazino-triazine, thiocarbonylhydrazide and N,N'-diaminoguanidine, as well as hydrazinopyridine derivatives of the type of 2-hydrazino-pyridine-5-carboxylic acid hydrazide, 3-chloro-2-hydrazino pyridine-5-carboxylic acid hydrazide, 6-chloro-2-hydrazinopyridine-4-carboxylic acid hydrazide and 2,5-dihydrazinopyridine-4-carboxylic acid, and bis-thiosemicarbazides as well as bis-hydrazines of alkylene-bis-acrylamides, dihydrazinoalkanes and dihydrazines of aromatic hydrocarbons, eg. 1,4-dihydrazinobenzene, 1,3-dihydrazinobenzene and 2,3-dihydrazinonaphthalene.

The compositions of the invention, if containing polyhydrazine (or polyhydrazone) compound(s) optionally contain 0.0002 to 0.02 mole per mole of hydrazine (or hydrazone) groups of a heavy metal ion. This may be added in the form of suitable water-soluble metal salts, particularly chlorides, sulphates, and acetates. Suitable heavy metal water-soluble salts are, in particular, those of Cu, Zn, Fe, Cr, Mn, Pb, V, Co and Ni.

The aqueous composition of the invention if desired may include at least one other polymer (i.e. a polymer other than a functionalised vinyl polymer of the type(s) described above). This is usually a free radical addition polymer, formed by the free radical addition polymerisation of at least one olefinically unsaturated monomer. The different polymers may be present in the composition in simple admixture but can also be present in such a way that there is at least a proportion of chemical bonding between the polymers to form (in effect) at least a proportion of grafting between the polymers.

The incorporation of the further polymer into the composition of the invention may be effected in various ways, the simplest method being to simply admix preformed dispersions of the two types of polymer.

Another method is to conduct the polymerisation to form the further polymer in the presence of an aqueous-based dispersion of the at least one vinyl polymer (and obviously in such a process some grafting to the vinyl polymer may also occur).

Monomers which may be polymerised to form the optional further polymer component in embodiments or variants of the types discussed above include any free radical-polymerisable olefinically unsaturated compounds or mixtures thereof. Thus, there may be mentioned hydrocarbon monomers, for example 1,3-butadiene, isoprene, styrene and divinylbenzene, acrylic and substituted acrylic monomers, for examples acrylic and methacrylic acids, acrylonitrile, methyl, ethyl, n-butyl, isobutyl and 2-ethylhexyl acrylates and methacrylates, acrylamide, methacrylamide, N-methylolacrylamide, allyl and methallyl acrylates and methacrylates, and other commonly used monomers such as vinyl esters, vinyl ethers, and heterocyclic vinyl compounds.

The aqueous compositions of the invention may be advantageously employed as coating compositions, e.g. protective coating compositions) or adhesive coating compositions (particularly in pressure sensitive adhesive systems). For such purposes they may be used "as is" or further diluted with water and/or organic solvents, or they may be supplied in more concentrated form by evaporation of water and/or organic components of the liquid medium. As coating compositions, they may be applied to a variety of substrates including wood, metals, glass, cloth, leather, paper, plastics, foam and the like, by any conventional method including brushing, dipping, flow coating, and spraying. The compositions may contain other conventional ingredients including organic solvents, pigments, dyes, emulsifiers, surfactants, thickeners, heat stabilizers, levelling agents, anti-cratering agents, fillers, sedimentation inhibitors, fire retardants, UV absorbers, and antioxidants introduced at any convenient stage of the production process or subsequently.

In many cases the compositions are useful in applications where treatment is effected at ambient or low temperatures. In other cases they may advantageously be employed in stoving applications (using higher temperatures, e.g. where the coating is subjected to temperatures within the range of from 80 to 160 °C).

The compositions, which are in the form of aqueous dispersions, suitably have solids contents of from about 20 to 60% by weight, preferably from about 30 to 50% by weight.

The present invention is now illustrated by the following examples. Unless otherwise specified, all parts and percentages are on a weight basis. The prefix C before an example number denotes that it is comparative.

Example 1

This example describes the preparation of an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of an acrylic copolymer having pendant carbonyl-groups and having pendant amine groups. The preparation of this polymer latex was as follows.

A precursor polymer having pendant carbonyl and pendant carboxyl groups was first made using the following procedure.

To a three necked flask provided with an agitator, reflux condensor, dropping funnel and nitrogen inlet tube, was added: 554.91 parts of water and 22.20 parts of a 30% emulsifier (Akyposal 9278 R) solution. To this vessel, 10% of the emulsified first-feed composition described below was added. In a nitrogen atmosphere the temperature of the vessel contents was brought to 85 °C (while stirring). When this temperature had been reached the remaining part of the first-feed was added in 80 minutes at the same temperature. When the first feed had been added, the second feed composition described below was added (emulsified) to the reactor in 40 minutes. When the second feed had been completed the

temperature was kept at 85 °C for another hour before cooling to room temperature.

Composition first feed:	
	parts
water	200,00
emulsifier (30%)	36.26
potassium persulphate	2.23
n-butyl acrylate	271.95
n-butyl methacrylate	181.30
methacrylic acid	31.08
acrolein	33.67

Composition Second Feed:	
	parts
water	123.00
emulsifier (30%)	15.54
potassium persulphate	0.96
n-butyl methacrylate	62.16
methyl methacrylate	135.42
methacrylic acid	13.32
diacetone acrylamide	11.10

The precursor polymer latex was treated with ammonia (12.5%) to adjust the pH of the medium to 6.5. After this the emulsion was heated to 33 °C. Within 45 minutes, 21.64 parts of propylene imine was added. When the propylene imine had been added completely, the temperature was brought to 45 °C and maintained for 30 minutes before cooling to room temperature. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

Films made on glass plates from the iminated polymer emulsion, showed a methyl ethyl ketone (MEK) double rub resistance of at least 200 double rubs, when the films were aged one night at room temperature. When the films were made from the emulsion before iminisation, only 18 MEK double-rubs could be achieved before the polymer was dissolved completely. (The double rub test assesses the solvent resistance of a film and is effected by rubbing the film to and from with a rag soaked with the solvent until the substrate is showing through, the result being quoted as the number of double rubs to effect this).

Example 2

This example describes the preparation of an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of an acrylic copolymer having pendant carbonyl-groups and having pendant amine groups. The preparation of this polymer latex was as follows.

A precursor polymer having pendant carbonyl and pendant carboxyl groups was first made using the following procedure. To a three necked flask provided with an agitator, reflux condensor, dropping funnel and nitrogen inlet tube, was added: 643.66 parts of water and 70.25 parts of a 20% emulsifier (Surfagene FAZ-109V) solution. To this vessel, 10% of the emulsified feed composition described below was added. In a nitrogen atmosphere, the temperature of the vessel contents was brought to 90 °C (while stirring). When this temperature had been reached the remaining part of the feed was added in 60 minutes at the same temperature. After this, the reactor was kept at 90 °C for another hour before cooling to room temperature.

Composition feed:	
	parts
water	496.46
emulsifier (20%)	35.07
NaHCO ₃	0.96
ammonium persulphate	2.41
styrene	151.29
n-butyl methacrylate	435.62
butyl acrylate	80.40
methacrylic acid	28.14
acrylic acid	28.14
acetoacetoxyethylmethacrylate	80.40

The precursor polymer latex was treated with ammonia (12.5%) to adjust the pH of the medium to 7.0. After this, the emulsion was heated to 33 °C and 20.49 parts of propylene imine were added over 45 minutes. When the propylene imine had been added, the temperature was kept at 35 °C for another hour before cooling to room temperature. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

Films made on glass plates from the iminated emulsion showed a MEK- and ethanol double-rub resistance of at least 200 double rubs when the films were aged one night at room temperature. When the films were made from the emulsion before iminisation, only 14 MEK double-rubs and 58 ethanol double rubs could be achieved before the polymer was dissolved completely.

Example C3

This example describes the preparation of a comparative aqueous-based selfcrosslinkable coating composition containing an aqueous latex of an acrylic copolymer having pendant carbonyl groups but no pendant amine groups, and also a polyhydrazide compound. The polymer latex was prepared as follows.

To a three necked flask provided with an agitator, reflux condenser, dropping funnel and nitrogen inlet tube was added : 520.00 parts of water, 1.33 parts of sodium hydrogen carbonate and 32.50 parts of a 30% sodium lauryl ether sulphate emulsifier (Akyposal 9278 R) solution. To this vessel, 10% of the emulsified monomer feed composition described below was added. In a nitrogen atmosphere, the temperature of the vessel contents was brought to 85 °C (while stirring). When this temperature had been reached the remaining part of the emulsified monomer feed was added in 120 minutes, at the same temperature. The diacetone acrylamide (DAAM) solution described below was simultaneously added with the emulsified monomer feed, but at a rate of 80% during the first 80 minutes and 20% during the last 40 minutes. After completing the monomer feeds and maintaining the temperature at 85 °C for 15 minutes, a postreaction was started by adding a solution of 15.00 parts of water and 0.70 parts of potassium persulphate. After maintaining the temperature at 85 °C for 0.5 hour the polymer latex was cooled to room temperature.

Composition monomer feed:	
	parts
water	269.30
sodium hydrogen carbonate	1.33
sodium lauryl ether sulphate (Akyposal 9278R, 30%)	48.84
potassium persulphate	3.18
n-butyl acrylate	334.33
methyl methacrylate	324.27
methacrylic acid	44.40

Composition DAAM solution	
	parts
water	109.50
diacetone acrylamide	36.50

The polymer latex was neutralized with 51.37 parts of ammonia (12.5%) to pH 8.6. The polymer had pendant carbonyl groups but no pendant amine groups. To this emulsion was added 217.27 parts of a 7.5% adipic acid dihydrazide solution (pH 8-8.5) and 31.95 parts of a 0.08% zinc sulphate solution, followed by mixing the latex for 30 minutes.

Example 4

This example describes an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of an acrylic copolymer having pendant carbonyl and pendant amine groups.

To 1713.23 parts of a polymer as described in Example C3 before neutralization were added 6.06 parts of ammonia (12.5%) for neutralization to pH 6.5. The emulsion was heated to 30 °C and 20.62 parts of propylene imine were added during 40 minutes while maintaining a temperature of 30-35 °C. When the propylene imine had been added completely, the temperature was kept at 30-35 °C for 60 minutes. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

Example 5

This example describes an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of an acrylic copolymer having pendant carbonyl and pendant amine groups, and also a polyhydrazide compound.

To 1713.23 parts of a polymer as described in Example C3 (before neutralization) were added 6.06 parts of ammonia (12.5%) for neutralization to pH 6.5. The emulsion was heated to 30 °C and 20.62 parts of propylene imine were added during 40 minutes while maintaining a temperature of 30-35 °C. When the propylene imine had been added completely, the temperature was kept at 30-35 °C for 60 minutes. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

To this latex was added 76.43 parts of a 7.5% adipic acid dihydrazide solution (pH 8-8.5) and 10.68 parts of a 0.08% zinc sulphate solution. The latex was stirred for 30 minutes.

The properties of the films made from the compositions of Examples C3, 4 and 5 are shown in the following Table.

	Example C3	Example 4	Example 5
Ethanol double rubs (no.)	145	> 200	> 200
MEK double rubs (no.)	87	76	> 200

Example 6

This example describes the preparation of an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of an acrylic copolymer having pendant carbonyl and pendant amine groups. The preparation of this polymer latex was as follows.

A precursor polymer having pendant carbonyl and pendant carboxyl groups was first made using the following procedure. To a three necked flask provided with an agitator, reflux condenser, dropping funnel and nitrogen inlet tube, was added: 866.48 parts of water, 3.85 parts of sodium hydrogen carbonate, 2.60 parts of potassium persulphate and 56.81 parts of a sodium lauryl sulphate (Akyposal SLS) solution (30%). To this vessel, 10% of the first-feed composition as described below was added. In a nitrogen atmosphere, the temperature of the vessel contents was brought to 90 °C (while stirring). When this temperature had been reached, the remaining part of the first-feed was added in 50 minutes at the same temperature. When the first feed had been added, the second feed composition as described below was added to the reactor in 20 minutes. After completing the second monomer feed and maintaining the temperature at 85 °C for 15

minutes, a postreaction was started by adding a solution of 30.00 parts of water, 1.00 part of SLS emulsifier (30%) and 0.70 parts of potassium persulphate. After maintaining the temperature at 90 °C for 45 minutes the polymer latex was cooled to room temperature.

Composition first feed:	
	parts
n-butyl acrylate	319.75
methyl methacrylate	144.97
methacrylic acid	31.08
acrolein	22.20

Composition second feed:	
	parts
methyl methacrylate	190.34
n-butyl acrylate	18.34
methacrylic acid	13.32

The precursor polymer latex was treated with ammonia (12.5%) to adjust the pH of the medium to 6.5. After this the emulsion was heated to 35 °C. During 40 minutes, a solution of 20.60 parts of propylene imine and 20.60 parts of water was added. When the propylene imine had been added completely, the temperature was brought to 40 °C and maintained for 1 hour before cooling to room temperature. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

Films made on glass plates from the iminated polymer emulsion showed a MEK double rub resistance of at least 200 double rubs when the films were aged one night at 50 °C. When the films were made from the emulsion before iminisation, only 97 MEK double rubs could be achieved.

Example 7

This example describes the preparation of an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of an acrylic copolymer having pendant carbonyl and pendant amine groups. The preparation of this polymer latex was as follows.

A precursor polymer having pendant carbonyl and pendant carboxyl groups was first made using the following procedure. To a three necked flask provided with an agitator, reflux condensor, dropping funnel and nitrogen inlet tube, was added: 620.47 parts of water, 1.85 parts of sodium hydrogen carbonates, 1.54 parts of potassium persulphate and 66.88 parts of an emulsifier (Surfagene FAZ-109) solution (20%). To this vessel, 10% of the emulsified monomer feed composition described below was added. In a nitrogen atmosphere the temperature of the vessel contents was brought to 90 °C (while stirring). When this temperature had been reached the remaining part of the monomer feed composition described below was added in 60 minutes at the same temperature. When the monomer feed had been completed the temperature was kept at 90 °C for another hour. Residual free monomer content was decreased by a postreaction through the addition of 0.96 parts of tert butylhydroperoxide and feeding a solution of 2.31 parts of i-ascorbic acid and 23.10 parts of water in 30 minutes at 80-82 °C. After maintaining this temperature for another 30 minutes the polymer latex was cooled to room temperature.

Composition feed:	
	parts
water	401.32
sodium hydrogen carbonate	0.93
Surfagene FAZ-109 emulsifier (20%)	33.39
potassium persulphate	2.31
2-ethyl hexylacrylate	220.33
n-butyl methacrylate	72.71
styrene	385.66
acrylic acid	30.85
methacrylic acid	30.85
methyl vinyl ketone	30.85

The precursor polymer latex was treated with 32.84 parts of ammonia (12.5%) to adjust the pH of the medium to 6.3. After this the emulsion was heated to 30 °C. Within 30 minutes, a solution of 28.30 parts propylene imine and 24.64 parts of water was added. When the propylene imine had been added completely, the temperature was brought to 45 °C and maintained for 30 minutes before cooling to room temperature. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

Films made on glass plates from the iminated polymer emulsion showed a MEK double rub resistance of at least 200 double rubs when the films were aged one night at 50 °C. When the films were made from the emulsion before iminisation, only 20 MEK double rubs could be achieved.

Example 8

This example describes the preparation of an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of a vinylidene chloride/acrylic copolymer having pendant carbonyl groups and having pendant amine groups. The preparation of this polymer latex was as follows:

A precursor polymer having pendant carbonyl groups and pendant carboxy groups was first made using the following procedure. To a reactor provided with an agitator, reflux condensor, dropping funnel and nitrogen inlet tube, was added: 442.47 parts of water, 40.13 parts of a 25% sodium lauryl sulphate solution and 1.75 parts of sodium metabisulphite. To the reactor 10% of the monomer feed described below was added and 5% of the initiator feed described below. In a nitrogen atmosphere the temperature of the reactor contents was brought to 40 °C (while stirring). When this temperature had been reached and maintained for 10 minutes, the remaining part of the monomer-feed was added in 4 hours at the same temperature. The initiator feed was fed in over a period of 4 hours and 20 minutes. After this the reactor was kept at 40 °C for another hour before cooling to room temperature.

Composition monomer feed:	
	parts
vinylidene chloride	261.60
n-butyl acrylate	139.52
methyl vinyl ketone	13.08
methacrylic acid	21.80

Composition initiator feed:	
	parts
water	77.46
potassium persulphate	2.19

200 parts of the prepared precursor polymer latex were heated to 30 °C. During 45 minutes, 0.90 parts of propylene imine were added. When the propylene imine had been added completely the latex was kept at 30 °C for another hour before adding 8.00 parts of a 25% solution of a nonionic surfactant ('Synperonic' NP30). After this the latex was cooled to room temperature. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

To 100 parts of the iminated latex, 2.03 parts of adipic acid dihydrazide were added. After this, the emulsion was kept at 50 °C for 30 minutes and subsequently cooled to room temperature.

Films on glass plates made from the iminated latex and with the added adipic acid dihydrazide showed an MEK double rub resistance of at least 200 double rubs when the films were aged 5 days at room temperature. When films were cast (under the same conditions) from the latex before adding the adipic acid dihydrazide 50 MEK double rubs could be achieved. When films from the latex were cast (under the same conditions) before imination, only 8 MEK double rubs could be achieved before complete dissolution of the film.

Example 9

This example describes the preparation of an aqueous-based selfcrosslinkable coating composition according to the invention containing an aqueous latex of a vinylidene chloride/acrylic copolymer having pendant carbonyl groups and having pendant amine groups. The preparation of this polymer latex was as follows:

A precursor polymer having pendant carbonyl groups and pendant carboxyl groups was first made using the following procedure. To a reactor provided with an agitator, reflux condensor, dropping funnel and nitrogen inlet tube, was added: 442.47 parts of water, 40.13 parts of a 25% sodium lauryl sulphate solution and 1.75 parts of sodium metabisulphite. To the reactor 10% of the monomer feed described below was added and 5% of the initiator feed described below. In a nitrogen atmosphere the temperature of the reactor contents was brought to 40 °C (while stirring). When this temperature had been reached and maintained for 10 minutes, the remaining part of the monomer feed was fed in over a period of 4 hours at the same temperature. The initiator feed was fed in over a period of 4 hours and 20 minutes. After this the reactor was kept at 40 °C for another hour before cooling to room temperature.

Composition monomer feed:	
	parts
vinylidene chloride	261.60
n-butyl acrylate	117.72
acetoacetoxyethyl methacrylate	34.88
methacrylic acid	21.80

Composition initiator feed:	
	parts
water	77.46
potassium persulphate	2.19

200 parts of the prepared precursor polymer latex were heated to 30 °C. During 45 minutes, 0.90 parts of propylene imine were added. When the propylene imine had been added completely the latex was kept at 30 °C for another hour before adding 8.0 parts of a 25% solution of a nonionic surfactant (Synperonic NP30). After this the latex was cooled to room temperature. In this way, pendant amine groups were formed from pendant carboxyl groups via imination.

To 100 parts of the iminated latex, 0.83 parts of adipic acid dihydrazide was added. After this, the emulsion was kept at 50 °C for 30 minutes and subsequently cooled to room temperature.

Films on glass plates made from the iminated latex and with the added adipic acid dihydrazide showed an MEK double rub resistance of 150 double rubs when the films were aged 7 days at room temperature. When films were cast (under the same conditions) from the latex before adding the adipic acid dihydrazide 81 MEK double rubs could be achieved. When films from the latex were cast (under the same conditions)

before imination, only 8 MEK double rubs could be achieved before complete dissolution of the film.

Claims

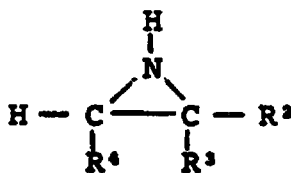
- 5 1. An aqueous selfcrosslinkable coating composition which comprises an aqueous dispersion comprising at least one vinyl polymer, wherein the polymer system constituted by said at least one vinyl polymer has chain-pendant amine functional groups and chain-pendant carbonyl functional groups to provide a selfcrosslinking reaction during and/or after coating formation from the composition, where by an amine functional group is meant an amine group which is bonded to a carbon atom and which can take part in selfcrosslinking with a carbonyl functional group, and by a carbonyl functional group is meant the carbonyl functionality of a ketone or aldehyde group.
- 10 2. A composition according to Claim 1 wherein the amine functional groups in a vinyl polymer of the composition comprise primary amine groups bonded to carbon atoms of aliphatic or aromatic groups.
- 15 3. A composition according to Claim 2 wherein the pendant primary amine groups in a vinyl polymer of the composition are incorporated by being part of chain-pendant aminoalkyl carboxylate groups of formula $-C(O)-O-R_1-NH_2$ where R_1 is an alkylene group.
- 20 4. A composition according to any one of the preceding claims wherein the carbonyl functional groups in a vinyl polymer of the composition are derived from at least one carbonyl-functional olefinically unsaturated monomer used in the preparation of the vinyl polymer.
- 25 5. A composition according to any one of the preceding claims wherein the ratio of amine functional groups to carbonyl functional groups is within the range of from 1:20 to 20:1.
- 30 6. A composition according to any one of the preceding claims which comprises at least one vinyl polymer bearing both chain-pendant amine functional groups and chain pendant carbonyl functional groups in the same polymer molecules.
- 35 7. A composition according to any one of Claims 1 to 5 wherein said at least one vinyl polymer consists of two or more vinyl polymers which bear chain-pendant amine functional groups and carbonyl functional groups in different polymer molecules.
- 40 8. A composition according to Claim 6 wherein said vinyl polymer thereof bearing both chain-pendant amine and carbonyl functional groups in the same polymer molecules is prepared by forming, using a free-radical polymerisation process, a precursor polymer comprising polymerised units of at least one olefinically unsaturated monomer having an amine precursor group, at least one carbonyl-functional olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer providing neither amine groups, amine precursor groups nor carbonyl functional groups, and subsequently reacting at least a proportion of the amine precursor groups to provide chain-pendant amine functional groups, where by an amine precursor group is meant a group which is subsequently reacted to provide a pendant amine functional group.
- 45 9. A composition according to Claim 8 wherein said vinyl polymer thereof bearing both chain-pendant amine and carbonyl functional groups comprises a free-radical addition polymer comprising polymerised units of at least one olefinically unsaturated monomer providing chain-pendant carboxyl groups at least a proportion of which have been subsequently reacted to provide chain-pendant amine functional groups, at least one carbonyl-functional olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer providing neither amine groups, carboxyl groups nor carbonyl functionality.
- 50 10. A composition according to Claim 9 wherein the amine-functional groups in said vinyl polymer are formed by an imination reaction involving the pendant carboxyl or carboxylate salt groups of the precursor polymer using an alkylene imine of formula
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before imination, only 8 MEK double rubs could be achieved before complete dissolution of the film.

Claims

- 5 1. An aqueous selfcrosslinkable coating composition which comprises an aqueous dispersion comprising at least one vinyl polymer, wherein the polymer system constituted by said at least one vinyl polymer has chain-pendant amine functional groups and chain-pendant carbonyl functional groups to provide a selfcrosslinking reaction during and/or after coating formation from the composition, where by an amine functional group is meant an amine group which is bonded to a carbon atom and which can take part in selfcrosslinking with a carbonyl functional group, and by a carbonyl functional group is meant the carbonyl functionality of a ketone or aldehyde group.
- 10 2. A composition according to Claim 1 wherein the amine functional groups in a vinyl polymer of the composition comprise primary amine groups bonded to carbon atoms of aliphatic or aromatic groups.
- 15 3. A composition according to Claim 2 wherein the pendant primary amine groups in a vinyl polymer of the composition are incorporated by being part of chain-pendant aminoalkyl carboxylate groups of formula $-C(O)-O-R_1-NH_2$ where R_1 is an alkylene group.
- 20 4. A composition according to any one of the preceding claims wherein the carbonyl functional groups in a vinyl polymer of the composition are derived from at least one carbonyl-functional olefinically unsaturated monomer used in the preparation of the vinyl polymer.
- 25 5. A composition according to any one of the preceding claims wherein the ratio of amine functional groups to carbonyl functional groups is within the range of from 1:20 to 20:1.
- 30 6. A composition according to any one of the preceding claims which comprises at least one vinyl polymer bearing both chain-pendant amine functional groups and chain pendant carbonyl functional groups in the same polymer molecules.
- 35 7. A composition according to any one of Claims 1 to 5 wherein said at least one vinyl polymer consists of two or more vinyl polymers which bear chain-pendant amine functional groups and carbonyl functional groups in different polymer molecules.
- 40 8. A composition according to Claim 6 wherein said vinyl polymer thereof bearing both chain-pendant amine and carbonyl functional groups in the same polymer molecules is prepared by forming, using a free-radical polymerisation process, a precursor polymer comprising polymerised units of at least one olefinically unsaturated monomer having an amine precursor group, at least one carbonyl-functional olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer providing neither amine groups, amine precursor groups nor carbonyl functional groups, and subsequently reacting at least a proportion of the amine precursor groups to provide chain-pendant amine functional groups, where by an amine precursor group is meant a group which is subsequently reacted to provide a pendant amine functional group.
- 45 9. A composition according to Claim 8 wherein said vinyl polymer thereof bearing both chain-pendant amine and carbonyl functional groups comprises a free-radical addition polymer comprising polymerised units of at least one olefinically unsaturated monomer providing chain-pendant carboxyl groups at least a proportion of which have been subsequently reacted to provide chain-pendant amine functional groups, at least one carbonyl-functional olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer providing neither amine groups, carboxyl groups nor carbonyl functionality.
- 50 10. A composition according to Claim 9 wherein the amine-functional groups in said vinyl polymer are formed by an imination reaction involving the pendant carboxyl or carboxylate salt groups of the precursor polymer using an alkylene imine of formula
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thereby to form chain-pendant amino ester groups, where R^2 and R^3 which may be the same or different are selected from hydrogen, benzyl, aryl, and alkyl of 1 to 5 carbon atoms; and where R^4 is hydrogen or alkyl of 1 to 5 carbon atoms.

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11. A composition according to Claim 10 wherein the alkylene imine employed is ethylene imine ($\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{hydrogen}$) or propylene imine ($\text{R}^2 = \text{R}^4 = \text{hydrogen}$; $\text{R}^3 = \text{methyl}$).

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12. A composition according to any one of Claims 8 to 11 wherein said at least one carbonyl-functional olefinically unsaturated monomer which is used in the preparation of the vinyl polymer is selected from one or more of acrolein, diacetone acrylamide, acetoacetoxyethyl methacrylate and methyl vinyl ketone.

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13. A composition according to any one of Claims 8 to 12 wherein said at least one other olefinically unsaturated monomer used in the preparation of the vinyl polymer which provides neither amine groups, amine precursor groups nor carbonyl-functional groups is selected from one or more of esters of acrylic acid and methacrylic acid of formula $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$ where R^9 is hydrogen or methyl and R^{10} is alkyl or cycloalkyl of 1 to 20 carbon atoms, and vinylidene chloride.

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14. A composition according to any one of Claims 8 to 13 wherein said vinyl polymer therein comprises at least the following polymerised units:

- a) units having pendant amine functional groups which are present in groups of formula $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}_2-\text{NH}_2$, or $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ and $-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$, derived from precursor carboxyl groups in a corresponding precursor polymer by imination thereof with ethylene imine or propylene imine respectively;
- (b) units derived from at least one carbonyl-containing monomer selected from acrolein, diacetone acrylamide, acetoacetoxyethyl methacrylate and methyl vinyl ketone; and
- (c) units derived from at least one olefinically unsaturated monomer selected from those of formula $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$, and vinylidene chloride.

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15. A composition according to any one of Claims 8 to 14 wherein said vinyl polymer thereof bearing both chain-pendant amine and carbonyl functional groups comprises 1 to 20 mole % of polymerised units bearing pendant amine groups, 1 to 20 mole % of polymerised units bearing pendant carbonyl groups and 60 to 90 mole% of polymerised units bearing neither pendant amine nor pendant carbonyl groups

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16. A composition according to any one of the preceding claims wherein said at least one vinyl polymer has a core/shell structure, the core providing a soft polymeric phase of $T_g \leq 20^\circ\text{C}$ and the shell providing a hard polymeric phase of $T_g \geq 50^\circ\text{C}$.

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17. A composition according to any one of the preceding claims wherein the polymer system contains a proportion of amine groups within the range 5 to 120 millimoles per 100 g of polymer solids and a proportion of carbonyl groups within the range 5 to 120 millimoles per 100 g of polymer solids.

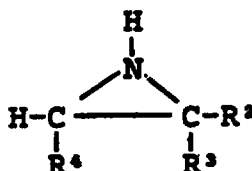
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18. A composition according to any one of the preceding claims wherein said composition also includes at least one polyhydrazine or polyhydrazone compound.

19. A vinyl polymer bearing chain-pendant amine functional groups and chain-pendant carbonyl functional groups in the same polymer molecules, where by an amine functional group is meant an amine group which is bonded to a carbon atom and which can take part in selfcrosslinking with a carbonyl functional groups, and by a carbonyl functional group is meant the carbonyl functionality of a ketone or aldehyde group.



20. A vinyl polymer according to Claim 19 wherein the amine functional groups therein comprise primary amine groups bonded to carbon atoms of aliphatic or aromatic groups.
21. A vinyl polymer according to Claim 20 wherein the pendant primary amine groups in said vinyl polymer of the composition are incorporated by being part of chain-pendant aminoalkyl carboxylate groups of formula $-C(O)-O-R_1-NH_2$ where R_1 is an alkylene group.
22. A vinyl polymer according to any one of Claims 19 to 21 wherein the carbonyl functional groups in said vinyl polymer are derived from at least one carbonyl-functional olefinically unsaturated monomer used in the preparation of the vinyl polymer.
23. A vinyl polymer according to any one of Claims 19 to 22 wherein said vinyl polymer is a polymer which is prepared by forming, using a free-radical polymerisation process, a precursor polymer comprising polymerised units of at least one olefinically unsaturated monomer having an amine precursor group, at least one carbonyl-functional olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer providing neither amine groups, amine precursor groups nor carbonyl functional groups, and subsequently reacting at least a proportion of the amine precursor groups to provide chain-pendant amine functional groups, where by an amine precursor group is meant a group which is subsequently reacted to provide a pendant amine functional group.
24. A vinyl polymer according to any one of Claims 19 to 23 wherein said vinyl polymer comprises a free-radical addition polymer comprising polymerised units of at least one olefinically unsaturated monomer providing chain-pendant carboxyl groups at least a proportion of which have been subsequently reacted to provide chain-pendant amine functional groups, at least one carbonyl-functional olefinically unsaturated monomer, and at least one other olefinically unsaturated monomer providing neither amine groups, carboxyl groups nor carbonyl functionality.
25. A vinyl polymer according to Claim 24 wherein the amine-functional groups in said vinyl polymer are formed by an imination reaction involving the pendant carboxyl or carboxylate salt groups of the precursor polymer using an alkylene imine of formula



- thereby to form chain-pendant amino ester groups, where R^2 and R^3 which may be the same or different are selected from hydrogen, benzyl, aryl, and alkyl of 1 to 5 carbon atoms, and where R^4 is hydrogen or alkyl of 1 to 5 carbon atoms.
26. A vinyl polymer according to Claim 25 wherein the alkylene imine employed is ethylene imine ($R^2 = R^3 = R^4 = \text{hydrogen}$) or propylene imine ($R^2 = R^4 = \text{hydrogen}$; $R^3 = \text{methyl}$).
27. A vinyl polymer according to any one of Claims 22 to 26 wherein said at least one carbonyl-functional olefinically unsaturated monomer which is used in the preparation of the vinyl polymer is selected from one or more of acrolein, diacetone acrylamide, acetoacetoxyethyl methacrylate and methyl vinyl ketone.
28. A vinyl polymer according to any one of Claims 19 to 26 which comprises polymerised units derived from at least one olefinically unsaturated monomer selected from one or more of esters of acrylic acid and methacrylic acid of formula $CH_2 = CR^9C(O)OR^{10}$ where R^9 is hydrogen or methyl and R^{10} is alkyl as cycloalkyl of 1 to 20 carbon atoms, and vinylidene chloride.
29. A vinyl polymer according to any one of Claims 19 to 28 wherein said vinyl polymer comprises at least the following polymerised units:



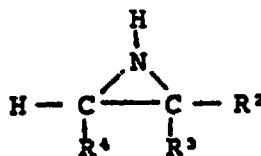
- (a) units having pendant amine functional groups which are present in groups of formula $-C(O)-O-CH_2CH_2-NH_2$, or $-C(O)-O-CH_2CH(CH_3)NH_2$ and $-C(O)-O-CH(CH_3)CH_2NH_2$, derived from precursor carboxyl groups in a corresponding precursor polymer by imination thereof with ethylene imine or propylene imine respectively;
- (b) units derived from at least one carbonyl-containing monomer selected from acrolein, diacetone acrylamide, acetoacetoxyethyl methacrylate and methyl vinyl ketone; and
- (c) units derived from at least one olefinically unsaturated monomer selected from those of formula $CH_2 = CR^9C(O)OR^{10}$ and vinylidene chloride.
30. A vinyl polymer according to any one of Claims 19 to 29 wherein said vinyl polymer comprises 1 to 20 mole % of polymerised units bearing pendant amine functional groups, 1 to 20 mole % of polymerised units bearing pendant carbonyl functional groups and 60 to 90 mole% of polymerised units bearing neither pendant amine nor pendant carbonyl functional groups.
31. A vinyl polymer according to any one of Claims 19 to 30 wherein said at least one vinyl polymer has a core/shell structure, the core providing a soft polymeric phase of $T_g \leq 20^\circ C$ and the shell providing a hard polymeric phase of $T_g \geq 50^\circ C$.
32. The use of a composition according to any one of Claims 1 to 18 in protective coating or adhesive coating applications.
33. The use of a composition according to Claim 32 in stoving applications wherein the coating is subjected to temperatures within the range of from 80 to 160 °C.

Patentansprüche

1. Wäßrige selbstvernetzbare Beschichtungszusammensetzung, die eine wäßrige Dispersion enthält, welche mindestens ein Vinyl-Polymer enthält, wobei das Polymer-System, das durch das mindestens eine Vinyl-Polymer gebildet wird, von der Kette überhängende funktionelle Amin-Gruppen und von der Kette überhängende funktionelle Carbonyl-Gruppen besitzt, um eine selbstvernetzende Reaktion während und/oder nach der Beschichtungsbildung aus der Zusammensetzung zu ergeben, wobei mit einer funktionellen Amin-Gruppe eine Amin-Gruppe gemeint ist, die an ein Kohlenstoffatom gebunden ist und an der Selbstvernetzung mit einer funktionellen Carbonyl-Gruppe teilnehmen kann, und mit einer funktionellen Carbonyl-Gruppe die Carbonyl-Funktionalität einer Keton- oder Aldehyd-Gruppe gemeint ist.
2. Zusammensetzung nach Anspruch 1, wobei die funktionellen Amin-Gruppen in einem Vinyl-Polymer der Zusammensetzung primäre Amin-Gruppen aufweisen, die an Kohlenstoffatome von aliphatischen oder aromatischen Gruppen gebunden sind.
3. Zusammensetzung nach Anspruch 2, wobei die überhängenden primären Amin-Gruppen in einem Vinyl-Polymer der Zusammensetzung dadurch einverleibt werden, daß sie Teil von von der Kette überhängenden Aminoalkylcarboxylat-Gruppen mit der Formel $-C(O)-O-R_1-NH_2$ sind, in der R_1 für eine Alkylen-Gruppe steht.
4. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die funktionellen Carbonyl-Gruppen in einem Vinyl-Polymer der Zusammensetzung von mindestens einem Carbonyl-funktionellen olefinisch ungesättigten Monomer abstammen, das bei der Herstellung des Vinyl-Polymers verwendet wird.
5. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Verhältnis von funktionellen Amin-Gruppen zu funktionellen Carbonyl-Gruppen im Bereich von 1:20 bis 20:1 liegt.
6. Zusammensetzung nach einem der vorhergehenden Ansprüche, die mindestens ein Vinyl-Polymer enthält, das sowohl von der Kette überhängende funktionelle Amin-Gruppen als auch von der Kette überhängende funktionelle Carbonyl-Gruppen in den gleichen Polymer-Molekülen trägt.



7. Zusammensetzung nach einem der Ansprüche 1 bis 5, wobei das mindestens eine Vinyl-Polymer aus zwei oder mehreren Vinyl-Polymeren besteht, die von der Kette überhängende funktionelle Amin-Gruppen und funktionelle Carbonyl-Gruppen in verschiedenen Polymer-Molekülen tragen.
8. Zusammensetzung nach Anspruch 6, wobei deren Vinyl-Polymer, das sowohl von der Kette überhängende funktionelle Amin- als auch Carbonyl-Gruppen in den gleichen Polymer-Molekülen trägt, dadurch hergestellt wird, daß unter Verwendung eines Polymerisations-Verfahrens mit freien Radikalen folgendes hergestellt wird: ein Vorläufer-Polymer, das polymerisierte Einheiten mindestens eines olefinisch ungesättigten Monomers mit einer Amin-Vorläufer-Gruppe enthält, mindestens ein Carbonyl-funktionelles olefinisch ungesättigtes Monomer und mindestens ein anderes olefinisch ungesättigtes Monomer, das weder Amin-Gruppen, Amin-Vorläufer-Gruppen noch funktionelle Carbonyl-Gruppen liefert, wobei anschließend zumindestens ein Teil der Amin-Vorläufer-Gruppen zur Bereitstellung von von der Kette überhängenden funktionellen Amin-Gruppen umgesetzt wird, wobei mit einer Amin-Vorläufer-Gruppe eine Gruppe gemeint ist, die anschließend umgesetzt wird, um eine überhängende funktionelle Amin-Gruppe bereitzustellen.
9. Zusammensetzung nach Anspruch 8, deren Vinyl-Polymer, das sowohl von der Kette überhängende funktionelle Amin- als auch Carbonyl-Gruppen trägt, ein Freie-Radikale-Additions-Polymer enthält, das polymerisierte Einheiten mindestens eines olefinisch ungesättigten Monomers enthält, das von der Kette überhängende Carboxyl-Gruppen liefert, wobei mindestens ein Teil davon anschließend umgesetzt wird, um von der Kette überhängende funktionelle Amin-Gruppen bereitzustellen, mindestens ein Carbonyl-funktionelles olefinisch ungesättigtes Monomer, und mindestens ein anderes olefinisch ungesättigtes Monomer, das weder Amin-Gruppen, Carboxyl-Gruppen noch Carbonyl-Funktionalität liefert.
10. Zusammensetzung nach Anspruch 9, wobei die funktionellen Amin-Gruppen in dem Vinyl-Polymer durch eine Iminierungs-Reaktion gebildet werden, an der die überhängenden Carboxyl- oder Carboxylat-Salz-Gruppen des Vorläufer-Polymers beteiligt sind, und zwar unter Verwendung eines Alkylens mit der Formel



so daß dadurch von der Kette überhängende Aminoester-Gruppen gebildet werden, wobei R^2 und R^3 , die gleich oder unterschiedlich sein können, ausgewählt sind aus Wasserstoff, Benzyl, Aryl und Alkyl mit 1 bis 5 Kohlenstoffatomen, und wobei R^4 für Wasserstoff oder Alkyl mit 1 bis 5 Kohlenstoffatomen steht.

11. Zusammensetzung nach Anspruch 10, wobei es sich bei dem verwendeten Alkylimin um Ethylenimin ($\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Wasserstoff}$) oder Propylenimin ($\text{R}^2 = \text{R}^4 = \text{Wasserstoff}$; $\text{R}^3 = \text{Methyl}$) handelt.
12. Zusammensetzung nach einem der Ansprüche 8 bis 11, wobei das mindestens eine Carbonyl-funktionelle olefinisch ungesättigte Monomer, das zur Herstellung des Vinyl-Polymers verwendet wird, aus einem oder mehreren aus Acrolein, Diacetonacrylamid, Acetacetoxyethylmethacrylat und Methylvinylketon ausgewählt ist.
13. Zusammensetzung nach einem der Ansprüche 8 bis 12, wobei das mindestens eine andere olefinisch ungesättigte Monomer, das zur Herstellung des Vinyl-Polymers verwendet wird, welches weder Amin-Gruppen, Amin-Vorläufer-Gruppen noch Carbonyl-funktionelle Gruppen bereitstellt, aus einem oder mehreren des folgenden ausgewählt ist: Estern von Acrylsäure und Methacrylsäure mit der Formel $\text{CH}_2 = \text{CR}^9 \text{C}(\text{O})\text{OR}^{10}$, wobei R^9 für Wasserstoff oder Methyl steht und R^{10} für Alkyl oder Cycloalkyl mit 1 bis 20 Kohlenstoffatomen steht, und Vinylidenchlorid.



14. Zusammensetzung nach einem der Ansprüche 8 bis 13, wobei das Vinyl-Polymer darin mindestens die folgenden polymerisierten Einheiten aufweist:
 - a) Einheiten mit überhängenden funktionellen Amin-Gruppen, die in Gruppen mit den folgenden Formeln vorhanden sind $-C(O)-O-CH_2CH_2-NH_2$ oder $-C(O)-O-CH_2CH(CH_3)NH_2$ und $-C(O)-O-CH(CH_3)-CH_2NH_2$, die von Vorläufer-Carboxyl-Gruppen in einem entsprechenden Vorläufer-Polymer abstammen, und zwar durch dessen Iminierung mit Ethylenimin bzw. Propylenimin;
 - b) Einheiten, die von mindestens einem Carbonylhaltigen Monomer abstammen, das aus Acrolein, Diacetonacrylamid, Acetoacetoxyethylmethacrylat und Methylvinylketon ausgewählt ist; und
 - c) Einheiten, die von mindestens einem olefinisch ungesättigten Monomer abstammen, das aus denen mit der Formel $CH_2 = CR^9C(O)OR^{10}$ und Vinylidenchlorid ausgewählt ist.

15. Zusammensetzung nach einem der Ansprüche 8 bis 14, wobei deren Vinyl-Polymer, das sowohl von der Kette überhängende funktionelle Amin- als auch Carbonyl-Gruppen enthält, 1 bis 20 Mol.-% an polymerisierten Einheiten enthält, die überhängende Amin-Gruppen tragen, 1 bis 20 Mol.-% polymerisierte Einheiten, die überhängende Carbonyl-Gruppen tragen und 60 bis 90 Mol.-% polymerisierte Einheiten, die weder überhängende Amin- noch überhängende Carbonyl-Gruppen tragen.

16. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das mindestens eine Vinyl-Polymer eine Kern/Schalen-Struktur aufweist, wobei der Kern eine weiche polymere Phase mit $T_g \leq 20^\circ C$ liefert und die Schale eine harte polymere Phase mit $T_g \geq 50^\circ C$.

17. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Polymer-System einen Anteil an Amin-Gruppen im Bereich von 5 bis 120 mMol pro 100 g Polymer-Feststoffe enthält und einen Anteil an Carbonyl-Gruppen im Bereich von 5 bis 120 mMol pro 100 g Polymer-Feststoffe.

18. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung außerdem mindestens eine Polyhydrazin- oder Polyhydrazon-Verbindung enthält.

19. Vinyl-Polymer, das von der Kette überhängende funktionelle Amin-Gruppen und von der Kette überhängende funktionelle Carbonyl-Gruppen in den gleichen Polymer-Molekülen trägt, wobei mit einer funktionellen Amin-Gruppe eine Amin-Gruppe gemeint ist, die an ein Kohlenstoffatom gebunden ist und an der Selbstvernetzung mit funktionellen Carbonyl-Gruppen teilnehmen kann, und mit einer funktionellen Carbonyl-Gruppe die Carbonyl-Funktionalität einer Keton- oder Aldehyd-Gruppe gemeint ist.

20. Vinyl-Polymer nach Anspruch 19, wobei die funktionellen Amin-Gruppen darin primäre Amin-Gruppen aufweisen, die an Kohlenstoffatome von aliphatischen oder aromatischen Gruppen gebunden sind.

21. Vinyl-Polymer nach Anspruch 20, wobei die überhängenden primären Amin-Gruppen in dem Vinyl-Polymer der Zusammensetzung dadurch einverleibt werden, daß sie Teil von von der Kette überhängenden Aminoalkylcarboxylat-Gruppen mit der Formel $-C(O)-O-R_1-NH_2$ sind, in der R_1 für eine Alkylengruppe steht.

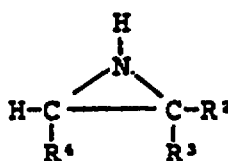
22. Vinyl-Polymer nach einem der Ansprüche 19 bis 21, wobei die funktionellen Carbonyl-Gruppen in dem Vinyl-Polymer von mindestens einem Carbonyl-funktionellen olefinisch ungesättigten Monomer abstammen, das zur Herstellung des Vinyl-Polymeres verwendet wird.

23. Vinyl-Polymer nach einem der Ansprüche 19 bis 22, wobei es sich bei dem Vinyl-Polymer um eine Polymer handelt, das hergestellt wird, indem unter Verwendung eines Polymerisations-Verfahrens mit freien Radikalen folgendes gebildet wird: ein Vorläufer-Polymer, das polymerisierte Einheiten mindestens eines olefinisch ungesättigten Monomers mit einer Amin-Vorläufer-Gruppe enthält, mindestens ein Carbonyl-funktionelles olefinisch ungesättigtes Monomer, und mindestens ein anderes olefinisch ungesättigtes Monomer, das weder Amin-Gruppen, Amin-Vorläufer-Gruppen noch funktionelle Carbonyl-Gruppen liefert, wobei anschließend mindestens ein Teil der Amin-Vorläufer-Gruppen zur Bereitstellung von von der Kette überhängenden funktionellen Amin-Gruppen umgesetzt wird, wobei mit einer Amin-Vorläufer-Gruppe eine Gruppe gemeint ist, die anschließend umgesetzt wird, um eine überhängende funktionelle Amin-Gruppe bereitzustellen.



24. Vinyl-Polymer nach einem der Ansprüche 19 bis 23, wobei das Vinyl-Polymer folgendes enthält: ein Freie-Radikale-Additions-Polymer, das polymerisierte Einheiten mindestens eines olefinisch ungesättigten Monomers enthält, das von der Kette überhängende Carboxyl-Gruppen bereitstellt, wobei mindestens ein Teil dieser anschließend umgesetzt wurde, um von der Kette überhängende funktionelle Amin-Gruppen bereitzustellen, mindestens ein Carbonyl-funktionelles olefinisch ungesättigtes Monomer, und mindestens ein anderes olefinisch ungesättigtes Monomer, das weder Amin-Gruppen, Carboxyl-Gruppen noch Carbonyl-Funktionalität bereitstellt.

25. Vinyl-Polymer nach Anspruch 24, wobei die funktionellen Amin-Gruppen in dem Vinyl-Polymer durch eine Iminierungs-Reaktion gebildet werden, an der die überhängenden Carboxyl- oder Carboxylat-Salz-Gruppen des Vorläufer-Polymers beteiligt sind, und zwar unter Verwendung eines Alkylenimins mit der folgenden Formel



wodurch von der Kette überhängende Aminoester-Gruppen gebildet werden, wobei R^2 und R^3 , die gleich oder unterschiedlich sein können, ausgewählt sind aus Wasserstoff, Benzyl, Aryl und Alkyl mit 1 bis 5 Kohlenstoffatomen, und wobei R^4 für Wasserstoff oder Alkyl mit 1 bis 5 Kohlenstoffatomen steht.

26. Vinyl-Polymer nach Anspruch 25, wobei es sich bei dem verwendeten Alkylenimin um Ethylenimin ($\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Wasserstoff}$) oder Propylenimin ($\text{R}^2 = \text{R}^4 = \text{Wasserstoff}$; $\text{R}^3 = \text{Methyl}$) handelt.

27. Vinyl-Polymer nach einem der Ansprüche 22 bis 26, wobei das mindestens eine Carbonyl-funktionelle olefinisch ungesättigte Monomer, das zur Herstellung des Vinyl-Polymers verwendet wird, aus einem oder mehreren aus Acrolein, Diacetonacrylamid, Acetoacetoxyethylmethacrylat und Methylvinylketon ausgewählt ist.

28. Vinyl-Polymer nach einem der Ansprüche 19 bis 26, das polymerisierte Einheiten aufweist, die von mindestens einem olefinisch ungesättigten Monomer abstammen, das aus einem oder mehreren des folgenden ausgewählt ist: Estern von Acrylsäure und Methacrylsäure mit der Formel $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$, wobei R^9 für Wasserstoff oder Methyl steht und R^{10} für Alkyl oder Cycloalkyl mit 1 bis 20 Kohlenstoffatomen steht, und Vinylidenchlorid.

29. Vinyl-Polymer nach einem der Ansprüche 19 bis 28, wobei das Vinyl-Polymer mindestens die folgenden polymerisierten Einheiten aufweist:

(a) Einheiten mit überhängenden funktionellen Amin-Gruppen, die in Gruppen mit der Formel $-\text{C}(\text{O})\text{O}-\text{CH}_2\text{CH}_2-\text{NH}_2$ oder $-\text{C}(\text{O})\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ und $-\text{C}(\text{O})\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$ vorhanden sind, die von Vorläufer-Carboxyl-Gruppen in einem entsprechenden Vorläufer-Polymer abstammen, und zwar durch dessen Iminierung mit Ethylenimin bzw. Propylenimin;

(b) Einheiten, die von mindestens einem Carbonylhaltigen Monomer abstammen, das aus Acrolein, Diacetonacrylamid, Acetoacetoxyethylmethacrylat und Methylvinylketon ausgewählt ist; und

(c) Einheiten, die von mindestens einem olefinisch ungesättigten Monomer abstammen, das aus denen mit der Formel $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$ und Vinylidenchlorid ausgewählt ist.

30. Vinyl-Polymer nach einem der Ansprüche 19 bis 29, wobei das Vinyl-Polymer folgendes aufweist: 1 bis 20 Mol.-% polymerisierte Einheiten, die überhängende funktionelle Amin-Gruppen tragen, 1 bis 20 Mol.-% polymerisierte Einheiten, die überhängende funktionelle Carbonyl-Gruppen tragen, und 60 bis 90 Mol.-% polymerisierte Einheiten, die weder funktionelle überhängende Amin- noch überhängende Carbonyl-Gruppen tragen.

31. Vinyl-Polymer nach einem der Ansprüche 19 bis 30, wobei das mindestens eine Vinyl-Polymer eine Kern/Schalen-Struktur besitzt, wobei der Kern eine weiche polymere Phase mit $T_g \leq 20^\circ\text{C}$ bereitstellt



und die Schale eine harte polymere Phase mit $T_g \geq 50^\circ\text{C}$ bereitstellt.

32. Verwendung einer Zusammensetzung nach einem der Ansprüche 1 bis 18 in Schutzbeschichtungs- oder Haftbeschichtungsanwendungen.

33. Verwendung einer Zusammensetzung nach Anspruch 32 in ofentrocknenden Anwendungen, wobei die Beschichtung Temperaturen im Bereich von 80 bis 160°C ausgesetzt wird.

Revendications

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1. Composition aqueuse de revêtement, autoréticulable, qui comprend une dispersion aqueuse renfermant au moins un polymère vinylique, dans laquelle la formulation polymérique constituée par ledit polymère vinylique d'au moins un type possède des groupes fonctionnels amine en position latérale sur la chaîne et des groupes fonctionnels carbonyle en position latérale sur la chaîne pour provoquer une réaction d'autoréticulation pendant et/ou après la formation du revêtement à partir de la composition, l'expression "groupe fonctionnel amine" désignant un groupe amine qui est lié à un atome de carbone et qui peut participer à l'autoréticulation avec un groupe fonctionnel carbonyle, et l'expression "groupe fonctionnel carbonyle" désignant la fonctionnalité carbonyle d'un groupe cétone ou aldéhyde.

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2. Composition suivant la revendication 1, dans laquelle les groupes fonctionnels amine dans un polymère vinylique de la composition comprennent des groupes amine primaires liés à des atomes de carbone de groupes aliphatiques ou aromatiques.

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3. Composition suivant la revendication 2, dans laquelle les groupes amine primaires latéraux dans un polymère vinylique de la composition sont incorporés en faisant partie de groupes carboxylate d'aminoalkyle, en position latérale sur la chaîne, de formule $-\text{C}(\text{O})-\text{O}-\text{R}_1-\text{NH}_2$ dans laquelle R_1 représente un groupe alkylène.

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4. Composition suivant l'une quelconque des revendications précédentes, dans laquelle les groupes fonctionnels carbonyle dans un polymère vinylique de la composition sont dérivés d'au moins un monomère à insaturation oléfinique et à fonctionnalité carbonyle utilisé dans la préparation du polymère vinylique.

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5. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le rapport des groupes fonctionnels amine aux groupes fonctionnels carbonyle est compris dans l'intervalle de 1:20 à 20:1.

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6. Composition suivant l'une quelconque des revendications précédentes, qui comprend au moins un polymère vinylique portant à la fois des groupes fonctionnels amine en position latérale sur la chaîne et des groupes fonctionnels carbonyle en position latérale sur la chaîne dans les mêmes molécules de polymère.

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7. Composition suivant l'une quelconque des revendications 1 à 5, dans laquelle le polymère vinylique d'au moins un type consiste en deux ou plus de deux polymères vinyliques qui portent des groupes fonctionnels amine et des groupes fonctionnels carbonyle en position latérale sur la chaîne dans des molécules de polymère différentes.

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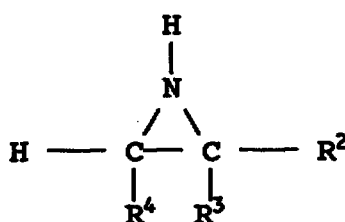
8. Composition suivant la revendication 6, dans laquelle le polymère vinylique présent qui porte à la fois des groupes fonctionnels amine et des groupes fonctionnels carbonyle, en position latérale sur la chaîne, dans les mêmes molécules de polymère est préparé en formant, au moyen d'un procédé de polymérisation radicalaire, un polymère précurseur comprenant des motifs polymérisés d'au moins un monomère à insaturation oléfinique possédant un groupe précurseur amine, d'au moins un monomère à insaturation oléfinique et à fonctionnalité carbonyle, et d'au moins un autre monomère à insaturation oléfinique ne fournissant ni groupes amine, ni groupes précurseurs d'amine ni groupes fonctionnels carbonyle, et en faisant ensuite réagir au moins une partie des groupes précurseurs d'amine pour produire des groupes fonctionnels amine en position latérale sur la chaîne, l'expression "groupe précurseur d'amine" désignant un groupe qui est soumis à une réaction ultérieure pour produire un groupe fonctionnel amine latéral.

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9. Composition suivant la revendication 8, dans laquelle le polymère vinylique présent portant à la fois des groupes fonctionnels amine et des groupes fonctionnels carbonyle, en position latérale sur la chaîne, comprend un polymère d'addition radicalaire comprenant des motifs polymérisés d'au moins un monomère à insaturation oléfinique fournissant des groupes carboxyle en position latérale sur la chaîne, dont au moins une partie a été soumise à une réaction ultérieure pour produire des groupes fonctionnels amine en position latérale sur la chaîne, d'au moins un monomère à insaturation oléfinique et à fonctionnalité carbonyle, et d'au moins un autre monomère à insaturation oléfinique ne fournissant ni groupes amine, ni groupes carboxy ni fonctionnalité carbonyle.
10. Composition suivant la revendication 9, dans laquelle les groupes à fonctionnalité amine dans le polymère vinylique sont formés par une réaction d'iminisation faisant intervenir les groupes carboxyle ou carboxylate latéraux du polymère précurseur au moyen d'une alkylène-imine de formule



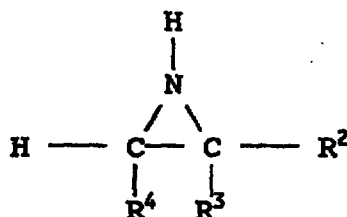
pour former ainsi des groupes amino-ester en position latérale sur la chaîne, formule dans laquelle R^2 et R^3 , qui peuvent être identiques ou différents, sont choisis entre l'hydrogène, un groupe benzyle, un groupe aryle et un groupe alkyle ayant 1 à 5 atomes de carbone ; et dans laquelle R^4 représente l'hydrogène ou un groupe alkyle ayant 1 à 5 atomes de carbone.

11. Composition suivant la revendication 10, dans laquelle l'alkylène-imine utilisée est l'éthylène-imine ($\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{hydrogène}$) ou la propylène-imine ($\text{R}^2 = \text{R}^4 = \text{hydrogène}$; $\text{R}^3 = \text{méthyle}$).
12. Composition suivant l'une quelconque des revendications 8 à 11, dans laquelle le monomère à insaturation oléfinique et à fonctionnalité carbonyle, d'au moins un type, qui est utilisé dans la préparation du polymère vinylique consiste en un ou plusieurs monomères choisis entre l'acroléine, le diacétone-acrylamide, le méthacrylate d'acétoacétoxyéthyle et la méthylvinylcétone.
13. Composition suivant l'une quelconque des revendications 8 à 12, dans laquelle l'autre monomère à insaturation oléfinique, d'au moins un type, utilisé dans la préparation du polymère vinylique qui ne fournit ni groupes amine, ni groupes précurseurs d'amine, ni groupes fonctionnels carbonyle consiste en un ou plusieurs monomères choisis entre des esters d'acide acrylique et d'acide méthacrylique de formule $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$ dans laquelle R^9 représente l'hydrogène ou un groupe méthyle et R^{10} représente un groupe alkyle ou cycloalkyle ayant 1 à 20 atomes de carbone, et le chlorure de vinylidène.
14. Composition suivant l'une quelconque des revendications 8 à 13, dans laquelle le polymère vinylique présent comprend au moins les motifs polymérisés suivants :
- des motifs possédant des groupes fonctionnels amine latéraux qui sont présents dans des groupes de formules $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}_2-\text{NH}_2$, $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ et $-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$, dérivés de groupes carboxyle précurseurs dans un polymère précurseur correspondant par iminisation de ce polymère avec, respectivement, l'éthylène-imine ou la propylène-imine ;
 - des motifs dérivés d'au moins un monomère à fonctionnalité carbonyle choisi entre l'acroléine, le diacétone-acrylamide, le méthacrylate d'acétoacétoxyéthyle et la méthylvinylcétone ; et
 - des motifs dérivés d'au moins un monomère à insaturation oléfinique choisi entre les monomères de formule $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$ et le chlorure de vinylidène.
15. Composition suivant l'une quelconque des revendications 8 à 14, dans laquelle le polymère vinylique présent portant à la fois des groupes fonctionnels amine et des groupes fonctionnels carbonyle, en position latérale sur la chaîne, comprend 1 à 20 modes % de motifs polymérisés portant des groupes



amine latéraux, 1 à 20 moles % de motifs polymérisés portant des groupes carbonyle latéraux et 60 à 90 moles % de motifs polymérisés ne portant ni groupes amine latéraux ni groupes carbonyle latéraux.

- 5 16. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le polymère vinylique d'au moins un type possède une structure de noyau/enveloppe, le noyau constituant une phase polymérique molle ayant une T_g inférieure ou égale à 20 °C et l'enveloppe constituant une phase polymérique dure ayant une T_g supérieure ou égale à 50 °C.
- 10 17. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le polymère contient une proportion de groupes amine comprise dans l'intervalle de 5 à 120 mmoles pour 100 g de matières solides polymériques et une proportion de groupes carbonyle comprise dans l'intervalle de 5 à 120 mmoles pour 100 g de matières solides polymériques.
- 15 18. Composition suivant l'une quelconque des revendications précédentes, qui comprend également au moins une polyhydrazine ou polyhydrazone.
- 20 19. Polymère vinylique portant des groupes fonctionnels amine en position latérale sur la chaîne et des groupes fonctionnels carbonyle en position latérale sur la chaîne dans les mêmes molécules de polymère, l'expression "groupe fonctionnel amine" désignant un groupe amine qui est lié à un atome de carbone et qui peut participer à une autoréticulation avec un groupe fonctionnel carbonyle, et d'expression "groupe fonctionnel carbonyle" désignant la fonctionnalité carbonyle d'un groupe cétone ou aldéhyde.
- 25 20. Polymère vinylique suivant la revendication 19, dans lequel les groupes fonctionnels amine présents comprennent des groupes amine primaires liés à des atomes de carbone de groupes aliphatiques ou aromatiques.
- 30 21. Polymère vinylique suivant la revendication 20, dans lequel les groupes amine primaires latéraux dans le polymère vinylique de la composition sont incorporés en faisant partie de groupes carboxylate d'amino-alkyle, en position latérale sur la chaîne, de formule $-C(O)-O-R_1-NH_2$ dans laquelle R_1 représente un groupe alkylène.
- 35 22. Polymère vinylique suivant l'une quelconque des revendications 19 à 21, dans lequel les groupes fonctionnels carbonyle dans ledit polymère vinylique sont dérivés d'au moins un monomère à insaturation oléfinique et à fonctionnalité carbonyle utilisé dans la préparation du polymère vinylique.
- 40 23. Polymère vinylique suivant l'une quelconque des revendications 19 à 22, qui est un polymère préparé en formant, au moyen d'un procédé de polymérisation radicalaire, un polymère précurseur comprenant des motifs polymérisés d'au moins un monomère à insaturation oléfinique possédant un groupe précurseur d'amine, d'au moins un monomère à insaturation oléfinique et à fonctionnalité carbonyle, et d'au moins un autre monomère à insaturation oléfinique ne fournissant ni groupes amine, ni groupes précurseurs d'amine, ni groupes fonctionnels carbonyle, et en faisant ensuite réagir au moins une partie des groupes précurseurs d'amine pour produire des groupes fonctionnels amine en position latérale sur la chaîne, l'expression "groupe précurseur d'amine" désignant un groupe qui est soumis à une réaction ultérieure pour produire un groupe fonctionnel amine latéral.
- 45 24. Polymère vinylique suivant l'une quelconque des revendications 19 à 23, qui comprend un polymère d'addition radicalaire renfermant des motifs polymérisés d'au moins un monomère à insaturation oléfinique fournissant des groupes carboxyle en position latérale sur la chaîne, dont au moins une partie a été soumise à une réaction ultérieure pour produire des groupes fonctionnels amine en position latérale sur la chaîne, d'au moins un monomère à insaturation oléfinique et à fonctionnalité carbonyle et d'au moins un autre monomère à insaturation oléfinique ne fournissant ni groupes amine, ni groupes carboxyle, ni fonctionnalité carbonyle.
- 50 25. Polymère vinylique suivant la revendication 24, dans lequel les groupes fonctionnels amine dans le polymère vinylique sont formés par une réaction d'imination faisant intervenir les groupes carboxyle ou carboxylate latéraux du polymère précurseur au moyen d'une alkylène-imine de formule
- 55



- 10 pour former ainsi des groupes amino-ester en position latérale sur la chaîne, formule dans laquelle R^2 et R^3 , qui peuvent être identiques ou différents, sont choisis entre l'hydrogène, un groupe benzyle, un groupe aryle et un groupe alkyle ayant 1 à 5 atomes de carbone, et dans laquelle R^4 représente l'hydrogène ou un groupe alkyle ayant 1 à 5 atomes de carbone.
- 15 26. Polymère vinylique suivant la revendication 25, dans lequel l'alkylène-imine utilisée est l'éthylèneimine ($\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{hydrogène}$) ou la propylène-imine ($\text{R}^2 = \text{R}^4 = \text{hydrogène}$; $\text{R}^3 = \text{méthyle}$).
- 20 27. Polymère vinylique suivant l'une quelconque des revendications 22 à 26, dans lequel le monomère à insaturation oléfinique et à fonctionnalité carbonyle qui est utilisé dans la préparation du polymère vinylique consiste en un ou plusieurs monomères choisis entre l'acroléine, le diacétone-acrylamide, le méthacrylate d'acétoacétoxyéthyle et la méthylvinylcétone.
- 25 28. Polymère vinylique suivant l'une quelconque des revendications 19 à 26, qui comprend des motifs polymérisés dérivés d'au moins un monomère à insaturation oléfinique consistant en un ou plusieurs monomères choisis entre des esters d'acide acrylique et d'acide méthacrylique de formule $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$ dans laquelle R^9 représente l'hydrogène ou un groupe méthyle et R^{10} représente un groupe alkyle ou cycloalkyle ayant 1 à 20 atomes de carbone, et le chlorure de vinylidène.
- 30 29. Polymère vinylique suivant l'une quelconque des revendications 19 à 28, qui comprend au moins les motifs polymérisés suivants :
- a) des motifs possédant des groupes fonctionnels amine latéraux qui sont présents dans des groupes de formules
 $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}_2-\text{NH}_2$, $-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ et $-\text{C}(\text{O})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$, dérivés de groupes carboxyle précurseurs dans un polymère précurseur correspondant par imination de ce polymère
35 avec, respectivement, l'éthylène-imine ou la propylène-imine ;
- b) des motifs dérivés d'au moins un monomère à fonctionnalité carbonyle choisi entre l'acroléine, le diacétone-acrylamide, le méthacrylate d'acétoacétoxyéthyle et la méthylvinylcétone ; et
- c) des motifs dérivés d'au moins un monomère à insaturation oléfinique choisi entre les monomères de formules $\text{CH}_2 = \text{CR}^9\text{C}(\text{O})\text{OR}^{10}$ et le chlorure de vinylidène.
- 40 30. Polymère vinylique suivant l'une quelconque des revendications 19 à 29, qui comprend 1 à 20 moles % de motifs polymérisés portant des groupes fonctionnels amine latéraux, 1 à 20 moles % de motifs polymérisés portant des groupes fonctionnels carbonyle latéraux et 60 à 90 moles % de motifs polymérisés ne portant ni groupes fonctionnels amine latéraux ni groupes fonctionnels carbonyle latéraux.
- 45 31. Polymère vinylique suivant l'une quelconque des revendications 19 à 30, dans lequel le polymère vinylique d'au moins un type possède une structure de noyau/enveloppe, le noyau constituant une phase polymérique molle ayant une T_g inférieure ou égale à 20°C et l'enveloppe constituant une phase polymérique dure ayant une T_g supérieure ou égale à 50°C .
- 50 32. Utilisation d'une composition suivant l'une quelconque des revendications 1 à 18 dans des applications de revêtements protecteurs ou de revêtements adhésifs.
- 55 33. Utilisation d'une composition suivant la revendication 32 dans des applications de cuisson au four dans lesquelles le revêtement est soumis à des températures comprises dans l'intervalle de 80 à 160°C .