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PROCESS FOR PREPARING WATER-DILUTABLE, ACRYLATE COPOLYMER-BASED LACQUER BINDERS, AND THEIR USE

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(71) Applicant(s)
VIANOVA RESINS AKTIENGESELLSCHAFT

(72) Inventor(s)
WERNER WILFINGER; INGO KRIESSMANN; KURT GOSSAK

(74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
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(57) Claim

1. Process for the preparation of water-dilutable coating binders based on acrylate copolymers, which are obtained by reacting a polycarboxy component with a polyhydroxy component followed by at least partial neutralisation of the carboxyl groups, characterised in that

(A) from 15 to 40wt%, based on solids content, of an acrylate copolymer as polycarboxy component having an acid number of from 70 to 240mg of KOH/g, which has been prepared in the form of a solution polymer from

(Aa) from 67 to 90wt% of alkyl (meth)acrylates which contain an alkyl radical of 1 to 12 carbon atoms, it being possible for these esters to be replaced in a proportion of up to 50wt% by aromatic vinyl compounds, and

(Ab) from 10 to 33wt% of α,β-ethylenically unsaturated carboxylic acids, is mixed with

(B) from 60 to 85wt% by weight, based on solids content, of an acrylate copolymer as polyhydroxy component having a hydroxyl number of from 90 to 250mg of KOH/g, and an epoxide equivalent of from 0.7 to 26.0 milliequivalents/100g of solids, which has been prepared in the form of a solution polymer from

(Ba) from 40 to 79.9wt% of alkyl (meth)acrylates which contain an alkyl radical of 1 to 12 carbon atoms, it being possible for these esters to be replaced in a proportion of up to 50wt% of aromatic vinyl compounds,

(Bb) from 20 to 59.9wt% of monoesters of (meth)acrylic acid with diols, which contain an alkylene radical of 2 to 4 carbon atoms or an oxyalkylene radical of 6 to 12 carbon atoms, and

(Bc) from 0.1 to 3wt% of a monomer which contains epoxide groups, the data for the acid number and hydroxyl number always relating to the solids content and the sums of the percentages for components (A) and (B) and, respectively, (Aa) and (Ab) and (Ba) to (Bc) necessarily giving 100 in each case,

with the proviso that the mixture has an acid number of at least 15mg of KOH/g, the solvent is removed *in vacuo* until the solids content of the batch is at least 95wt%, the batch is diluted with an auxiliary solvent to a solids content of from 85 to 93wt%, and then the mixture is maintained at a temperature of from 100 to 150°C, until the epoxide equivalent of the batch has fallen to less than 0.2 milliequivalent/100g of solids.

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VIANOVA RESINS AKTIENGESELLSCHAFT

(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: ~~VIANOVA KUNSTHARZ AKTIENGESELLSCHAFT~~ [AT/AT]; Bundesstrasse 175, A-8402 Werndorf (AT).

see folio 4

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: WILFINGER, Werner [AT/AT]; Händelstrasse 52, A-8042 Graz (AT). KRIESSMANN, Ingo [AT/AT]; Stiftingtalstrasse 324, A-8010 Graz (AT). GOSSAK, Kurt [AT/AT]; Wöbling 31, A-8042 Graz (AT).

(74) Anwalt: PFEIFER, Otto; Schütz u. Partner, Fleischmanngasse 9, A-1040 Wien (AT).

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(54) Title: PROCESS FOR PREPARING WATER-DILUTABLE, ACRYLATE COPOLYMER-BASED LACQUER BINDERS, AND THEIR USE

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON WASSERVERDÜNNBAREN LACKBINDEMITTELN AUF DER BASIS VON ACRYLATCOPOLYMERISATEN UND DEREN VERWENDUNG

(57) Abstract

A process is disclosed for preparing water-dilutable, acrylate copolymer-based lacquer binders. A polycarboxylic component is reacted with an epoxide group-containing polyhydroxylic component, and the carboxylic groups are then at least partially neutralised. As epoxide group-containing monomers for the polyhydroxylic components, glycidyl(meth)acrylate and/or glycidylallylether are used in proportions from 0.1 to 3 % by weight. Associated with cross-linking components and if required with other lacquer binders, these lacquer binders are suitable for producing water-dilutable baking enamels with a low auxiliary organic solvent content.

(57) Zusammenfassung

Die Erfindung betrifft ein Verfahren zur Herstellung von wasserverdünnbaren Lackbindemitteln auf der Basis von Acrylatcopolymerisaten, die durch die Umsetzung einer Polycarboxylkomponente mit einer Epoxidgruppen aufweisenden Polyhydroxylkomponente und eine nachfolgende, zumindest teilweise Neutralisation der Carboxylgruppen erhalten werden. Als Epoxidgruppen enthaltende Monomere für die Polyhydroxylkomponente werden Glycidyl(meth)acrylat und/oder Glycidylallylether in Anteilen von 0,1 bis 3 Gew.-% verwendet. Die Lackbindemittel eignen sich in Kombination mit Vernetzungskomponenten und gegebenenfalls mit anderen Lackbindemitteln zur Formulierung von wasserverdünnbaren Einbrennlacken mit einem niedrigen Gehalt an organischen Hilfslösemitteln.

Process for the preparation of water-dilutable coating binders based on acrylate copolymers, and their use

The invention relates to a process for the preparation of water-dilutable coating binders based on acrylate copolymers and to their use for the formulation of water-thinnable baking enamels having a low content of organic auxiliary solvents.

Water-dilutable binders which are obtained by partial condensation of a polycarboxy component, which is soluble in water following neutralization of the carboxyl groups, with a resin-like polyhydroxy component which is essentially not dilutable in water, and which are distinguished by favourable viscosity characteristics on dilution with water, are claimed in a series of protective documents, for example in AT Patent 328 587, AT Patent 379 607, AT Patent 388 738, AT Patent 388 382 and EP 0 496 079 A2.

The preparation of acrylate copolymers in accordance with EP 0 496 079 A2 requires a high level of concomitant analytical control measures in order to ensure that the quality of these products remains constant.

It has now been found that it is possible, by reacting a polycarboxy component with a polyhydroxy component which contains epoxide groups, to carry out the preparation of such water-dilutable acrylate copolymers in a more simple, more rapid and more reproducible manner.

The invention accordingly relates to a process for the preparation of water-dilutable coating binders based on acrylate copolymers, which are obtained by reacting a polycarboxy component with a polyhydroxy component followed by at least partial neutralization of the carboxyl groups, which is characterized in that

(A) from 15 to 40% by weight, based on solids content, of an acrylate copolymer as polycarboxy component having an acid number of from 70 to 240 mg of KOH/g, preferably from 100 to 200 mg of KOH/g, which has been prepared in the form of a solution polymer from

(Aa) from 67 to 90 % by weight of alkyl (meth)-acrylates which contain an alkyl radical of 1 to 12 carbon atoms, it being possible for these esters to be replaced in a proportion of up to 50% by weight by aromatic vinyl compounds, preferably styrene, and

(Ab) from 10 to 33 % by weight of α,β-ethylenically unsaturated carboxylic acids, preferably (meth)acrylic acid,

is mixed with

(B) from 60 to 85% by weight, based on solids content, of an acrylate copolymer as polyhydroxy component having a hydroxyl number of from 90 to 250 mg of KOH/g, preferably from 110 to 180 mg of KOH/g, and an epoxide equivalent of from 0.7 to 26.0 milliequivalents/100 g of solids, which has been prepared in the form of a solution polymer from

(Ba) from 40 to 79.9 % by weight of alkyl (meth)-acrylates which contain an alkyl radical of 1 to 12 carbon atoms, it being possible for these esters to be replaced in a proportion of up to 50% by weight of aromatic vinyl compounds, preferably styrene,

(Bb) from 20 to 59.9 % by weight of monoesters of (meth)acrylic acid with diols, which contain an alkylene radical of 2 to 4 carbon atoms or an oxyalkylene radical of 6 to 12 carbon atoms, and

(Bc) from 0.1 to 3 % by weight of a monomer which contains epoxide groups,

the data for the acid number and hydroxyl number always relating to the solids content and the sums of the percentages for components (A) and (B) and, respectively, (Aa) and (Ab) and (Ba) to (Bc) necessarily giving 100 in each case,

with the proviso that the mixture has an acid number of at least 15 mg of KOH/g, the solvent is removed in vacuo until the solids content of the batch is at least 95% by weight, the batch is diluted with an auxiliary solvent to a solids content of from 85 to 93% by weight, and then the mixture is maintained at a temperature of from 100 to 150°C, preferably from 110 to 130°C, until the epoxide equivalent of the batch has fallen to less than 0.2 milliequivalent/100 g of solids.

The invention also relates to the use of the binders prepared by this process, in combination with crosslinking components and optionally with other coating binders, for the formulation of water-thinnable baking enamels having a low content of organic auxiliary solvents.

In comparison with the process described in EP 0 496 079 A2 it is possible with the aid of the process according to the invention to prepare water-dilutable acrylate copolymers of similar composition with a simple procedure, a short duration of reaction and without risk of gelation.

Components (A) and (B) are prepared in a known manner by solution polymerization, preferably in alcohols or glycol ethers. In this polymerization the monomers are employed in the proportions indicated in the main claim.

Monomers which are used as components (Aa) and/or (Ba) are (meth)acrylic esters of alkanols of 1 to 12 carbon atoms and also, if desired, proportions - that is, up to 50% by weight - of aromatic vinyl monomers, especially styrene.

Component (Ab) preferably comprises acrylic or methacrylic acid, although it is possible for other α,β-ethylenically unsaturated carboxylic acids such as maleic acid and its monoesters to be employed if desired.

As component (Bb) monoesters of (meth)acrylic acid with diols, which contain 2 to 4 carbon atoms, are employed, such as ethylene glycol, propylene glycol and butylene glycol and/or the corresponding isomeric compounds. In addition, it is also possible to use monoesters of alkanediols of 6 to 12 carbon atoms which contain ether groups, for example tri- or corresponding poly-ethylene glycol mono(meth)acrylates and/or di- or corresponding poly-propylene glycol mono(meth)acrylates.

Monomers containing epoxide groups as component (Bc) are preferably glycidyl (meth)acrylate and/or glycidyl allyl ether.

The polycarboxy component (A) has an acid number of from 70 to 240 mg of KOH/g, preferably from 100 to 200 mg of KOH/g.

The hydroxyl number of the polyhydroxy component (B) is between 90 and 250 mg of KOH/g, preferably between 110 and 180 mg of KOH/g, and the epoxide equivalent is from 0.7 to 26.0 milliequivalents/100 g of solids.

Components (A) and (B) are mixed in a proportion, based on solids content, of between 15 : 85 and 40 : 60, with the proviso that the mixture has an acid number of at least 15 mg of KOH/g. Subsequently the solvents are substantially removed in vacuo and are replaced in part by auxiliary solvents such as alcohols or glycol ethers, such that the solids content of the mixture is from 85 to 93% by weight.

The reaction of the polycarboxy component (A) with the polyhydroxy component (B) which contains epoxide groups is carried out at from 100 to 150°C, preferably at from 110 to 130°C, until the epoxide equivalent of the batch has fallen to less than 0.2 milliequivalent/100 g of solids. An appropriate neutralizing agent, such as ammonia and/or an alkylamine and/or an alkanolamine, is then added, and the batch is diluted with water to the desired solids content.

The binders prepared in accordance with the invention are used, in combination with crosslinking components and optionally with other coating binders, for the formulation of baking enamels having a very low content of organic auxiliary solvents.

The binders are particularly suitable for the production of water-dilutable basecoats as are employed, for example, in the production-line finishing of cars for two-coat finishes consisting of a coloured and/or special-effect basecoat and a clearcoat.

Such water-dilutable basecoats additionally contain - optionally in combination with additional water-dilutable binders - crosslinking components, preferably amino resins and/or blocked polyisocyanates, and also the additives, fillers and pigments which are familiar to the person skilled in the art.

Suitable additional water-dilutable binders, which can also be used as paste resins, are, in particular, polyester resins, polyacrylate resins and polyurethane resins.

The water-dilutable basecoats are applied in a known manner in combination with clearcoats and are crosslinked at temperatures of up to 160°C.

The examples which follow illustrate the invention without limiting its scope. All parts and percentages are by weight unless stated otherwise.

1. Preparation of the polycarboxy components (A) and polyhydroxy components (B) used in the examples

The copolymers were prepared in a known manner by solution polymerization in isopropanol, in accordance with a calculated solids content of 50% by weight for components (A) and 65% by weight for components (B). The quantitative proportions and characteristics are compiled in Table 1.

2. Examples 1 to 5

Preparation of the acrylate copolymers (AB1) to (AB5)

Components (A) and (B) are mixed in the proportions indicated in Table 2. The isopropanol is removed in vacuo until the solids content of the batch is at least 95% by weight. After dilution of the batch with dipropylene glycol monomethyl ether to a solids content of about 90% by weight, the mixture is maintained at a temperature of from 110 to 120°C until the epoxide equivalent of the batch has fallen to less than 0.2 milliequivalent/100 g of solids. After the end of the reaction the batch is cooled to 95°C, neutralized and diluted with deionized water.

The characteristics of the products according to Examples 1 to 5 are likewise to be found in Table 2.

Analytical determination of the epoxide equivalent:

(milliequivalents of epoxide groups/100 g of solids)

About 0.2 g of the sample is weighed accurately on an analytical balance and is dissolved with gentle heating in 25 ml of a mixture of 4 parts of dichloromethane/1 part of glacial acetic acid. After the solution has been cooled to room temperature 0.5 g of tetrabutylammonium iodide is added. Following the addition of 3 drops of crystal violet (0.1% in glacial acetic acid) the mixture is titrated with 0.1 N perchloric acid in glacial acetic acid, from blue-violet until the change-over point to grass green (green without a hint of blue!). In parallel with the sample, a control with no resin added must be determined.

$$\text{Epoxide equivalent} = \frac{(A - B) \times 0.1 \times f}{\text{Sample weight (g)}}$$

A = Consumption in ml of 0.1 N perchloric acid for sample

B = Consumption in ml of 0.1 N perchloric acid for control

f = Factor for 0.1 N perchloric acid

Determination of the factor of 0.1 N perchloric acid:

About 200 mg of potassium hydrogen phthalate AR are weighed accurately on an analytical balance in a 300 ml conical flask, 30 ml of glacial acetic acid and 3 drops of crystal violet (0.1% in glacial acetic acid) are added, and the mixture is titrated with 0.1 N perchloric acid in glacial acetic acid to the colour change-over point from violet to a definite green.

$$f = \frac{W}{C \times 20.422}$$

W = Weight of potassium hydrogen phthalate AR in milligrams

C = Consumption in ml of 0.1 N perchloric acid in glacial acetic acid

Table 1

		COMPONENT				
		(A1)	(A2)			
(Aa)	Ethyl acrylate	-	25			
	Butyl acrylate	-	35			
	2-Ethylhexyl acrylate	30	-			
	Methyl methacrylate	-	30			
	Isobutyl methacrylate	27	-			
	Styrene	18.5	-			
(Ab)	Acrylic acid	-	10			
	Methacrylic acid	24.5	-			
	Acid number mg of KOH/g	160	78			
		COMPONENT				
		(B1)	(B2)	(B3)	(B4)	(B5)
(Ba)	Ethyl acrylate	-	19	-	-	-
	Butyl acrylate	-	14	-	30	23
	2-Ethylhexyl acrylate	26	-	-	-	-
	Methyl methacrylate	-	27	20	-	12
	Isobutyl methacrylate	18	-	24	10	22.6
	Styrene	24.2	-	-	31.8	10
(Bb)	4-Hydroxybutyl acrylate	-	9	33	22	15
	2-Hydroxyethyl methacrylate	31	30	21	-	17
	Tripropylene glycol methacrylate	-	-	-	6	-
(Bc)	Glycidyl acrylate	-	1	-	-	0.4
	Glycidyl methacrylate	0.8	-	1	0.2	-
	Glycidyl allyl ether	-	-	1	-	-
	Hydroxyl number mg of KOH/g	137	169	228	95	134
	Epoxide equivalent meq/100 g of solid resin	5.6	7.8	15.8	1.4	3.1

Table 2

(all quantities relate to solids content)

Example	1	2	3	4	5
	(AB1)	(AB2)	(AB3)	(AB4)	(AB5)
Quantity/Component (A)	25 (A1)	30 (A1)	40 (A2)	20 (A2)	25 (A2)
Quantity/Component (B)	75 (B1)	70 (B2)	60 (B3)	80 (B4)	75 (B5)
Acid number mg of KOH/g of the mixture Solids content % by wt.[1]	40 91.5	48 91.3	31 92.0	16 90.8	20 91.5
Addition reaction min/°C Epoxide equivalent[2] meq/100 g of solid resin	30/ 120 0.12	15/ 115 0.18	30/ 115 0.08	60/ 120 0.12	45/ 120 0.09
Neutralizing agent	DMA	TEA	DMA	DMA	DMA
Degree of neutralization (% of the COOH groups)	90	80	100	100	100
Dilution with H_2O to % by wt. solids content/supply form	42.3	43.5	41.8	43.2	44.6
pH of 10% strength solution (20°C)	8.7	8.3	8.9	8.8	8.7
% by wt. of organic solvent and amine in supply form	6.3	7.5	5.7	5.5	5.6

[1] % by weight solids content of the mixture after the addition of dipropylene glycol monomethyl ether

[2] after the end of the reaction

DMA = Dimethylethanolamine

TEA = Triethylamine

3. Coating performance testing of the acrylate copolymers (AB1) to (AB5)

3.1. Clearcoats in a metallic basecoat/clearcoat system and white coating materials

The formulations are compiled in Tables 3 and 4.

The indices 1) to 9) in Tables 3 and 4 denote:

1) Commercial melamine resin, of moderate reactivity, 85% strength in water (Cymel® 373, Cyanamid)
2) Commercial silicone levelling agent for water-thinnable coating materials (Additol® XW 329, Hoechst)
3) Commercial light stabilizer combination of benzotriazole UV absorber (Tinuvin® 1130, Ciba-Geigy) with sterically hindered amine (Tinuvin® 292, Ciba-Geigy) in a ratio of 1 : 1
4) Commercial antifoam based on acetylenediols (Surfinol® E 104/50%, Air Products)
5) Fully deionized water
6) HS value, as a measure of the content of volatile organic solvents:

$$\text{HS value} = \frac{\%\text{ by wt. of coating solids content (CS) X }100}{\%\text{ by wt. of CS}+\%\text{ by wt. of aux. solvent} + \%\text{ by wt. of amine}}$$

7) Flow time according to DIN 53211/23°C in seconds

8) Content of organic auxiliary solvents and amine in % by weight

9) Commercial titanium dioxide (Kronos® CL 310, Kronos)

The batches of coating material were adjusted to a pH of from 7.5 to 9.0 with dimethylethanolamine and were diluted with deionized water to a viscosity corresponding to a flow time according to DIN 53211/23°C of about 32 seconds.

The clearcoats were applied to coated steel panels (zinc phosphatization, cathodic electrodeposition coating, filler, metallic basecoat, using products which are employed in the automotive industry) by spraying at 23°C and a relative atmospheric humidity of 60%. After a flash-off time of 10 minutes and a preliminary drying time of 10 minutes at 80°C, the coatings were baked for 30 minutes at 140°C.

The white coating materials were applied to coated steel panels (zinc phosphatization, cathodic electrodeposition coating, filler, using products which are employed in the automotive industry) in an analogous manner and baked.

The results are compiled in Tables 5 and 6, where indices (1) to (4) denote:

(1) measured with a Byk Type Colourgloss 2 gloss meter at an angle of 60°

(2) an acetone-soaked cotton wool pad is placed on the coating film and the time taken for the film to soften is measured

(3) +: the coating film is unchanged after storage in water at 40°C for 240 hours

(+): the coating film has softened after storage in water at 40°C for 240 hours, but is regenerated after storage at room temperature for about 2 hours

(4) with the coating applied in a wedge formation (max. 60 µm, min. 15 µm), blistering and/or runs are noted in the baked coating film from the coat thickness indicated.

Table 3

Acrylate copolymer (AB) /supply form	Clearcoat			
	1	2	3	4
(AB1)	75.0			
(AB2)		69.1		
(AB4)			74.1	
(AB5)				70.6
Melamine resin1)	16.0	15.3	9.4	12.4
Levelling agent2)	0.2	0.2	0.3	0.3
Light stabilizer3)	1.2	1.2	1.4	1.3
Antifoam4)	0.5	0.5	0.5	0.5
H_2O5) 7.1	13.8	14.3	14.9	
	100	100	100	100
(AB) : MF resin*)	70:30	70:30	80:20	75:25
Solids content in % by wt.	46.9	44.6	42	43.7
HS value6)	90.4	89.2	90.7	91.2
pH	8.7	8.7	8.7	8.6
Viscosity7)	30	30	30	30
Solvent + amine in the coating material8)	5.0	5.4	4.3	4.3

*) based on solids

Table 4

Acrylate copolymer (AB) /supply form	White coating material	
	1	2
(AB1)	46.3	
(AB3)		51.0
Melamine resin[1)]	9.9	10.7
TiO_2[9)]	24.8	23.3
Levelling agent[2)]	0.2	0.2
Antifoam[4)]	0.4	0.4
H_2O[5)]	18.4	14.4
	100	100
(AB) : MF resin[*)]	70:30	70:30
Solids content in % by wt.	53.2	54.1
HS value[6)]	94.5	94.6
pH	8.5	8.4
Viscosity[7)]	32	35
Solvent + amine in the coating material[8)]	3.1	3.1

[*)] based on solids

Table 5

Clearcoat	1	2	3	4
Pendulum hardness DIN 53157 in sec.	165	180	190	195
Cross-hatch (DIN 53151)	0-1	0-1	0	0-1
Gloss (1)	89	86	86	84
Acetone resistance in min. (2)	2	3	2	2
Water resistance (3)	(+)	(+)	+	+
Blistering tendency, µm (4)	37	39	40	40
Tendency to run, µm (4)	42	40	40	38

Table 6

White coating material	1	2
Pendulum hardness DIN 53157 in sec.	175	160
Cross-hatch (DIN 53151)	1-2	2
Gloss (1)	82	78
Acetone resistance in min. (2)	2	2
Water resistance (3)	(+)	(+)
Blistering tendency, µm (4)	41	37
Tendency to run, µm (4)	40	42

3.2. Lime green water-dilutable basecoat

3.2.1. Preparation of a green pigment paste

20 parts of a chlorinated phthalocyanine pigment are predispersed using a dissolver in a mixture of 20 parts of a paste resin according to EP 0438090 A1 (paste resin 1), 35 parts of butoxyethanol and 0.5 parts of dimethylethanolamine, and this mixture is then dispersed in a bead mill. The pigment paste is subsequently diluted with 24.5 parts of deionized water.

3.2.2. Preparation of a white pigment paste

60 parts of titanium dioxide are predispersed using a dissolver in a mixture of 10 parts of a paste resin according to EP 0438090 A1 (paste resin 1), 15 parts of butoxyethanol and 0.5 parts of dimethylethanolamine and this mixture is then dispersed in a bead mill. The pigment paste is subsequently diluted with 14.5 parts of deionized water.

3.2.3. Preparation and application of the lime green water-dilutable basecoat

In a dissolver, 25 parts of the acrylate copolymer (AB3) are neutralized with 0.5 part of dimethylethanolamine. 8 parts of a 2:1 mixture of butylglycol and butyldiglycol, 2 parts of a commercially available antifoam, 4 parts of an acidic acrylate thickener, 12 parts of a paste resin according to EP 0438090 A1 (paste resin 1) and 5 parts of crosslinking agent (Cymel 323) are added. After homogenization of the mixture, 10 parts of the green pigment paste obtained under 3.2.1. and 3 parts of the white pigment paste obtained under 3.2.2. are added to the mixture. Homogeneous mixing is again carried out, and the mixture is diluted with 30.5 parts of deionized water.

The basecoat is applied to a phosphatized bodywork panel, which has been precoated with a cathodic deposition coat and with a filler, by spraying, in a dry-film thickness of 20 µm. This coating is then flashed off at room temperature for 10 minutes, predried at 80°C for 10 minutes, and overcoated with a commercial, acrylate resin-based automotive production-line clearcoat, which cures by means of melamine resin, in a dry-film thickness of 35 µm. The two-coat topcoat is baked at 130°C (panel temperature) for 30 minutes.

The multi-coat paint system thus obtained meets, in terms of its optical and mechanical properties, all of the requirements set by the automotive industry.

The Claims defining the invention are as follows:

1. Process for the preparation of water-dilutable coating binders based on acrylate copolymers, which are obtained by reacting a polycarboxy component with a polyhydroxy component followed by at least partial neutralisation of the carboxyl groups, characterised in that

(A) from 15 to 40wt%, based on solids content, of an acrylate copolymer as polycarboxy component having an acid number of from 70 to 240mg of KOH/g, which has been prepared in the form of a solution polymer from

(Aa) from 67 to 90wt% of alkyl (meth)acrylates which contain an alkyl radical of 1 to 12 carbon atoms, it being possible for these esters to be replaced in a proportion of up to 50wt% by aromatic vinyl compounds, and

(Ab) from 10 to 33wt% of α,β-ethylenically unsaturated carboxylic acids, is mixed with

(B) from 60 to 85wt% by weight, based on solids content, of an acrylate copolymer as polyhydroxy component having a hydroxyl number of from 90 to 250mg of KOH/g, and an epoxide equivalent of from 0.7 to 26.0 milliequivalents/100g of solids, which has been prepared in the form of a solution polymer from

(Ba) from 40 to 79.9wt% of alkyl (meth)acrylates which contain an alkyl radical of 1 to 12 carbon atoms, it being possible for these esters to be replaced in a proportion of up to 50wt% of aromatic vinyl compounds,

(Bb) from 20 to 59.9wt% of monoesters of (meth)acrylic acid with diols, which contain an alkylene radical of 2 to 4 carbon atoms or an oxyalkylene radical of 6 to 12 carbon atoms, and

(Bc) from 0.1 to 3wt% of a monomer which contains epoxide groups, the data for the acid number and hydroxyl number always relating to the solids content and the sums of the percentages for components (A) and (B) and, respectively, (Aa) and (Ab) and (Ba) to (Bc) necessarily giving 100 in each case,

with the proviso that the mixture has an acid number of at least 15mg of KOH/g, the solvent is removed *in vacuo* until the solids content of the batch is at least 95wt%, the batch is diluted with an auxiliary solvent to a solids content of from 85 to 93wt%, and then the mixture is maintained at a temperature of from 100 to 150°C, until the epoxide equivalent of the batch has fallen to less than 0.2 milliequivalent/100g of solids.

2. Process according to claim 1, characterised in that glycidyl (meth)acrylate and/or glycidyl allyl ether is employed as component (Bc).

3. Process for the preparation of water-dilutable coating binders based on acrylate copolymers, which are obtained by reacting a polycarboxy component with a polyhydroxy component followed by at least partial neutralisation of the carboxyl groups,substantially as hereinbefore described with reference to any one of the Examples.

4. A water-dilutable coating binder produced by the process of any one of claims 1 to 3.

5. A water- thinnable baking enamel with a low content of organic auxiliary solvents containing a binder according to claim 4 in combination with crosslinking components and optionally other coating binders.

6. A water-dilutable basecoat containing a binder of claim 4 in combination with crosslinking components and further coating raw materials.

7. Process for the production of two-coat paint systems, characterised in that after the application of a basecoat to a substrate a further clearcoat is applied, the basecoat containing the binders according to claim 4.

Dated 14 June, 1996
Vianova Resins Aktiengesellschaft

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON

INTERNATIONAL SEARCH REPORT

International Application No
PCT/AT 94/00203

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G81/02 C09D133/06 B05D7/26 //(C09D133/06,133:14), (C09D133/06,161:20)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C09D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 496 079 (VIANOVA KUNSTHARZ AG) 29 July 1992 cited in the application see claim 1 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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

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Date of the actual completion of the international search
15 February 1995

Date of mailing of the international search report
08.03.95

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/AT 94/00203

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0496079	29-07-92	AT-A-	79091	15-09-93
		AT-B-	396244	26-07-93
		CA-A-	2058371	28-06-92
		JP-A-	4304277	27-10-92

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/AT 94/00203

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 6 C08G81/02 C09D133/06 B05D7/26 //(C09D133/06,133:14),(C09D133/06,161:20)

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 6 C08G C09D

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	EP,A,0 496 079 (VIANOVA KUNSTHARZ AG) 29.Juli 1992 in der Anmeldung erwähnt siehe Anspruch 1 -----	1

☐ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :

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Datum des Abschlusses der internationalen Recherche 15.Februar 1995	Absendedatum des internationalen Recherchenberichts 08.03.95
Name und Postanschrift der Internationale Recherchenbehörde Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Bevollmächtigter Bediensteter Schueler, D

INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Internationales Aktenzeichen
PCT/AT 94/00203

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
EP-A-0496079	29-07-92	AT-A- 79091	15-09-93
		AT-B- 396244	26-07-93
		CA-A- 2058371	28-06-92
		JP-A- 4304277	27-10-92