

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 February 2003 (06.02.2003)

PCT

(10) International Publication Number
WO 03/010253 A1

(51) International Patent Classification⁷: **C09D 163/10**,
167/06, 175/16, 177/12

(21) International Application Number: PCT/EP02/08194

(22) International Filing Date: 23 July 2002 (23.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01118132.8 26 July 2001 (26.07.2001) EP

(71) Applicant (*for all designated States except US*): **UCB, S.A.** [BE/BE]; Allée de la Recherche, 60, B-1070 Bruxelles (BE).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **MOENS, Luc** [BE/BE]; Ijsvogellaan, 30, B-1640 Sint-Genesius-Rode (BE). **BUYSENS, Kris** [BE/BE]; Marollestraat 5A, B-9700 Oudenaarde (BE). **MAETENS, Daniel** [BE/BE]; Avenue René Comhaire, 108, B-1070 Bruxelles (BE).

(74) Agent: **ROELANTS, François**; UCB, S.A., Intellectual Property Department, Allée de la Recherche, 60, B-1070 Bruxelles (BE).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POLYMERIC COMPOSITIONS

(57) Abstract: There is described a radiation curable powder composition which comprises a) 10 to 90% weight of a (meth)acryloyl group containing hydrogenated polyphenoxy resin b) 10 to 90% weight of a (meth)acryloyl group containing resin, different from the (meth)acryloyl group containing hydrogenated polyphenoxy resin; and c) 0 to 30% weight of a (meth)acryloyl group containing oligomer.



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POLYMERIC COMPOSITIONS

The present invention concerns powder compositions, hardenable by radiation usable as paint or varnish, comprising a mixture of at least one (meth)acryloyl group containing hydrogenated polyphenoxy resin and at least one (meth)acryloyl group containing resin different from the hydrogenated polyphenoxy resin, and optionally at least one (meth)acryloyl group containing oligomer.

The powder compositions of the present invention may be especially suited for coating over metal and heat-sensitive substrates and combine, upon melting at low temperatures and curing by radiation, a series of properties such as good flow along with an outstanding solvent resistance, flexibility and outdoor durability. Thus these radiation curable powders may exhibit improved weathering and chemical resistance.

Powder coatings, which are dry, finely divided, free flowing, solid materials at room temperature, have gained considerable popularity in recent years over liquid coatings. Despite their many advantages, nowadays thermosetting powder coatings generally are cured at temperatures of at least 140°C. Below this recommended temperature the coatings have poor appearance as well as poor physical and chemical properties. In consequence of this restriction, powder coatings are generally not employed in coating heat-sensitive substrates such as wood and plastic or assembled metallic parts containing heat-sensitive compounds. Heat-sensitive substrates or compounds both demand low curing temperatures, preferably below 140°C, to avoid significant degradation and/or deformation.

Low temperature radiation curable powders have recently been proposed as a solution to this problem.

The use of unsaturated resins, eventually in combination with unsaturated oligomers, as a binder for radiation curable powder coatings already is subject of a considerable number of patents and patent applications.

UV curable powder coating compositions derived from ethylenically unsaturated group containing polyesters, acrylic copolymers or epoxy resins, among others, already have been extensively illustrated.

US 3,974,303 (Kansai Paint Co Ltd.) describes different unsaturated resins such as methacryloyl group containing polyesters or acrylic copolymers.

EP 2164254 (BASF) describes powder coatings based on unsaturated polyesters, acrylic copolymers, epoxy resins and other polymers containing unsaturated double bonds.

US 4,129,488 (SCM Corporation N.Y.) discloses powder paint coatings suitable for UV curing comprising a specific spatial arrangement of ethylenically unsaturated polymers. The (meth)acrylic unsaturated polymer is a spatial specific epoxy-polyester polymer, produced in a step-wise process, with a number average molecular weight between 1000 and 10 000, providing suitable crystallinity to the free flowing powder and exhibiting a sharp melting point, between 80 and 200°C, for excellent flow.

The powder paints derived from the spatial specific epoxy polyester polymer prove excellent hardness, desirable flexibility and good MEK resistance.

Radiation curable powder coatings, especially developed for those applications where an outstanding flexibility and chemical resistance is needed, all fall short when outdoor durability is concerned.

It now has been surprisingly found that radiation curable powder coating compositions based on a binder comprising a particular mixture of at least one (meth)acryloyl group containing hydrogenated polyphenoxy resin, at least (meth)acryloyl group containing resin, different from the hydrogenated polyphenoxy resin, and optionally at least one (meth)acryloyl group containing oligomer, upon application and curing exhibit an excellent combination of flexibility, solvent resistance and outdoor durability.

It is accordingly the object of this invention to provide a powder coating composition, capable of being cured by radiation upon melting, the composition comprising:

- (a) 10 to 90% weight of at least one (meth)acryloyl group containing hydrogenated polyphenoxy resin
- (b) 10 to 90% weight of at least one (meth)acryloyl group containing polyester, polyesteramide, polyurethane or polyacrylic copolymer used in a mixture or alone
- (c) 0 to 30% weight of a (meth)acryloyl group containing oligomer

The (meth)acryloyl group containing hydrogenated polyphenoxy resin may be prepared from the reaction of the glycidyl group of the hydrogenated polyphenoxy resin with: (meth)acrylic acid and the reaction product of an hydroxyalkylester of (meth)acrylic acid such as hydroxyethyl(meth)acrylate with an anhydride such as phthalic anhydride or succinic anhydride.

For the preparation of the (meth)acryloyl group containing hydrogenated polyphenoxy resin, use is generally made of a conventional reactor equipped with a stirrer, an inlet for oxygen, an inlet for the (meth)acryloyl group containing carboxylic acid group containing compound and a thermometer connected to a thermoregulator. To the epoxy resin standing at a temperature between 100 and 150°C, a radical polymerisation inhibitor is added in a proportion of e.g. 0.01

to 1 % with respect to the weight of the epoxy resin. A substantial equivalent amount of the (meth)acryloyl group containing carboxylic acid group containing compound is then slowly added to the molten epoxy resin. A catalyst for the acid/ epoxy reaction can optionally be used. Examples of such catalysts include amines (e.g. 2-phenylimidazoline), phosphines (e.g. tri-phenyl phosphine), ammonium salts (e.g. tetrabutylammonium bromide or tetra-propyl ammonium chloride), phosphonium salts (e.g. ethyl triphenyl phosphonium bromide or tetra propyl phosphonium chloride). These catalysts are preferably used in an amount of 0.05 to 1% with respect to the weight of the epoxy resin.

- 10 The degree of progression of the reaction is monitored by determination of the properties of the ethylenically unsaturated group containing resin obtained, such as acid number, hydroxyl number and the degree of unsaturation.

15 The (meth)acryloyl group containing hydrogenated polyphenoxy resins incorporated in the compositions in accordance with the present invention, preferably exhibit a degree of unsaturation of 0.2 to 6.0, particularly of 0.5 to 4.5 milliequivalents of double bonds per gram of resin, and in a specifically preferred embodiment additionally exhibit one or more of following characteristics:

- 20 a number average molecular weight (M_n) from 450 to 5000, preferably between 650 and 3500, measured by gel permeation chromatography (GPC)
a glass transition temperature (T_g) determined by differential scanning calorimetry (DSC) according to ASTM D3418, from 30 to 80°C and/or
a viscosity in the molten state measured at 200°C with a cone/plate viscometer (known under the name of ICI viscosity) according to ASTM D4287, of less than 20 000 mPa.s.

25 The (meth)acryloyl group containing polyesters of the present invention are amorphous or semi-crystalline and are prepared from the reaction of a hydroxyl or carboxylic acid functional polyester with a (meth)acryloyl group containing monomer having functional groups reactable with the functional groups of the polyester.

30 For the preparation of the hydroxyl or carboxylic acid functional polyester use is being made of one or more aliphatic, cycloaliphatic or aromatic polyacids and one or more aliphatic or cycloaliphatic polyols.

35 Examples of suitable aliphatic, cycloaliphatic or aromatic acids include among others: phthalic acid, isophthalic acid, terephthalic acid, 1,2-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,12-dodecanedioic acid, trimellitic acid, pyromellitic acid and their anhydrides, alone or as a mixture.

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Examples of suitable aliphatic or cycloaliphatic polyols include among others: ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, 2-methyl-1,3-propanediol, neopentyl glycol, 2-butyl-2-methyl-1,3-propanediol, hydroxy pivalate ester of neopentyl glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, hydrogenated Bisphenol A, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 4,8-bis(hydroxymethyl)-tricyclo-[5,2,1,0^{2,6}]-decane.

The hydroxyl or carboxylic acid group containing polyesters of the present invention are prepared according a procedure comprising one or more reaction steps.

On completion of the polycondensation, the hydroxyl or carboxyl functional group containing polyester in the molten state, which is found in the reactor, is allowed to cool to a temperature between 100 and 160°C, and a radical polymerisation inhibitor, such as phenothiazine or an inhibitor of the hydroquinone type, is added in a proportion of e.g. 0.01 to 1% with respect to the weight of the polyester and the nitrogen is replaced by an oxygen inlet.

When started from a hydroxyl group containing polyester, a substantially equivalent amount of hydroxyalkyl(meth)acrylate is added thereto. When all the hydroxyalkyl(meth)acrylate is added, an equivalent amount of diisocyanate is slowly added to the mixture. A catalyst for the hydroxyl/isocyanate reaction can optionally be used. Examples of such catalysts include organo-tin compounds (e.g. dibutyltin dilaurate, dibutyltin dimaleate, dibutyltin oxide, stannous octoate, 1,3-diacetoxy-1,1,3,3-tetrabutyl-distanoxane). These catalysts are preferably used in an amount of 0 to 1% with respect to the weight of the polyester.

Otherwise, when started from a polyester containing carboxyl groups, a substantially equivalent amount of glycidyl(meth)acrylate is added thereto. A catalyst for the acid/epoxy reaction can optionally be used. Examples of such catalysts include amines (e.g. 2-phenylimidazoline), phosphines (e.g. triphenylphosphine), ammonium salts (e.g. tetrabutylammonium bromide or tetrapropylammonium chloride), phosphonium salts (e.g. ethyltriphenylphosphonium bromide or tetrapropylphosphonium chloride). These catalysts are preferably used in an amount of 0.05 to 1% with respect to the weight of the polyester.

The degree of progression of the reaction is monitored by determination of the properties of the polyester obtained, for example the hydroxyl number, the acid number, the degree of unsaturation and/ or the content of free glycidyl(meth)acrylate or hydroxyalkyl(meth)acrylate.

The (meth)acryloyl group containing polyesters of the present invention are characterised with a number average molecular weight (Mn) from 800 to 16 000 and preferably from 1 300 to 8 500, a glass transition temperature (Tg) from 35 to 85°C when the polyester is amorphous, or a melting temperature from 60 to 150°C and a glass transition temperature of less than 50°C

when the polyester is semi-crystalline, a degree of unsaturation ranging from 0.15 to 2.00 and preferably from 0.35 to 1.50 milliequivalents of double bonds per gram of polyester and an ICI cone/plate viscosity of less than 50 000 mPa.s measured at 200°C.

5 The (meth)acryloyl group containing polyesteramides of the present invention are prepared from the reaction of glycidyl(meth)acrylate with a carboxyl group terminated polyesteramide, said polyesteramide being prepared from the reaction of a carboxyl group terminated polyester with a diamine.

10 The carboxyl group terminated polyesters used for the synthesis of the polyesteramides are prepared from aliphatic, cycloaliphatic or aromatic polyacids used in a mixture or alone, and aliphatic or cycloaliphatic polyols used in a mixture or alone, both, the polyacids and the polyols being selected among these examples as recited earlier for the preparation of the (meth)acryloyl group containing polyesters.

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Examples of the diamines which can be used, either alone or in combination, for the preparation of the polyesteramides are selected from ethylenediamine, 1,3-propanediamine, 1,5-pentanediamine, 1,6-hexanediamine, 1,2-cyclohexanediamine, 1,3-cyclohexanediamine, 1,4-cyclohexanediamine, 2,2-dimethyl-1,3-propanediamine, N-(2-aminoethyl)-1,2-ethanediamine, 20 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 4,4'-diaminodicyclohexylmethane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane and analogous compounds.

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The polyesteramides used for the preparation of the (meth)acryloyl group containing polyesteramides are prepared accordingly a two or more step procedure process as claimed in US 5,306,786.

30

On completion of the synthesis of the carboxylic acid group containing polyesteramide, a substantially equivalent amount of glycidyl(meth)acrylate is added thereto, accordingly a procedure as described above for the preparation of the (meth)acryloyl group containing polyesters starting from the carboxylic acid group functional polyester, to end up with a (meth)acryloyl group containing polyesteramide characterised by a number average molecular weight (Mn) from 800 to 16 000 and preferably from 1 300 to 8 500, a glass transition temperature (Tg) from 40 to 70°C when the polyester is amorphous, a degree of unsaturation 35 ranging from 0.15 to 2.00 and preferably from 0.35 to 1.50 milliequivalents of double bonds per gram of polyester and an ICI cone/plate viscosity of less than 50 000 mPa.s measured at 200°C.

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The (meth)acryloyl group containing polyurethanes of the present invention are prepared from the reaction of an hydroxyalkyl(meth)acrylate and a polyol with a polyisocyanate.

The polyol used for the preparation of the (meth)acryloyl group containing polyurethanes are chosen among the C2 - C15 aliphatic or cycloaliphatic diols, polyester polyols or polyether polyols.

5 Examples of C₂₋₁₅aliphatic or cycloaliphatic diols are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-undecanediol, 1,12-dodecanediol, 2-methyl-1,3-propanediol, neopentyl glycol, 2-butyl-2-methyl-1,3-propanediol, hydroxypivalate ester of neopentyl glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, hydrogenated Bisphenol A, 2,2,4,4-tetramethyl-
10 1,3-cyclobutanediol, 4,8-bis(hydroxymethyl)-tricyclo-[5,2,1,0^{2,6}]-decane.

The polyester polyols, characterised by number average molecular weight (Mn) from 8200 to 4000, are prepared from a stoichiometric excess of an aliphatic or cycloaliphatic polyol with an aromatic, aliphatic or cycloaliphatic polyacid, the polyacids and the polyols being selected
15 among those recited earlier for the preparation of the (meth)acryloyl group containing polyesters of polyesteramides.

Examples of the polyether polyols are polyoxyethylene glycol, polyoxypropylene glycol, polyoxybutylene glycol, polytetramethylene glycol, block copolymers, for example, combinations
20 of polyoxypropylene and polyoxyethylene glycols, poly-1,2-oxybutylene and polyoxyethylene glycols, poly-1,4-tetramethylene and polyoxyethylene glycols, and copolymer glycols prepared from blends or sequential addition of two or more alkylene oxides. The polyalkylene polyether polyols may be prepared by any known process such as, for example, the process disclosed in Encyclopaedia Technology, Vol. 7, pp. 257 - 262, published by Interscience Publishers, Inc.
25 (1951).

Examples of polyisocyanates that can be used for the preparation of the (meth)acryloyl group containing polyurethanes of the present invention are 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorondiisocyanate, IPDI), tetramethylxylenediisocyanate
30 (TMXDI), hexamethylenediisocyanate (HDI), trimethylhexamethylenediisocyanate, 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanatodiphenylmethane, these technical mixtures with 2,4-di-isocyanatodiphenylmethane and also the higher homologues of above mentioned diisocyanates, 2,4-di-isocyanatotoluene and technical mixtures of them with 2,6-diisocyanatotoluene, as well as the copolymerisation product of α,α' -dimethyl-meta-isopropenylbenzylisocyanate (TMI).
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The hydroxyalkyl(meth)acrylate used for the preparation of the (meth)acryloyl group containing polyurethanes are hydroxyalkylesters of acrylic or methacrylic acid preferably having 2 to 4 carbon atoms in the hydroxyalkyl group such as hydroxyethyl(meth)acrylate, 2- and 3-
40 hydroxypropyl(meth)acrylate and 2-, 3- and 4-hydroxybutyl(meth)acrylate.

Preparation of the polyurethanes by reacting the above mentioned starting components may be carried out in inert solvents such as acetone, ethyl acetate, butyl acetate or toluene, preferably at reaction temperatures of 20 to 100°C. The reaction is preferably carried out by reacting the polyisocyanate with the hydroxyalkyl(meth)acrylate in a first reaction step and then
5 reacting the resulting reaction product with the polyol.

The reaction may be accelerated by the use of suitable catalysts such as tin octoate, dibutyltin dilaurate or tertiary amines such as dimethylbenzylamine. The polyurethane or urethane acrylate obtained as the reaction product may be protected against premature, unwanted
10 polymerisation by the addition of suitable inhibitors and antioxidants such as phenols and/or hydroquinones in quantities of 0.001 to 0.300% by weight, based on the polyurethane. These auxiliary agents may be added before, during and/or after the reaction which results in the polyurethane.

The (meth)acryloyl group containing polyurethanes of the present invention are characterised by a number average molecular weight (M_n) from 800 to 15 000 and preferably from 1 300 to 8 500, a glass transition temperature (T_g) from 40 to 100°C, a degree of unsaturation ranging from 0.15 to 0.20 and preferably from 0.35 to 1.50 milliequivalents of double bonds per gram of polyurethane and an ICI cone/plate viscosity of less than 100 000 mPa.s measured at 200°C.
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The (meth)acryloyl group containing acrylic copolymers of the powder composition of the present invention are prepared from the reaction of (meth)acryloyl group containing monomers having functional groups with an acrylic copolymer having functional groups being capable of reacting with the functional groups of the (meth)acryloyl group containing monomers.
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The acrylic copolymer having reactable functional groups is composed of from 40 to 95% mole of at least one acrylic or methacrylic monomer, from 0 to 60% mole of at least one other ethylenically unsaturated monomer and from 5 to 60% mole of an (meth)acryloyl group containing monomer having functional groups selected from epoxy, carboxyl, hydroxyl or
30 isocyanate groups.

The (meth)acryloyl group containing acrylic copolymer of the powder composition of the present invention is prepared accordingly a two step process.

In a first step the acrylate copolymer is prepared in a conventional polymerisation process, such as polymerisation in bulk, in emulsion, or in solution in an organic solvent, in which a certain portion of functional monomer is copolymerised to obtain a functionalised acrylate copolymer.
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This functional monomer, which is usually present in amounts of between 5 and 60% mole, is preferably an epoxy - functional monomer, for example on the basis of glycidyl (meth)acrylate.
40

However, acid-functional monomers, for example on the basis of (meth)acrylic acid, hydroxyl-functional monomers, for example on the basis of hydroxyethyl (meth)acrylate, or isocyanate-functional monomers, for example on the basis of TMI (benzene, 1-(1-isocyanato-1-methylethyl)-4-(1-methylethenyl)) or MOI (2-isocyanatoethylmethacrylate) also can be used.

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The monomers are copolymerised in the presence of free-radical initiator such as benzoyl peroxide, tert.-butyl peroxide, decanoyl peroxide, azo-bis-isobutyronitrile, and the like, in an amount of from 0.1 to 5% by weight of the monomers. Useful monomers for the preparation of the acrylic copolymer are methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, n-butyl(meth)acrylate, isobutyl(meth)acrylate, tert.-butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, stearyl(meth)acrylate, tridecyl(meth)acrylate, cyclohexyl(meth)acrylate, benzyl(meth)acrylate, benzyl(meth)acrylate, phenyl(meth)acrylate, dimethylaminoethyl(meth)acrylate, diethylaminoethyl(meth)acrylate, polysiloxane (meth)acrylate and caprolactone(meth)acrylate. These monomers usually are present in amounts between 40 and 95% mole.

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Other copolymerisable monomers, which can be present in amounts between 0 and 60% mole, are for example styrene, α -methylstyrene, vinyltoluene, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate, acrylamide, methacrylamide, methylolmethacrylamide, vinylchloride, ethylene, propylene and C4-20 α -olefins.

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In the second step an addition reaction is carried out between the functionalised monomer of the acrylate copolymer obtained from the first step and the (meth)acryloyl group containing compound that can react with said functional monomer. The compound that can react respectively is for example (meth)acrylic acid, maleic anhydride, (β -methyl)glycidyl(meth)acrylate, allylglycidylether, MOI, hydroxyethyl (meth)acrylate, hydroxy butylvinylether, allyl alcohol.

25

The addition reaction of the second step can be done either in bulk or in solvent. Typical solvents are toluene, xylene, n-butylacetate, etc. The compound containing an (meth)acryloyl group that can react with the functionalised acrylate polymer is added at temperatures between 50 and 150°C. The mixture is stirred for several hours. The progress of the reaction is followed by titration.

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The (meth)acryloyl group containing acrylic copolymer of the powder composition of the present invention exhibit following characteristics:

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a number average molecular weight (M_n) from 1000 to 8000 and preferably from 2 000 to 6 000 measured by GPC

a degree of unsaturation from 0.35 to 3.50 and preferably from 0.5 to 2.5 milliequivalents of double bonds per gram of acrylic copolymer

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an ICI cone/plate melt viscosity of less than 50 000 mPa.s measured at 200°C according to ASTM D4287

a glass transition temperature (T_g) from 45 to 100°C as determined by DSC according to ASTM D3418.

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Besides, up to 30% weight of the (meth)acryloyl group containing resin optionally is replaced by a (meth)acryloyl group containing oligomer selected from the triacrylate and the tri(meth)acrylate of tris(2-hydroxyethyl)isocyanurate, the epoxy acrylates and methacrylates which are formed by the reaction of an epoxy compound (for example, the diglycidyl ether of Bisphenol A) with acrylic or methacrylic acid, the urethane acrylates and methacrylates which are formed by the reaction of an organic di- or polyisocyanate with an hydroxyalkylacrylate or a hydroxyalkylmethacrylate and optionally a mono- and/or polyhydroxylated alcohol (for example, the reaction product of hydroxyethyl(meth)acrylate with toluenediisocyanate or isophoronediiisocyanate), the acrylic acrylates or methacrylates, such as, for example, the reaction product of (meth)acrylic acid with a copolymer containing glycidyl groups and methylmethacrylate, and the like.

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The hydrogenated polyphenoxy resin, the semi-crystalline and/or the amorphous polyester and/or the polyesteramide and/or polyurethane and/or acrylic copolymer optionally along with one or more oligomers all containing (meth)acryloyl groups all described above, intended to be used as binders in the preparation of powder compositions curable by UV radiation or by accelerated electron beams, it being possible for the said compositions to be used in particular as varnishes and paints which e.g. lend themselves to application according to the technique of deposition by means of a triboelectric or electrostatic spray gun or according to the technique of deposition in a fluidised bed. The radiation curable powder compositions can be used as varnishes or paints as such or, if desired, the compositions can be used to prepare the varnishes or paints by adding, further constituents conventionally used in the preparation of powder varnishes and paints.

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Therefore, the present invention also relates to the powder varnish or paint obtained using these compositions.

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Finally, the present invention also relates to a process for coating an article more particularly a metal article comprising the application to the said article of a radiation curable powder composition in accordance with the invention by deposition such as by spraying with a triboelectric or electrostatic spray gun or by deposition in a fluidised bed, followed by the melting of the coating thus obtained such as by heating at a temperature of 80 to 150°C for a time of e.g. approximately 0.5 to 10 minutes and by the curing of the coating in the molten state by UV irradiation or by accelerated electron beams.

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For the radiation curing of the powder compositions in accordance with the invention with accelerated electron beams, it is not necessary to use a photo-initiator, seeing that this type of radiation provides by itself alone a production of free radicals which is sufficiently high for the curing to be extremely rapid. In contrast, when it concerns the photo-curing of the powder composition according to the invention with radiation where the wavelengths are between 200 and 600 nm (UV radiation), the presence of at least one photo-initiator is essential.

The photo-initiators which can be used according to the present invention are chosen from those commonly used for this purpose.

The appropriate photo-initiators which can be used, are aromatic carbonyl compounds, such as benzophenone and its alkylated or halogenated derivatives, anthraquinone and its derivatives, thioxanthone and its derivatives, benzoin ethers, aromatic or non-aromatic aliphadiones, benzil dialkyl acetals, acetophenone derivatives and phosphine oxides.

Photo-initiators which may suitably be, for example, 2,2'-diethoxyacetophenone, 2-, 3- or 4-bromoacetophenone, 2,3-pentanedione, hydroxycyclohexylphenylketone, benzaldehyde, benzoin, benzophenone, 9,10-dibromoanthracene, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 4,4'-dichlorobenzophenone, xanthone, thioxanthone, benzildimethylketal, diphenyl(2,4,6-trimethylbenzyl)phosphine oxide, and the like. It may be optionally advantageous to use a photo-activator, such as tributylamine, 2-(2-aminoethylamino)ethanol, cyclohexylamine, diphenylamine, tribenzylamine or aminoacrylates such as, for example, the addition product of a secondary amine, such as dimethylamine, diethylamine, diethanolamine, and the like, with a polyol polyacrylate, such as the diacrylate of trimethylolpropane, 1,6-hexanediol, and the like.

The powder compositions in accordance with the invention can contain 0 to 15 and preferably 0.5 to 8.0 parts of photo-initiators for 100 parts by weight of the binder in the composition in accordance with the invention.

The radiation curable powder compositions and powder varnishes or paints, respectively, in accordance with the invention can also contain various additional substances conventionally used in the manufacture of powder paints and varnishes. The additional substances optionally added to the radiation-curable powder compositions in accordance with the invention, e.g. to prepare the powder varnishes or paints are, inter alia, compounds which absorb UV radiation, such as Tinuvin 900 (Ciba), light stabilisers based on sterically hindered amines (for example Tinuvin 144 from Ciba), fluidity-regulating agents such as Resiflow PV5 (Worlee), Modaflow (Monsanto), Acronal 4F (BASF) or Crylcoat 109 (UCB), degassing agents such as benzoin and the like.

To the radiation-curable powder composition according to the present invention, further can be added a variety of coating properties modifying substances such as polytetrafluoroethylene

modified polyethylene waxes (e.g. Lanco Wax TF 1830 from Lubrizol), polyethylene waxes (e.g. Ceraflour 961 from BYK Chemie), polypropylene waxes (e.g. Lanco Wax PP1362 from Lubrizol), polyamide waxes (e.g. Orgasol 3202 D NAT from ELF Atochem), organosilicones (e.g. Modarez S304P from Protex), etc., or blends of them. These modifying substances are optionally added from 0 to 10 parts for 100 parts by weight of the binder in the composition according to the invention. A variety of pigments and inorganic fillers can also be added to the radiation curable powder compositions in accordance with the invention. Mention will be made, as examples of pigments and fillers, of metal oxides, such as titanium oxide, iron oxide, zinc oxide, and the like, metal hydroxides, metal powders, sulphides, sulphates, carbonates, silicates such as, for example, aluminium silicate, carbon black, talc, kaolins, barytes, iron blues, lead blues, organic reds, organic maroons, and the like.

These additional substances are used in the usual amounts, it being understood that if the radiation curable powder compositions in accordance with the present invention are used as varnishes, the addition of additional substances having opacifying properties should be omitted.

For the preparation of the radiation curable powder compositions of the present invention the hydrogenated polyphenoxy resin, the semi-crystalline and/or the amorphous polyester and/or the polyesteramide and/or polyurethane and/or acrylic copolymer optionally along with one or more oligomers all containing (meth)acryloyl groups, optionally the photo-initiator, optionally the various additional substances conventionally used for the manufacturing of powder paints and varnishes, and optionally the coating properties modifying substances are dry mixed, for example in a tumbler mixer. The mixture is then homogenised at a temperature ranging from 60 to 150°C in an extruder, for example in a Buss Ko-Kneter single screw extruder or a twin screw extruder of Werner-Pfleiderer, APV-Baker or Prism type. The extrudate is then allowed to cool, is ground and sieved in order to obtain a powder in which the size of the particles is preferably between 10 and 150 µm.

Instead of the above methods, it is also possible to dissolve/suspend the different unsaturated constituents of the binder system of the present invention, optionally the photo-initiator, and the various additional substances in a solvent such as dichloromethane, to grind in order to obtain a homogeneous suspension containing approximately 30% by weight of solid matter and subsequently to evaporate the solvent, for example by spray drying at a temperature of approximately 50°C, according to methods known per se.

The powder paints and varnishes thus obtained, are entirely suitable for application to the article to be coated by conventional techniques, that is to say by the well-known technique of e.g. deposition in a fluidised bed or by application with a triboelectric or electrostatic spray gun.

After having been applied to the article concerned, the coatings deposited are heated e.g. in a forced circulation oven or by means of infrared lamps at a temperature of 80 to 150°C for a time of e.g. approximately 0.5 to 10 minutes for the purpose of obtaining the melting and the spreading of the powder particles as a smooth, uniform and continuous coating at the surface of the said article. The molten coating is then cured by radiation, such as UV light emitted, for example, by medium pressure mercury vapour UV radiators, of preferably at least 80 to 250 W/linear cm, or by any other well-known source of the state of the art, at a distance of e.g. approximately 5 to 20 cm and for a time sufficient to cure the coating, such as 1 to 60 seconds.

The molten coating can also be cured with accelerated electron beams of preferably at least 150 keV, the power of the devices employed being a direct function of the thickness of the composition layer to be cured by polymerisation.

The invention is also concerned with articles partially or entirely coated by the coating processes.

Further aspects and features of the invention are given in the claims.

The radiation curable powder compositions in accordance with the invention though they can be applied to the most diverse substrates, such as, for example, metal, paper, cardboard, wood, fibre board, textiles, plastics, such as polycarbonates, poly(meth)acrylates, polyolefins, polystyrenes, poly(vinylchloride)s, polyesters, polyurethanes, polyamides, copolymers such as acrylonitrile-butadiene-styrene (ABS) or cellulose acetate butyrate, and the like.

The radiation curable powder compositions in accordance with the invention can also be formulated in toner compositions.

The examples which follow, illustrate the invention without limiting it. Except when otherwise indicated, the parts mentioned throughout the description and in the examples are parts by weight.

Example 1

A mixture of 372.8 parts of neopentyl glycol, 10.2 parts of trimethylolpropane along with 2.3 parts of n-butyltin trioctoate catalyst is placed in a conventional four-neck round bottom flask equipped with a stirrer, a condenser, an inlet for nitrogen and a thermoprobe attached to a thermoregulator.

The flask contents are heated while stirring, under nitrogen to a temperature of circa 140°C. Thereupon 661.8 parts of isophthalic acid is added while stirring and the mixture is gradually heated to a temperature of 230°C. Distillation starts from about 190°C. When the distillation

under atmospheric pressure stops, a vacuum of 50 mm Hg is gradually applied. After 3 hours at 230°C and 50 mm Hg, a product is obtained with the following characteristics (measured in a conventional manner): acid value of 38 mg KOH/g; and hydroxy value of 3 mg KOH/g.

- 5 Subsequently the carboxyl functionalised polyester is cooled down and the methacrylation is carried out accordingly the procedure of example 1. When the polyester stands at 150°C, 0.5 parts of di-t-butylhydroquinone along with 4.6 parts of ethyltriphenylphosphonium bromide are added along with a slow alimentation of 81.1 parts of glycidylmethacrylate. The mixture is stirred for 1 hour at 150°C under oxygen until a product is obtained with the following
- 10 characteristics (measured in a conventional manner): acid value of 1 mg KOH/g; hydroxy value of 35 mg KOH/g; unsaturation of 0.6 meq/g; $ICI^{200^{\circ}C} = 4600$ mPa.s; $Tg^{quenched}$ (DSC, 20°/min) = 46°C; Mn (GPC) = 4030

Example 2

- 15 358.7 parts of n-butylacetate are brought in a double walled flask of 5 l equipped with a stirrer, a water cooled condenser an inlet for nitrogen and a thermoprobe is attached to a thermoregulator.

- The flask content is heated and stirred continuously while nitrogen is purged through the solvent. At a temperature of 92°C a mixture of 89.6 parts of n-butylacetate with 5.67 parts of 2,2'-azobis(2-methylbutanenitrile) is fed in the flask during 215 minutes with a peristaltic pump. Five minutes after the start of this feed, a second feed is started with another pump and is a mixture of: 127.5 parts of glycidylmethacrylate; 170.8 parts of isobornylacrylate; 3.78 parts of butylmethacrylate; 146.3 parts of styrene; 17.93 parts of n-dodecylmercaptan; and 2.24
- 25 parts of ditridecylthiodipropionate. This feed takes 180 minutes.

After 315 minutes of total synthesis time, the flask content is emptied and dried in a rotary evaporator at 150°C during 45 minutes. The dry polymer is characterised by:

E.E.W. = 1.89 meq/g; $ICI^{125^{\circ}C} = 50\ 000$ mPa.s

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- The dry resin of step 1 is transversed in a round bottom single walled flask of 5 l equipped with an air inlet, a thermoprobe, and an inlet for the methacrylic acid to be fed. The resin is heated to 100°C and air is continuously purged through. After 30 minutes 0.08 parts of di-t-butylhydroquinone is added to the polymer. After 60 minutes 77.21 parts of methacrylic acid
- 35 are fed with a peristaltic pump in the mixture during 30 minutes. The temperature is kept constant during the synthesis. The acid number is checked regularly through titration. At an acid number of 6.2 mg KOH/g the polymer is cooled down.

- The resin is characterised by: unsaturation of 1.63 meq/g; $ICI^{125^{\circ}C} = 65\ 000$ mPa.s; $Tg^{quenched}$ (DSC, 20°/min) = 58°C; Mn (GPC) = 5642.
- 40

Example 3

In a conventional four-neck round bottom flask equipped with a stirrer, an inlet for oxygen, an inlet for (meth)acrylic acid and a thermocouple attached to a thermoregulator, 934 parts of
 5 ST4100D, a hydrogenated Bisphenol A-type epoxy resin (KUKDO Chem. Ind. Co., Ltd.), are heated under oxygen to a temperature of 140°C. Subsequently 0.8 parts of ethyl tri-phenyl phosphonium bromide are added and the addition of 66 parts of acrylic acid containing 0.2 parts of di-*t*-butylhydroquinone, is started. The acrylic acid addition is completed in a 3 hour period. One and an half hour after the completion of the acrylic acid addition, a resin with the
 10 following characteristics is obtained: acid value of 5 mg KOH/g; unsaturation of 0.92 meq/g; $ICI^{200^{\circ}C}=2\ 700\ mPa.s$; $T_{gquenchd}$ (DSC, 20°/min) = 55°C and M_n (GPC) = 3 320.

Example 4 and 5

15 Two white powders which can be used for the manufacturing of coatings by spraying with the aid of an electrostatic spray gun are prepared from blends of the methacryloyl group containing resins of example 1 and 2 respectively, with the methacryloyl group containing hydrogenated polyphenoxy resin of example 3, the formulation of these powders being as follows:

20 *White powder formulation*

binder	750.0 parts
titanium dioxide (Kronos 2310 (Kronos))	250.0 parts
α -hydroxyketone (Irgacure 2959 (Ciba))	12.5 parts
bisacylphosphineoxide (Irgacure 819 (Ciba))	12.5 parts
25 fluidity regulating agent (Resiflow PV5 (Worlee Chemie))	10.0 parts

These powder compositions are prepared by dry mixing the different ingredients. The mixture obtained is homogenised at a temperature of approximately 70 to 140°C in a Prism 16 mm (L/D = 15/1) twin screw extruder (from the company Prism), and the extrudate is ground in a grinder
 30 of Alpine 100UPZ (from the company Alpine). To complete, the powder is sieved in order to obtain a size of the particles between 10 and 110 μm .

The powders thus obtained respectively comprise a binder system composed of:

	<u>Example 4</u>	<u>Example 5</u>
35	Example 2: 375 parts	Example 1: 563 parts
	Example 3: 375 parts	Example 3: 187 parts

Example 6

Characteristics of the coating

The powders formulated as described in example 4 and 5 are applied with an electrostatic spray gun at a voltage of 60 kV on untreated cold rolled steel as well as on yellow chromated aluminium (Cr⁶⁺) with a film thickness of 40 to 100 µm.

- 5 The coatings deposited are then subjected to melting in a medium infrared/convection oven (Triab) at a temperature of 140°C during a time of approximately 3 minutes, and are then subjected to irradiation with ultraviolet light emitted by a 160 W/cm Gallium-doped followed by a 160 W/cm medium pressure mercury vapour UV-bulb (Fusion UV Systems Ltd.) with a total UV dose of 4000 mJ/cm².

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The powder coatings obtained were tested; following results are perceived: visual assessment: Example 4= good, Example 5= good.

For both powders a smooth and glossy appearance without any defect was perceived

- 15 MEK resistance: Example 4 > 200 double rubs, Example 5 > 200 double rubs, which corresponds to the number of twofold rubbing movements (to and fro) with a cotton pad impregnated with MEK which does not detrimentally affect the appearance of the surface of the cured film

- 20 Reverse impact: Example 4 > 100 kg.cm, Example 5= 60 kg.cm, the value of resistance to reverse impact (RI) in kg.cm, according to ASTM D2795 on cold rolled steel

Direct impact: Example 4 > 100 kg.cm, Example 5= 60 kg.cm, the value of resistance to direct impact (DI) in kg.cm, according to ASTM D2795 on cold rolled steel

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Outdoor durability: QUV-A exposure: Example 4= 6200 hours, Example 5= 5500 hours. Gloss reductions until 50% of the maximum value are mentioned. Weathering measurements are conducted in a very severe environment, i.e. the Q-UV accelerated weathering tester (Q-Panel Co.) according to ASTM G53 (standard practice for operating light and water exposure apparatus - fluorescent UV/condensation type - for exposure of non metallic materials)

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While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

1. Radiation curable powder composition which comprises:
 - a) a first component comprising from about 10 to about 90% by weight of non aromatic polyoxy resin comprising a (meth)acryloyl group;
 - b) a second component comprising from about 10 to about 90% by weight of a resin comprising a (meth)acryloyl group, the resin being different from the first component;
 - c) optionally a third component comprising up to about 30% by weight of a polymer precursor comprising a (meth)acryloyl group.
2. Radiation curable powder composition which comprises:
 - a) a first component comprising from about 10 to about 90% by weight of a hydrogenated polyphenoxy resin comprising a (meth)acryloyl group;
 - b) a second component comprising from about 10 to about 90% by weight of a resin comprising a (meth)acryloyl group, the resin being different from the first component;
 - c) a third component comprising from about 0 to about 30% weight of an oligomer comprising a (meth)acryloyl group.
3. A composition according to either preceding claim, in which the first component is obtained and/or obtainable by reacting (meth)acrylic acid with a non aromatic polyoxy resin comprising a glycidyl group.
4. A composition according to any preceding claim, in which the first component is characterised by at least one of the following properties or any combinations thereof:
 - (I) a number averaged molecular weight from about 450 to about 5,000 (preferably from 650 to 3,500) daltons;
 - (II) a glass transition temperature from about 30 to about 80°C;
 - (III) a degree of unsaturation from about 0.2 to about 6.0 (preferably from about 0.5 to about 4.5) milliequivalents of double bonds per gram of resin;
 - (IV) a melt viscosity (measured by the cone / plate method at 200°C) of less than about 20,000 mPa.s.
5. A composition according to any preceding claim, in which the second component is selected from any polyester, polyesteramide, polyurethane and/or acrylic copolymers that comprise at least one (meth)acryloyl group.
6. A composition according to any preceding claim, in which the first component is obtained and/or obtainable by reacting
 - (a) a diisocyanate with an hydroxyalkyl(meth)acrylate and polyester comprising at least one hydroxyl group; and/or

(b) a glycidyl(meth)acrylate with a polyester comprising at least one carboxylic acid group.

7. A composition according to claim 6, where polyester used to prepare the first component is obtained and/or obtainable by reacting one or more aliphatic, cycloaliphatic and/or aromatic polyacids with one or more aliphatic and/or cycloaliphatic polyols.

8. A composition according to any preceding claim, in which the second component comprises a polyester characterised by at least one of the following properties or any combinations thereof:

(I) a number averaged molecular weight from about 800 to about 16 000 (preferably from about 1,300 to about 8,500) daltons;

(II) a melt viscosity (as measured by the cone/plate method at 200°C) of less than about 50,000 mPa.s.

(III) a degree of unsaturation from about 0.15 to about 2.00 (preferably from about 0.35 to about 1.50) milliequivalents of double bonds per gram of polyester;

(IV) a glass transition temperature from about 35 to about 85°C; and/or

(V) a melting point from about 60 to about 150°C and a glass transition temperature of less than about 50°C for semi-crystalline polyesters.

9. A composition according to any preceding claim, in which the second component comprises a polyester amide obtained and/or obtainable by reacting a glycidyl(meth)acrylate with a polyester amide terminated with one or more carboxylic acid groups.

10. A composition according to claim 9, in which the polyester amide is obtained and/or obtainable from the carboxylic acid group terminated polyesteramide obtained and/or obtainable from the reaction of a diamine with a carboxylic acid group containing polyester and where the polyester is obtained and/or obtainable by reacting one or more aliphatic, cycloaliphatic and/or aromatic polyacids with one or more aliphatic and/or cycloaliphatic polyols.

11. A composition according to any preceding claim, in which the second component comprises a polyester amide characterised by at least one of the following properties or any combinations thereof:

(I) a number averaged molecular weight from about 800 to about 16 000 (preferably from about 1,300 to about 8,500) daltons;

(II) a degree of terminal unsaturation from about 0.15 to about 2.00 (preferably from about 0.35 to about 1.50) milli-equivalents of double bonds per gram of polyester amide;

(III) a glass transition temperature from about 40 to about 70°C; and/or

(IV) a melt viscosity (measured by the cone/plate method at 200°C) of less than about 50,000 mPa.s.

12. A composition according to any preceding claim, in which the second component comprises a polyurethane obtained and obtainable by reacting an hydroxyalkyl(meth)acrylate, polyol and polyisocyanate.

5 13. A composition according to claim 12, in which the polyurethane is obtained and/or obtainable from a polyol selected from a C₂₋₁₅aliphatic diol; C₃₋₁₅ cycloaliphatic diol, polyester polyol and/or a polyether polyol.

10 14. A composition according to any preceding claim, in which the second component comprises a polyurethane characterised by at least one of the following properties or any combinations thereof:

(I) a number averaged molecular weight from about 800 to about 15,000 (preferably from about 1,300 to about 8,500);

15 (II) a degree of terminal unsaturation from about 0.15 to about 2.00 (preferably from about 0.35 to about 1.50) milli-equivalents of double bonds per gram of polyurethane;

(III) a glass transition temperature from about 40 to about 100°C; and/or

(IV) a melt viscosity (measured by the cone/plate method at 200°C) of less than about 100,000 mPa.s.

20 15. A composition according to any preceding claim, in which the second component comprises an acrylic copolymer obtained and/or obtainable by reacting:

(a) an acrylic copolymer having functional groups and which is obtained and/or obtainable from

25 (i) about 40 to about 95 mole % of at least one monomer having (meth)acrylic groups,

(ii) optionally up to about 60 mole % of another ethylenically unsaturated monomer; and

30 (iii) about 5 to about 60 mole % of an ethylenically unsaturated monomer having functional groups capable of reacting with one or more epoxy, carboxylic acid, hydroxy and/or isocyanate;

(b) a monomer having a (meth)acryloyl group and a functional group capable of reacting with one or more epoxy, carboxylic acid, hydroxy and/or isocyanate.

35 16. A composition according to any preceding claim, in which the second component comprises an acrylic copolymer characterised by at least one of the following properties or any combinations thereof:

(I) a number averaged molecular weight from about 1,000 to about 8 000 (preferably from about 2,000 to about 6000) daltons;

(II) a glass transition temperature from about 45 to about 100°C;

(III) a degree of unsaturation from about 0.35 to about 3.50 (preferably from about 0.5 to about 2.5) milliequivalents of double bonds per gram of acrylic copolymer; and/or

(IV) a melt viscosity (measured by the cone/plate method at 200°C) of less than about 50,000 mPa.s.

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17. A composition according to any preceding claim in which the third component comprises from about 0 to about 30% by weight of a (meth)acryloyl group containing oligomer.

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18. A radiation curable powder composition which additionally comprises up to about 15 (preferably up to about 8) parts by weight of a photo-initiator for every 100 parts by weight of (as a binder) a composition according to any preceding claim.

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19. A radiation curable powder composition which additionally comprises up to about 10 parts by weight of at least one substance which is effective in modifying coating properties for every 100 parts by weight of (as a binder) a composition according to any preceding claim.

20. A powder varnish and/or powder paint comprising a radiation curable powder composition according to any preceding claim.

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21. A process for coating an article with a composition as claimed in any preceding claim which comprises the steps of

(a) depositing the composition on the article

(b) melting the coating thus obtained; and

(c) exposing the molten coating to radiation sufficient to form a cured coating.

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22. A process according to claim 21, in which the coating is melted by heating at a temperature of from about 80 to about 150°C (preferably for a time of about 0.5 to about 10.0 minutes).

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23. A process according to claim 21 or 22, in which the curing radiation is UV radiation or an accelerated electron beam.

24. An article partially or entirely coated by the process of any of claims 21 to 23.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/08194

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D163/10 C09D167/06 C09D175/16 C09D177/12

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 7 C09D C08F

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)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 956 425 A (HEFNER JR ROBERT E ET AL) 11 September 1990 (1990-09-11) column 4, line 25-30	2
A	US 4 835 228 A (HEFNER JR ROBERT E ET AL) 30 May 1989 (1989-05-30) the whole document	2
A	US 4 579 925 A (UENO KAZUO ET AL) 1 April 1986 (1986-04-01) the whole document	2

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

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 November 2002

Date of mailing of the international search report

27/11/2002

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,
Fax: (+31-70) 340-3016

Authorized officer

Meulemans, R

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No
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