ELECTRO IMMERSION LACQUER PRODUCED BY MELT EMULSIFICATION

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ABSTRACT
Novel electrodeposition coating material preparable by (i) melting at least one self-crosslinking binder, or (ii) separately melting at least one externally crosslinking binder and at least one crosslinking agent and supplying the melts to a mixing unit in which the melts are homogenized, introducing the resultant melt into an aqueous medium, and emulsifying it therein; and the use of the novel electrodeposition coating material to coat electrically conductive substrates.
ELECTRO IMMERSION LACQUER PRODUCED BY MELT EMULSIFICATION

[0001] The present invention relates to a novel electrodeposition coating material preparable by melt emulsification. The present invention further relates to a novel process for preparing the novel electrodeposition coating material. The present invention relates not least to the use of the novel electrodeposition coating materials to coat electrically conductive substrates.

[0002] In the preparation of electrodeposition coating materials it is common to employ organic solvents in order to reduce the viscosity of the binders and/or of the crosslinking agents, in order that they may be dispersed more readily at low temperatures in the aqueous media. A disadvantage of this process is the need to remove the organic solvents from the electrodeposition coating materials subsequently by means of distillation.

[0003] For reasons of environmental protection and of cost, however, attempts are being made to forego the use of solvents. In particular, the distillation process is time-consuming and, moreover, presents safety problems.

[0004] If no organic solvents are used in preparing electrodeposition coating materials, the viscosity of the binders and/or of the crosslinking agents must be lowered by increasing their temperature in order to facilitate, or indeed enable, their dispersion. The high temperatures, however, prevent the introduction even of crosslinking agents of very low reactivity, since unwanted premature crosslinking reactions occur with the binders. The introduction of reactive crosslinking agents as commonly used for so-called low-bake applications is then completely impossible.

[0005] Similar problems also occur when using self-crosslinking binders.

[0006] It is an object of the present invention to find a new electrodeposition coating material from which the disadvantages of the prior art are now absent and which instead may be prepared at least using a smaller amount of organic solvent than is usually required for the electrodeposition coating materials of the prior art, preferably without organic solvents, without premature crosslinking of the constituents of the electrodeposition coating material. This should also be reliably so even when using highly reactive crosslinking agents or highly reactive self-crosslinking binders. Moreover, the new electrodeposition coating materials should have the same advantageous profile of properties as their prior art counterparts, if not indeed exceeding them.

[0007] Accordingly, we have found the novel electrodeposition coating material which is preparable by

[0008] (i) melting at least one self-crosslinking binder, or

[0009] (ii) separately melting at least one externally crosslinking binder and at least one crosslinking agent and supplying the melts to a mixing unit in which the melts are homogenized,

[0010] introducing the resultant melt into an aqueous medium, and emulsifying it therein.

[0011] In the text below, the novel electrodeposition coating material is referred to as the “electrodeposition coating material of the invention”.

[0012] Additional subject-matter of the invention will emerge from the description.

[0013] The electrodeposition coating material of the invention comprises at least one self-crosslinking binder.

[0014] In the context of the present invention, the term “self-crosslinking” refers to the ability of a binder (regarding that term cf. Römm Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, “Binders”, pages 73 and 74) to enter into crosslinking reactions with itself. This requires that the binders contain complementary reactive functional groups which react with one another and so lead to crosslinking. Or else the binders contain reactive functional groups which react “with themselves”.

[0015] Or else the electrodeposition coating material of the invention comprises at least one external crosslinking binder and at least one crosslinking agent.

[0016] Binders are termed externally crosslinking if they contain one kind of the complementary reactive functional groups and the other kind is provided by a curing agent, hardener, or crosslinking agent. For further details, reference is made to Römm Lexikon Lacke und Druckfarben, Georg Thieme Verlag, Stuttgart, New York, 1998, “Curing”, pages 274 to 276, especially page 275, bottom.

[0017] Suitable reactive functional groups of the binders are preferably thio, amino, hydroxyl, carbamate, aliphatic, carboxyl and/or (meth)acrylate groups, but especially hydroxyl groups, and suitable complementary functional reactive groups of the crosslinking agents are preferably anhydride, carbonyl, epoxy, blocked isocyanate, urethane, methylol, methylol ether, amino, hydroxyl and/or beta-hydroxyalkylamide groups, but especially blocked isocyanate groups.

[0018] In the self-crosslinking binders, in contrast, both types of complementary reactive functional groups are present, preferably hydroxyl groups and blocked isocyanate groups, and/or reactive functional groups which are able to react “with themselves”, such as methylol ether groups, for example.

[0019] In accordance with the invention, the externally crosslinking binders are of advantage and are therefore used with preference.

[0020] In order that the binders may be dispersed in water and electrophoretically deposited, they contain functional groups which are ionic or are convertible to ionic groups.

[0021] These groups comprise

[0022] (a) functional groups convertible to cations by neutralizing agents and/or quaternizing agents, and/or cationic groups, or

[0023] (b) functional groups convertible to anions by neutralizing agents, and/or anionic groups.

[0024] The binders with functional groups (a) are used in cathodically depositable (cathodic) electrodeposition coating materials of the invention, whereas the binders with functional groups (b) are employed in anodically depositable (anodic) electrodeposition coating materials of the invention.

[0025] Examples of suitable functional groups (a) for use in accordance with the invention, which are convertible to
ations by neutralizing agents and/or quaternizing agents, are primary, secondary or tertiary amino groups, second sulfide groups or tertiary phosphine groups, especially tertiary amino groups or secondary sulfide groups.

[0026] Examples of suitable cationic groups (a) for use in accordance with the invention are primary, secondary, tertiary or quaternary ammonium groups, tertiary sulfonium groups or quaternary phosphonium groups, preferably quaternary ammonium groups of tertiary sulfonium groups, but especially quaternary ammonium groups.

[0027] Examples of suitable functional groups (b) for use in accordance with the invention, which are convertible to anions by neutralizing agents, are carboxylic acid, sulfonic acid or phosphonic acid groups, especially carboxylic acid groups.

[0028] Examples of suitable anionic groups (b) for use in accordance with the invention are carboxylate, sulfonate or phosphate groups, especially carboxylate groups.

[0029] The selection of the groups (a) or (b) is to be made so as to rule out the possibility of disruptive reactions with the above-described complementary reactive functional groups. The skilled worker will therefore be able to make the selection in a simple manner on the basis of his or her knowledge.

[0030] Examples of suitable neutralizing agents for functional groups (a) convertible to cations are organic and inorganic acids such as sulfuric acid, amidosulfuric acid (amidosulfonic acid), C₄-C₈ sulfonic acids such as methanesulfonic acid or hexafluorosulfonic acid, hydrochloric acid, phosphoric acid, formic acid, acetic acid, lactic acid, dimethylolpropionic acid or citric acid, especially formic acid, acetic acid or lactic acid.

[0031] Examples of suitable neutralizing agents for functional groups (b) convertible to anions are ammonia, ammonium salts such as ammonium carbonate or ammonium hydrogen-carbonate, for example, and also amines, such as trimethylenamine, triethylamine, tributylamine, dimethylamline, diethylamine, triphenylamine, dimethyl-ethanolamine, diethylthanolamine, methyl-diethanol-amine, triethanolamine and the like, for example.

[0032] In general, the amount of neutralizing agent is chosen so that from 1 to 100 equivalents, preferably from 30 to 90 equivalents, of the functional groups (a) or (b) of the binder are neutralized.

[0033] Examples of suitable binders for anodic electrodeposition coating materials of the invention are disclosed in the patent DE-A 28 24 418. These are preferably polyesters, epoxy resin esters, poly(methylacrylates), maleate oils or polybutadiene oils having a weight-average molecular weight of from 300 to 20,000 daltons and an acid number of from 35 to 300 mg KOH/g.


[0035] The amount of the above-described binders in the electrodeposition coating materials of the invention may vary very widely.

[0036] In the case of the self-crosslinking binders, it may be up to 100% by weight, based on the solids of the electrodeposition coating material of the invention.

[0037] In the case of the externally crosslinking binders, it is preferably from 40 to 95, more preferably from 50 to 90, and in particular from 55 to 85% by weight, based in each case on the solids of the electrodeposition coating material of the invention.

[0038] In the context of the present invention, the “solids” is that fraction of the electrodeposition coating material of the invention that forms the electrodeposition coating following the thermal curing of the electrophoretically deposited coating film.

[0039] Preference is given to the use of cathodic electrodeposition coating materials of the invention.

[0040] Preferably, the electrodeposition coating materials of the invention comprise crosslinking agents.

[0041] Examples of suitable crosslinking agents are blocked organic polyisocyanates, especially blocked polyisocyanates known as paint polyisocyanates, having blocked isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic moieties.

[0042] They are preferably prepared using polyisocyanates having 2 to 5 isocyanate groups per molecule and having viscosities of from 100 to 10,000, preferably from 100 to 5000, and in particular from 100 to 2000 mPa·s at 23° C. Furthermore, the polyisocyanates may have been hydrophilically or hydrophobically modified by conventional means.

[0043] Examples of suitable polyisocyanates are described, for example, in “Methoden der organischen Chemie” [Methods of organic chemistry], Houben-Weyl, volume 14/2, 4th edition, Georg Thieme Verlag, Stuttgart 1963, pages 61 to 70, and by W. Siecklen, Liebig's Annalen der Chemie, volume 562, pages 75 to 136.

[0044] Further examples of suitable polyisocyanates are polyisocyanates containing isocyanurate, biuret, aliphanoate, iminoxazolidinedione, urethane, urea and/or ureidone groups. Polyisocyanates containing urethane groups, for example, are obtained by reacting some of the isocyanate groups with polyols, such as trimethylolpropane and glycerol, for example. It is preferred to use aliphatic or cycloaliphatic polyisocyanates, especially dimerized and
trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane 2,4'-diisocyanate, dicyclohexylmethane 4,4'-diisocyanate or 1,3-bis(isocyanatomethyl)cyclohexane (BIC), diisocyanates derived from dimeric fatty acids, as marketed under the commercial designation DDI 1410 by Henkel, 1,6-diisocyanato-4-isocyanatomethyloctane, 1,7-diisocyanato-4-isocyanatomethylheptane and/or 1-isocyanato-2-(3-isocyanatopropyl)cyclohexane.

[0045] Examples of suitable blocking agents for preparing the blocked polycyocyanates are the blocking agents known from U.S. Pat. No. 4,444,954, such as

- i) phenols such as phenol, cresol, xlenol, nitro-phenol, chlorophenol, ethylphenol, t-butylphenol, hydroxybenzoin acid, esters of this acid, or 2,5-di-t-tert-butyl-4-hydroxytoluene;
- ii) lactams, such as ε-caprolactam, β-valerolactam, γ-butrolactam or β-propiolactam;
- iii) active methylene compounds, such as diethyl malonate, dimethylmalonate, ethyl or methyl acetoacetate or acetylactone;
- iv) alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, n-amyl alcohol, t-amyl alcohol, lauryl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monopropyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, methoxymethanol, glyceric acid, glyceric esters, lactic acid, lactic esters, methylolurea, methylolmelamine, diacetone alcohol, ethylenechlorohydrin, ethylenebromohydrin, 1,3-dichloro-2-propanol, 1,4-cyclohexyldimethanol, trimethylolpropane or acectyolohydrin;
- v) mercaptans such as butyl mercaptan, hexyl mercaptan, t-butyl mercaptan, t-dodecyl mercaptan, 2-mercaptobenzothiazole, thiophenol, methythiophenol or ethylthiophenol;
- vi) acid amides such as acetoanilide, acetoaminidamide, acrylamide, methacrylamide, acetamide, stearamide or benzamide;
- vii) imides such as succinimide, phthalimide or maleimide;
- viii)amines such as diphenylamine, phenyl-naphthylamine, xylidine, N-phenylxydilidine, carbazole, aniline, naphthylamine, butylamine, dibutylamine or tetraphenylamine;
- ix) imidazoles such as imidazole or 2-ethylimidazole;
- x) ureas such as urea, thiourea, ethylenurea, ethylenethiourea or 1,3-diphenylurea;
- xi) carbamates such as phenyl N-phenylcarbamate or 2-oxazolidone;
- xii) imines such as ethylenimine;
- xiii)oximes such as acetone oxime, formaldoxime, acetaldoxime, acetoxime, methyl ethyl ketoxime, diisobutyl ketoxime, diacetyl monoxime, benzophenone oxime or chlorohexanone oximes;

[0059] xiv) salts of sulfurous acid such as sodium bisulfite or potassium bisulfite;
[0060] xv) hydroxamic esters such as benzyl methacryloxyhydroxamate (BMAH) or allyl methacryloxyhydroxamate; or
[0061] xvi) substituted pyrazoles, imidazoles or triazoles; and
[0062] xvii) mixtures of these blocking agents, especially dimethylpyrazole and triazoles, malonic esters and acetoacetic esters, dimethylpyrazole and succinimide, or ethylene glycol monopropyl ether and trimethylolpropane.

[0063] Further examples of suitable crosslinking agents are all known aliphatic and/or cycloaliphatic and/or aromatic polypeoxides, based for example on bishenol A or bishenol F. Examples of further suitable polypeoxides are the polypeoxides available commercially under the designations Epikote® from Shell, Denacol® from Nagase Chemicals Ltd., Japan, such as, for example, Denacol EX-411 (pentacyrtritol polyglycidyl ether), Denacol EX-321 (trimethylolpropane polyglycidyl ether), Denacol EX-512 (polyglycerol polyglycidyl ether) and Denacol EX-521 (polyglycerol polyglycidyl ether).

[0064] As crosslinking agents it is also possible to use tris(alkoxy carbonylaminotriazines (TACT) of the general formula

\[
\text{RO} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{OR} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}
\]

[0065] Examples of suitable tris(alkoxy carbonylaminotriazines (B) are described in the patents U.S. Pat. No. 4,949,213 A 1, U.S. Pat. No. 5,084,541 A 1, and EP 0 624 577 A 1. In particular, the tris(methoxy-, tris(butoxy- and/or tris(2-ethylhexoxycarbonylamino)triazines are used.

[0066] Of advantage are the methyl butyl mixed esters, the butyl-2-ethylhexyl mixed esters, and the butyl esters. These have the advantage over the straight methyl ester of improved solubility in polymer melts, and also tend less toward crystallizing out.

[0067] Further examples of suitable crosslinking agents are amino resins, examples being melamine, guanamine, benzoguanamine or urea resins. Also suitable are the conventional amino resins some of whose methyl and/or methoxymethyl groups have been defunctionalized using carbamate or allophanate groups. Crosslinking agents of this kind are described in the patents U.S. Pat. No. 5,710,542 A 1 and EP 0 245 700 B 1 and also in the article by B. Singh and coworkers. “Carbamylmethylated Melamines, Novel

Further examples of suitable crosslinking agents are beta-hydroxyalkylamides such as \( \text{N,N',N''-tetraakis(2-hydroxyethyl)adipamide} \) or \( \text{N,N',N''-tetraakis(2-hydroxypropyl)adipamide} \).

Further examples of suitable crosslinking agents are compounds having on average at least two groups capable of transesterification, examples being reaction products of malonic diesters and polyisocyanates or of esters and partial esters of polyhydric alcohols of malonic acid with monoisocyanates, as described in European Patent Application EP 0 596 460 A1.

Particular preference is given to the use of the block polyisocyanates.

The amount of the crosslinking agents in the electrodeposition coating materials of the invention may vary widely and is guided in particular first by the functionality of the crosslinking agents and second by the number of complementary reactive functional groups present in the binder, and also by the target crosslinking density. The skilled worker will therefore be able to determine the amount of the crosslinking agents on the basis of his or her general art knowledge, possibly with the aid of simple ranging tests. Advantageously, the crosslinking agent is present in the electrodeposition coating material of the invention in an amount of from 5 to 60% by weight, with particular preference from 10 to 50% by weight, and in particular from 15 to 45% by weight, based in each case on the solids of the electrodeposition coating material of the invention. It is advisable in this context, moreover, to choose the amounts of crosslinking agent and binder such that in the electrodeposition coating materials of the invention the ratio of reactive functional groups in the crosslinking agent to complementary reactive functional groups in the binder is from 2:1 to 1:2, preferably from 1.5:1 to 1:1.5, with particular preference from 1.2:1 to 1:1.2, and in particular from 1:1.1 to 1:1.1.

The electrodeposition coating material of the invention may comprise customary coating additives in effective amounts. Examples of suitable additives are:

- organic and/or inorganic pigments, anticorrosion pigments and/or fillers such as calcium sulfate, barium sulfate, silicates such as talc or kaolin, silicas, oxides such as aluminum hydroxide or magnesium hydroxide, nanoparticles, organic fillers such as textile fibers, cellulose fibers, polyethylene fibers or wood flour, titanium dioxide, carbon black, iron oxide, zinc phosphate or lead silicate; these additives may also be incorporated into the electrodeposition coating materials of the invention by way of pigment pastes, suitable dispersing resins being the binders described above;

- anticrater agents, as described in European Patent Application EP 0 301 293 A1;

- water-soluble polymers such as polyvinyl alcohols or water-soluble cellulose ethers, as disclosed in European Patent Application 0 640 700 A1;

- free-radical scavengers;
- organic corrosion inhibitors;
- crosslinking catalysts such as organic and inorganic salts and complexes of tin, of lead, of antimony, of bismuth, of iron or of manganese, preferably organic salts and complexes of bismuth and of tin, especially bismuth lactate, ethylhexanate or dimethylpropionate, bismuth-amino acid complexes, dibutyltin oxide or dibutyltin dilaurate or dioleate;
- slip additives;
- polymerization inhibitors;
- defoamers;
- emulsifiers, especially nonionic emulsifiers such as alkoxylated alkanols, polyls, phenols and alkylphenols or anionic emulsifiers such as alkali metal salts or ammonium salts of alkanecarboxylic acids, alkanesulfonic acids, and sulfonic acids of alkoxylated alkanols, polyls, phenols and alkylphenols;
- wetting agents such as siloxanes, fluoro compounds, carboxylic monoesters, phosphoric esters, polycarboxylic acids and their copolymers or polyurethanes;
- adhesion promoters;
- leveling agents;
- film-forming auxiliaries such as cellulose derivatives;
- flame retardants;
- thermally crosslinkable reactive diluents, such as positionally isomeric diethyloctanediol, hydroxyl-containing hyperbranched compounds or dendrimers, as described in the patent applications DE 198 09 643 A1, DE 198 40 605 A1 or DE 198 05 421 A1;
- biocides;


The electrodeposition coating material of the invention is preparable by the process of the invention.

In one preferred variant of the process of the invention, at least one of the above-described self-crosslinking binders is melted, after which the resultant melt is introduced into an aqueous medium and emulsified therein.

In a particularly preferred variant of the process of the invention, at least one of the above-described externally crosslinking binders and at least one of the above-described crosslinking agents are melted separately and supplied to a mixing unit in which the melts are homogenized. The resultant melt is introduced into an aqueous medium and emulsified therein.

Both the binders and/or the crosslinking agents may comprise at least one of the above-described additives,
provided they do not disrupt the melting operation, through decomposition or chemical reactions, for example.

[0095] Preferably, the aqueous medium comprises at least one of the above-described neutralizing agents in amounts sufficient to stably disperse the above-described binders. Particularly preferred neutralizing agents are the above-described acids. Furthermore, the aqueous medium may comprise at least one of the above-described additives.

[0096] The temperatures of the melts may vary widely. Thus, the temperatures chosen should not be so high that the binders or the crosslinking agents undergo thermal decomposition and/or premature crosslinking. On the other hand, the temperatures ought not to be so low that the excessive viscosity of the melts means that they can no longer be readily mixed with one another and dispersed in the aqueous medium. It is preferred to employ temperatures of between 40 and 160, preferably 50 and 140, and in particular 70 and 130 °C.

[0097] Mixing units which can be used in connection with the process of the invention are all conventional mixing units suitable for the homogenous mixing of comparatively viscous melts. Examples of suitable mixing units are static mixers of the Sulzer type, marketed by Sulzer Chemtech GmbH. The melts may be run once or a number of times in circulation through the mixing units. An alternative option is to connect up at least two mixing units in series.

[0098] To emulsify the melt in water, it is possible in the process of the invention to use all conventional equipment as commonly used in the emulsification of liquid or melted substances in water.

[0099] Examples of suitable equipment of this kind include the above-described static mixers, rotor-stator systems, and high-pressure homogenizers.

[0100] Examples of suitable rotor-stator systems are high-speed stirrers (Ultraturrax), wet rotor mills, in-line dissolvers, or toothed-wheel dispersing units as described, for example, in European Patent Application EP 0 648 537 A 1 and marketed under the tradename "K-Generatoren" by Kinematica AG, Lucerne, Switzerland.

[0101] Examples of suitable high-pressure homogenizers are those which operate in accordance with the opposed-jet principle, as are described, for example, in European Patent Application EP 0 401 565 A 1.

[0102] In the process of the invention, the melt and the aqueous medium may be passed once or several times in circulation through one of the above-described apparatuses. It is also possible, however, to connect up at least two of these apparatuses in series.

[0103] On the emulsification of the melt in the aqueous medium, the discontinuous phase of the emulsion is formed as droplets. Their average size can vary very widely and is guided in particular by the temperature of the melt, its viscosity, and the shear field prevailing within the apparatus. Preferably, the average droplet size is from 40 to 1000, more preferably from 60 to 500, and in particular from 70 to 200 nm.

[0104] In the subsequent course of the process of the invention the resultant emulsion is cooled preferably to room temperature by being passed, for example, through a cooling unit, in particular a heat exchanger.

[0105] The resultant electrodeposition coating material of the invention may be used as it is for electrophoretic deposition. Preferably, it is diluted further with water so as to give, preferably, a solids content of from 5 to 60, with particular preference from 6 to 55, and in particular from 7 to 50% by weight, based in each case on the solids of the electrodeposition coating material of the invention.

[0106] Furthermore, there may be added to the electrodeposition coating material of the invention at least one of the above-described additives, preferably at least one pigment and/or filler, especially in the form of at least one pigment paste.

[0107] The process of the invention described above may be conducted continuously or batchwise.

[0108] The electrodeposition coating material of the invention may be applied to substrates by means of a very wide variety of application techniques. In accordance with the invention, however, it is of advantage to deposit it electrophoretically onto electrically conductive substrates such as motor vehicle bodies or parts thereof.

[0109] For this purpose, the electrically conductive substrate is immersed in an electrodeposition bath of the invention, in accordance with the above remarks, the substrate is connected as the cathode and anode, preferably the cathode, a film is deposited on the substrate by means of direct current, the coated substrate is removed from the electrodeposition bath, and the electrodeposited coating film is either baked or just dried.

[0110] The baked electrodeposition coating may subsequently be further coated with a surfacer or with an antistonechip coat and a solid-color topcoat or, alternatively, with a basecoat and a clearcoat. Thereafter, the surface or film of the antistonechip film and the solid-color topcoat film are normally baked separately, whereas the basecoat and the clearcoat are preferably applied by the wet-on-wet technique and the resulting basecoat film and clearcoat film are baked together.

[0111] The dried electrodeposition coating film may be coated wet-on-wet with a surfacer or antistonechip coat or a basecoat, after which the electrodeposition coating film and the surface or film or antistonechip film or the basecoat film are baked together (cf. European Patent Application EP 0 817 614 A 1).

[0112] The resultant electrodeposition coatings of the invention exhibit excellent throw, outstanding edge protection, and, if any, only a very small number of surface defects such as craters. The adhesion of the electrodeposition coatings to the substrate and to the surfacer coatings or antistonechip primer coats or basecoats is excellent. Owing to the excellent smooth surface of the electrodeposition coatings of the invention, the overlying coatings also have a particularly good, defect-free surface.

[0113] The resultant multicoat color and/or effect finishes of the invention exhibit an excellent profile of properties, and so may also be used with advantage in the especially demanding technical field of automotive OEM finishing.
EXAMPLES

Preparation Example 1

The Preparation of a Crosslinking Agent for Use in Accordance with the Invention

[0114] A reactor equipped with reflux condenser, internal thermometer, and inert gas inlet was charged with 810 parts by weight of isomers and higher-functionality oligomers based on 4,4'-diphenylmethane diisocyanate, having an isocyanate equivalent weight of 135 (Basonat® A 270 from BASF Aktiengesellschaft), under a nitrogen atmosphere. 0.6 part by weight of dibutyltin dilaurate was added and 988 parts by weight of butyl diglycol were added dropwise, with stirring, at a rate such that the temperature of the reaction mixture remained below 60° C. Following the addition, the reaction mixture was held at 100° C. for two hours. Thereafter, no free isocyanate groups were detectable. The resultant blocked polyisocyanate was admixed to 87 parts by weight of phenoxypentanol and 87 parts by weight of butoxypropylol and cooled to 70° C. The solids content was 90%.

Preparation Example 2

The Preparation of a Binder for Use in Accordance with the Invention

[0115] A reactor equipped with reflux condenser, internal thermometer and inert gas inlet was charged with 1177 parts by weight of a commercial epoxy resin based on bisphenol A, having an epoxide equivalent weight of 188, 92 parts by weight of phenol, 268 parts by weight of bisphenol A and 46 parts by weight of butoxypropylol and this initial charge was heated to 130° C. under nitrogen and with stirring. Thereafter, 1.5 parts by weight of triphenylphosphine were added with stirring, whereupon there was an exothermic reaction and the temperature rose to 155° C. The reaction mixture was subsequently cooled to 130° C. and the epoxide equivalent weight was measured. The target value was from 520 to 530. When this value had been reached, 160 parts by weight of a commercial polyalkylene glycol (Pluronic® P 600 from BASF Aktiengesellschaft) were added with cooling. When the temperature reached 95° C., 113 parts by weight of diethanolamine were added, whereupon there was an exothermic reaction and the temperature rose to 115° C. After a further 40 minutes at 115° C., 55 parts by weight of N,N-dimethyaminopropylamine were added. At this point the temperature rose briefly to 140° C. Subsequently, the reaction mixture was left to continue reacting for two hours at 130° C. until its viscosity remained constant. The solids content of the reaction mixture was 97.5%.

Preparation Example 3

The Preparation of an Aqueous Medium

[0116] 2024 parts by weight of deionized water and 41 parts by weight of an 85% strength aqueous formic acid solution were mixed with one another in a preparation vessel.

Preparation Example 4

The Preparation of a Pigment Paste

[0117] The pigment paste was prepared as described in International Patent Application WO 98/33835, page 22, line 23 to page 23, line 30, 3. Cationic, water-soluble dispersing resins, 3. 1. Dispersing resin A, Table 1: aqueous pigment pastes, pigment paste B.

Example 1

The Preparation of an Electrodeposition Coating Material of the Invention by Melt Emulsification

[0118] Example 1 was conducted using

[0119] 888 parts by weight of the crosslinking agent of Preparation Example 1,

[0120] 1913 parts by weight of the epoxy resin of Preparation Example 2, and

[0121] 2065 parts by weight of the aqueous medium of Preparation Example 3.

[0122] The epoxy resin and the crosslinking agent were heated separately to 100° C., and melted. Using separate pumps, the epoxy resin melt and the crosslinking agent melt in a weight ratio of 68:3:5:1.7 were conveyed uniformly through a static mixer and so homogenized. The static mixer used was a mixer of the Sulzer SMX type. The resultant melt was run into the aqueous medium, heated to 23° C., and divided therein into fine droplets by stirring, so giving an emulsion. Following the melt emulsification, the resultant electrodeposition coating material was diluted further with 1330 parts by weight of deionized water and cooled to room temperature. The dilute electrodeposition coating material was completely stable with respect to settling even after three months of storage. The electrodeposition coating material had the following characteristics:

[0123] Solids content (1 hour/30° C.): 43% by weight,

[0124] MEQ-base: 0.8 meq/g solid resin,

[0125] MEQ-acid: 0.28 meq/g solid resin,

[0126] pH: 5.8,

[0127] Viscosity: 20 s (DIN 4 cup at 23° C.), and

[0128] z-average particle diameter: 50 to 100 nm.

Example 2

The Preparation of an Electrodeposition Coating Material of the Invention by Melt Emulsification

[0129] Example 1 was repeated except that the homogenized melt was conveyed uniformly into the aqueous medium via an injection tube and the resultant mixture was pumped uniformly into a three-stage toothed-wheel dispersing unit ("K-Generator" from Kinematics AG, Lucerne, Switzerland) and dispersed therein.

[0130] The resultant dilute electrodeposition coating material had the same advantageous properties as that of Example 1.

Examples 3 and 4

The Use of the Electrodeposition Coating Materials of the Invention of Examples 1 and 2 to Produce Electrodeposition Coatings

[0131] For Example 3, an electrodeposition bath comprising 2135 parts by weight of the electrodeposition coating
material of Example 1, 603 parts by weight of the pigment paste of Preparation Example 3 and 2263 parts by weight of deionized water was prepared.

[0132] For example 4, an electrodeposition bath comprising 2135 parts by weight of the electrodeposition coating material of Example 2, 603 parts by weight of the pigment paste of Preparation Example 3 and 2263 parts by weight of deionized water was prepared.

[0133] The electrodeposition baths were aged with stirring at room temperature for 3 days. Their key performance properties and the conditions of the deposition are compiled in the table.

<table>
<thead>
<tr>
<th>Performance properties of the electrodeposition baths and conditions of their deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature</td>
</tr>
<tr>
<td>Example</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
</tr>
<tr>
<td>Bath temperature (°C)</td>
</tr>
<tr>
<td>Removal voltage (V)</td>
</tr>
<tr>
<td>Deposition voltage (V)</td>
</tr>
</tbody>
</table>

[0134] The electrodeposition coating films were deposited in the course of two minutes on zinc-phosphated steel test panels connected as cathodes, which had not been given a subsequent chromium(VI) rinse. The coated steel test panels were removed from the electrodeposition baths. The electrodeposition coating films on the panels were rinsed with deionized water and subsequently baked at 175° C. (panel temperature) for 15 minutes.

[0135] The resultant electrophatings of Examples 3 and 4 have a dry film thickness of 22 μm. Their leveling was outstanding. They were completely solvent-stable and withstood more than 100 double strokes with a cotton pad soaked with methyl ethyl ketone. Their Erichsen cupping was 7 mm. Their corrosion protection effect was outstanding.

What is claimed is:

1. An electrodeposition coating material preparable by (i) melting at least one self-crosslinking binder, or (ii) separately melting at least one externally crosslinking binder and at least one crosslinking agent and supplying the melts to a mixing unit in which the melts are homogenized, introducing the resultant melt into an aqueous medium, and emulsifying it therein.

2. The coating material as claimed in claim 1, wherein the aqueous medium comprises at least one neutralizing agent.

3. The coating material as claimed in claim 2, wherein the neutralizing agent is at least one acid.

4. The coating material as claimed in any of claims 1 to 3, wherein the mixing unit is a static mixer.

5. The coating material as claimed in any of claims 1 to 4, wherein the melt is emulsified in the aqueous medium in a static mixer, in a rotor-stator system or in a high-pressure homogenizer.

6. The coating material as claimed in claim 5, wherein a high-pressure homogenizer is used, which operates in accordance with the opposed-jet principle.

7. The coating material as claimed in claim 5, wherein said rotor-stator system comprises a high-speed stirrer (Ultraturrax), a wet rotor mill, an in-line disolver, or a toothed-wheel dispersing unit.

8. The coating material as claimed in any of claims 1 to 7, wherein the discontinuous phase of the emulsion has an average droplet size of 40 to 1000 nm.

9. The use of the coating material as claimed in any of claims 1 to 8 to coat electrically conductive substrates.

10. A process for coating electrically conductive substrates by electrophoretically depositing an electrodeposition coating material on the substrates and thermally curing the resultant electrodeposition coating film alone or together with at least one further coating film present thereon, which comprises using an electro-deposition coating material as claimed in any of claims 1 to 8.

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