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Adhesion promoter additive comprising an unsaturated, amorphous polyester

The invention relates to an adhesion promoter additive comprising an unsaturated, amorphous polyester and to the use of unsaturated, amorphous polyesters as adhesion promoter additives.

Unsaturated polyester resins (UP resins) are well known. They are prepared by condensing saturated and unsaturated dicarboxylic acids or their anhydrides with diols. Their properties depend substantially on the nature and proportion of the starting materials.

The carrier of the polymerizable double bonds used are usually α,β -unsaturated acids, primarily maleic acid and its anhydride or fumaric acid; unsaturated diols are of minor importance. The higher the amount of double bonds, i.e., the smaller the separation of the double bonds in the chain molecules, the more reactive the polyester resin. It polymerizes very rapidly with intense development of heat and extensive contraction to give a highly crosslinked and therefore comparatively brittle end product. For this reason, the reactive double bonds in the polyester molecule are "diluted" by co-condensing saturated aliphatic or aromatic dicarboxylic acids. The alcohol components used are straight-chain and/or branched diols. The individual UP resin types differ not only in the components used to prepare them but also in the ratio of saturated to unsaturated acids, which determines the crosslinking density in the polymerization, the degree of condensation, i.e., the molar mass, the acid number and the OH number, i.e., the type of end groups in the chain molecules, the monomer content, and the type of additives (Ullmann's Encyclopedia of Industrial Chemistry, VOL A21, p. 217ff, 1992).

UP resins based on dicidol as the diol component are known, for example, from DE 924 889, DE 953 117, DE 22 45 110, DE 27 21 989, EP 114 208 and EP 934 988.

The use of unsaturated polyester resins to promote adhesion is known, for example, from DE 24 09 800, EP 114 208, and EP 934 988.

It is an object of the present invention to find an adhesion promoter additive



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which enhances properties of coating materials, such as the adhesion of coating materials, and at the same time exhibits high corrosion protection, high hardness, improved gloss and solids content, and lower contraction in the case of crosslinked systems.

The invention provides an adhesion promoter additive composed of at least one unsaturated, amorphous polyester substantially comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component,

wherein

the alcohol component comprises a dicidol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)-tricyclo[5.2.1.0^{2,6}]decane,

where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%,

and at least 5% of the mixture is present in the alcohol component of the polyester.

The invention also provides for the use of unsaturated, amorphous polyesters substantially comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component, wherein the alcohol component comprises a dicidol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%, and at least 5% of the mixture is present in the alcohol component of the polyester, as an adhesion promoter additive.

It has been found that said additive is universally compatible with further ingredients of coating materials and/or adhesives and/or sealants. For example, the adhesion promoter additives may be mixed with polyacrylates, polyolefins, saturated and/or unsaturated polyesters and copolyesters, cellulose nitrate, phenol- and/or melamine-formaldehyde resins, phenolic resins, alkyd resins, acrylated polyesters, polyamides, phenol-formaldehyde resins and ketone-formaldehyde resins, ketone

resins, polyurethanes, polyureas, epoxy resins, polyvinyl chloride and its derivatives, such as copolymers and terpolymers, polyvinyl alcohols, PVDF, polyethers, silicone resins, chlorinated rubber, cyclorubber, and cellulose acetobutyrate.

The adhesion promoter additives may be used, for example, as binders in filling compounds, where through oxidative drying or free-radical reaction they form corrosion-resistant layers. The good adhesion and the possibility of participating in crosslinking reactions predestine the resins according to the invention for corrosion protection. In addition to increasing the adhesion, there is also an improvement in the intercoat adhesion to overlying and underlying, adjacent coats. A further advantage of the resins according to the invention is their high stability to hydrolysis. Coating materials comprising an additive according to the invention are also distinguished by high gloss and effective leveling.

In spray coating materials, moreover, there is a significant increase in over-spray absorption.

The adhesion promoter additives are used together with the above polymers in aqueous, solventborne (normal, medium, high, and very high solids) and/or solvent-free (powder and/or liquid) heat-curable, radiation-curable, air-drying (oxidatively and physically) coating materials, filling compounds and/or sealants, and adhesives, and are suitable as modifying resins for primers, surfacers, basecoats, single-coat topcoats, clearcoats, adhesives, sealants, traffic marking paints, and corrosion protection paints.

The adhesion promoter additives of the invention comprising the unsaturated, amorphous polyester are described in greater detail below.

The unsaturated, amorphous polyester resins according to the invention are obtained by reacting the alcohol component with the acid component.

According to the invention, the alcohol component used is a didiol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the

three isomers is from 90 to 100%, preferably from 95 to 100%, and at least 5% of the mixture is present in the alcohol component of the polyester. The isomer content of the didiol mixture may be determined qualitatively and quantitatively, for example by GC analysis, or quantitatively by separating by means of preparative GC or HPLC and subsequent NMR spectroscopy. All corresponding isomers of didiol in the 9-position are equally suitable but, owing to the mirror symmetry of the abovementioned isomers, like the cis- and trans-isomers, cannot be differentiated under normal, practical conditions.

The didiol mixture may further comprise up to 10% of further isomers of didiol and/or trimeric and/or higher isomeric diols of the Diels-Alder reaction product of cyclopentadiene. The alcohol component preferably consists of 20%, of 50%, preferably of 90%, more preferably of 100%, of didiol mixture which more preferably comprises from 95 to 100% of the abovementioned three isomeric compounds.

In addition to the didiol mixture, the alcohol component may comprise further linear and/or branched, aliphatic and/or cycloaliphatic and/or aromatic diols and/or polyols. The additional alcohols used are preferably ethylene glycol, 1,2- and/or 1,3-propanediol, diethylene glycol, dipropylene glycol, triethylene glycol or tetraethylene glycol, 1,2- and/or 1,4-butanediol, 1,3-butylethylpropanediol, 1,3-methylpropanediol, 1,5-pentanediol, cyclohexane dimethanol, glycerol, hexanediol, neopentyl glycol, trimethylolethane, trimethylolpropane and/or pentaerythritol and also bisphenol A, B, C, F, norbornylene glycol, 1,4-benzylidimethanol and – ethanol, and 2,4-dimethyl-2-ethylhexane-1,3-diol.

The starting acid component present in the unsaturated, amorphous polyester resins according to the invention comprises at least one α,β -unsaturated dicarboxylic acid. The unsaturated polyester resins preferably comprise citraconic acid, fumaric acid, itaconic acid, maleic acid and/or mesaconic acid.

In addition, aromatic and/or aliphatic and/or cycloaliphatic monocarboxylic acids and/or dicarboxylic acids and/or polycarboxylic acids may also be present, for example phthalic acid, isophthalic acid, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, succinic acid, sebacic acid,

methyltetrahydrophthalic acid, methylhexahydrophthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, dodecanedioic acid, adipic acid, azelaic acid, isononanoic acid, 2-ethylhexanoic acid, pyromellitic acid and/or trimellitic acid. Preference is given to phthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, adipic acid and/or azelaic acid.

The acid component may partly or entirely consist of anhydrides and/or alkyl esters, preferably methyl esters.

In general, the alcohol component is present in a molar ratio of from 0.5:1 to 2.0:1 to the acid component, preferably from 0.8:1 to 1.5:1. The reaction of the alcohol component more preferably takes place in a molar ratio of from 1.0:1 to 1.1:1 to the acid component.

The unsaturated, amorphous polyesters according to the invention may have an acid number of from 1 to 200 mg KOH/g, preferably from 1 to 100 mg KOH/g, more preferably from 1 to 50 mg KOH/g, and an OH number of from 1 to 200 mg KOH/g, preferably from 1 to 100 mg KOH/g, more preferably from 1 to 50 mg KOH/g.

The T_g of the unsaturated, amorphous polyesters according to the invention varies from -30 to +80°C, preferably from -20 to +50°C, more preferably from -10 to +40°C.

In one preferred embodiment I, the saturated polyesters (UP resins) according to the invention consist of an alcohol component comprising at least 90%, preferably 95%, more preferably 100%, of the dicidol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, and of fumaric acid and/or maleic acid/anhydride. In a further preferred embodiment II, the polyesters comprise the abovementioned starting components as under I, but additionally a further acid selected from adipic acid and phthalic acid/anhydride, where the ratio of α,β -unsaturated acid to the additional acid may vary from 2:1 to 1:4. Preference is given to ratios of approx. 1:1 to 1:2. These polyesters generally have acid numbers of from 1 to 200 mg KOH/g, preferably 1-100 mg KOH/g, more preferably 1-50 mg KOH/g, OH

numbers of from 1 to 200 mg KOH/g, preferably 1-100 mg KOH/g, more preferably 1-50 mg KOH/g, and a Tg of from -30 to +80°C, preferably from -20 to +50°C, more preferably from -10 to +40°C.

The polyesters according to the invention may also comprise assistants and additives which are selected from inhibitors, water and/or organic solvents, neutralizing agents, surface-active substances, oxygen scavengers and/or radical scavengers, catalysts, light stabilizers, color brighteners, photosensitizers, thixotropic agents, antiskinning agents, defoamers, antistats, thickening agents, thermoplastic additives, dyes, pigments, flame retardants, internal release agents, fillers and/or blowing agents.

The polyesters according to the invention are prepared by (semi)continuous or batchwise esterification and condensation of the starting acids and alcohols in a one-stage or two-stage procedure.

Examples

Starting component: dicidol mixture (claim 1) in an isomer ratio of approximately 1:1:1

Example 1

Dodecanedioic acid and fumaric acid (ratio 0.6:0.4) are reacted with dicidol in a ratio of 1:1.05 at 180°C in a nitrogen atmosphere until an acid number of 24 mg KOH/g and an OH number of 34 mg KOH/g are attained. To this end, the fumaric acid is initially esterified with dicidol over the course of one hour and then the dodecanedioic acid is added. $M_n = 2200$ g/mol, $M_w = 5500$ g/mol, glass transition temperature 4°C.

Example 2

Adipic acid and maleic acid (ratio 1:1) are reacted with dicidol in a ratio of 1:1.05 at 180°C in a nitrogen atmosphere until an acid number of 26 mg KOH/g and an OH number of 37 mg KOH/g are attained. To this end, the maleic acid is initially esterified with dicidol over the course of one hour and then the adipic acid is added. $M_n = 1800$ g/mol, $M_w = 4300$ g/mol, glass transition temperature 12°C.

Use Examples

Use Example 1

In a red corrosion protection paint based on a soluble VC copolymer, 5% by weight of the binder is replaced by each of the resins according to the invention from Examples 1 and 2, in the form of their 60% strength solutions in xylene. The original poor adhesion on zinked metal panels, measured as the characteristic cross-cut value "G5", is improved by the additives to reach the very good figures of in each case "G0".

Formulations:	1	2	3
Vilit ® MB 30	13.4	13.1	13.1
Hordaresin NP 70	9.2	9.0	9.0
Vestinol ® AH	4.1	4.0	4.0
Araldit ® GY 250	0.5	0.5	0.5
Butyl acetate	2.0	2.0	2.0
Xylene	13.3	13.0	13.0
Solvesso ® 100	12.6	12.2	12.2
Adhesion resin from Example 1 – 60% in xylene	-	2.2	-
Adhesion resin from Example 2 – 60% in xylene	-	-	2.2
Thixotrol ® ST 10% in xylene	9.2	9.0	9.0
Perenol ® F 1	0.3	0.3	0.3
Bayfferox ® 130	5.1	5.0	5.0
Zinc oxide Harzsiegel S-NT	2.3	2.3	2.3
Blanc fixe N	14.0	13.7	13.7
Micro Talc AT 1	14.0	13.7	13.7
	100.0	100.0	100.0

Substrate: zinked steel

Film thickness (dry): approx. 30 µm

Drying: 24 h, room temperature

Cross-cut value [Gt]:

Formula 1: 5

Formula 2: 0

Formula 3: 0

Use Example 2

In a white corrosion protection paint based on chlorinated rubber, 5% by weight of the binder is replaced by each of the resins according to the invention from Examples 1 and 2, in the form of their 60% strength solutions in xylene. These additives improve the adhesion of such paints to unpretreated steel, zinked steel, and aluminum significantly.

Formulations:	1	2	3
Pergut ® S 10	24.0	22.8	22.8
Xylene	43.2	42.1	42.1
Vestinol ® AH	7.6	7.2	7.2
Edenol ® D 81	1.5	1.4	1.4
TiO ₂ Kronos ® 2059	23.7	23.7	23.7
Adhesion resin from Example 1 – 60% in xylene	-	2.8	-
Adhesion resin from Example 2 – 60% in xylene	-	-	2.8
	100.0	100.0	100.0

Film thickness: 25 – 30 µm

Drying: 24 h, room temperature

Substrate	Steel	Zinked steel	Aluminum
Formula 1	Gt5	Gt3	Gt5
Formula 2	Gt0	Gt0	Gt0
Formula 3	Gt0	Gt0	Gt0

Use Example 3

In a white baking varnish based on a hydroxyl-containing polyacrylate resin crosslinked with a fully methyl-etherified melamine resin, 5% by weight of

the binder is replaced by each of the adhesion resins according to the invention from Examples 1 and 2, in the form of their 60% strength solutions in xylene. The moderate adhesion to zinked steel in the blank sample is significantly improved.

Formulations:	1	2	3
Paraloid ® AT 410	43.0	40.5	40.5
Cymel ® 303	8.2	7.8	7.8
Methoxypropanol	5.3	5.1	5.1
Butanol	2.1	2.0	2.0
Dynapol ® Catalyst 1203	2.0	2.0	2.0
TiO ₂ Kronos ® 2059	39.4	39.4	39.4
Adhesion resin from Example 1 – 60% in xylene	-	3.2	-
Adhesion resin from Example 2 – 60% in xylene	-	-	3.2
	100.0	100.0	100.0

Baking conditions: 30 min at 130°C

Substrate: zinked steel

Film thickness (dry): 25 - 30 µm

Cross-cut value [Gt]:

Formula 1: 2 - 3

Formula 2: 0 - 1

Formula 3: 0

Use Example 4

In a white baking varnish based on a hydroxyl-containing, saturated polyester resin crosslinked with a blocked polyisocyanate, 5% by weight of the binder is replaced by each of the adhesion resins according to the invention from Examples 1 and 2, in the form of their 60% strength solutions in xylene. The original moderate adhesion to zinked steel is greatly improved.

Formulations:	1	2	3
Dynapol ® H 905-07	42.5	40.3	40.3
VESTANAT ® B 1370	15.5	14.8	14.8
DBTL, 10% in xylene	1.0	1.0	1.0
Xylene	4.1	4.0	4.0
Butyl acetate	1.9	1.9	1.9
TiO ₂ Kronos ® 2059	35.0	35.0	35.0
Adhesion resin from Example 1 – 60% in xylene	-	3.0	-
Adhesion resin from Example 2 – 60% in xylene	-	-	3.0
	100.0	100.0	100.0

Baking conditions: 15 min at 170°C

Substrate: zinked steel

Film thickness (dry): 25 - 30 µm

Cross-cut value [Gt]:

Formula 1: 2 - 3

Formula 2: 0 - 1

Formula 3: 0

CLAIMS :

1. An adhesion promoter additive composed of at least one unsaturated, amorphous polyester substantially comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component,
wherein
the alcohol component comprises a didiol mixture of the isomeric compounds 3,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxy-methyl)tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis-(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane,
where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%,
and at least 5% of the mixture is present in the alcohol component of the polyester.
2. The additive as claimed in claim 1,
wherein
up to 10% of further isomers of didiol and/or trimeric and/or higher isomeric diols of the Diels-Alder reaction product of cyclopentadiene are present.
3. The additive as claimed in either of the preceding claims,
wherein
the acid component additionally comprises aromatic and/or aliphatic and/or cycloaliphatic mono-carboxylic acids and/or dicarboxylic acids and/or polycarboxylic acids.
4. The additive as claimed in any of the preceding claims,
wherein
the acid component consists partly or entirely of anhydrides and/or alkyl esters.
5. The additive as claimed in any of the preceding claims,
wherein
the alcohol component comprises further linear and/or branched, aliphatic and/or cycloaliphatic and/or aromatic diols and/or polyols.

6. The additive as claimed in any of the preceding claims,
wherein
the α,β -unsaturated dicarboxylic acid present is citraconic, fumaric, itaconic, maleic and/or mesaconic acid.
7. The additive as claimed in any of the preceding claims,
wherein
the additional acids present are phthalic acid, isophthalic acid, terephthalic acid, 1,4-cyclohexanedicarboxylic acid, succinic acid, sebacic acid, methyltetrahydrophthalic acid, methylhexahydrophthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid, dodecanedioic acid, adipic acid, azelaic acid, pyromellitic acid and/or trimellitic acid, their anhydrides and/or methyl esters, and also isononanoic acid and 2-ethylhexanoic acid.
8. The additive as claimed in any of the preceding claims,
wherein
the additional alcohols present are ethylene glycol, 1,2- and/or 1,3-propanediol, diethylene glycol, dipropylene glycol, triethylene glycol or tetraethylene glycol, 1,2- and/or 1,4-butanediol, 1,3-butylethylpropanediol, 1,3-methylpropanediol, 1,5-pentanediol, cyclohexanedimethanol, glycerol, hexanediol, neopentyl glycol, trimethylolethane, trimethylolpropane and/or pentaerythritol, bisphenol A, B, C, F, norbornylene glycol, 1,4-benzylidimethanol and -ethanol, or 2,4-dimethyl-2-ethylhexane-1,3-diol.
9. The additive as claimed in any of the preceding claims,
wherein
at least 20% of the alcohol component consists of the isomers of claim 1 or 2.
10. The additive as claimed in any of the preceding claims,
wherein
at least 50% of the alcohol component consists of the isomers of claim 1 or 2.
11. The additive as claimed in any of the preceding claims,

wherein

at least 90% of the alcohol component consists of the isomers of claim 1 or 2.

12. The additive as claimed in any of the preceding claims,
wherein
at least 100% of the alcohol component consists of the isomers of claim 1 or 2.
13. The additive as claimed in any of the preceding claims,
wherein
the α,β -unsaturated acid component present is fumaric acid and/or maleic acid/anhydride.
14. The additive as claimed in any of the preceding claims,
wherein
the further dicarboxylic acid component present is adipic acid and/or phthalic acid/anhydride.
15. The additive as claimed in any of the preceding claims,
wherein
the alcohol component is present in a molar ratio of from 0.5:1 to 2.0:1 to the acid component.
16. The additive as claimed in any of the preceding claims,
wherein
the alcohol component is present in a molar ratio of from 0.8:1 to 1.5:1 to the acid component.
17. The additive as claimed in any of the preceding claims,
wherein
the alcohol component is present in a molar ratio of from 1.0:1 to 1.1:1 to the acid component.
18. The additive as claimed in any of the preceding claims,
which
has an acid number of from 1 to 200 mg KOH/g, preferably from 1 to 100 mg KOH/g, more preferably from 1 to 50 mg KOH/g.

19. The additive as claimed in any of the preceding claims,
which
has an OH number of from 1 to 200 mg KOH/g, preferably from 1 to 100 mg KOH/g, more preferably from 1 to 50 mg KOH/g.
20. The additive as claimed in any of the preceding claims,
wherein
assistants and additives are present.
21. The additive as claimed in any of the preceding claims,
wherein
assistants and additives are present which are selected from inhibitors, water and/or organic solvents, neutralizing agents, surface-active substances, oxygen scavengers and/or radical scavengers, catalysts, light stabilizers, color brighteners, photosensitizers, thixotropic agents, antiskinning agents, defoamers, antistats, thickening agents, thermoplastic additives, dyes, pigments, flame retardants, internal release agents, fillers and/or blowing agents.
22. The additive as claimed in any of the preceding claims,
wherein
the alcohol component consists of at least 90% of the dicidol mixture of claim 1 and/or 2, and fumaric acid and/or maleic acid/anhydride are present in a diol/acid ratio of from 0.9:1 to 1.1:1.
23. The additive as claimed in any of the preceding claims,
wherein
adipic acid and/or phthalic acid/anhydride are additionally present as the acid component in a ratio of α,β -unsaturated to additional acid of from 3:1 to 1:4, preferably from 1:1 to 1:2.
24. The use of an unsaturated, amorphous polyester as claimed in any of the preceding claims, substantially comprising at least one α,β -unsaturated dicarboxylic acid component and one alcohol component,
wherein

the alcohol component comprises a didiol mixture of the isomeric compounds 3,8-bis(hydroxy-methyl)tricyclo[5.2.1.0^{2,6}]decane, 4,8-bis(hydroxy-methyl)tricyclo[5.2.1.0^{2,6}]decane and 5,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, where each isomer may be present in the mixture in a proportion of from 20 to 40% and the sum of the three isomers is from 90 to 100%, and at least 5% of the mixture is present in the alcohol component of the polyester, as an adhesion promoter additive.

25. The use as claimed in claim 24, wherein compounds of claims 2 to 23 are present as starting components.
26. The use as claimed in claim 24 or 25 as an adhesion promoter additive in coating compositions which include water and/or solvent or are free from organic solvents and/or water.
27. The use as claimed in claim 26 as an adhesion promoter additive in coating compositions selected from paints, varnishes, glazes, traffic markings, filling compounds, and pigment pastes.
28. The use as claimed in claim 27 as an adhesion promoter additive in primers, surfacers, basecoats, topcoats, and clearcoats.