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(54) A METHOD FOR COATING A SUBSTRATE WITH A RADIATION CURABLE COATING COMPOSITION

(71) We, AKZO N.V., a company organised and existing under the laws of the Kingdom of the Netherlands, of Ijssellaan 82, Arnhem, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method for coating a substrate by applying thereto a radiation curable coating composition based on a urethane compound and subjecting the coating to radiation having a wavelength of 90 to 600 nm.

A method of this type indicated above is described in U.S. Patent Specification No. 3,719,638, according to which an acrylic urethane compound free of isocyanate groups, which is the reaction product of a polyisocyanate, a (meth)acrylic ester having a hydroxy group and a polyfunctional hydroxy compound, is applied to a substrate and cured. Preferably the urethane compound is prepared stepwise in such a way that first an adduct is prepared by reacting 2 equivalents of a polyisocyanate with 1 equivalent of a (meth)-acrylic ester having a hydroxy group, and subsequently reacting the intermediate product with a polyfunctional hydroxy compound to obtain the final monomer free of isocyanate groups. More particularly, a styrene-alkyl alcohol copolymer having a molecular weight in the range of from 200 to 30,000 is used as the polyfunctional hydroxy compound, the number of acrylate groups per molecule determining the speed of radiation curing. British Patent Specification No. 1,159,551 describes a coating composition which also contains as a binder an acrylic urethane compound free of isocyanate groups. This composition is exclusively cured by ionizing radiation in the form of a beam of accelerated electrons.

Although radiation having a wave length of 90 to 600 nm as curing means offers the advantages of low energy consumption and rapid curing without the substrate increasing greatly in temperature, the inside of a coating composition containing a pigment is not cured sufficiently rapidly because the pigment arrests the radiation. Furthermore, it is not easy to radiate and cure every part of the coating layer of non-flush substrates such as automobile bodies and chassis, partly because the distance from the radiation source(s) to the substrate is not constant. Furthermore, because of oxygen inhibition at the surface too low a scratch hardness of the coating layer is generally obtained and the adhesion of the composition to the substrate is unfavourably influenced as a result of shrinkage.

We have now developed a method which does not display the above-mentioned disadvantages, in which curing is carried out in two, mainly separate, steps, primary curing being effected by radiation and further curing taking place as a result of a chemical reaction in which the isocyanate groups of the urethane compound are cross-linked by means of moisture from the ambient air (so-called moisture curing), in combination with a specific polyfunctional hydroxy compound also contained in the composition.

Accordingly, the present invention provides a method for coating a substrate which comprises applying thereto a radiation curable coating composition comprising A) an at least one isocyanate group-containing adduct of a at least one acrylic or methacrylic hydroxy ester containing one hydroxy group and containing from 5 to 20 carbon atoms and b) at least one polyisocyanate containing from 4 to 42 carbon atoms and from 2 to 4 isocyanate groups per molecule, B) at least one polyfunctional hydroxy compound having a molecular weight in the range of from 178 to 12,000 and a hydroxyl content of from 0.5 to 30% by weight in an amount of from 0.5 to 1.5 equivalents of hydroxy groups per equivalent of isocyanate groups of component A, and C) at least one photoinitiator in an amount of from 0.1 to 10% by weight of component A and subjecting the coating layer to radiation having a wavelength of 90 to 600 nm, and after the irradiation reacting the coating with water vapour.

The use of the method of the present invention results in rapid drying upon radiation of the surface of the composition, which may optionally contain a pigment, as a result of which the coated object is hardly susceptible to depositing dust and can be handled and transported very shortly after being treated. Accordingly, a high rate of passage during manufacture and an effective use of the spraying and drying booths are achieved. The commonly used pigments can furthermore be ground in the presence of the polyfunctional hydroxy compound(s) and dispersed therein. This offers the advantage that the pigments need not be ground together with the radiation curable adduct, so that premature curing as a result of the free isocyanate groups of the adduct reacting with moisture from the pigment and thermal instability of the radiation curable adduct as a result of the ethylenically unsaturated groups resulting from temperature rise during grinding are avoided. The second curing step used in the present invention has the important advantage that the coating layer finally has a hardness which is adequate in those places which were not or insufficiently radiated and cured in the first curing step.

The adduct used in the present invention is built up from (a) one or more acrylic or methacrylic hydroxy esters containing from 5 to 20 carbon atoms and preferably from 5 to 15 carbon atoms (hereinafter referred to as hydroxy(meth)acrylate). The hydroxy(meth)acrylate contains one hydroxy group. Examples of suitable hydroxy(meth)acrylates are 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 3-hydroxypropylacrylate, 3-hydroxypropylmethacrylate, 4-hydroxybutylacrylate, 8-hydroxyoctylacrylate, 12-hydroxydodecanylacrylate, 2-hydroxy-3-chloropropylacrylate, 2-hydroxy-3-acryloxypropylacrylate, 2 - hydroxy - 3 - methacryloxypropylmetha crylate, trimethylol propanediacrylate, trimethylol propanedimethacrylate, pentaerythritoltriacrylate and pentaerythritoltrimethacrylate. Mixtures of 2 or more hydroxy-(meth)acrylates may also be used. Preferably 2-hydroxyethylacrylate, 4-hydroxybutylacrylate or pentaerythritoltriacrylate are used.

The adduct is also built up from (b) one or more polyisocyanates containing from 4 to 40 carbon atoms and from 2 to 4, preferably 2 or 3, isocyanate groups per molecule. The polyisocyanate may be an aliphatic, cycloaliphatic, arcliphatic or aromatic polyisocyanate and should preferably contain from 15 to 40 carbon atoms. For a priming coat preferably an adduct with an aromatic polyisocyanate is used and for a top coat preferably an adduct with a (cyclo) aliphatic polyisocyanate is employed.

Examples of suitable (ar) aliphatic or (cyclo) aliphatic diisocyanates are tetramethylene-1, 4-diisocyanate, hexamethylene-1, 6-diisocyanate, ω, ω′-dipropylether diisocyanate, thiodipropyl diisocyanate, 2, 2, 4-trimethylhexane-1, 6-diisocyanate, 2, 4, 4-trimethylhexane-1, 6-diisocyanate, cyclohexyl-1, 4-diisocyanate, isophoron diisocyanate, the adduct of 1 molecule of 1, 4-butanediol and 2 molecules of isophoron diisocyanate, the adduct of 1 molecule of 1, 4-butanediol and 2 molecules of hexamethylene diiscoyanate, dicyclohexylmethane-4, 4′-diisocyanate, dicyclohexyldimethylmethane-4, 4′-diisocyanate, xylylene diisocyanate, 1, 5-dimethyl (2, 4-ω-diisocyanatomethyl) benzene, 1, 5-dimethyl (2, 4-ω-diisocyanatoethyl) benzene, 1, 3, 5-trimethyl (2, 4-ω-diisocyanatomethyl) benzene and 1, 3, 5-triethyl (2, 4-ω-diisocyanatomethyl) benzene. As examples of suitable aromatic diisocyanates may be mentioned toluene diisocyanate, diphenylmethane-4, 4′-diisocyanate, naphthalene diisocyanate, 3, 3′-bistoluene-diisocyanate and 5, 5′-dimethyldiphenylmethane-4, 4′-diisocyanate. Examples of suitable triisocyanates are the adduct of 3 molecules of hexamethylene-1, 6-diisocyanate and 1 molecule of water (marketed by Bayer under the trade name Desmodur N — Registered Trade Mark) the adduct of 1 molecule of trimethylol propane and 3 molecules of isophoron diisocyanate and the adduct of 1 molecule of trimethylol propane and 3 molecules of toluene diisocyanate (marketed by Bayer under the trade name Desmodur L). A suitable tetraisocyanate, is for example, the adduct of 1 molecule of pentaerythritol and 4 molecules of hexamethylene-1, 6-diisocyanate. Mixtures of two or more of the above-envisaged polyisocyanates may also be used. Preferably the adduct of 3 molecules of hexamethylene-1, 6-diisocyanate and 1 molecule of water, or the adduct of 1 molecule of trimethylol propane and 3 molecules of toluene diisocyanate or the adduct of 1 molecule of trimethylol propane and 3 molecules of isophoron diisocyanate are used.

The formation of an adduct from a polyisocyanate and a hydroxy-(meth)acrylate may generally be carried out by adding the reaction components together in any arbitrarily chosen way, optionally at elevated temperature. Preferably, the reaction should be carried out under anhydrous conditions in an atmosphere of an inert gas at a temperature in the range of from 5° to 100°C, more preferably in the range of from 20° to 80°C. Although generally the reaction components may be added together in any arbitrarily chosen way, it is usually preferred to add the hydroxy-(meth)acrylate to the polyisocyanate, which may be effected in several stages, if desired. As a rule, the reaction will be carried out in the presence of an inert solvent, for example: acetone, methylisobutyl ketone, toluene, xylene, or esters such as butyl acetateor ethyl glycol acetate, but the use of a solvent is not strictly necessary. Optionally the reaction between the isocyanate groups and the hydroxy groups may be carried out in the presence of a catalyst. Examples of suitable catalysts are tertiary amines and organic tin salts or zinc salts such as dibutyl tin dilaurate, tin octoate and zinc octoate. Mixtures of catalysts may also be used.

The radiation curable composition contains one or more photoinitiators in an amount of from 0.1 to 10% by weight, based on the adduct. Examples of suitable initiators are benzophenone, acetophenone, diethoxyacetophenone, chlorothioxanthone, benzoin and benzoin ethers, such as benzoin methyl ether, benzoin ethyl ether or benzoin tert.-butyl ether. Preferably diethoxyacetophenone should be used because it does not or hardly causes the composition to yellow. If desired, the composition may also contain photosensitizers. A suitable example thereof is Michler's ketone.

The isocyanate groups of the adduct used in the present invention are cross-linked not only with the aid of moisture from the ambient air, but also by means of a polyfunctional hydroxy compound contained in the radiation curable composition. To prevent premature curing or cross-linking, the adduct containing at least one isocyanate group and the polyfunctional hydroxy compound(s) preferably are intermixed shortly before the radiation curable compound is applied to the substrate. The polyfunctional hydroxy compounds, which contain at least 2 hydroxyl groups per molecule, may be those polyols usually employed for the preparation of polyurethane coating compositions, for example the polyester polyols, polyether polyols, acrylate polyols and polycaprolactones. Examples of representative polyhydroxy compounds are polyester polyols modified with a fatty acid and having a hydroxyl content of about 1 to 8% by weight, branched polyether polyols having a hydroxyl content of 8 to 15% by weight, alkyd resins based on phthalic acid, propylene glycol and a synthetic fatty acid and having a hydroxyl content of about 2 to 5% by weight, epoxy resins based on the diglycidyl ether of Bisphenol A having a hydroxyl content of about 4% by weight, hydroxyacrylate resins made up of e.g. styrene, an alkyl acrylate or methacrylate and a hydroxyalkyl acrylate which have a hydroxyl content of about 3to 10% by weight and polycaprolactone polyols, having a hydroxy content of about 3 to 10% by weight and esterpolyols such as the reaction product of 1 mole of maleic acid and 2 moles of trimethylol propane and the reaction product of 1 mole of maleic acid with 2 moles of ethylene glycol. The molecular weight of the polyfunctional hydroxy compounds is preferably in the range of from 300 to 8000. The hydroxy content is preferably in the range of from 1 to 22% by weight.

The polyfunctional hydroxy compound is present in the coating composition in such an amount that from 0.5 to 1.5, and preferably 0.9 to 1.1 equivalents of hydroxy groups, are present in the composition per 1 equivalent of isocyanate groups of the adduct.

The coating composition may, if desired, contain additives, such as pigment dispersing agents, levelling agents, fillers, pigments, colouring agents, polymerization inhibitors, solvents, catalysts for curing the free isocyanate groups of the adduct with the aid of water vapour and the polyfunctional hydroxy compound(s), for example: organic tin salts or zinc salts and tertiary amines such as triethylene diamine, trimethylamine and N-methylmorpholine. The coating composition may also contain monomers such as methyl methacrylate, ethyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, ethylene glycol diacrylate, neopentyl glycol diacrylate, glycerol triacrylate and trimethylol propane triacrylate.

The application of the coating composition to a particular substrate may be carried out in any known manner for example by rolling, brushing, sprinkling, casting, dipping or by electrostatic spraying, and preferably by spraying. The coating composition may advantageously be applied to a substrate of a synthetic material, such as polyurethane elastomers and to metal substrates, for example as automobile paint or automobile repair paint, as coil coating or can coating and as shop primer to sandblasted steel. The composition may furthermore be applied as furniture lacquer to, for example, chip board, plywood, board and veneered core board.

According to the invention the hardening of the radiation curable coating composition is effected in 2 stages. In the first stage the composition, after application to a particular substrate is subjected to radiation having a wave length of 90 to 600 nm (UV-light and blue light). The radiation source may be, for example, a mercury or xenon lamp, which works at high, medium or low pressure. The composition need be radiated only for from a few seconds to a few minutes in order to ensure such drying that the coating layer is tack-free and of such hardness that it can be handled.

In the second curing stage the coating is given its final hardness as a result of the progressive reaction of the isocyanate groups of the adduct with water vapour and with the hydroxyl groups of the polyfunctional hydroxy compound. The second curing stage may take place at a temperature in the range of, say, 0° to 160°C, over a period ranging from 5 minutes to a few days. It is preferred that this curing should take place over a period of several days at room temperature. It is found that after the coating has been cured for seven days at about 10°C, it has about the same hardness as after a curing treatment of 10 minutes at 120°C. Carrying out the second curing stage at room temperature offers the considerable advantage that it does not require any energy or any capital expenditure.

The invention will be further described with reference to the following examples, which are not to be considered to limit the scope of the present invention. The following polyfunctional hydroxy compounds were used therein:—

Polyol A: a fatty acid modified polyester polyol having a hydroxyl content of about 4% by weight and an acid number lower than 20 (available under the trade name Desmophen 1300 — Registered Trade Mark of Bayer). The polyol was employed as a 75% by weight solution in xylene.

Polyol B: a branched polyether polyol having a hydroxyl content of about 11.5% by weight and an acid number lower than 0.5 (available under the trade name Desmophen 550 U of Bayer).

Polyol C: an alkyd resin modified with a synthetic fatty acid and obtained by the reaction of 47 parts by weight of phthalic acid, 37 parts by weight of propylene glycol and 26 parts by weight of fatty acid. The alkyd resin had a hydroxyl content of about 3.0% by weight.

Polyol D: an epoxy resin based on the diglycidyl ether of Bisphenol A and having a hydroxyl content of about 3.8% by weight (marketed by Shell under the trade name Epikote 1001 — Registered Trade Mark). The polyol was used as a 75% by weight solution in xylene.

Polyol E: a hydroxyacrylate resin made up of 35% by weight of styrene, 30% by weight of methylmethacrylate and 35% by weight of hydroxypropyl acrylate, and having a hydroxyl content of 5.0% by weight and a molecular weight of 3000. The polyol was used as a 55% by weight solution in xylene.

Polyol F: a polycaprolactone polyol having a hydroxyl content of 6.3% by weight and a molecular weight of 500.

The radiation curable polyurethane compounds used were:

Adduct P: the adduct obtained by the reaction of 1 mole of the adduct of 1 mole of trimethylol propane and 3 moles of toluene diisocyanate, with 1½ moles of hydroxybutyl acrylate.

Adduct Q: the adduct obtained by the reaction of 1 mole of the adduct of 1 mole of trimethylol propane and 3 moles of toluene diisocyanate, with 1½ moles of pentaerythritol triacrylate.

Adduct R: the adduct obtained by the reaction of 1 mole of the adduct of 3 moles of hexamethylene diisocyanate and 1 mole of water, with 1½ moles of hydroxybutyl acrylate.

Adduct S: the adduct obtained by the reaction of 1 mole of the adduct of 3 moles of hexamethylene diisocyanate and 1 mole of water, with 1½ moles of pentaerythritol triacrylate.

The adducts P to S are used as 70% by weight solutions in butyl acetate.

In the preparation of each coating composition according to the invention 100 parts by weight of the polyfunctional hydroxy compound (polyols A and C to E as solutions) were mixed with the amount by weight of a solution of the respective adduct P to S given in Table 1.

TABLE 1

Polyol	Adduct			
	P	Q	R	S
A	230	319	170	260
B	660	916	499	747
C	172	239	128	195
D	218	303	162	247
E	287	398	213	325
F	362	502	268	409

In all of the Examples a UV lamp of the HOK type (Philips — Registered Trade Mark) was used for the curing treatment in the first phase. The coatings obtained were tested for tackiness and for resistance to rotational pressure. i.e. the resistance to damage of the coating upon rotation of a punch applied to the coating at a pressure of 9.8 N/cm^2. The punch, which had a pressure surface area of 1 cm^2, was turned for 1 second through an angle of $\frac{1}{2}\pi$ rad. The values determined were classified in the range of 1 to 10. In the test for tackiness a value 1 denotes that the surface remained dust free and a value 10 denotes a 100%-tacky surface. In the determination of the resistance to rotational pressure the value 1 denotes that no damage has occured, whereas a value 10 indicates that the punch had penetrated into the paint to such a degree that the coating of the area subjected to the test had been entirely removed. The hardness, of the coating was tested manually. The final curing of the coatings takes place in the presence of water vapour.

Examples 1 to 24

In all of these examples the adducts P, Q, R and S were each mixed with one of the afore-mentioned polyhydroxy compounds A to F in the weight ratios given in Table 1. Chlorothioxanthone was added as photoinitiator in an amount of 4% by weight, based on the adduct to each of the resulting mixtures. The compositions obtained were applied to steel panels to a coating thickness of 35 μm (in the cured state), after which the panels were immediately passed under a UV lamp at a speed of 5 m/min. The distance between the lamp and the panels was 40 cm. Immediately after radiation, the tackiness, the resistance to rotational pressure and the duration between the exposure to radiation and the moment each coating was tack-free or had a resistance to rotational pressure of 1 was determined. The resulting coatings were satisfactorily cured in all cases after they had been kept at room temperature for 5 days. The values determined are given in Table 2.

TABLE 2

Example	Polyol	Immediately after radiation		Drying time in min. after radiation until:	
		Tackiness	Resist. to rot. press.	Tack-free	Value 1 for resist. to rot. pressure
		Adduct P			
1	A	8	8	8	29
2	B	7	7	8	25
3	C	8	8	4	12
4	D	8	9	8	32
5	E	8	8	9	16
6	F	3	2	1	1
		Adduct Q			
7	A	9	9	3	4
8	B	8	8	5	5
9	C	9	9	3	4
10	D	7	7	1	2
11	E	6	9	9	12
12	F	1	2	1	1
		Adduct R			
13	A	9	7	15	39
14	B	9	7	15	35
15	C	9	9	12	30
16	D	9	9	8	24
17	E	8	9	20	20
18	F	2	1	1	0.5
		Adduct S			
19	A	8	9	6	9
20	B	5	7	7	12
21	C	9	9	4	8
22	D	3	4	2	2
23	E	6	9	5	5
24	F	1	1	0	0

Examples 25 to 35

The adducts given in Table 3 were mixed with the afore-mentioned polyhydroxy compounds and subsequently pigmented to a pigment volume concentration of 30% using a mixture of 6 parts by weight of talc and 1 part by weight of iron oxide red. Chlorothioxanthone in an amount of 2.5% by weight, based on the adduct was added as photoinitiator. Triethanolamine in an amount of 2% by weight, based on the adduct was added as sensitizer. Butyl acetate was added as solvent in order to bring the composition to a sprayable viscosity (20 seconds efflux time, DIN-cup 4).

The resulting compositions were applied to steel panels to a layer thickness of 16 to 18 μm (in the cured state). Two minutes later the panels were passed under a UV lamp at a speed of 5 m/min. The distance between the lamp and the panels was 40 cm. The duration between radiation and the moment each coating was tack-free or had a resistance to rotational pressure of 1 was determined. All of the coatings obtained except that of Example 29, were cured after they had been kept at room temperature for 14 days. The values obtained are given in Table 3.

TABLE 3

Example	Polyol	Adduct	Drying time in min. after radiation until:	
			Tack-free	Value 1 for resist. to rotational pressure
25	A	P	3	16
26	A	Q	2.5	9
27	A	R	8	23
28	A	S	1	6
29	B	Q	2	12
30	C	Q	0.75	3.5
31	C	S	0.50	1.75
32	D	P	2.5	10
33	D	Q	2.5	8.5
34	D	R	2	18
35	D	S	0.25	1.5

Example 36 to 39

The Examples 30 to 33 were repeated in such a way that the compositions were applied with a spray and after the panels had been left for only 15 seconds they were passed under a UV lamp. Immediately after radiation the coatings were tack-free and it was after only 10, 15, 13 and 20 seconds, respectively, that the coatings had a value for resistance to rotational pressure.

All of the coatings were satisfactorily cured.

Examples 40 to 47

The compositions of Examples 30, 31, 33 and 35 were applied to steel panels to a layer thickness of 16 to 18 μm (in the cured state) with the aid of a spray gun. After the panels had been left for 15 seconds or 1 minute, they were passed under a UV lamp at a rate of 10 m/min. The distance between the lamp and the panels was 40 cm. Immediately after radiation the coatings were tack-free. The duration between radiation and the moment each coating reached a value 1 for resistance to rotational pressure is given in Table 4. All of the coatings were satisfactorily cured after they had been kept at room temperature for 14 days.

TABLE 4

Example	Polyol	Adduct	Waiting time	Drying time in sec. after radiation until value 1 for resistance to rotational pressure
40	C	Q	15 sec.	30
41	C	Q	1 min.	0
42	C	S	15 sec.	15
43	C	S	1 min.	0
44	D	Q	15 sec.	25
45	D	Q	1 min.	0
46	D	S	15 sec.	30
47	D	S	1 min.	15

WHAT WE CLAIM IS:—

1. A method for coating a substrate which comprises applying thereto a radiation curable coating composition comprising A) an at least one isocyanate group-containing adduct of a) at least one acrylic or methacrylic hydroxy ester containing one hydroxy group and containing from 5 to 20 carbon atoms and b) at least one polyisocyanate containing from 4 to 42 carbon atoms and from 2 to 4 isocyanate groups per molecule, B) at least one polyfunctional hydroxy compound having a molecular weight in the range of from 178 to 12,000 and a hydroxyl content of from 0.5 to 30% by weight in an amount of from 0.5 to 1.5 equivalents of hydroxy groups per equivalent of isocyanate groups of component A, and C) at least one photoinitiator in an amount of from 0.1 to 10% by weight of component A and subjecting the coating layer to radiation having a wavelength of 90 to 600 nm and after the irradiation reacting the coating with water vapour.

2. A method as claimed in claim 1, wherein the acrylic or methacrylic hydroxy ester contains from 5 to 15 carbon atoms.

3. A method as claimed in claim 1 or 2, wherein the acrylic or methacrylic hydroxy ester is 2-hydroxyethylacrylate, 4-hydroxybutylacrylate or pentaerythritoltriacrylate.

4. A method as claimed in any one of the preceding claims wherein the polyisocyanate contains from 15 to 40 carbon atoms.

5. A method as claimed in any one of the preceding claims wherein the polyisocyanate contains 2 or 3 isocyanate groups per molecule.

6. A method as claimed in any one of the preceding claims wherein the polyisocyanate is the adduct of 3 molecules of hexamethylene-1,6-diisocyanate and 1 molecule of water, the adduct of 1 molecule of trimethylol propane and 3 molecules of toluene diisocyanate or the adduct of 1 molecule of trimethylol propane and 3 molecules of isophoroneidisocyanate.

7. A method as claimed in any one of the preceding claims wherein the polyfunctional hydroxy compound is contained in the composition in an amount of 0.9 to 1.1 equivalents of hydroxy per equivalent of isocyanate groups of component A.

8. A method as claimed in any one of the preceding claims wherein the polyfunctional hydroxy compound contained in the composition is a polyester polyol, a polyether polyol, an acrylate polyol or a polycaprolactone.

9. A method as claimed in any one of the preceding claims wherein the polyfunctional hydroxy compound contained in the composition has a molecular weight in the range of from 300 to 8000.

10. A method as claimed in any one of the preceding claims wherein the polyfunctional hydroxy compound contained in the composition has a hydroxyl content of 1 to 22% by weight.

11. A process as claimed in any one of the preceding claims wherein the reaction with water vapour takes place over a period of several days at room temperature.

12. A process as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

13. A substrate when coated with a cured coating composition obtained by the method claimed in any one of the preceding claims.

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