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(54) **Coated polycarbonate**

(57) Improved coatings on polycarbonate are formed by polymerizing a mixture containing (1) an oligomer or a reactive resin having a molecular weight between 400 and 4,000 and containing at least two acrylic groups per molecule, and (2) an N-vinyl derivative of straight-chain or cyclic secondary amide, the polymerization being carried out in the presence of a photoinitiator.

GB 2 082 606 A

SPECIFICATION

Coated polycarbonate

- 5 This invention relates to coated polycarbonate such as coated polycarbonate of Bisphenol A. 5
 - Polycarbonates have excellent properties such as transparency, shock resistance and tensile strength.
 However, the surface of polycarbonate has a poor resistance to abrasion and scratching and a poor
 resistance to solvents. More particularly, the surface of polycarbonate, due to the effect of weathering agents
 or even gentle contact with other materials, becomes scratched and tends to become opaque. Some
- 10 methods have been suggested for overcoming these defects. These methods are based on the use of 10
 particular coatings based on siloxane or melamine resins. These coatings involve cost problems. Also, they
 are difficult to use and have unsatisfactory properties, since they are in the form of varnishes in solvents and
 generally require a heat treatment to bring about cross-linking, this treatment being such as to jeopardize the
 properties of the polycarbonate, more particularly the impact resistance thereof.
- 15 We have found a polycarbonate coating which has good properties as to adhesion, hardness and abrasion 15
 resistance.
 According to the present invention, there is provided polycarbonate having on a surface thereof a coating
 of a copolymer of (a) an oligomer or reactive resin having a molecular weight of from 400 to 4000 and
 containing at least two acrylic groups, and (b) an N-vinyl derivative of a linear or cyclic secondary amine.
- 20 The present invention also provides a process for forming a coating on a surface of polycarbonate, which 20
 comprises coating the surface with a mixture of (a) an oligomer or reactive resin having a molecular weight
 of from 400 to 4000 and containing at least two acrylic groups, and (b) an N-vinyl derivative of a linear or
 cyclic secondary amide; and copolymerising the components of the mixture, in the presence of a
 photoinitiator, by exposure of the mixture to radiation.
- 25 The polymerisation mixture may contain, moreover, reactive compounds having a low molecular weight 25
 (less than 4000) and containing at least a functional group of acrylate type, methacrylate type, maleate type
 or fumarate type. Examples of such compounds are butanediol diacrylate, ethyl hexyl acrylate, dimethyl
 maleate, diethyl fumarate and ethylene glycol diacrylate.
- The method of the invention as compared with conventional procedures, enables the mixture to be
 30 completely hardened at room temperature without modifying the properties of the polycarbonate, such as 30
 its shock resistance and its transparency.
 The oligomer used is preferably (a) a urethane resin containing, at the ends of the molecule, at least two
 acrylic groups; (b) a resin obtained by oligomerising acrylic monomer(s) functionalised by at least two
 acrylic groups per molecule; or (c) a resin obtained by condensing a saturated or unsaturated dicarboxylic
 35 acid with a glycol and subsequently esterifying their terminal hydroxy groups with acrylic acid. 35
 Examples of resins (a) above are the condensation product of one mol of hexamethylene diisocyanate with
 two mols of trimethylolpropane diacrylate; the condensation product of one mol of hexamethylene
 diisocyanate with two mols of hydroxyethyl diacrylate; and the condensation product of one mol of toluene
 diisocyanate with two mols of hydroxyethyl acrylate.
- 40 Examples of resins (b) above are an oligomer containing monomeric units deriving from the 40
 copolymerization of methyl acrylate, ethyl acrylate and glycidyl acrylate, the oligomer being reacted with an
 amount of acrylic acid which is stoichiometric relative to the glycidyl group, thus forming an acrylated acrylic
 resin; and an oligomer obtained by copolymerizing methyl acrylate with ethyl acrylate and 2-hydroxyethyl
 acrylate, the oligomer being reacted with acrylic acid to form an acrylated acrylic resin.
- 45 An example of resin (c) above is an oligomer obtained by condensation of maleic acid anhydride, adipic 45
 acid and ethylene glycol, the oligomer, which has two terminal hydroxy groups, being subsequently
 esterified with acrylic acid.
 Examples of N-vinyl derivatives of straight-chain or cyclic secondary amides are N-vinyl pyrrolidone,
 N-vinyl caprolactam, N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl-propionamide and N-vinyl-N-methyl
 50 propionamide. 50
 The quantity of N-vinyl compound which is present in the mixture is preferably from 5 to 60% by weight of
 the mixture.
 The photoinitiators used are compounds capable of producing free radicals under the action of UV
 radiation. Examples of these are benzoin isopropyl ether, benzoin ethyl ether, benzyl dimethyl ketal,
 55 benzophenone, 2,2-dimethyl-2-phenyl acetophenone, 2-chlorothioxanthone and anthraquinone. 55
 The mixture is preferably spread on the polycarbonate by spreading, spraying or dipping. The thickness of
 the coating is preferably from 5 to 200 microns.
 The UV radiation used for the cross-linking of the mixture can easily be produced by using mercury-vapour
 lamps operating under medium or high pressures. It is possible to use also other types of radiations (e.g.
 60 electron rays and X-rays). 60
 The possible uses for the coated polycarbonate are manifold. Thus, for example, they can be used as
 transparent slabs, machine parts and various other articles. As a matter of fact, the coated polycarbonate has
 the basic and inherent properties of the polycarbonates (i.e. shock resistance, transparency and resistance to
 high temperatures) and very good surface properties such as resistance to scratching, to abrasion, to
 65 solvents, to radiation and to hydrolysis, so that outdoor use of the composite material is possible, since it can 65

withstand weathering agents and contact with other chemicals as well.

The invention will now be illustrated by the following Examples.

Example 1

5 A urethane-acrylic resin (Resin A), obtained by condensing one mol of hexamethylene diisocyanate with two mols of trimethylolpropane diacrylate, was used. The resin had a viscosity at 25°C of 13,500 cps and an acrylic functionality of 4. The resin was used to propose the following composition: 5

10	Resin A	80 parts by weight	10
	N-vinyl pyrrolidone	20 parts by weight	
	Benzyl-methyl ketal	5 parts by weight	

15

The mixture had a viscosity at 25°C of 830 cps. It was spread over sample plates cut from a planar extruded slab of a typical commercial polycarbonate so as to form a coating having a thickness of 30 microns. For this operation a film-spreader K-Control Coater with spiral bars was used. The coating was cross-linked by passing the sample plates in air through a UV tunnel equipped with a mercury vapour lamp having a power of 80 W/cm and placed at a distance of 11 cm from the surface to be cross-linked, the speed of the conveyor being 24 metres per minute. The surface hardness (König Hardness, FN Unichim No. 91) and the scratch resistance of the plates was measured as a function of the number of passes through the tunnel. The resistance to scratching was measured by reading the minimum load (in grams) which is necessary to scratch the surface with a diamond point with an angle of 120° under conditions of a slow rectilinear motion. The results given in the following Table were obtained. 25

TABLE 1

30	No. of passes	König Hardness (s)	Resistance to scratching (g)	30
35	2	169	26	35
	4	170	29	
40	8	176	32	40
	12	178	33	
45	16	181	34	45
	20	185	35	

50 It can be seen that the surface has a high hardness and a high resistance to scratching even after 2 passes. The resistance to scratching of an uncoated sample plate was 6.2 g so that it can be appreciated that the coating considerably improves the resistance of the plates to scratching. The adhesion of the coating to the plates, measured after 20 tunnel passes was 100%. Also, the adhesion of adhesive tape to the coating (measurement through FN Unichim No. 37 grid) was 100%. These two adhesion tests are referred to hereinbelow as "adhesion without tape" and "adhesion with tape", respectively. The resistance to shocks of the coated plates was equal to that (75 kg.cm/cm²) of the uncoated plates. The same is true of their transparency. 55

For determining the impact resistance of the plates, the Izod method, ASTM-D-256, was used. Accelerated ageing tests were carried out in a Weatherometer (WOM) and by immersion of the plates in water. The results given in the following Table 2 were obtained.

5		TABLE 2		5
	After 1,000 hours in the WOM	Adhesion without tape	100%	
10		Adhesion with tape	100%	10
		Scratch resistance	37g	
15		Colour	unaffected	15
	After 10 days in water at 23°C	Adhesion without tape	100%	
		Adhesion with tape	100%	
20		Scratch resistance	31g	20
		Colour	unaffected	

25 It can thus be seen that there are no visible alterations in the plates during the ageing test and the water immersion test. The same tests were repeated, using a plate coated with a coating composed of resin A alone. The coating had the same properties as tabulated above, but its adhesion was zero. This shows that the presence of both the resin and the vinyl amide are necessary in order that the expected properties may be obtained.

30 The resistance of the coated plates to abrasion was measured with a Taber Abrasion-meter having CS 10F grinding wheels, according to ASTM-D10 44. A determination of the extent of abrasion was carried out by an optical method, namely the ASTM 1003 Haze test. The results which have been obtained for various cycles of treatment, employing plates coated with resin A and vinyl pyrrolidone, in comparison with a commercial polycarbonate coated with a siloxane varnish coating, given in the following Table 3.

35

40		TABLE 3		40
		Haze test (%)		
	No. of cycles	Polycarbonate + Resin Resin A+vinyl pyrrolidone	Commercial Polycarbonate	
45	10	1.2	1.2	45
	20	2.5	1.6	
50	40	3.8	3.9	50
	60	5.0	5.6	
55	100	7.5	10.0	55
	150	10.8	15.6	
	200	13.9	26.8	
60				60

Polycarbonate as such, under these conditions, displays, even after 10 cycles, a value in the Haze test higher than 20%. These results show that the composition described above has a high abrasion resistance, namely a resistance which is higher than that of the commercial varnish coated articles.

Example 2

Using the same procedure as in the previous Example, a mixture having the following composition was prepared:

5	Resin A	50 parts by weight	5
	Vinyl pyrrolidone	50 parts by weight	
10	Benzyl dimethyl ketal	5 parts by weight	10

The mixture had a viscosity at 25°C of 75 cps. It was spread on plates as used in Example 1 so as to form a coating having a thickness of 30 microns. After 20 UV-tunnel passes, the coating had the following properties:

	König Hardness	176 s	
20	Adhesion without tape	100%	20
	Adhesion with tape	100%	
25	Resistance to scratching	24 g.	25

The resistance to shock and the transparency of the coated sample plates were the same as those of the uncoated sample plates. When a different amount of the photoinitiator was used, and when a nitrogen atmosphere was used, the coated plates, after 20 passes, had the properties given in the following Table 4.

30

TABLE 4

35	Hardness	Adhesion		Resistance to scratching	35	
		without tape	with tape			
	(s)	(%)	(%)	(g)		
40	Benzyl dimethyl ketal (2 parts)	181	100	100	22	40
45	Benzyl dimethyl ketal (2 parts) + N ₂ atmosphere	189	100	100	26	45

It can be seen that, within the limits above, the concentration of the initiator and the presence of nitrogen do not involve any appreciable variations in the properties of the coated plates.

50

Example 3

The procedure was the same as in Example 1. A mixture having the following composition was prepared.

5	Resin A	60 parts by weight	5
	N-vinyl caprolactam	40 parts by weight	
10	Benzyl dimethyl ketal	5 parts by weight	10

The mixture had a viscosity at 25°C of 230 cps. It was spread on polycarbonate plates so as to form a coating having a thickness of 30 microns. After 20 UV-tunnel passes, the coating had the following properties:

15	König Hardness	180 s	15
	Adhesion without tape	100%	
20	Adhesion with tape	100%	20
	Resistance to Scratching	27 g.	

25 The shock resistance and the transparency of the sample plates were the same as those of the pure polycarbonate. 25

Example 4

30 A mixture having the following composition was prepared: 30

	Resin A	70 parts by weight	
35	N-vinyl pyrrolidone	15 parts by weight	35
	Methyl maleate	15 parts by weight	
40	Benzoin ethyl ether	5 parts by weight	40

The mixture was spread on polycarbonate plates in a thickness of 30 microns, and, upon cross-linking by 20 UV-tunnel passes, the coating obtained had the following properties:

45	König Hardness	177 s	45
	Adhesion without tape	100%	
50	Adhesion with tape	100%	50
	Resistance to Scratching	28 g	

55 The shock resistance and the transparency of the plates were the same as those of uncoated polycarbonate. 55

Example 5

There is used a resin of acryl-acrylate type (Resin B), obtained by copolymerising methyl acrylate with ethyl acrylate and glycidyl acrylate to form a terpolymer in which the three monomers are present in the molar proportions 55:35:10, respectively. The terpolymer is reacted with a stoichiometric amount of acrylic acid relative to the glycidyl group, thus forming an acryl-acrylate type resin having an average molecular weight, M_n , of 1650. The resin was used to form a mixture having the following composition:

10	Resin B	50 parts by weight	10
	Butanediol diacrylate	30 parts by weight	
	N-vinyl pyrrolidone	20 parts by weight	
15	Benzyl dimethyl ketal	5 parts by weight	15

The mixture had a viscosity at 25°C of 330 cps. It was spread on polycarbonate sample plates to a thickness of 30 microns. After 20 UV-tunnel passes, the coating had the following properties:

20	König hardness	149 s	20
25	Adhesion without tape	100%	25
	Adhesion with tape	100%	
	Resistance to Scratching	18 g.	

The shock resistance and the transparency of the plates were the same as those of uncoated polycarbonate.

An accelerated ageing test in a WOM and an immersion test in water were carried out as in Example 1. The results given in following Table 5 were obtained.

TABLE 5				
40	After 1,000 hours in WOM	Adhesion without tape	100%	40
		Adhesion with tape	100%	
45		Resistance to Scratching	17 g	45
	After 10 days in water at 23°C	Colour	unaffected	
50		Adhesion without tape	100%	50
		Adhesion with tape	100%	
55		Resistance to scratching	14 g	55
		Colour	unaffected	

These results shows that there are no appreciable alterations of the sample plates in the two tests. When the tests were repeated under the same conditions, but without any N-vinyl pyrrolidone in the mixture, the coatings had the same properties but their adhesion to the plate was nil.

Example 6

Using resin B of Example 5, the following blend was prepared:

5	Resin B	30 parts by weight	5
	Ethylene glycol diacrylate	20 parts by weight	
10	Vinyl pyrrolidone	50 parts by weight	10
	Benzoin ethyl ether	5 parts by weight	

The mixture had a viscosity at 25°C of 85 cps. After 20 UV-tunnel passes of polycarbonate plates coated to a thickness of 30 microns, the coating had the following properties: 15

	König hardness	147 s	
20	Adhesion without tape	100%	20
	Adhesion with tape	100%	
25	Resistance to Scratching	13 g.	25

The other properties of the coated plates were found to be similar to those of the previous Example.

Example 7

Resin A of Example 1 was used to form the following mixture: 30

	Resin A	70 parts by weight	
35	N-vinyl-N-methyl butyramide	30 parts by weight	35
	Benzyl-dimethyl-ketal	5 parts by weight	

A coating having a thickness of 5 microns was formed on polycarbonate plates and, after 10 UV-tunnel passes, the coatings had the following properties: 40

45	König hardness	162 s	45
	Adhesion without tape	100%	
	Adhesion with tape	100%	
50	Resistance to Scratching	18 g.	50

The other properties of the coated plates were similar to those of Example 1.

Example 8

The same mixture as used in Example 1 was spread in different thicknesses on three sample plates of commercial polycarbonate of different brands. These sample plates had the following resistances to scratching:

5		5
	Sample No. 1	6.2 g
	Sample No. 2	7.5 g
10	Sample No. 3	7.0 g.

Upon coating the plates with the mixture in different thicknesses and after 20 UV cross-linking passes, the coating had the properties given in the following Table 6.

TABLE 6

20	Sample	5 microns thickness		30 microns thickness		20
	No.	Resistance to Scratching (g)	Adhesion with tape (%)	Resistance to Scratching (g)	Adhesion with tape (%)	
25						25
	1	16	100	35	100	
30	2	13	100	32	100	30
	3	13	100	30	100	

These results show that the adhesion is not influenced by the thickness, whereas the resistance to scratching is increased as the film thickness is increased.

Example 9

A resin C of polyester acrylate type was used. This resin was obtained by polycondensing a mixture of one mol of maleic acid anhydride with one mol of adipic acid and 3 mols of ethylene glycol. The product thus obtained was esterified by reacting it with acrylic acid to obtain a semi-solid resin having an \bar{M}_n of 460 and an acrylic functionality of 2. This resin was used to form the following mixture:

45	Resin C	70 parts by weight	45
	N-vinyl pyrrolidone	30 parts by weight	
50	Benzyl dimethyl ketal	5 parts by weight	50

The mixture, spread to a thickness of 30 microns on polycarbonate plates and UV-cross-linked by 20 tunnel passes, gave coatings having the following properties:

55	König hardness	172 s	55
	Adhesion without tape	100%	
60	Adhesion with tape	100%	60
	Resistance to Scratching	22 g.	

The other properties of the sample plates were similar to those of Example 1. The test was repeated without adding the vinyl amide. The coated sample plates obtained has similar properties to the foregoing

65

plates, but the adhesion of the coatings to the plates was nil.

CLAIMS

- 5 1. Polycarbonate having on a surface thereof a coating of a copolymer of (a) an oligomer or reactive resin 5
having a molecular weight of from 400 to 4000 and containing at least two acrylic groups, and (b) an N-vinyl
derivative of a linear or cyclic secondary amine.
2. Coated polycarbonate as claimed in claim 1, wherein the oligomer is a urethane resin containing at
least two terminal acrylic groups.
- 10 3. Coated polycarbonate as claimed in claim 1, wherein the oligomer is one obtained by oligomerising 10
acrylic monomer(s) functionalised with at least two acrylic groups.
4. Coated polycarbonate as claimed in claim 1, wherein the oligomer is a resin obtained by condensing a
saturated or unsaturated dicarboxylic acid with a glycol and by subsequently esterifying the terminal hydroxy
groups of the condensate with acrylic acid.
- 15 5. Coated polycarbonate as claimed in any of claims 1 to 4, wherein the N-vinyl derivative of a secondary 15
amine is N-vinyl pyrrolidone, N-vinyl caprolactain, N-vinyl-N-methyl acetamide, N-vinyl-N-ethyl propiona-
mide or N-vinyl-N-methyl propionamide.
6. Coated polycarbonate as claimed in claim 1, substantially as described in any of the foregoing
Examples.
- 20 7. A process for forming a coating on a surface of polycarbonate, which comprises coating the surface 20
with a mixture of (a) an oligomer or reactive resin having a molecular weight of from 400 to 4000 and
containing at least two acrylic groups, and (b) an N-vinyl derivative of a linear or cyclic secondary amide; and
copolymerising the components of the mixture, in the presence of a photoinitiator, by exposure of the
mixture to radiation.
- 25 8. A process according to claim 7, wherein the amount of component (b) in the mixture is from 5 to 60% 25
by weight, based on the weight of the mixture.
9. A process according to claim 7 or 8, wherein the photoinitiator is benzoin isopropyl ether, benzoin
ethyl ether, benzyl dimethyl ketal, benzophenone, 2,2-dimethyl-2-phenyl acetophenone, 2-
chlorothioxanthone or anthraquinone.
- 30 10. A process according to any of claims 7 to 9, wherein the radiation is UV radiation. 30
11. A process according to any of claims 7 to 10, wherein the mixture contains a reactive compound
having a molecular weight of less than 400 and containing at least one functional group of acrylate type,
methacrylate type, maleate type or fumarate type.
12. A process according to claim 7, substantially as described in any of the foregoing Examples.
- 35 12. Coated polycarbonate prepared by a process according to any of claims 7 to 12. 35