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(54) **Titre :** UTILISATION DE COMPOSITION DE REVETEMENT EN VUE DE REVETIR L'ENDOS D'UNE PELLICULE D'UN MODULE PHOTOVOLTAIQUE ET MODULE PHOTOVOLTAIQUE

(54) **Title:** USE OF A COATING COMPOSITION TO COAT THE BACKING FILM OF A PHOTOVOLTAIC MODULE, AND PHOTOVOLTAIC MODULE

(57) **Abrégé/Abstract:**

The invention relates to the use of a coating agent for coating the rear face film of a photovoltaic module. The coating agent is a two-component coating agent comprising a resin component (A) and a crosslinker component (B). The resin component (A) contains a1) a polyester having a hydroxyl number of 60 to 300 mg KOH/g and a glass transition temperature (T_g) of -65 °C to 50 °C, a2) a poly(meth)acrylate(co)polymer having a hydroxyl number of 50 to 250 mg KOH/g and a glass transition temperature of -65 °C to 50 °C, a3) pigments and/or fillers, a4) lacquer additives, a5) optionally a light stabilizer, a6) a phosphoric acid ester and a7) organic solvents. The crosslinker component (B) contains b1) a polyisocyanate and b2) optionally organic solvents. The invention also relates to a corresponding photovoltaic module.

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(54) Title: USE OF A COATING AGENT FOR COATING THE REAR FACE FILM OF A PHOTOVOLTAIC MODULE AND PHOTOVOLTAIC MODULE

(54) Bezeichnung : VERWENDUNG EINES BESCHICHTUNGSMITTELS ZUR BESCHICHTUNG DER RÜCKSEITENFOLIE EINES PHOTOVOLTAIKMODULS UND PHOTOVOLTAIKMODUL

(57) Abstract: The invention relates to the use of a coating agent for coating the rear face film of a photovoltaic module. The coating agent is a two-component coating agent comprising a resin component (A) and a crosslinker component (B). The resin component (A) contains a1) a polyester having a hydroxyl number of 60 to 300 mg KOH/g and a glass transition temperature (T_g) of -65 °C to 50 °C, a2) a poly(meth)acrylate(co)polymer having a hydroxyl number of 50 to 250 mg KOH/g and a glass transition temperature of -65 °C to 50 °C, a3) pigments and/or fillers, a4) lacquer additives, a5) optionally a light stabilizer, a6) a phosphoric acid ester and a7) organic solvents. The crosslinker component (B) contains b1) a polyisocyanate and b2) optionally organic solvents. The invention also relates to a corresponding photovoltaic module.

(57) Zusammenfassung: Die Erfindung betrifft die Verwendung eines Beschichtungsmittels zur Beschichtung der Rückseitenfolie eines Photovoltaikmoduls. Das Beschichtungsmittel ist ein 2-Komponenten-Beschichtungsmittel, das eine Harzkomponente (A) und eine Vernetzerkomponente (B) umfasst. Die Harzkomponente (A) enthält a1) einen Polyester mit einer Hydroxylzahl von 60 bis 300 mg KOH/g und einer Glasübergangstemperatur (T_g) von -65°C bis 50°C, a2) ein Poly(meth)acrylat(co)polymer mit einer Hydroxylzahl von 50 bis 250 mg KOH/g und einer Glasübergangstemperatur von -65°C bis 50°C, a3) Pigmente und/oder Füllstoffe, a4) Lackadditive, a5) ggf. ein Lichtschutzmittel, a6) einen Phosphorsäureester, und a7) organisches Lösemittel. Die Vernetzerkomponente (B) enthält b1) ein Polyisocyanat und b2) ggf. organisches Lösemittel. Die Erfindung betrifft auch ein entsprechendes Photovoltaikmodul.

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BASF Coatings GmbH
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Use of a coating composition to coat the backing film of a photovoltaic module, and photovoltaic module

The present invention relates to the use of a coating composition for coating the backing film of a photovoltaic module, and to a photovoltaic module having a coated backing film.

Photovoltaic modules generally have a glass cover layer on their front. Beneath the cover layer there is an elastic layer in which solar cells are embedded. To protect against mechanical damage and to protect against weathering effects, the back of the photovoltaic module finishes with a plate or a backing film. At the sides, the layer system described is closed off with a frame, which gives the module the necessary mechanical stability and also prevents penetration of moisture or dust.

The backing film, also referred to as barrier film, may consist of a multi-ply laminate with, for example, a polyethylene terephthalate core. The core is laminated on either side with a film, consisting of polyvinyl fluoride or polyvinylidene fluoride, for example. Also possible is the use of a single-ply, unlaminated film as backing film. In this case the film in question may be a polyethylene terephthalate film.

To enhance the protection from weathering it is usual to coat the single-ply or multi-ply backing film, at least on the side which lies on the outside in the completed module, with a coating composition.

Known from international patent applications WO 2013/173629 A1 is a backing film for a photovoltaic module that has a coating on its outside, this coating comprising a fluoropolymer resin and a crosslinking agent. The patent application does include acrylate resins and polyurethanes as suitable polymer resins. No details of the composition of such resins are given, however. The resins are preferably fluoropolymer resins, which to improve the adhesion include at least one acid group. Resins containing fluorine impose a burden on the environment in their preparation, in their processing and especially in their disposal.

It is an object of the present invention to specify an eco-friendly alternative to fluorine-containing resins that nevertheless results in good weathering stability and in effective adhesion to the film base.

This object is achieved in accordance with the invention through the use of a coating composition for coating the backing film of a photovoltaic module, the coating composition being a 2-component coating composition comprising a resin component (A) and a crosslinker component (B), the resin component (A) comprising

a1) 3 to 20 wt%, based on the nonvolatile fraction of the resin component, of a polyester having a hydroxyl number of 60 to 300 mg KOH/g and a glass transition temperature T_g of -65°C to 50°C,

a2) 10 to 40 wt%, based on the nonvolatile fraction of the resin component, of a poly(meth)acrylate (co)polymer having a hydroxyl number of 50 to 250 mg KOH/g and a glass transition temperature of -65°C to 50°C,

a3) 40 to 86 wt%, based on the nonvolatile fraction of the resin component, of pigment and/or fillers,

a4) 0.1 to 10 wt%, based on the nonvolatile fraction of the resin component, of coating additives,

a5) 0 to 6 wt%, based on the nonvolatile fraction of the resin component, of a light stabilizer,

a6) 0.01 to 1 wt%, based on the nonvolatile fraction of the resin component, of phosphoric esters of the general formula

$$PO\ (OR)_n\ (OH)_m,$$

in which

$n = 1 - 3$,

$m = 0 - 2$, and

$n + m = 3$,

R is selected from the group consisting of straight-chain or branched alkyl radicals having 1 to 16 carbon atoms, which may be substituted by aromatic radicals and/or may contain ether oxygen atoms (-O-), and aromatic radicals, which may be substituted by alkyl radicals having 1 to 6 carbon atoms, where if n= 2 or 3 the radicals R may be identical or different, the sum total of constituents a1) to a6) being 100 wt%, and

a7) 20 to 50 wt%, based on the total weight of the resin component (A), of organic solvent, and

the crosslinker component (B)

b1) 30 to 100 wt% polyisocyanate and

b2) 0 to 70 wt% of organic solvent, the sum total of the constituents b1) and b2) being 100 wt%. The hydroxyl number is determined according to DIN 53240-2 and the glass transition temperature Tg by means of dynamic scanning calorimetry DSC according to DIN 53765. The nonvolatile fraction (NVF) is determined according to DIN EN ISO 3251 under the following test conditions: test duration 60 min, test temperature 150°C and initial mass 1.5 g +/- 0.1 g.

The coating composition used for the coating of the backing film is known per se. It is used, for example, in automotive refinishing and in original (OEM) finishing, and also in the refinishing of trucks and construction machinery. It was surprising that this coating composition is suitable for the coating of backing films of photovoltaic modules and results in high weathering resistance and effective adhesion to the films.

Suitable phosphoric esters are, for example, dibutyl hydrogenphosphate, butyl dihydrogenphosphate, 2-ethylhexyl dihydrogenphosphate, phenyl dihydrogenphosphate, benzyl dihydrogenphosphate, 2-ethoxybutyl dihydrogenphosphate and the like. Dialkyl hydrogenphosphates and alkyl dihydrogenphosphates are preferred. Mixtures of phosphoric esters may also be used.

Advantageous embodiments of the invention are apparent from the dependent claims.

The organic solvents present in the resin component (A) and in the crosslinker component (B) are, advantageously, acetates, such as butyl acetate or ethyl acetate, or aromatics such as solvent naphtha or toluene.

The backing film consists advantageously of polyethylene terephthalate, polyvinyl fluoride, or polyvinylidene fluoride.

The outside of the backing film is advantageously coated. It is also possible, however, to coat the outside and the inside of the backing film.

The wet-film thickness of the coating is advantageously 10 to 40 μm.

The coating composition is applied advantageously by spraying, rolling, or knife coating to the backing film.

Following the application of the coating composition, it is cured advantageously at a temperature of 110 to 150°C within a period of 20 to 40 s.

The invention also relates to a photovoltaic module having a coated backing film, the coating having been produced by application and curing of a 2-component coating composition comprising a resin component (A) and a crosslinker component (B), the resin component (A) comprising a1) 3 to 20 wt%, based on the nonvolatile fraction of the resin component, of a polyester having a hydroxyl number of 60 to 300 mg KOH/g and a glass transition temperature T_g of -65°C to 50°C,

a2) 10 to 40 wt%, based on the nonvolatile fraction of the resin component, of a poly(meth)acrylate (co)polymer having a hydroxyl number of 50 to 250 mg KOH/g and a glass transition temperature of -65°C to 50°C,

a3) 40 to 86 wt%, based on the nonvolatile fraction of the resin component, of pigment and/or fillers,

a4) 0.1 to 10 wt%, based on the nonvolatile fraction of the resin component, of coating additives,

a5) 0 to 6 wt%, based on the nonvolatile fraction of the resin component, of a light stabilizer,

a6) 0.01 to 1 wt%, based on the nonvolatile fraction of the resin component, of phosphoric esters of the general formula

$$PO\ (OR)_n\ (OH)_m,$$

in which

$n = 1 - 3,$

$m = 0 - 2$, and

$n + m = 3$,

R is selected from the group consisting of straight-chain or branched alkyl radicals having 1 to 16 carbon atoms, which may be substituted by aromatic radicals and/or may contain ether oxygen atoms (-O-), and aromatic radicals, which may be substituted by alkyl radicals having 1 to 6 carbon atoms, where if n= 2 or 3 the radicals R may be identical or different, the sum total of constituents a1) to a6) being 100 wt%, and

a7) 20 to 50 wt%, based on the total weight of the resin component (A), of organic solvent, and
the crosslinker component (B)

b1) 30 to 100 wt% polyisocyanate and

b2) 0 to 70 wt% of organic solvent, the sum total of the constituents b1) and b2) being 100 wt%.

Advantageous embodiments of the photovoltaic module are apparent from the dependent claims.

The backing film consists advantageously of polyethylene terephthalate.

Advantageously at least the outside of the backing film is coated. It is also possible, however, for the outside and the inside of the backing film to be coated.

The dry-film thickness of the coating is advantageously 20 to 35 µm.

The invention is illustrated in more detail below, using working examples.

Preparation example for resin component A:

The component A can be manufactured by the following preparation method. This method consists of a number of steps.

In the first step, the binders, optionally a portion of the solvents, and the entire pulverulent pigments are processed to millbase in a suitable batching vessel. For this processing, first the two binders, the acrylate, and the polyester are charged to a drum. If the viscosity of the binders makes it necessary to do so, a portion of the solvent can be added, in order to prevent excessive introduction of air during stirring. The mixture is stirred for about 10 min with slight vortexing, using an inclined blade stirrer, until the resulting mixture is homogeneous and has no streaks or the like.

Thereafter the silica is added cautiously with stirring. When the components have been wetted, the mixture can be dissolver-treated for about 30 minutes until the paste is free from lumps. The temperature of the millbase here must not exceed 50°C.
Subsequently, the remainder of the pulverulent pigments are added, with slow stirring. The mixture, which has a high viscosity, is dissolver-treated again until the resulting paste is homogenous to the eye. In order to prevent a temperature increase above 50°C, the batch must be cooled as and when necessary.

Toward the end of the dispersing time, the remaining solvent is added, to dilute the millbase batch appropriately for dispersing by circulation in an agitator mill. In the mill, the millbase is circulated until a fineness of grind of 10-15 μm is attained. Here as well, it may be necessary to attach a water cooling facility. The fineness of grind is determined using a Hegmann 50 gage.

The discharged millbase can then be made up with the appropriate weight % of additives. These additives are likewise added with stirring.

Preparation of the coating composition

Component A is adjusted by addition of component B (HDI trimer) and the solvent for adjusting the viscosity for processability. The amount of isocyanate selected should be such as to enable ideally the attainment of 20% overcrosslinking. The completed 2-component mixture has a pot life of >5 hours. This means that no earlier than after 5 hours, depending on the amount of solvent added, from the moment of mixing, is a doubling in the flow time from a DIN 4 cup observable at 23°C. The coating composition, consequently, is fundamentally suitable for application in a roll-to-roll process. The corresponding parameters must always be determined on the specific line.

To produce a test specimen for the mechano-technological tests, ambient conditions tests, and weathering, the coating composition is knife-coated onto the appropriate substrate - PET, for example. The knife coater must be selected so as to achieve a dry-film thickness of between 10 and 15 µm, depending on the solids. Following paint application, the test specimen is baked immediately, without flashing, in a convection oven at 150°C for 30 seconds.

Table 1: composition of the coating materials

		Example I		**Example II**	
Item	**Commercial product**	**Initial mass [g]**	**NVF-m [g]**	**Initial mass [g]**	**NVF-m [g]**
	Component A				
1	Macrynal SM 685 (OH number 77-93, OH content (NVF) 2.6%, 55% in butyl acetate as per TDS)	17	9.35	36.8	20.24
2	Desmophen 670 (OH number 115, OH content (NVF) 3.5%, 80% fraction in butyl acetate as per TDS)	5	4	5.1	4.08
3	Talco HM1	12.5	12.5	6.3	6.3
5	Zinkphosphat PZ 20	2.6	2.6	1.3	1.3
6	Blanc Fixe PLV. HD 80	16.4	16.4	8.2	8.2
7	Tiona 595	29.5	29.5	28.3	28.3
8	Baysilon OL 17	0.2	0.17	0.2	0.2
9	Duraphos BAP	0.1	0.1	0.1	0.1
10	Aerosil 200	0.6	0.6	0.3	0.3
12	Butyl acetate	16.1	0	13.4	0
	Component B				
13	Desmodur N3600 56% in butyl acetate	8.9	5.0	15.27	8.4

	sum total	108.9	80.204	115.27	77.42

Macrynal SM 685:	OH-functional acrylate resin
Desmophen 670:	OH-functional polyester
Talco HM1:	talc
Zinkphosphat PZ 20:	zinc phosphate
Blanc Fixe PLV.HD 80:	barium sulfate
Tiona 595:	titanium dioxide (rutile type)
Baysilon OL 17:	polyether-modified polysiloxane
Duraphos BAP:	mixture of dibutyl hydrogenphosphate (48-57%) and butyl dihydrogenphosphate (40-48%)
Aerosil 200:	hydrophilic fumed silica
Desmodur N3600:	polyfunctional aliphatic polyisocyanate resin based on hexamethylene diisocyanate

Testing of the coating composition

After cooling, freedom from tack is verified by the Zapon Tack Test (ZTT). For this test, a strip of aluminum with a thickness of about 0.5 mm, a width of 2.5 cm, and a length of about 11 cm is bent in a 110° angle so as to produce an area of 2.5 x 2.5 cm. The long side of the metal is bent by about 15° for a further 2.5 cm in such a way that the metal is just held in balance by a 5 g weight placed centrally on the square area. For the measurement of the freedom from tack by the ZTT method, the bent metal, directly after the test specimen has cooled, is placed on the paint film and loaded with a 100 g weight for 30 seconds. After the weight has been removed, the paint is considered tack-free if the metal angle falls over within 5 seconds. The baked paint system (variants A and B) is tack-free after 30 seconds at 150°C.

In addition, a blocking test was carried out. For this purpose, a further PET film was placed all over the surface and loaded briefly (~10 seconds) with a 2 kg weight. If the applied film could be removed thereafter without any resistance, the drying was scored as OK. According to this test, the drying of the paint system (variants A and B) is OK.

For further tests, the test specimen is aged in a convection oven at 150°C for 20 minutes. This accelerates the process of aftercrosslinking, which would occur in the case of the storage of the applied rolls prior to further processing.

The test specimen is thereafter subjected to a boiling test. For this purpose, fully demineralized water in a stainless steel bowl is brought to boiling on a hob plate, i.e., to a test temperature of 100°C, and the test specimen is introduced for two 8-hour cycles so that it is completely under water. After each cycle, the test specimen is removed, dried, and inspected. There must be no visible changes to the paint surface. This is followed by a DIN ISO 2409 cross-cut procedure, directly after exposure and again after 1 hour of regeneration. The lattice spacing is set at 1 mm in line with the plastic substrate and the low paint film layer thickness. The cross-cut classification is to be < 2. Testing of variants A and B produced a cross-cut classification of 0 after each cycle, both directly after exposure, and after 1 hour of regeneration. The inspection also yields no adverse comments.

Following the successful quick test, long-term ambient conditions tests are conducted, firstly in the form of a constant condensation condition (CC) test according to DIN EN ISO 6270-2. The test specimen is stored for 240 hours at 40°C +/- and at a relative humidity of 100%, with condensation being made to form on the test specimen.

Secondly, the test specimen is stored in an individually adjustable conditioning cabinet. The parameters selected, 504 hours at 85°C and 85% relative humidity, are intended to approximate to the conditions of the DIN EN ISO 60068 damp heat test required in the photovoltaics industry.

After exposure on both sets of conditions, the paint film is tested in the same way as after the boiling test: verification of adhesion by cross-cut directly after exposure and after 1 hour of regeneration (target cross-cut classification <2). The paint film is also inspected, and here again must not show any visual changes. After both tests, variants A and B show no changes at all after inspection. Both directly after exposure and after 1 hour of regeneration, the cross-cut classifications were 0.

Lastly, the weathering stability was tested in accordance with SAE J2527_04 in the WOM-CAM. The total test duration is 3000 hours. Evaluation takes place after each 1000 hours by means of colorimetric measurement relative to the unexposed standard, and inspection of the surface. The total color difference after 3000 hours by comparison with the unexposed sample has a mDE* of 1.0.

What is claimed is:

1. The use of a coating composition for coating the backing film of a photovoltaic module, wherein the coating composition is a 2-component coating composition comprising a resin component (A) and a crosslinker component (B), the resin component (A) comprising

a1) 3 to 20 wt%, based on the nonvolatile fraction of the resin component, of a polyester having a hydroxyl number of 60 to 300 mg KOH/g and a glass transition temperature T_g of -65°C to 50°C,

a2) 10 to 40 wt%, based on the nonvolatile fraction of the resin component, of a poly(meth)acrylate (co)polymer having a hydroxyl number of 50 to 250 mg KOH/g and a glass transition temperature of -65°C to 50°C,

a3) 40 to 86 wt%, based on the nonvolatile fraction of the resin component, of pigment and/or fillers,

a4) 0.1 to 10 wt%, based on the nonvolatile fraction of the resin component, of coating additives,

a5) 0 to 6 wt%, based on the nonvolatile fraction of the resin component, of a light stabilizer,

a6) 0.01 to 1 wt%, based on the nonvolatile fraction of the resin component, of phosphoric esters of the general formula

$$PO(OR)_n(OH)_m,$$

in which

$n = 1 - 3$,

$m = 0 - 2$, and

$n + m = 3$,

R is selected from the group consisting of straight-chain or branched alkyl radicals having 1 to 16 carbon atoms, which may be substituted by aromatic radicals and/or may contain ether oxygen atoms (-O-), and aromatic radicals, which may be substituted by alkyl radicals having 1 to 6 carbon atoms, the sum total of constituents a1) to a6) being 100 wt%, and

a7) 20 to 50 wt%, based on the total weight of the resin component (A), of organic solvent, and

the crosslinker component (B)

b1) 30 to 100 wt% polyisocyanate and

b2) 0 to 70 wt% of organic solvent, the sum total of the constituents b1) and b2) being 100 wt%.

2. The use as claimed in claim 1, wherein the organic solvents present in the resin component (A) and in the crosslinker component (B) are acetates or aromatics.

3. The use as claimed in claim 1 or 2, wherein the backing film consists of polyethylene terephthalate, polyvinyl fluoride, or polyvinylidene fluoride.

4. The use as claimed in claim 1 to 3, wherein the outside of the backing film is coated.

5. The use as claimed in claim 1 to 3, wherein the outside and the inside of the backing film are coated.

6. The use as claimed in claim 1 to 5, wherein the wet-film thickness of the coating is 10 to 40 µm.

7. The use as claimed in claim 1 to 6, wherein the coating composition is applied by spraying, by rolling, or knife coating to the backing film.

8. The use as claimed in claim 1 to 7, wherein the

coating composition is cured at a temperature of 110 to 150°C within from 20 to 40 s.

9. A photovoltaic module having a coated backing film, the coating having been produced by application and curing of a coating composition, wherein the coating composition is a 2-component coating composition comprising a resin component (A) and a crosslinker component (B), the resin component (A) comprising

a1) 3 to 20 wt%, based on the nonvolatile fraction of the resin component, of a polyester having a hydroxyl number of 60 to 300 mg KOH/g and a glass transition temperature T_g of -65°C to 50°C,

a2) 10 to 40 wt%, based on the nonvolatile fraction of the resin component, of a poly(meth)acrylate (co)polymer having a hydroxyl number of 50 to 250 mg KOH/g and a glass transition temperature of -65°C to 50°C,

a3) 40 to 86 wt%, based on the nonvolatile fraction of the resin component, of pigment and/or fillers,

a4) 0.1 to 10 wt%, based on the nonvolatile fraction of the resin component, of coating additives, a5) 0 to 6 wt%, based on the nonvolatile fraction of the resin component, of a light stabilizer,

a6) 0.01 to 1 wt%, based on the nonvolatile fraction of the resin component, of phosphoric esters of the general formula

$$PO\ (OR)_n\ (OH)_m,$$

in which

$n = 1 - 3,$

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$n + m = 3,$

R is selected from the group consisting of straight-chain or branched alkyl radicals having 1 to 16 carbon atoms, which may be substituted by aromatic radicals and/or may contain ether oxygen atoms (-O-), and aromatic radicals, which may be substituted by alkyl radicals having 1 to 6 carbon atoms, the sum total of constituents a1) to a6) being 100 wt%, and

a7) 20 to 50 wt%, based on the total weight of the resin component (A), of organic solvent, and

the crosslinker component (B)

b1) 30 to 100 wt% polyisocyanate and

b2) 0 to 70 wt% of organic solvent, the sum total of the constituents b1) and b2) being 100 wt%.

10. The photovoltaic module as claimed in claim 9, wherein the backing film consists of polyethylene terephthalate, polyvinyl fluoride, or polyvinylidene fluoride.

11. The photovoltaic module as claimed in claim 9 or 10, wherein the outside of the backing film is coated.

12. The photovoltaic module as claimed in claim 8 to 9, wherein the outside and the inside of the backing film are coated.

13. The photovoltaic module as claimed in claim 8-12, wherein the dry-film thickness of the coating is 20 to 35 µm.