

(19) **DANMARK**

(10) **DK/EP 2238210 T3**



(12)

Oversættelse af
europæisk patentskrift

Patent- og
Varemærkestyrelsen

-
- (51) Int.Cl.: **C 09 D 175/04 (2006.01)** **C 08 G 18/10 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2015-09-21**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2015-08-12**
- (86) Europæisk ansøgning nr.: **09705026.4**
- (86) Europæisk indleveringsdag: **2009-02-02**
- (87) Den europæiske ansøgnings publiceringsdag: **2010-10-13**
- (86) International ansøgning nr.: **NL2009000020**
- (87) Internationalt publikationsnr.: **WO2009096778**
- (30) Prioritet: **2008-02-01 NL 1034986**
- (84) Designerede stater: **AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR**
- (73) Patenthaver: **Durable Compliant Coatings B.V., Zilverenberg 9, 5234 GL 's-Hertogenbosch, Holland**
- (72) Opfinder: **DUIJGHUISEN, Gerardus, Johannes, Jozef, Leenhoflaan 1A, NL-5282 PV Boxtel, Holland**
BROEDERS, Johannes, Petrus, Rocus, Maria, Van Beverenlaan 5, 4931 HW GEERTRUIDENBERG, Holland
- (74) Fuldmægtig i Danmark: **Hegner & Partners A/S, Banemarksvej 50, 2605 Brøndby, Danmark**
- (54) Benævnelse: **MALINGSAMMENSÆTNING**
- (56) Fremdragne publikationer:
EP-A- 1 038 897
EP-A2- 1 277 876
WO-A1-2005/087874
US-A- 4 138 299
US-A1- 2005 106 395
US-A1- 2005 119 438
US-A1- 2005 282 933
US-A1- 2006 046 068

DESCRIPTION

[0001] The present invention relates to an object of which at least one surface is coated with at least one layer of a paint composition comprising a component A, being a basic binder, and a component B, being an isocyanate compound.

[0002] Such a paint composition is known from US patents US 6.833.424 and US 7.169.876, which disclose a two-component coating composition comprising a polyisocyanate (in an excess amount) combined with a polyaspartic ester.

[0003] Such a paint composition is referred to as a "dual cure" composition. This relates to the two separate reaction mechanisms that play a role in the curing of the paint composition, viz. in the first place the chemical crosslinking (also known as "fast curing" on account of the short reaction time) that results from the reaction between the -NH group of the polyaspartic ester and the isocyanate group of the polyisocyanate. The second reaction mechanism playing a role is the so-called wet curing of the excess amount of polyisocyanate when it comes into contact with water.

[0004] The coating composition according to these two US patents consists of the combination of a polyaspartic ester with an amount of polyisocyanate that is greater than the normal stoichiometric amount.

[0005] Such compositions combine the fast curing properties of the reaction of the polyisocyanate with the polyaspartic ester with the slower wet curing properties of the reaction of the polyisocyanate with moisture. This curing results in the formation of urea compounds according to the aforementioned two reaction mechanisms.

[0006] Polyisocyanates as used in the aforementioned US patents are typically obtained from isocyanate monomers.

[0007] A polymeric coating is disclosed in EP 1 038 897. Due to the high viscosity of such a paint coating, said coating is only suitable for thick film technologies. A drawback of this technology is the fact that the applied coating does not degas easily, so that gas bubbles may remain behind in the paint coating, which adversely affects the quality of the coating. In thick film technologies, one-layer coatings having a thickness of at least 250 µm to a few millimetres are usually applied.

[0008] US 2005/282,933 discloses a coating comprising a modified polyisocyanate and a polyaspartic acid. Said coating has an index of 1.05. Said polyisocyanates have an NCO weight percentage of 23 wt.%. A coating according to said US application is suitable for use as road marking paint.

[0009] US 2006/046068 discloses a coating comprising a prepolymer and polyaspartic acid having an index of 1.05. A prepolymer according to said application is prepared from an isoforon diisocyanate having an NCO weight percentage of 37.8 wt.%.

[0010] One object of the present invention is to provide a paint composition having improved drying properties.

[0011] Another object of the present invention is to provide a paint composition having good adhesion to the surface to which the paint composition will be applied.

[0012] Yet another object of the present invention is to provide a paint composition that offers excellent protection against weather influences.

[0013] It is also an object of the present invention to provide a paint composition that degases easily.

[0014] One or more of the above objects is/are achieved by the present paint composition according to claim 1.

[0015] Via the use of the isocyanate prepolymer, the present invention provides the possibility of using other basic binders as component A in the paint composition besides polyaspartic acid (component A). That way the paint composition can be enhanced with special properties.

[0016] Isocyanate prepolymers are typically obtained in a reaction between polyisocyanates and polyols. Isocyanate prepolymers have a so-called NCO content of maximally 16 wt.%. The NCO weight percentage indicates the percentage of the molecular weight of the isocyanate prepolymers that consists of NCO groups. NCO stands for isocyanate group (N= nitrogen; C= carbon; O= oxygen). Polyisocyanates, on the other hand, have an NCO weight percentage in excess of 16 wt.%.

[0017] Component A according to the present invention is selected from the group consisting of hydroxyacrylate, polyaspartic ester, polyester polyol, epoxy, silicone epoxide, and one or more combinations hereof.

[0018] The present paint composition is a composition whose index, being the ratio between reactive groups of component B and the reactive groups of component A, ranges between 1.5 and 3.0.

[0019] The paint composition according to the present invention comprises a basic binder (component A) which is in a certain ratio caused to react with an isocyanate prepolymer (component B). The ratio is such that the reactive groups of component B are present in an amount that is higher than the stoichiometric amount relative to the reactive groups of the basic binder, viz. index ≥ 1.5 . The use of an excess amount, resulting in an index greater than 1, is also known as overindexing.

[0020] Some examples of suitable basic components (component A) will follow below.

[0021] Examples of a hydroxyacrylate are the commercially available Desmophen A160, Desmophen A365 (both supplied by Bayer) and Setalux 1152 (supplied by Nuplex Resins). Hydroxyacrylate contains hydroxyl groups as its reactive groups.

[0022] Examples of a polyaspartic ester are the commercially available Desmophen NH1420 and NH1520 (supplied by Bayer). Polyaspartic ester contains amine groups as its reactive groups.

[0023] Examples of a polyester polyol are the commercially available Desmophen 670, 651 and RD181 (supplied by Bayer). Polyester polyol contains hydroxyl groups as its reactive groups.

[0024] Examples of an epoxy are the commercially available Epikote 1007, 1009, 1001 and 828 (Hexion Specialty Chemicals). Epoxy contains epoxy groups as its reactive groups.

[0025] Examples of a silicone epoxide are the commercially available Silikofтал ED and Silikopon EF (both supplied by Degussa). Silicone epoxide contains epoxy groups as its reactive groups.

[0026] The index ranges between 1.5 and 3.0 because the best properties are obtained in this range, with respect to for example tack-free time and adhesion (see the examples). The index preferably ranges between 1.7 and 3.0, more preferably between 1.7 and 2.7, most preferably between 1.7 and 2.5. If component A has been selected from the group comprising hydroxyacrylate and polyester polyol, it is preferable for the index to range between 1.7 and 3.0, more preferably between 1.7 and 2.7, most preferably between 1.7 and 2.5. The inventors have found that within these ranges the paint compositions according to the present invention in particular have good properties in the fields of tack-free time, adhesion and gloss properties (see the examples).

[0027] The isocyanate prepolymers used in the present invention are preferably aromatic isocyanate prepolymers, aliphatic isocyanate prepolymers or one or more combinations thereof. Use of an aliphatic isocyanate prepolymer in the present paint composition results in a paint coating having improved durability. Use of an aromatic isocyanate prepolymer in the paint composition results in faster curing of the paint coating. By using both aliphatic and aromatic isocyanate prepolymers in the paint composition, the favourable properties of both isocyanate prepolymers will be combined.

[0028] The isocyanate prepolymers used in the present invention have an NCO weight percentage of maximally 16 wt.%. The present inventor has found that a paint composition comprising such prepolymers having the aforesaid NCO weight percentages produces good results regarding adhesion, tack-free time, gloss properties and film formation compared to paint compositions based on isocyanate (see the examples).

[0029] The present isocyanate prepolymers have a functionality of more than 2.0, which leads to good results as regards adhesion, tack-free time, gloss properties and film formation in comparison with paint compositions based on isocyanate polymers having a functionality of maximally 2.0.

[0030] Some commercially available aromatic isocyanate prepolymers are known under the names of Desmodur E21, E23, E28 and E1361 (supplied by Bayer). Some examples of commercially available aliphatic isocyanate prepolymers are known under the names of Desmodur E3265 and E3370 (supplied by Bayer).

[0031] It is preferable for the composition according to the present invention to comprise one or more aliphatic isocyanate prepolymers on account of the improved durability.

[0032] As already mentioned above, it is possible to use a mixture of different basic binders as component A. The use of such

mixtures will make it possible to obtain different paint compositions, each having different properties that are advantageous under different conditions. This gives the paint composition according to the present invention a broad range of application.

[0033] Hydroxyacrylate is particularly suitable for use as a basic binder for obtaining a top layer having good weather resistance. It can also be used to obtain corrosion-resistant single-layer systems having excellent adhesion to different surfaces.

[0034] Polyaspartic ester is particularly suitable for use as a basic binder to obtain so-called "super high solids" top coats having good weather resistance. There are possible formulations having a solids content of more than 60%, up to even more than 90 volume %.

[0035] Polyester polyol is particularly suitable for use as a basic binder to obtain top coats having a very high gloss and excellent flow behaviour.

[0036] Epoxy is particularly suitable for use as a basic binder to obtain rust-resistant primers and/or intermediate coats having very short tack-free times. Epoxy moreover allows excellent adhesion to moist, poorly cleaned substrates and/or surfaces.

[0037] Silicone epoxide is particularly suitable for obtaining "super high solids" top coats having excellent weather resistance, chemical resistance and flexibility, and corrosion-resistant intermediate coats.

[0038] The paint composition according to the present invention may also contain certain components such as pigments, colour and functional pigments (for example for obtaining corrosion-resistant properties), surfactants, anti-foaming agents, solvents, diluents, fillers, carrier materials, binders, plasticizers, drying agents, catalysts, preservatives, wetting agents, barrier-strengthening agents such as clay and mica, and capillary-active substances, agents influencing the viscosity and softeners.

[0039] The paint composition according to the present invention preferably has a viscosity of lower than or equal to 5 Pa.s (50 poise) at room temperature (25 °C).

[0040] As a result of the low viscosity, the applied paint composition can degas easily after being applied to the desired surface. The advantage of proper degassing is that the gas bubbles that have formed can easily escape due to the low viscosity of the composition. Paint coatings in which said gas bubbles remain behind are sensitive to, for example, moisture, cold, heat and other weather conditions. As a result of the presence of said gas bubbles, cracks may for example form in the paint coating under the influence of such conditions. Furthermore, said paint coatings will be easily damaged when an object impacts with the paint coating. Since the paint coating consisting of the paint composition according to the present invention does not contain any gas bubbles, because gas bubbles can easily escape, the paint coating is thus less sensitive to the aforesaid conditions, and the paint coating will less easily crack or be damaged.

[0041] The paint composition according to the present invention more preferably has a viscosity of lower than or equal to 3 Pa.s (30 poise) at room temperature, even more preferably a viscosity lower than or equal to 2 Pa.s (20 poise).

[0042] As a result of the low viscosity of the paint composition according to the present invention, said paint composition can be applied to a surface as a thin film. A single layer of the paint composition has a thickness of maximally 150 µm, preferably maximally 100 µm. Since the paint composition can be applied as a thin film, less paint composition is required for coating a surface in comparison with a paint composition having a higher viscosity, which is advantageous from an economic point of view.

[0043] The present invention also relates to the use of the present paint composition as a paint or top coat.

[0044] The present paint composition is suitable for application to surfaces that may or may not have been treated, such as metal, for example steel and aluminium, plastics, for example PVC, and wood. It will of course be clear that this list is not limitative and that other surfaces are also possible.

[0045] The present invention thus relates to an object of which at least one surface is coated with at least one layer of the present paint composition.

[0046] The layer of paint on the object concerned has a loss of gloss that ranges between 0 and 10, in particular 1-8, measured according to ISO11507:1997 (after 1000 hours of irradiation with UV-A light).

[0047] It is also preferable for the layer of paint on the object concerned to have a flexibility ranging between 1 and 9 mm

measured according to ISO1520:1999. At a lower flexibility the layer of paint may be brittle, resulting in insufficient durability.

[0048] In addition to that the layer of paint on the present object has a thickness of maximally 150 µm, preferably maximally 100 µm, if one layer is used.

[0049] The present invention will be further elucidated with reference to a number of examples.

Examples

[0050] Table 1 describes a number of paint compositions which the present inventors subjected to a number of measurements whose results are shown in the subsequent Tables. Compositions according to the present invention are referred to as "example" and compositions used for comparison are referred to as "comparative example".

Table 1: Survey of examples

Example No.	Component A	Component B
Example 1 (E 1)	hydroxyacrylate	isocyanate prepolymer
Comparative example 1 (C E 1)	hydroxyacrylate	polyisocyanate
Example 2 (E 2)	polyaspartic acid	isocyanate prepolymer
Comparative example 2 (C E 2)	polyaspartic acid	polyisocyanate
Example 3 (E 3)	polyester polyol	isocyanate prepolymer
Comparative example 3 (C E 3)	polyester polyol	polyisocyanate
Example 4 (E 4)	epoxy	isocyanate prepolymer
Comparative example 4 (C E 4)	epoxy	polyamino amide
Example 5 (E 5)	silicone epoxide	isocyanate prepolymer
Comparative example 5 (C E 5)	silicone epoxide	aminosilaan

[0051] A first test carried out by the present inventors is the determination of the so-called tack-free time, viz. the drying rate of the paint. This test was carried out using a drying time recorder according to ASTM D 5895-03.

[0052] Table 2 shows the tack-free time of the various paint compositions as a function of the employed index. The paint compositions shown in Table 2 comprise a basic binder (component A) selected from the group consisting of hydroxyacrylate, polyaspartic ester, polyester polyol, epoxy or silicone epoxide.

Table 2: tack-free time (in minutes) of examples 1-5 and comparative examples 1-5 at different index values.

Index	E1	C E 1	E 2	C E 2	E 3	C E 3	E 4	C E 4	E 5	C E 5
0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 240	n.d.	< 90
1	< 30	< 60	< 10	< 30	< 45	< 90	< 120	< 300	< 90	< 120
1.3	< 45	< 90	< 10	< 45	< 60	< 150	< 120	> 360	< 90	< 240
1.5	< 60	< 150	< 10	< 45	< 60	< 240	< 120	> 360	< 120	> 360
1.7	< 60	< 240	< 15	< 45	< 90	> 360	< 150	n.d.	< 150	> 360
2	< 90	> 360	< 15	< 45	< 120	> 360	< 150	n.d.	< 150	> 360
2.2	< 120	> 360	< 20	< 60	< 150	> 360	< 150	n.d.	< 240	> 360
2.5	< 240	> 360	< 30	< 60	< 240	> 360	< 180	n.d.	< 240	> 360
3	> 360	> 360	< 30	< 120	> 360	> 360	< 180	n.d.	< 240	> 360
4	> 360	> 360	< 120	> 360	> 360	> 360	> 360	n.d.	> 360	> 360
n.d. = not determined										

[0053] The results of the tack-free time measurement clearly show that paint compositions according to the present invention have shorter tack-free times than the comparative paint compositions. This holds for both low and high indexes. The advantage of

this is that the paint dries faster, so that any additional coats of paint or lacquer can be applied sooner, or the coated object can be stacked or transported sooner. In addition, it will in many cases no longer be necessary to accelerate the drying process by means of heating, for example in an oven.

[0054] Table 3 shows the results of adhesion tests using different surfaces and paint compositions according to the present invention as a function of the index. The adhesion tests were carried out according to ISO2409:1992.

Table 3: adhesion tests

Example No.	Index	Blasted steel	Galvanized steel	Aluminium	PVC	St 2 steel#
E 1	1.0	2	1	0	1	n.d.
	1.7	4	4	2	4	n.d.
	2.0	5	4	2	4	n.d.
	2.5	5	5	4	5	n.d.
E 2	1.0	3	3	2	2	n.d.
	1.7	4	4	3	3	n.d.
	2.0	5	5	4	4	n.d.
	2.5	5	5	4	5	n.d.
E 3	1.0	2	1	0	1	n.d.
	1.7	4	4	2	4	n.d.
	2.0	5	4	2	4	n.d.
	2.5	5	5	4	5	n.d.
E 4	1.0	5	2	4	3	4
	1.7	5	4	5	4	4
	2.0	5	4	5	5	5
	2.5	5	5	5	5	5
E 5	1.0	2	1	0	1	n.d.
	1.7	4	4	2	4	n.d.
	2.0	5	4	2	4	n.d.
	2.5	5	5	4	5	n.d.

#: Steel thoroughly cleaned by hand so that it can be observed by the naked eye that the surface is free of visible oil, grease, dirt and of loose mill scale, rust, coats of paint and foreign materials.

n.d.: not determined

The following criteria were used:

0: totally unsatisfactory adhesion

1: almost totally unsatisfactory adhesion

2: partially unsatisfactory adhesion

3: unsatisfactory adhesion

4: satisfactory adhesion

5: excellent adhesion

[0055] These results clearly show that the paint compositions according to the present invention have excellent adhesion properties with respect to different substrates and/or surfaces.

[0056] Tables 2 and 3 clearly show that the paint compositions according to the present invention have better properties than comparative paint compositions. This is evident from both the tack-free times and the adhesion properties. It may hence be concluded that one or more of the objects of the present invention are achieved by the present paint compositions.

[0057] Table 4 shows the loss of gloss (angle of 60°) after 1000 hours of irradiation with UV-A light measured according to ISO11507:1997, and the water resistancy measured according to ISO2812-1:1993, method 2, of paint compositions according to the present invention. The figures given in Table 4 for loss of gloss are all the values at the beginning of the measurement (initial gloss) and at the end of the measurement, with the loss of gloss calculated from these values indicated between brackets.

Table 4: loss of gloss measured according to ISO11507:1997 and water resistancy (minutes) measured according to ISO2812-1:1993 of examples 1-4 at different index values.

Index	Loss of gloss				Water resistancy			
	E 1	E 2	E 3	E 4	E 1	E 2	E 3	E 4
1.0	92>89 (3)	90>81 (9)	91 >76 (15)	n.d.	< 15	< 5	< 20	< 20
1.3	92>90 (2)	91>85 (6)	92>82 (10)	n.d.	< 20	< 5	< 30	< 30
1.5	94>92 (2)	94>90 (4)	94>87 (7)	n.d.	< 30	< 5	< 30	< 30
1.7	94>93 (1)	94>91 (3)	94>89 (5)	n.d.	< 30	< 5	< 60	< 60
2	94>93 (1)	94>93 (1)	94>90 (4)	n.d.	< 60	< 10	< 90	< 90
2.2	94>93 (1)	94>93 (1)	94>91 (3)	n.d.	< 90	< 10	< 120	< 120
2.5	94>93 (1)	94>93 (1)	94>91 (3)	n.d.	<180	< 10	< 180	< 180
3	94>93 (1)	94>93 (1)	94>91 (3)	n.d.	> 360	< 10	> 360	> 360
4	n.d.	n.d.	n.d.	n.d.	> 360	< 30	> 360	> 360

n.d. = not determined

[0058] Table 5 shows the flexibility of compositions according to the present invention (E1 - E5). The flexibility is measured according to ISO 1520:1999, and is also referred to as "cupping".

Table 5: flexibility (in mm) measured according to ISO 1520:1999 as a function of the index.

Index	E 1	E 2	E 3	E 4	E 5
1	1	3	2	6	5
1,7	5	> 9	7	> 9	> 9
2	> 9	> 9	> 9	> 9	> 9
2,5	> 9	> 9	> 9	> 9	> 9

[0059] Table 5 clearly shows that the paint compositions according to the present invention have good flexibility at different indices.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- [US6833424B \[0002\]](#)
- [US7169876B \[0002\]](#)
- [EP1038897A \[0007\]](#)
- [US2005282933A \[0008\]](#)
- [US2006046068A \[0009\]](#)

Patentkrav

1. Objekt, på hvilket mindst én overflade er belagt med mindst ét lag af en malingsammensætning, som omfatter en bestanddel A, der er et basisbindemiddel, og en bestanddel B, der er en isocyanatpræpolymer, hvor isocyanatpræpolymeren har en NCO-vægtprocentandel på 16 vægtprocent eller derunder, og hvor bestanddel A er valgt fra gruppen bestående af hydroxyacrylat, polyasparaginsyreester, polyesterpolyol, epoxy, siliconeepoxid og en eller flere kombinationer heraf, og hvor indekset, som er forholdet mellem reaktive grupper i bestanddel B og de reaktive grupper i bestanddel A, er på mellem 1,5 og 3,0, og kendetegnet ved, at laget har en tykkelse på maksimalt 150 µm, og at laget har et glanstab i intervallet fra 0 til 10, som målt i henhold til ISO11507:1997, efter 1000 timers bestråling med UVA-lys.
2. Objekt ifølge krav 1, hvor forholdet mellem reaktive grupper i bestanddel B og de reaktive grupper i bestanddel A af malingsammensætningen er på mellem 1,7 og 3,0, mere fortrinsvis mellem 1,7 og 2,7, mest fortrinsvis mellem 1,7 og 2,5.
3. Objekt ifølge et eller flere af de foregående krav, kendetegnet ved, at bestanddel A er hydroxyacrylat og/eller polyesterpolyol, og at indekset er på mellem 1,7 og 3,0, mere fortrinsvis mellem 1,7 og 2,7, særligt fortrinsvis mellem 1,7 og 2,5.
4. Objekt ifølge et hvilket som helst eller flere af kravene 1-3, kendetegnet ved, at bestanddel B af malingsammensætningen er en aromatisk isocyanatpræpolymer og/eller en alifatisk isocyanatpræpolymer.
5. Objekt ifølge krav 4, kendetegnet ved, at bestanddel B af malingsammensætningen er en alifatisk isocyanatpræpolymer.

6. Objekt ifølge et hvilket som helst af de foregående krav, kendetegnet ved, at laget har en fleksibilitet i intervallet fra 1 til 9 mm, som målt i henhold til ISO1520:1999.

- 5 7. Anvendelse af en malingsammensætning, som omfatter en bestanddel A, der er et basisbindemiddel, og en bestanddel B, der er en isocyanatpræpolymer, hvor isocyanatpræpolymeren har en NCO-vægtprocentandel på 16 vægtprocent eller derunder, og hvor bestanddel A er
- 10 valgt fra gruppen bestående af hydroxyacrylat, polyasparaginsyreester, polyesterpolyol, epoxy, siliconeepoxid og en eller flere kombinationer heraf, og hvor indekset, som er forholdet mellem reaktive grupper i bestanddel B og de reaktive grupper i bestanddel A, er på mellem 1,5 og 3,0, som et maling-
- 15 eller dæklag med en tykkelse på maksimalt 150 µm, og hvor laget har et glanstab i intervallet fra 0 til 10, som målt i henhold til ISO11507:1997, efter 1000 timers bestråling med UVA-lys.