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(54) Title: PROCESS FOR THE PREPARATION OF A COATING, A COATED SUBSTRATE, AN ADHESIVE, FILM OR SHEET

(57) **Abstract:** The present invention relates to a process for the preparation of a coating, a coated substrate, an adhesive, film or sheet and the like, which process comprises the application of a coating mixture containing a reactive system onto a substrate. According to the invention a coating mixture is used which comprising at least two reactive systems and after application of the coating mixture the first reactive system is substantially reacted under conditions where the second reactive system is substantially not reacted. Thereafter the coated substrate is remoulded at elevated temperature and the second reactive system is substantially reacted during or after the remoulding of the coated substrate resulting in a fixed remoulded coating.

Process for the preparation of a coating, a coated substrate, an adhesive, film or sheet.

The present invention relates to a process for the preparation of a coating, a coated substrate, an adhesive, film or sheet, to the thus obtained product and to a coating mixture to be used in the process.

In the course of years several methods have been developed for solvent-free application of polyurethanes in the preparation of coatings, films and the like. An overview of these methods is presented in WO-123451. Further, in this patent application an invention is described which caused a breakthrough in the development of high solid systems. This invention describes a process for the preparation of coatings in which a mixture of a polyisocyanate-, polyepoxide-, polyanhydride-, or polyketone- functional compound and a compound containing reactive hydrogen, which mixture is not reactive at room temperature, is applied onto a substrate, whereafter the mixture reacts at elevated temperatures. The compound containing reactive hydrogen is a solid, which may be present in the mixture as a fine powder or as a dispersion in a medium.

In some applications the known systems, including the system described in WO-123451, have the disadvantage that after reaction the material retains its form so well that treatment such as embossing or otherwise moulding and subsequent fixing of the form, poses problems.

The object of the present invention is to provide a process in which the disadvantages mentioned are eliminated and in which is taken advantage of the invention described in WO-123451.

According to the present invention there is provided a process for the preparation of a coating, coated substrate, adhesive, film, sheet and the like which comprises:

- the preparation of a coating mixture comprising a reactive system,
- applying of the coating mixture onto a substrate resulting in a substrate coated with the coating mixture and

- reacting the reactive system, characterized, in that,
- the coating mixture is prepared as a mixture comprising a first and a second reactive system, after the application of the coating mixture the first reactive system is substantially reacted under conditions where the second reactive system is substantially not reacted,
- after substantially reacting the first reactive system at elevated temperatures the coated substrate is remoulded resulting in a remoulded coating, and
- the second reactive system is substantially reacted during or after the remoulding of the coated substrate, resulting in a fixed remoulded coating; which means that the first reactive system and the second reactive system are essentially reacted as a sequential two-step reaction.

Surprisingly the technical problems known in the art are solved. After the first reaction step a remouldable material is formed and after the second reaction step the remoulding is fixed by using the two-step reaction. A second advantage is that the material formed in the two-step reaction is extra strong and resistant. Moreover crosslinking or the formation of polymer networks can be achieved by the use of the two-step reaction.

Advantageously a coating mixture is prepared in which one reactive system from the first and the second reactive system comprises i) a compound with at least one isocyanate functionality, preferably a polyisocyanate, and ii) a compound with at least one reactive hydrogen, and the selected reactive system is non-reactive or hardly reactive at room temperature.

Preferably the compound containing reactive hydrogen is a polyhydrazide- and/or polysemicarbazide- functional compound and/or carbodihydrazide.

Preferably the polyhydrazide- or polysemicarbazide functional compound and/or carbodihydrazide are present in the mixture as a fine powder or as dispersion in a material that is non-reactive towards the hydrazide or semicarbazide function. This is favourable for reasons described in WO-123451.

By applying the conditions mentioned above a very useful and effective process is obtained.

The other functional groups which are present in the coating mixture may be incorporated in the polyisocyanate or are present in another compound or polymer. The other functional group may be a ketone, anhydride, epoxide, hydrazide or semicarbazide with a lower reactivity or a different particle size, isocyanate with a different reactivity, blocked isocyanate, hydroxide, melamine, hindered amine, chlorinated amine, azetidine, aspartate, carboxyl, aromatic amine, siloxane, unsaturated compound and/or cyclic carbonate.

During the second reaction step of the process, the ketone, anhydride, epoxide, isocyanate with a different reactivity, blocked isocyanate and cyclic carbonate, as well as the isocyanate in the first reaction step, react with the hydrazide or semicarbazide, but the reaction speed is lower or an increased reaction temperature is required. An alternative is that the isocyanate, ketone, anhydride, epoxide, isocyanate with a different reactivity, blocked isocyanate and cyclic carbonate react in the second step with hydroxide, carboxyl, hydrazide or semicarbazide with a lower reactivity or with a different particle size, amine, hindered amine, chlorinated amine, a polymer protected amine, blocked amine, azetidine, aspartate and aromatic amine, which may be present in the coating mixture. The melamine may either undergo a self-condensation reaction or react with the isocyanate or with likewise present ketone, anhydride, epoxide or cyclic carbonate functions. The siloxane function undergoes a self-condensation reaction after the addition of water and/or acid or after exposure to ambient moisture. The unsaturated compound undergoes a self-addition reaction after radical or UV-initiation.

When necessary, suitable conventional catalysts may be added prior to the second reaction step.
This catalytic effect may also be achieved by incorporation of an acid function in the polyisocyanate functional compound, which is preferably a carboxylic acid function.

After the application of the coating mixture onto a substrate, the substrate coated with the coating mixture is preferably treated at an elevated temperature between 50 to 200°C to effect the first reaction step in which the first reactive system substantially reacts and the second reactive system is only slightly or not reacted.

In the process of the invention the polyisocyanate-functional compound, the hydrogen-functional compound and, optionally, a compound with one or more of the other functional groups described above and/or a catalyst are mixed together, whereafter the obtained mixture is applied onto a substrate and the thus obtained coated or impregnated substrate is heated in a first reaction step to a temperature from 50 to 200°C for 0.5 to 10 min, whereafter the formed intermediate material is treated in a second step by:

- embossing or otherwise remoulding, followed by heating to a temperature from 10 to 100°C above that of the first reaction step, or
- heating to a temperature from 10 to 100°C above that of the first reaction step, under which conditions the intermediate material melts or softens, followed by embossing and/or remoulding the material, or
- applying of a second substrate onto the intermediate material, followed by, whether or not under pressure, lamination of the second substrate in the intermediate coating at a temperature between 10 and 100°C above that of the first reaction step, under which conditions the intermediate material further cures, followed by elimination of the first substrate, or
- embossing and/or remoulding otherwise, optionally at elevated temperatures, for example at a temperature between 10 and 100°C above that of the first reaction step, followed by curing after radical or UV-initiation, or
- welding or applying as sealing to other materials or to the same material at a temperature between 10 and 100°C above that of the first reaction step.

If the mixture contains polyisocyanate- as well as, ketone-, epoxide-, anhydride- or cyclic carbonate-functional compounds, the stoichiometric ratio of the total amount of isocyanate and/or ketone and/or epoxide and/or anhydride and/or cyclic carbonate to the polyhydrazide- and/or semicarbazide- functional compound, carbodihydrazide, hydrazide- or semicarbazide functional compound with a lower reactivity or with a different particle size, amine, hindered amine, chlorinated amine, a polymer protected amine, blocked amine, azetidine, aspartate, carboxyl, aromatic amine, hydroxide, and/or melamine is between 3:1 and 1:3 and preferably between 1.5 : 1 and 1 :1.5.

Systems which contain polyisocyanate- as well as ketone-, epoxide-, anhydride-, melamine-, siloxane-, unsaturated- and/or cyclic carbonate-functional groups, the ratio of the isocyanate groups to the ketone-, epoxide-, anhydride-, melamine-, siloxane-, unsaturated- and/or cyclic carbonate- functional group is between 20:1 and 1:20 and preferably between 10:1 and 1:10.

The two-step reaction can be used in several applications. After the formation of the intermediate coating this can be embossed or remoulded otherwise.

In a manner similar to the one described in the above mentioned patent publication all the necessary and for the coating relevant additives that are essential for the application and properties may be present, the mixture may be applied to various substrates and various techniques may be used.

The invention will now be further elucidated with reference to the following non-limiting examples. It goes without saying that many other embodiments are possible, all within the protective scope of the invention.

Examples

Example 1: Preparation of an isocyanate functional polyurethane prepolymer.

Under a nitrogen atmosphere 112.78 g (507.56 mmol) 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (obtainable from Huls as isophoronediisocyanate, and in the following indicated as IPDI) was added at 60-70°C to a mixture of 139.21 g (138.24 mmol) of polypropylene glycol with a molecular weight of 1007, 163.77 g (81.89 mmol) of polypropylene glycol with a molecular weight of 2000 and 4.2 g (31.34 mmol) of trimethylolpropane while stirring. The mixture was heated to 100°C and was reacted for two hours at this temperature under formation of a polyurethane prepolymer. After 1 hr of reaction time 0.1 g of tinoctoate was added as a catalyst. The reaction mixture was cooled down. The remaining NCO-content was measured and was 4.26 %.

Example 2: Preparation of an isocyanate functional polyurethane prepolymer.

The procedure of Example 1 was repeated, with the exception that a polyurethane prepolymer was prepared from 188.89 g (850 mmol) of IPDI, 402.8 g (400 mmol) of polypropylene glycol with a molecular weight of 1007 and 9.0 g (100 mmol) of 1,3-butanediol. The remaining NCO-content was measured and was 4.48 %.

Example 3: Preparation of an isocyanate- and ketone-functional polyurethane prepolymer.

The procedure of Example 1 was repeated, with the exception that a polyurethane prepolymer was prepared from 188.89 g (850 mmol) of IPDI, 314.66 g (157.33 mmol) of polypropylene glycol with a molecular weight of 2000, 172.78 g (171.58 mmol) of polypropylene glycol with a molecular weight of 1007 and 169.1 g (120.61 mmol) of a ketone functional polyester diol (obtainable from NeoResins as PEC 205). The remaining NCO-content was measured and was 3.77 %.

Example 4: Preparation of an isocyanate- and trimethylsiloxane-functional polyurethane.

Under a nitrogen atmosphere 4.72 g 3-(trimethoxysilyl)propylamine was added to 120 g of the product of Example 1 while stirring. The mixture was stirred for 15 min. The remaining NCO-content was 3.26 %.

Example 5: Preparation of an isocyanate functional polyurethane containing incorporated unsaturated groups.

Under a nitrogen atmosphere 4.55 g of a hydroxy functional polyesteracrylate (obtainable as Tone M-100 from Union Carbide) and 0.02 g of dibutyltindilaureate was added to 120 g of the product of Example 1 while stirring. The mixture was stirred for 1.5 hr at 90°C and cooled down. The remaining NCO-content was 3.40 %. Just before testing of the product in Example 7, 0.4 g of an UV-initiator (CGI-1800 van Ciba) in 4 g of dipropylene glycol-dimethylether was stirred into 50 g of the mixture.

Example 6: Preparation of a mixture of an isocyanate-functional polyurethane and a melamine functional compound.

Under a nitrogen atmosphere 100 g of the product of Example 2 was mixed with 3 g of a melamine-functional resin (obtainable as Cymel 303 from Cytec). The remaining NCO-content was 4.12 %.

Example 7: Evaluation of the two-step reactions using the products of the Examples 1 to 6.

50 g of the products of the examples 1 to 6 were mixed with an equivalent amount (with respect to the remaining NCO content) of a 1:1 dispersion of adipic dihydrazide in castor oil and with 1 g of a black pigment dispersion (obtainable as PermaQure EX-60-266/15 from Stahl Holland). An additional amount of 3.27 g of the dispersion of adipic dihydrazide in castor oil was added to the product of Example 3 as an equivalent amount of the ketone functions. Films of a thickness of 200 μm were prepared and they were heated for 2 min at 160°C. The films obtained were flexible and dry. The films were embossed by pressing a pattern into the films for 20 sec at 200°C and 6.10^5 Pa (6 atm.). The results of the embossing test are presented in Table I. A film of Example 5 was, after the embossing, further cured by exposing the film to UV-radiation at 240 nm and a total of

energy of 4000 mJ/cm.

Next, the embossed films were placed for 24 hrs at 120°C to test the stability of the embossing. The results are presented in Table I.

Table I:

Product of example:	Embossability	Stability of the print at 120°C
1	poor	print remains poor
2	good	print disappears
3	good	good
4	good	good
5 – without UV-radiation	good	moderate
- with UV-radiation	good	good
6	good	good

Remarks relating to Table I:

– The second reaction step occurs during the embossing (Examples 3, 4, 6) or during the UV-curing (Example 5);

– By adding a melamine resin to the product of Example 2, a better stability of the print in the film is obtained

– By adding additional functions to the polyurethane prepolymer of Example 1 a better embossing is acquired and the print is fixed by the second reaction step.

– By curing of the embossed film of product 5 with UV-radiation the print is fixed.

CLAIMS

1. A process for the preparation of a coating, a coated substrate, an adhesive, film, sheet and the like which comprises:

- the preparation of a coating mixture containing a reactive system,
- applying of the coating mixture onto a substrate resulting in a substrate coated with the coating mixture,
- reacting the reactive system, **characterized,** in that,
- the coating mixture is prepared as a mixture comprising a first and a second reactive system, after the application of the coating mixture the first reactive system is substantially reacted under conditions where the second reactive system is substantially not reacted,
- after substantially reacting the first reactive system at elevated temperatures the coated substrate is remoulded, resulting in a remoulded coating, and
- the second reactive system is substantially reacted during or after the remoulding of the coated substrate, resulting in a fixed remoulded coating; which means that the first reactive system and the second reactive system are essentially reacted as a sequential two-step reaction.

2. The process according to claim 1, **characterized,** in that a coating mixture is prepared in which one reactive system from the first and the second reactive system comprises i) a compound with at least one isocyanate functionality, preferably a polyisocyanate, and ii) a compound with at least one reactive hydrogen, and the selected reactive system is non-reactive or hardly reactive at room temperature.

3. The process according to claim 1 and 2, **characterized,** in that the compound containing reactive hydrogen is a polyhydrazide- and/or polysemicarbazide-functional compound and/or carbodihydrazide

4. The process according to claim 3, **characterized,** in that the compound containing reactive hydrogen is present

in the mixture at ambient temperature as a fine powder or as a dispersion in a material which is non-reactive towards the reactive hydrogen.

5. The process according to claims 2 - 4, **characterized,** in that the other reactive system comprises on one hand a ketone, anhydride, epoxide, a polyisocyanate with a different reactivity, a blocked isocyanate and/or a cyclic carbonate function, or the isocyanate functional compound from claim 2 and on the other hand a hydrazide or semicarbazide with a lower reactivity or with a different particle size, an amine, hindered amine, chlorinated amine, a polymer protected amine, blocked amine, azetidine, aspartate, carboxyl, aromatic amine, hydroxide and/or melamine function and/or that the other reactive system comprises polyalkylsiloxane or melamine functions which are polymerisable by self-condensation, and/or that the other reactive system comprises an unsaturated compound which undergoes an addition polymerisation.

6. The process according to claims 2 - 5, **characterized,** in that the compound containing at least one isocyanate functionality also contains another functional group according to claim 5 which is not reactive towards the isocyanate function.

7. The process according to claims 2 - 6 **characterized,** in that the compound containing the isocyanate functionality also contains another functionality according to claim 5 which is reactive with the compound with at least one reactive hydrogen.

8. The process according to claims 4 - 7 **characterized,** in that the dispersion with the polyhydrazide- and/or polysemicarbazide-functional compound and/or carbodihydrazide also contains another functional group according to claim 5 which is not reactive with the polyhydrazide- and/or polysemicarbazide-functional compound and/or carbodihydrazide.

9. The process according to claims 2 - 8 **characterized,** in that the polyisocyanate functional compound contains an acid function, which is preferably a carboxylic

acid function.

10. The process according to claims 1 - 9 **characterized,** in that after the application of the coating mixture onto a substrate to provide a substrate coated with the coating mixture, the coated substrate is preferably treated at an elevated temperature between 50 to 200°C to effect the first reaction step in which the first reactive system substantially reacts and the second reactive system is only slightly or not reacted.

11. The process according to claims 2 - 10 **characterized,** in that the polyisocyanate-functional compound, the reactive hydrogen-functional compound and, optionally, a compound with one or more of the other functional groups described in claims 5-9 and/or a catalyst are mixed together, whereafter the obtained mixture is applied onto a substrate and the thus obtained coated or impregnated substrate is heated in a first reaction step to a temperature from 50 to 200°C for 0.5 to 10 min, whereafter the formed intermediate material is treated in a second step by:

- embossing or remoulding otherwise, followed by heating to a temperature from 10 to 100°C above that of the first reaction step, or
- heating to a temperature from 10 to 100°C above that of the first reaction step, under which conditions the intermediate material melts or softens, followed by embossing and/or remoulding of the material, or
- applying of a second substrate onto the intermediate material, followed by, whether or not under pressure, lamination of the second substrate in the intermediate coating at a temperature between 10 and 100°C above that of the first reaction step, under which conditions the intermediate material further cures, followed by elimination of the first substrate, or
- embossing and/or remoulding, optionally at elevated temperatures, for example at a temperature between 10 and 100°C above that of the first reaction step, followed by curing after radical or UV-initiation, or

- welding or applying as sealing to other materials or to the same material at a temperature between 10 and 100°C above that of the first reaction step.

12. The process according to claims 2 - 11 **characterized,** in that the stoichiometric ratio of the total amount of the isocyanate-, ketone-, epoxide-, anhydride- or cyclic carbonate- functional compounds to the polyhydrazide and/or semicarbazide functional compound, carbodihydrazide, hydrazide- or semicarbazide- functional compound with a lower reactivity or with different particle size, amine, hindered amine, chlorinated amine, an amine protected by a polymer, blocked amine, azetidine, aspartate, carboxyl, aromatic amine, hydroxide, and/or melamine is between 3:1 and 1:3 and preferably between 1.5 : 1 and 1 :1.5.

13. The process according to claims 2 - 12 **characterized,** in that the ratio of the isocyanate groups to the ketone-, epoxide-, anhydride-, melamine-, siloxane-, unsaturated and/or cyclic carbonate-functional groups is between 20:1 and 1:20 and preferably between 10:1 and 1:10.

14. Cured product obtained by a process according to one of the preceding claims 1-13.

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00555

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/12 C09D175/16 C09J175/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 23451 A (STAHL INTERNATIONAL) 5 April 2001 (2001-04-05) page 2, line 24 -page 5, line 10; claims 1-6; examples 1-7,14-21 ---	1-10
X	US 4 912 152 A (NEJIGAKI ET AL) 27 March 1990 (1990-03-27) column 1, line 43 -column 7, line 39; claims 1-13 ---	1
A	DE 40 41 753 A (HENKEL) 25 June 1992 (1992-06-25) column 3, line 5 -column 7, line 63 ---	1
A	EP 0 287 736 A (W.L. GORE & ASSOCIATES) 26 October 1988 (1988-10-26) column 1, line 43 -column 5, line 2; claims 1-3 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 02/00555

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0123451 A	05-04-2001	NL 1013179 C2	02-04-2001
		AU 7971900 A	30-04-2001
		BR 0014669 A	01-10-2002
		EP 1233991 A2	28-08-2002
		WO 0123451 A2	05-04-2001
US 4912152 A	27-03-1990	JP 2000614 A	05-01-1990
		JP 2632939 B2	23-07-1997
DE 4041753 A	25-06-1992	DE 4041753 A1	25-06-1992
		AT 133442 T	15-02-1996
		DE 59107322 D1	07-03-1996
		WO 9211335 A1	09-07-1992
		EP 0564483 A1	13-10-1993
		US 5478427 A	26-12-1995
EP 287736 A	26-10-1988	AT 96834 T	15-11-1993
		AU 594500 B2	08-03-1990
		AU 7839787 A	27-10-1988
		DE 3788061 D1	09-12-1993
		DE 3788061 T2	17-03-1994
		DK 217988 A	09-01-1989
		EP 0287736 A2	26-10-1988
		FI 881861 A	22-10-1988
		GB 2204049 A	02-11-1988
		JP 63278922 A	16-11-1988
		NO 880245 A	24-10-1988
		PT 87264 A ,B	01-05-1988