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(54) **SYSTEMES DE POLYURETHANNE A DEUX CONSTITUANTS THIXOTROPES**

(54) **THIXOTROPIC TWO-COMPONENT POLYURETHANE SYSTEMS**

(57) L'invention concerne des systèmes de polyuréthanne à deux constituants thixotropes contenant un constituant polyol et un constituant isocyanate. Le constituant polyol contient au moins deux amines A1 et A2, la réactivité R1 de l'amine 1 par rapport à l'isocyanate étant largement supérieure à la réactivité R2 de l'amine 2 par rapport à l'isocyanate. Il se produit ainsi deux réactions décalées dans le temps, conférant aux systèmes décrits une faible viscosité souhaitée pour l'application et une thixotropie après l'application, qui permet d'empêcher le glissement même de couches épaisses sur des surfaces verticales. Ces systèmes de polyuréthanne à deux constituants sont utilisés pour la production de modèles d'estimation, de prototypes ou similaires dans l'industrie automobile, et pour la production de corps structurés, de revêtements épais et de cordons d'étanchéité.

(57) The invention relates to two-component polyurethane systems, consisting of one polyol component and one isocyanate component. Said polyol component contains at least two amines A1 and A2, the reactivity R1 of amine A1 with isocyanate being considerably greater than the reactivity R2 of amine A2 with isocyanate. As a result, two time-delayed reactions take place. This gives the inventive systems the desired low level of viscosity, and the thixotropic properties which prevent even thick layers from sliding off of vertical surfaces. The inventive two-component polyurethane systems can be used for producing cubing models, master models and similar in the automobile industry and for producing structured bodies and thick films and sealing beads.

## ABSTRACT

The invention relates to two-component polyurethane systems, consisting of one polyol component and one isocyanate component. Said polyol component contains at least two amines A1 and A2, the reactivity R1 of amine A1 with isocyanate being considerably greater than the reactivity R2 of amine A2 with isocyanate. As a result, two time-delayed reactions take place. This gives the inventive systems the desired low level of viscosity, and the thixotropic properties that prevent even thick layers from sloughing off of vertical surfaces. The inventive two-component polyurethane systems can be used for producing cubing models, master models and the like in the automobile industry and for producing structured bodies and thick coatings and sealing beads.

# THIXOTROPIC TWO-COMPONENT POLYURETHANE SYSTEMS

## DESCRIPTION

The invention concerns thixotropic two-component polyurethane systems, processes for the production thereof, and methods for employment thereof.

In many applications involving two-component polyurethane systems, in particular in the manufacture of shaped bodies for cubing-models, prototypes, and the like in the automobile industry, it is desired that these two-component systems become thixotropic immediately after the mechanical mixing of the components and the coating thereof, so that after coating onto vertical surfaces even to a high layer thickness the layer does not slough off.

Until now, pasty polyurethane systems with fillers were employed for this purpose which, at least in the polyol component, contained inorganic and/or organic thickeners. A thixotropic coating composition is known from DE-PS 27 51 761 comprising a binder and a reaction product of a diisocyanate with a primary or secondary polyamine, in particular a benzylamine, as anti-running agent. As compositions providing thixotropism, polyamine resins with free amino groups are also known, which are included for gel formation in varnish resins, as described in EP-A 0 006 252, page 1.

It is likewise known, that following the reaction of primary and/or secondary polyamines, mono-functional alcohols and/or

amines with diisocyanate compounds, the resulting urea- or carbamide-adducts, which are produced in situ with the binder or a component of the binder, are thixotropic (DE-PS 23 60 019).

In DE-A 40 23 005 there are described thixotropic polyurethane systems on the basis of a polyol component and an isocyanate component, of which the polyol component contains a mixture of polyamideamine (polyamide polyamine) and low molecular, multi-functional, particularly aromatic, amines. The mixture of polyol, isocyanate and amino components exhibits the desired low viscosity for a short period of time for application or coating; the thixotropism which is necessary for application to overhead or vertical work surfaces has an onset which occurs later on in the mixture. In the illustrative embodiments, polyurethane systems are applied in layer thicknesses of 5 mm, and are used as adhesive systems, for example, for vitrification. The polyurethane systems described in this reference may comprise a combination of two amines; these, however, react simultaneously with the isocyanate in order to provide the desired result with respect to low viscosity and thixotropism. These systems are however not suitable for the application of coatings with higher layer thicknesses (approximately 20-50 mm), because they cannot completely prevent the sloughing off of these layers, which occurs particularly during the exothermic curing reaction due to the significant evolution of heat.

Beginning therewith, it is the task of the present invention to provide improved two-component polyurethane systems, of which the components develop a sufficient thixotropism within a short period of time following the mechanical mixing as a result of a

chemical reaction, such that, on the one hand, sufficient flowability remains while brushing on such that the brush strokes blend sufficiently, and on the other hand, it becomes possible to apply strokes to vertical surfaces with a high coating thickness, without a sliding or sloughing off after the onset of the exothermic curing reaction.

The task of the invention is inventively solved by the provision of a two-component polyurethane system of a polyol component and an isocyanate component, which is characterized in that the polyol component contains at least two amines - A1 and A2 - wherein the reactivity R1 of amine A1 with the isocyanate component is considerably greater than the reactivity R2 of amine A2 with the isocyanate component.

Advantageous embodiments of the invention can be seen from the dependent claims.

The invention also includes a process for the manufacture of the polyurethane system (Claim 12) and processes for the employment thereof (Claim 13).

Advantageous characteristics of the inventive two-component polyurethane system include:

1. A fluid consistency of the two starting components, which makes an easy mixing of the components possible;
2. Good flowability of the individual applied strokes into each other, whereby the occurrence of air

inclusions (bubbles) is reduced and flat surfaces are obtained;

3. Good flow resistance of the coated material, and thus small tendency to slough off from vertical surfaces;
4. Long follow-up work time for smoothing out and the like;
5. Possibility of the application of multiple layers, one over the other, with good layer adhesion;
6. Depending upon the applied amount and applied surface, a variable consistency at the point of time of the application.

The polyurethane system according to the present invention is based upon a two-component system of fluid components. The resin component is comprised of a modified polyetherpolyol and/or polyesterpolyol with filler components, and the hardener component is a low viscosity isocyanate based on 4,4'-diphenylmethane-diisocyanate (MDI).

According to the invention, it is most important that the timing of the thixotropism of the system is so adjusted, that the system after mixing is made thixotropic in a first stage by the reaction of amine A1 with the isocyanate such that it polymerizes or gels the base coat to the point that it flows to smooth out applied strokes and flows into the recesses, and at the same time however remains so resistant to flow, that it can be applied to vertical surfaces in a layer thickness of approximately 20 mm and adheres well thereto and does not slough off. Since the structural viscosity produced in the first stage, however, as a rule does not suffice to prevent the

weakening of the inter-molecular adhesiveness and the resulting sloughing off of the applied layer after onset of the polymerization reaction of the polyol-isocyanate and the therefrom resulting exothermic reaction temperature, a further, time-delayed onset reaction is necessary. There is thus produced, in a second stage in the system, a stronger structural viscosity or as the case may be thixotropism, by the reaction of amine A2 with the isocyanate, which remains temperature stable, and which does not allow running which would occur after the reaction in the first stage.

The inventive modified polyol/isocyanate system, with respect to its environment of use, has to be able to satisfy two criteria, wherein criterion 1 comprises good networking or polymerization and good flowability with respect to surface smoothness immediately after the application upon the base or undercoating, which maintains good flow resistance at temperatures of up to approximately 40° C, and criteria 2 comprises good inter-molecular adhesion after onset of the exothermic curing reaction of the polyol/isocyanate with increasing temperatures up to approximately 80°C, whereby a sloughing off of layers applied even in high layer-thicknesses to vertical surfaces is prevented.

Both tasks or criteria cannot be achieved by utilization of only one amine or, as the case may be, by utilizing mixtures of simultaneously reacting amines. By increasing the amount of amine, or as the case may be, a corresponding selection of the amine types, it may be possible to satisfy criteria 2 with respect to the prevention of the sloughing off of the applied

layers, but, however, not simultaneously criteria 1 with respect to the good networking and the flowing onto the base or undercoating. It was however now been discovered, that both criteria can be solved simultaneously, when at least two amines are employed, which are significantly different in their reactivity. Therein the reactivity R1 of amine A1 to the isocyanate component must be higher than the reactivity R2 of amine A2 to the isocyanate component. It was inventively discovered, that the relation of reactivity of amine A1 with respect to the isocyanate to the reactivity of amine A2 with respect to the isocyanate (R1:R2) must be approximately 1000 to 5 (1000:1 to 5:1) and preferably approximately 100 to 5.

At time 0, the material components are mechanically mixed with each other. In the first stage, the amine A1 reacts within a few seconds with the isocyanate. Thereupon this first reaction is substantially concluded. In the second stage, immediately following the reaction of the first stage, the amine A2 reacts with the isocyanate in approximately 1 to 2 minutes and forms, by hydrogen bridges and other inter-molecular forces, and inter-connected framework, so that a sloughing off of the applied layer does not occur during the pot life, during which the polyol is reacting with the isocyanate. The pot life is approximately 30 to 40 minutes; the layers applied to vertical surfaces would slide off after approximately 20 minutes if it were not for the reaction of amine A2.

Amines A1 which are particularly suited as components of the polyol for the first reaction stage include the following amines, of which the reactivity is R1 > R2.

1 a) aromatic amines such as
2,4- or 2,6-toluylenediamine (TDA),
3,5-diethyl-toluylenediamine (DETDA),
methylene-bis-(2,6-diisopropylaniline) (M-DIPA),
methylene-bis-(2-methyl-6-isopropylaniline) (M-MIPA),
methylene-bis-(2,6-diethylaniline) (M-DEA),
4,4' methylene-bis-(6-methyl-aniline),
2,6-diisopropylaniline (DIPA),
2-methyl-6-isopropylaniline (MIPA)
4,4'-diamino-diphenyl-methane (MDA),

1 b) cycloaliphatc amines such as
3-isocyanomethyl-3,5,5-trimethylcyclohexylamine
(isophorondiamine, IPD),
4,4' diamino-3,3' dimethyl-cyclohexylmethane (Laromin C 260),
cyclohexanediamine,
piperazine, N-aminoethylpiperazine,

1 c) araliphatic amines such as
m-xylylendiamine (M-XDA) and derivatives
or other types with an aromatic and an
aliphatic bound amino group,

1 d) aliphatic amines and polyamines such as
butylamine,
diethylenetriamine,
triethylenetetramine,
trimethyl-hexamethylenediamine,

pentaethylenehexamine,
polyetherpolyamines such as $H_2N-(CH_2-CH_2-0)_x-CH_2-CH_2-NH_2$ and derivatives.

The following amines, of which the reactivity is R2 < R1 are examples of particularly suitable amines A2 to be used in the polyol component for the second reaction stage:

2 methylene-bis-(3-chlor-2,6-diethylaniline) (M-CDEA), 3,5-dimethylthio-(2,4- or 2,6-)toluylenediamine, available under the trademark ETHACURE 300 from Ethyl Corp.,
3,5-diamino-4-chloro-benzoic acid-isobutylester (DACB),
methylene-bis-anthranilate methylester (MBMA),
4,4'-diamino-3,3'-dichlorodiphenylmethane (MOCA),
or similar compounds.

In the amines of type A2, these are characterized by electron withdrawing or mesomeric effects as a consequence of lowering of basicity and/or stearic hindrance of strongly masked amines. The distinction is, that the amines A2 must exhibit a significantly lower reactivity than amines A1 with respect to the isocyanate. It is also possible to combine an amine A1 from groups 1 b) - 1 d) with an amine A2 of group 1 a), when in this combination a sufficient differentiation in reactivity is present. Mixtures of amines of the different groups can also be employed.

A comparison of the relative reactivity of the amines of the groups 1 a), 1 b) through d), and 2 is presented in the following table.

TABLE 1

| Amines of the Group | Relative Reactivity |
|---|---|
| 2 | 0,1 to 1 |
| 1 a) | 5 to 200 |
| 1 b), c), d) | 100 to > 1000 |

In practice this means that in the conditions under which Examples 1 and 2 are carried out the amines of groups 1 b) through 1 d) begin reacting with the isocyanate instantaneously, the amines of group 1 a) within approximately 5-10 seconds and the amines of group 2 within approximately 30-90 seconds.

The above-mentioned amino-compounds in the form of fluid preparations can be mixed with suitable polyols. As such, the polyols known from polyurethane chemistry, which exhibit at least two alcoholic bonded hydroxy groups, come into consideration. Included therein are the known linear or branched polyether polyols in the molecular weight range of 75 to 6000, or the known linear or polyester polyols with a molecular weight range of 75 to 6000, as described for example in DE-PS 21 60 589 or DE-A 33 40 588. The formulated polyol components have a viscosity at 25°C of approximately 1000 to 60,000 mPa.s. In the polyol components, other ingredients, for example drying aids, pigments, dispersion aids, softeners, anti-foaming agents and, in certain cases, catalysts can also be contained. Included therein are, for example, conventional potassium-sodium-alumino-silicate of the zeolite type (drying aid), chalk, calcium carbonate, pigments, softeners based on

carbohydrates and, in certain cases, tertiary amines or organic tin compounds as catalysts.

As isocyanate components which are also suitable for use in these two-component polyurethane systems, there are included for example those disclosed in DE-PS 21 60 589 or DE-A 33 40 588. Particularly preferred are aromatic diisocyanates, for example derivatives of 4,4'-diphenylmethane diisocyanate (MDI) and toluylene diisocyanate (TDI). The isocyanate component has a viscosity at 25°C of approximately 10-10,000 mPa.s.

The stoichiometric relationship of the polyol components inclusive of all additives to the isocyanate component can be 100:10 parts by wt. to 100:200 parts by wt.

The portion of amine A1 in the polyol component corresponds approximately to 0.25 to 5 wt.%, preferably 0.5 to 2 wt.% of the total weight of the polyol component of the two component system. The portion of amine A2 in the polyol component corresponds approximately to 0.3 to 5 wt.%, preferably 1-2 wt.% of the total weight of the polyol component. The addition of a combination of amine A1 to amine A2 in the ratio 0.5:1 to 2:1 (wt.%), for example of 1.5:1.5 wt.%, is most preferred with respect to the desired results.

The amines according to the invention are added into the polyol component prior to the reaction with the isocyanate component. The polyol components inclusive of all additives are mixed mechanically with the isocyanate prior to the application to the desired surfaces.

The invention will now be described in greater detail on the basis of the embodiments.

Example 1

4,4'-methylene-2-(3-chloro-2,6-diethylaniline) (M-CDEA), melting point approximately 85°C, which can be obtained from Lonza AG, Basel Switzerland, is dissolved with heat in the polyether polyol component as amine A2. As polyol P1, a polypropylene glycol with a hydroxy number of 380 mg KOH/g and a viscosity at 25°C of 650 mPa.s was employed. The remaining components, that is, a drying agent D1, which is a conventional K-Na-aluminosilicate of the zeolith type A and available under the trademark BAYLITH L POWDER from the company Bayer AG, Leverkusen, Germany; diazabicyclooctane, which is available as a 33% solution in dipropylene glycol, for example under the trademark DABCO 33 LV from the company Biesterfeld and Co., Hamburg, Germany, as catalyst; calcium carbonate, which is available as chalk under the trademark OMYA BLR 2 from the company Omya, Koeln, Germany; and 4,4'-diamino-3,3'-dimethyl-cyclohexyl methane (LAROMIN C 260) as amine A1, which can be obtained from the company BASF, Ludwigshafen, Germany, were added to the solution and dispersed using a tooth-disc dissolver. The total mixture was subjected to vacuum treatment for removal of gasses.

| | | |
|---|---|---|
| Polyol P1 | 100 | g |
| Amine A2 | 6 | g |
| Drying Agent D1 | 15 | g |

| | |
|---|---|
| Catalyst | 0.05 g |
| Calcium Carbonate, Chalk | 285 g |
| Amine A1 | 6 g |
| Viscosity of the Mixture: | approximately 25 Pa.s |
| Density of the Mixture: | approximately 1.8 kg/l |

The thus produced mixture is mixed, using a conventional two-component-polyurethane mixing-and-dosing-device, with a pre-polymer-modified 4,4'-diphenyl methane-diisocyanate with polymeric components, density 1.23 kg/l, NCO-content 28%, viscosity at 25° C:250 mPa.s as isocyanate I1 in a stoichiometric relationship of 100:30 in parts by wt. The result was a thixotropic mass, which could be applied in one step to vertical surfaces using a flexible hose to a layer thickness of 20 mm and greater, and which hardens to a hard material with a shore hardness of approximately D 90.

Example 2

4,4'-methylene-bis-(3-chlor-2,6-diethylaniline) (M-CDEA), melting point approximately 85°C, which can be obtained from Lonza AG, Basel Switzerland, is dissolved with heat in the polyether polyol component as amine A2. As polyol P2, there is employed a polypropylene glycol with a hydroxy number of 76 mg KOH/g and a viscosity at 25°C of 900 mPa.s. The remaining components, that is, drying agent D2, which is available as a pasty preparation of zeolith in ricinus oil and available under the trademark BAYLITH L PASTE from the company Bayer AG, Leverkusen, Germany; 1,4-butanediol; diazabicyclooctane, which

is available as a 33% solution in dipropylene glycol, for example under the trademark DABCO 33 LV from the company Biesterfeld and Co., Hamburg, Germany, as catalyst; 4,4'-diamino-3,3'-dimethyl-cyclohexyl methane (LAROMIN C 260) as amine A1, which can be obtained from the company BASF, Ludwigshafen, Germany, were added to the solution and dissolved with a stirrer.

| | |
|---|---|
| Polyol 2 | 100 g |
| Amine A2 | 1,3 g |
| Drying Agent D2 | 12 g |
| Butanedial-1,4 | 9 g |
| Catalyst | 0.05 g |
| Calcium Carbonate, Chalk | 285 g |
| Amine A1 | 1.8 g |

| | |
|---|---|
| Viscosity of the Mixture: | 1.3 Pa.s at 25° C |
| Density of the Mixture: | 1.05 kg/l |

This mixture was mixed using a conventional two-component mixing-and-dosing device with a prepolymer-modified, aromatic diisocyanate, density 1.21 kg/l, NCO-content 25%, viscosity at 25°C: 300 mPa.s as isocyanate I2 in a stoichiometric relationship of 100:60 parts by wt. This results a thixotropic mass, which was applied to a vertical surface in a single step using a flexible hose to layer thicknesses of 20 mm and greater and which hardened to an elastic material with a shore hardness of approximately A-90.

# PATENT CLAIMS

1. Two-component polyurethane system comprised of a polyol component and an isocyanate component, which react exothermically, thereby characterized, that the polyol component comprises at least two amines A1 and A2, wherein the reactivity R1 of amine A1 to the isocyanate component is greater than the reactivity R2 of amine A2, wherein amine A1 is so selected, that it reacts with the isocyanate component within a few seconds for transformation to such a structural viscosity, that the system is not fully cured but is non-flowing and wherein amine A2 is so selected, that its reaction with the isocyanate component is delayed with respect to that of amine A1, so that an increased thermally stable structural viscosity is produced.

2. Two-component polyurethane system according to Claim 1, thereby characterized, that the relationship of the reactivity R1 of amine A1 to reactivity R2 of amine A2 with respect to the isocyanate component is from 1000 to 5.

3. Two-component polyurethane system according to Claim 2, thereby characterized, that the relationship of the reactivity R1 of amine A1 to the reactivity R2 of amine A2 with respect to the isocyanate component is from 100 to 5.

4. Two-component polyurethane system according to Claims 1-3, thereby characterized, that amine A1 is selected from aromatic amines (Group 1 a), cycloaliphatic amines (Group 1 b), araliphatic amines (Group 1 c), and aliphatic amines and polyamines (Group 1 d).

5. Two-component polyurethane system according to Claims 1-3, thereby characterized, that amine A2 is selected from Group 2 which includes:
methylene-bis-(3-chlor-2,6-diethylanilin) (M-CDEA),

3,5-dimethylthio-(2,4 or 2,6)-toluylenediamine,
3,5-diamino-4-chlor-benzoesaure-isobutylester (DACB),
methylene-to-anthranilate methylester (MBMA),
4,4'-diamino-3,3'-dichlordiphenylmethane (MOCA)
and similar compounds.

6. Two-component polyurethane system according to one of Claims 1-5, thereby characterized, that amine A1 is selected from Group 1 a) through 1 d) and amine A2 is selected from Group 2.

7. Two-component polyurethane system according to one of Claims 1-5, thereby characterized, that amine A1 is selected from Groups 1 b) through 1 d) and amine A2 is selected from Group 1 a), wherein the reactivity R1 of amine A1 from Groups 1 b) through 1 d) is greater than the reactivity R2 of amine A2 from Group 1 a).

8. Two-component polyurethane system according to one of Claims 1-7, thereby characterized, that amine A1 is 4,4'-diamino-3,3'-dimethyl-cyclohexylmethane and amine A2 is 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline).

9. Two-component polyurethane system according to one of Claims 1-8, thereby characterized, that the weight relationship of amine A1 to amine A2 is 0.5:1 to 2:1 in wt.%.

10. Two-component polyurethane system according to one of Claims 1-8, thereby characterized, that amine A1 comprises

0.25 to 5 wt.% of the total polyol component and amine A2 comprises 0.3 to 5 wt.%. of the total polyol component.

11. Two-component polyurethane system according to one of Claims 1-10, thereby characterized, that the polyol is at least one of a polyether polyol and a polyester polyol with a molecular weight in the range of 75 to 6000, and the diisocyanate is a 4,4'-diphenylmethane-diisocyanate-derivative.

12. Process for production of the two-component polyurethane system according to the preceding claims, thereby characterized, that the amine component is dissolved in the polyol component, the two amine components and the desired additives are added using a stirring device and the resulting mixture is mixed with the diisocyanate in a mixing-and-dosing device.

13. Use of the two-component polyurethane system according to the preceding claims for production of shaped bodies for cubing-models, prototypes and the like in the automobile industry, as well as for production of structured bodies and thick coatings and sealing beads.