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(54) Titre : METHODE DE PREPARATION DE POLYISOCYANATES AU MOINS PARTIELLEMENT BLOQUES A L'AIDE DE 3,5-DIMETHYLPYRAZOLE

(54) Title: A PROCESS FOR THE PRODUCTION OF POLYISOCYANATES AT LEAST PARTIALLY BLOCKED WITH 3,5-DIMETHYLPYRAZOLE

(57) Abrégé/Abstract:
The present invention relates to a process for preparing a blocked polyisocyanate which comprises reacting in a first reaction stage an equimolar mixture of acetylacetone and hydrazine hydrate via a condensation reaction in a water-immiscible solvent with separation and removal of the introduced and formed water to form a liquid organic product containing 3,5-dimethylpyrazole and in a second reaction stage reacting said liquid organic product, without separation of 3,5-dimethylpyrazole as a solid, with an organic polyisocyanate, which is optionally dissolved in a solvent, to at least partially block the isocyanate groups with 3,5-dimethylpyrazole.

Mo4317
LeA 30,784

A PROCESS FOR THE PRODUCTION OF POLYISOCYANATES AT LEAST PARTIALLY BLOCKED WITH 3,5-DIMETHYLPYRAZOLE

ABSTRACT OF THE DISCLOSURE

The present invention relates to a process for preparing a blocked polyisocyanate which comprises reacting in a first reaction stage an equimolar mixture of acetylacetone and hydrazine hydrate via a condensation reaction in a water-immiscible solvent with separation and removal of the introduced and formed water to form a liquid organic product containing 3,5-dimethylpyrazole and in a second reaction stage reacting said liquid organic product, without separation of 3,5-dimethylpyrazole as a solid, with an organic polyisocyanate, which is optionally dissolved in a solvent, to at least partially block the isocyanate groups with 3,5-dimethylpyrazole.

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A PROCESS FOR THE PRODUCTION OF POLYISOCYANATES AT LEAST PARTIALLY BLOCKED WITH 3,5-DIMETHYLPYRAZOLE

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a novel process for the production of polyisocyanates at least partially blocked with 3,5-dimethylpyrazole (DMP) using DMP produced in situ from acetylacetone and hydrazine hydrate.

Background of the Invention

The use of DMP as a blocking agent for isocyanates is known (US-PS 3,248,398 or EP-A-0,159,117). Lacquer polyisocyanates blocked with DMP may be used as crosslinking agents in high-grade one-component polyurethane coating compositions. The advantage of DMP over other blocking agents, such as butanone oxime, resides in a substantially lower thermal yellowing of the coatings and a comparatively low stoving temperature of approximately 130°C.

DMP is prepared by the condensation of acetylacetone with hydrazine and is a solid which melts at above 100°C. For this reason, large-scale industrial handling of DMP has been more complicated than, for example, the use of liquid blocking agents.

An object of the present invention is to provide a novel process for the production of polyisocyanates blocked with DMP in which the separate production of the blocking agent and the need to handle it as a solid is omitted.

Surprisingly, it proved possible to achieve this object with the process according to the invention described in greater detail below. It has been found that the crude product produced by the condensation reaction in an organic solution between acetylacetone and hydrazine hydrate may be used directly for the blocking reaction for organic

polyisocyanates without isolation of the DMP present. The use of this crude product does not result in any appreciable impairment of the quality of the blocked polyisocyanate obtained in this manner. A further advantage of the process according to the invention is that the yield of blocked polyisocyanate relative to the introduced starting materials is virtually quantitative. To the contrary the previous isolation of DMP and its subsequent use as a blocking agent inevitably resulted in unavoidable losses in yield.

SUMMARY OF THE INVENTION

The present invention relates to a process for preparing a blocked polyisocyanate which comprises reacting in a first reaction stage an equimolar mixture of acetylacetone and hydrazine hydrate via a condensation reaction in a water-immiscible solvent with separation and removal of the introduced and formed water to form a liquid organic product containing 3,5-dimethylpyrazole and in a second reaction stage reacting said liquid organic product, without separation of 3,5-dimethyl-pyrazole as a solid, with an organic polyisocyanate, which is optionally dissolved in a solvent, to at least partially block the isocyanate groups with 3,5-dimethylpyrazole.

DETAILED DESCRIPTION OF THE INVENTION

The polyisocyanates to be blocked in the process according to the invention are selected from organic polyisocyanates having at least two (cyclo)aliphatically or aromatically bound isocyanate groups. Examples of these polyisocyanates include 2,4- and/or 2,6-diisocyanatotoluene (TDI), hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 4,4'-diisocyanato-dicyclohexyl-methane (HMDI) and in particular the polyisocyanates, which have isocyanurate, urethane, allophanate, biuret and/or uretidione groups and are prepared from these diisocyanates. Higher molecular weight NCO prepolymers prepared from the previously disclosed di- and/or

polyisocyanates may also be used in the process according to the invention. Preferred di- or polyisocyanates have a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%. Derivatives of HDI, IPDI and/or HMDI having isocyanurate groups are especially preferred for use in the process according to the invention.

The first stage of the process according to the invention is the condensation reaction between acetylacetone (pentane-1,3-dione) and hydrazine, which is generally used as hydrazine monohydrate, in a water-immiscible solvent. Suitable solvents include toluene, xylene, 2-methoxy-propyl acetate, solvent naphtha 100 and mixtures of these solvents. The condensation reaction generally takes place at a temperature of 50 to 150, preferably 70 to 110°C, wherein 4 to 7, preferably 5 to 6, moles of each of the two starting components are used per liter of the stated solvent. The exothermic reaction is complete once the water introduced with the hydrazine hydrate and the water formed during the condensation reaction has been separated.

After isolation of the separated water, the organic solution is used directly in the second stage of the process according to the invention. In this stage one of the two reactive components (either the polyisocyanate dissolved in an inert solvent such as methoxypropyl acetate or the above-stated solution of the blocking agent produced in situ) is initially introduced and the other component is then mixed into the starting batch. The blocking reaction generally proceeds at 50 to 110, preferably 70 to 90°C. The quantities of the reaction components used in the second stage of the process according to the invention are selected such that 0.3 to 1.05 moles (30 to 105 equivalent percent) of DMP are available for each equivalent of unblocked isocyanate groups. If blocked polyisocyanates are to be produced in which DMP is present as the sole blocking agent, 0.95 to 1.05 moles (95 to 105 equivalent percent) of the DMP are used per equivalent of isocyanate groups. In this case an

equivalent quantity of the blocking agent is preferably used. The course of the reaction may be monitored by the decrease in NCO content.

The process according to the invention is also very well suited to the production of co-blocked polyisocyanates, i.e. polyisocyanates having isocyanate groups blocked with different blocking agents. During production of such co-blocked polyisocyanates, at least one other blocking agent is used in addition to DMP. Other suitable blocking agents include butanone oxime, 1,2,4-triazole, diisopropylamine, ethyl malonate and ethyl acetoacetate.

For the production of co-blocked polyisocyanates using the process according to the invention, at least 0.3 moles (30 equivalent percent), preferably 0.3 to 0.9 moles (30 to 90 equivalent percent) and more preferably 0.4 to 0.5 moles (40 to 50 equivalent percent) of DMP are used per equivalent of isocyanate groups of the unblocked polyisocyanate.

The co-blocked polyisocyanates may be produced in accordance with either of two embodiments. In the first embodiment isocyanates already partially blocked with at least one "other" blocking agent are used in the second stage of the process according to the invention. The quantity of the DMP previously produced in situ is calculated such that 0.95 to 1.05 moles of DMP are present for each equivalent of unblocked isocyanate groups. It may be seen from these and previous ratios that the "other" blocking agent may be used in an amount of up to 75 equivalent percent, based on the isocyanate groups originally present in the starting polyisocyanate.

According to the second embodiment for the production of co-blocked polyisocyanates, unblocked starting polyisocyanates and a subequivalent quantity of DMP, based on the free isocyanate groups present, are used for the blocking reaction according to the invention. The quantity of DMP is at least 0.3 moles per equivalent of free

isocyanate groups. Subsequent to the partial blocking of the starting polyisocyanate, blocking with the "other" blocking agent proceeds in known manner. The quantity of the "other" blocking agent is also calculated such that 0.95 to 1.05 moles of this blocking agent are present per equivalent of the remaining unblocked isocyanate groups.

The blocked polyisocyanates produced using the process according to the invention are valuable starting materials for the production of one-component polyurethane lacquers for any heat resistant substrates. Particularly preferred reaction partners for the products according to the invention are the known polyhydroxyl compounds, preferably polyacrylate resins having hydroxyl groups.

All percentages in the following examples are weight percentages.

EXAMPLES

Example 1 (according to the invention)

Starting materials:

85.0 g	(0.85 moles)	acetylacetone
42.5 g	(0.85 moles)	hydrazine hydrate
170.0 g	(0.85 NCO equiv)	polyisocyanate having isocyanurate groups and prepared from 1,6-diisocyanatohexane, NCO content: 21%
100.0 g		xylene
70.0 g		2-methoxypropyl acetate
467.5 g		
-45.9 g	(2.55 moles)	water
421.6 g	(0.85 equiv blocked NCO groups)	blocked NCO content: 8.4%, solids content 60%, viscosity at 22°C: 225 mPa·s

Stage 1: Production of 3,5-dimethylpyrazole solution

Acetylacetone and the two solvents were initially introduced into a stirred apparatus fitted with a water separator, reflux condenser and dropping funnel, and heated to 70°C. Hydrazine hydrate was added dropwise to this initial mixture, which caused the temperature of the reaction mixture to rise to 90 to 100°C, i.e., weak refluxing. After the addition of hydrazine hydrate was complete, the mixture was heated such that it was constantly refluxing (bottom temperature 120 to 140°C). After approximately 30 minutes, 45 ml of water had collected in the water separator. The clear, almost colorless reaction solution was cooled to approximately 70°C and further processed in stage 2.

Stage 2: Production of the blocked polyisocyanate

The liquid polyisocyanate based on 1,6-diisocyanatohexane (viscosity at 23°C approximately 3000 mPa·s) was initially introduced, heated to approximately 70°C and combined in portions with stirring with the reaction solution from stage 1. On completion of addition, the reaction was continued for a further 1 hour at 100°C. No NCO content was then detectable by IR spectroscopy.

An almost colorless, 60% solution of a blocked polyisocyanate was obtained having a blocked NCO content of 8.4% and a viscosity at 22°C of 225 mPa·s. Yield: 100%, based on the polyisocyanate.

Example 2 (according to the invention)

Starting materials:

85.0 g	(0.85 moles)	acetylacetone
42.5 g	(0.85 moles)	hydrazine hydrate
79.4 g	(1.15 moles)	1,2,4-triazole
700.0 g	(2.0 equiv)	polyisocyanate having isocyanurate groups prepared from isophorone diisocyanate (IPDI), and present as a 70% solution in 2-methoxy-propyl-acetate/xylene (1/1), NCO content: 12.0%
124.0 g		2-methoxypropyl acetate
100.0 g		xylene
1130.9 g		
-45.9 g	(2.55 moles)	water
1085.0 g	(2.0 equiv blocked NCO groups)	blocked NCO content: 7.7%, solids content 60%, viscosity at 22°C: 8000 mPa·s

Stage 1: Production of 3,5-dimethylpyrazole solution

Acetylacetone, xylene and 70 g of methoxypropyl acetate were initially introduced into a stirred apparatus fitted with a water separator, reflux condenser and dropping funnel, and heated to 70°C. Hydrazine hydrate was added dropwise to this initial mixture, which caused the temperature of the reaction mixture to rise to 90 to 100°C, i.e., weak refluxing. After addition of the hydrazine hydrate, the mixture was heated such that it was constantly refluxing (bottom temperature 120 to 140°C). After approximately 30 minutes, 45 ml of water had collected in the water separator. The clear, almost colorless reaction solution was cooled to approximately 70°C and further processed in stage 2.

Stage 2: Production of the blocked polyisocyanate

The polyisocyanate based on IPDI and 54 g of methoxypropyl acetate were initially introduced and heated to 60°C. The white, crystalline flakes of 1,2,4-triazole were added to this stirred solution and heated in stages to 100 to 105°C, wherein the 1,2,4-triazole dissolved. No significant exothermic reaction was detectable at this point. After reacting for 30 minutes at 100 to 105°C, an NCO content of 4.3% was measured (calculated value 4.2%). The solution was allowed to cool to approximately 70°C and the solution of 3,5-dimethylpyrazole from stage 1 at approximately 70°C was added in portions. The temperature was raised to 100°C and the reaction continued until no NCO content was detectable by IR spectroscopy (approximately 1 hour).

A pale yellow solution of a polyisocyanate co-blocked with both triazole and dimethylpyrazole was obtained for use in yellowing-resistant one-component clear coating compositions. The blocked NCO content of this solution was 7.7% (calculated), the solids content was 60% (calculated) and the viscosity at 22°C was approximately 8000 mPa·s. Yield: 100%, based on the polyisocyanate.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for preparing a blocked polyisocyanate which comprises reacting in a first reaction stage an equimolar mixture of acetylacetone and hydrazine hydrate via a condensation reaction in a water-immiscible solvent with separation and removal of the introduced and formed water to form a liquid organic product containing 3,5-dimethylpyrazole and in a second reaction stage reacting said liquid organic product, without separation of 3,5-dimethylpyrazole as a solid, with an organic polyisocyanate, which is optionally dissolved in a solvent, to at least partially block the isocyanate groups with 3,5-dimethylpyrazole.

2. The process of Claim 1 wherein 0.95 to 1.05 moles of the 3,5-dimethylpyrazole produced in said first reaction stage are used for each equivalent of isocyanate groups of said organic polyisocyanate.

3. The process of Claim 1 wherein said organic polyisocyanate has a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%.

4. The process of Claim 3 wherein said organic polyisocyanate is a lacquer polyisocyanate having isocyanurate groups and based on 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane and/or 4,4'-diisocyanatodicyclohexyl-methane.

5. The process of Claim 2 wherein said organic polyisocyanate has a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%.

6. The process of Claim 5 wherein said organic polyisocyanate is a lacquer polyisocyanate having isocyanurate groups and based on 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane and/or 4,4'-diisocyanatodicyclohexyl-methane.

7. The process of Claim 1 wherein said organic polyisocyanate is a polyisocyanate prepared by blocking a portion of the isocyanate groups of an unblocked polyisocyanate with a blocking agent other then 3,5-dimethylpyrazole, and wherein the total quantity of blocking agent used to block the polyisocyanate is at least 95 equivalent percent, based on the isocyanate groups of the unblocked polyisocyanate, and the quantity of 3,5-dimethylpyrazole is sufficient to blocked 30 to 90 equivalent percent of the isocyanate groups, based on the isocyanate groups of the unblocked polyisocyanate.

8. The process of Claim 7 wherein the quantity of 3,5-dimethylpyrazole is sufficient to blocked 40 to 50 equivalent percent of the isocyanate groups, based on the isocyanate groups of the unblocked polyisocyanate.

9. The process of Claim 7 wherein said other blocking agent comprises butanone oxime, 1,2,4-triazole, diisopropylamine, diethyl malonate or ethyl acetoacetate.

10. The process of Claim 7 wherein said organic polyisocyanate has a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%.

11. The process of Claim 10 wherein said organic polyisocyanate is a lacquer polyisocyanate having isocyanurate groups and based on 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane and/or 4,4'-diisocyanatodicyclohexyl-methane.

12. The process of Claim 9 wherein said organic polyisocyanate has a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%.

13. The process of Claim 12 wherein said organic polyisocyanate is a lacquer polyisocyanate having isocyanurate groups and based on 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-

isocyanatomethyl-cyclohexane and/or 4,4'-diisocyanatodicyclohexyl-methane.

14. The process of Claim 1 wherein 30 to 90 equivalent percent of the isocyanate groups of said polyisocyanate are reacted with said liquid organic product containing 3,5-dimethylpyrazole, without separation of 3,5-dimethylpyrazole as a solid, and the resulting partially blocked polyisocyanate is then reacted with another blocking agent in an amount sufficient to block at least 95 equivalent percent of the remaining unblocked isocyanate groups.

15. The process of Claim 14 wherein 40 to 50 equivalent percent of the isocyanate groups of said polyisocyanate are reacted with said liquid organic product containing 3,5-dimethylpyrazole, without separation of 3,5-dimethylpyrazole as a solid.

16. The process of Claim 14 wherein said other blocking agent comprises butanone oxime, 1,2,4-triazole, diisopropylamine, diethyl malonate or ethyl acetoacetate.

17. The process of Claim 14 wherein said organic polyisocyanate has a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%.

18. The process of Claim 17 wherein said organic polyisocyanate is a lacquer polyisocyanate having isocyanurate groups and based on 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane and/or 4,4'-diisocyanatodicyclohexyl-methane.

19. The process of Claim 16 wherein said organic polyisocyanate has a molecular weight of 168 to 1000 and an NCO content of 15 to 50 wt.%.

20. The process of Claim 19 wherein said organic polyisocyanate is a lacquer polyisocyanate having isocyanurate groups and based on 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-

isocyanatomethyl-cyclohexane and/or 4,4'-diisocyanatodicyclohexyl-methane.