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(54) **Titre :** PROCEDE DE PREPARATION D'UN AGENT THIXOTROPE ET SON UTILISATION
(54) **Title:** PROCESS FOR PREPARING A THIXOTROPIC AGENT AND ITS USE

(57) **Abrégé/Abstract:**

The invention relates to a process for preparing a solution that is active as a thixotropic agent and contains urea urethanes, in which monohydroxyl compounds are reacted with an excess of toluylene diisocyanate, the unreacted portion of the toluylene diisocyanate is removed from the reaction mixture and the monoisocyanate adduct obtained is further reacted with diamines in the presence of a lithium salt to form urea urethanes. The invention also relates to the use of the solution for imparting thixotropic properties to coating compounds.

BYK-Chemie GmbH

Abstract

Process for preparing a thixotropic agent and its use

The invention relates to a process for preparing a solution that is active as a thixotropic agent and contains urea urethanes, in which monohydroxyl compounds are reacted with an excess of toluylene diisocyanate, the unreacted portion of the toluylene diisocyanate is removed from the reaction mixture and the monoisocyanate adduct obtained is further reacted with diamines in the presence of a lithium salt to form urea urethanes. The invention also relates to the use of the solution for imparting thixotropic properties to coating compounds.

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Process for preparing a thixotropic agent and its use

The invention relates to a process for preparing a solution that is active as a thixotropic agent and contains urea urethanes, in which monohydroxyl compounds are reacted with diisocyanate and the monoisocyanate adducts formed are further reacted with diamines in aprotic solvent in the presence of a lithium salt to form urea urethanes and to the use of the solution, in particular, for imparting thixotropic properties to coating compounds, such as, for Example, solvent-containing, solvent-free and aqueous paints and lacquers, PVC plastisols and coatings based on epoxide and based on unsaturated polyester resins.

To control the rheology of liquid coating compounds, organically modified bentonites, silicic acids, hydrogenated castor oil and polyamide waxes are predominantly used. A disadvantage of these substances is that they are generally dry solids that have to be dispersed by means of solvents and shear forces to form semi-finished products or be introduced into the liquid coating compound by systematic temperature control. If these temperatures are not maintained, crystallites, which may result in defects in the coating, occur in the finished coating compound.

The general disadvantage of these rheological auxiliaries used at present is that they result in turbidities and clouds (haze) in clear, transparent coatings. In addition, handling dry, powdered products causing dusts during processing is undesirable.

Other achievements relating to rheology control were disclosed in European Patent Application EP-A-0 198 519. In the latter, an isocyanate is reacted with an amine in the presence of paint resin solutions to form a urea that forms needle-shaped crystals in very finely dispersed form. These paint binders modified in this way are offered as rheology-control agents and sag-preventing binders, as so-called "sag control agents".

The disadvantage of these products is the result of the fact that they are always bound to the binder in which they have been prepared and do not permit any subsequent universal correction of finished coating agents.

European Patent EP-B-0 006 252 describes a process for preparing a thixotropic agent that eliminates some of the abovementioned disadvantages by describing urea urethanes that are prepared in aprotic solvents in the presence of LiCl by reacting isocyanate adducts with polyamines. The disadvantage of the products prepared in this way is the undefined structure of said urea urethanes due to the preparation process. Although isocyanate monoadducts are described, there are in fact no monoadducts at all in this case, as becomes clearly apparent from the Example, but mixtures of different adducts. In the process described, one mole of a diisocyanate is first reacted with one mole of a monoalcohol. This process partly produces the desired NCO-functional monoadducts, but also diadducts with no NCO-functionality. In addition, a proportion of the monomeric diisocyanate remains unreacted.

The proportions of these different compounds may vary, depending on the accessibility of the NCO group and the reaction conditions applied, such as temperature and time. The reason for the greatest disadvantage is, however, that all these adducts prepared in this way contain fairly large amounts of unreacted diisocyanate that, during the further reaction with polyamines in the presence of lithium chloride, results in uncontrolled chain extension of the urea urethane and in polymeric ureas. These products then have a tendency to precipitation and can be kept in solution only with the greatest difficulty.

The object of the present invention is therefore to find a process to generate thixotropic agent of a defined structure and consequently to enable a greater storage stability over several months of solutions prepared in this way and to enable a more reliable application of the products.

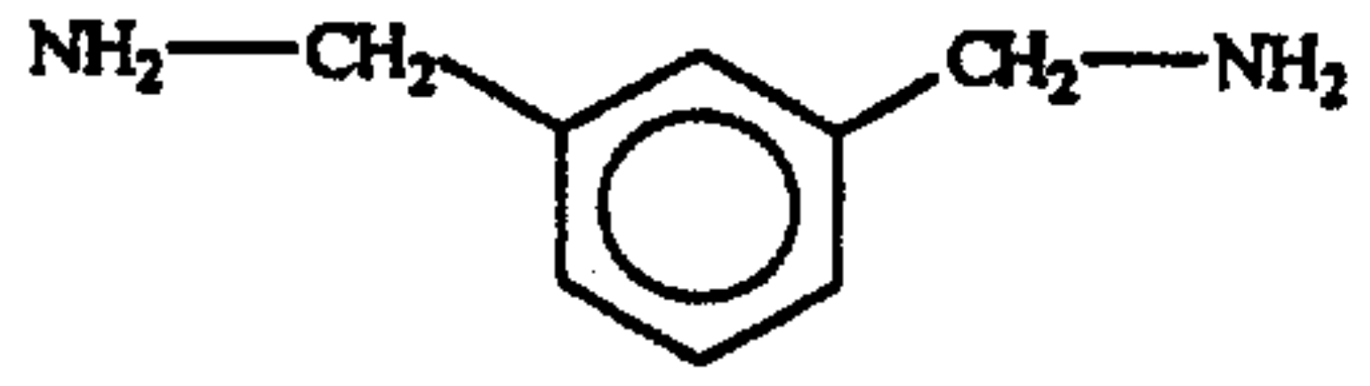
Surprisingly, it was found that this problem solution can be achieved in that monohydroxyl compounds of the general formula (I)

$$R\text{-}OH \qquad (I)$$

in which R is n-alkyl or isoalkyl containing 4 to 22 carbon atoms, cycloalkyl containing 6 to 12 carbon atoms, aralkyl containing 7 to 12 carbon atoms or a radical of the formula $C_mH_{2m+1}(O\text{-}C_nH_{2n})_x\text{-}$ or $C_mH_{2m+1}(OOC\text{-}C_vH_{2v})_x\text{-}$, where $m = 1 - 22$, $n = 2 - 4$, $x = 1 - 15$ and $v = 4$ or 5, are reacted with a 1.5 times to 5 times molar excess of toluylene diisocyanate, the unreacted part of the toluylene diisocyanate is removed from the reaction mixture and the monoisocyanate adduct obtained is reacted with diamines of the general formula (II)

$$H_2N\text{-}R''\text{-}NH_2 \qquad (II)$$

where $R'' = -C_yH_{2y}$ with $y = 2\text{-}12$ and/or with



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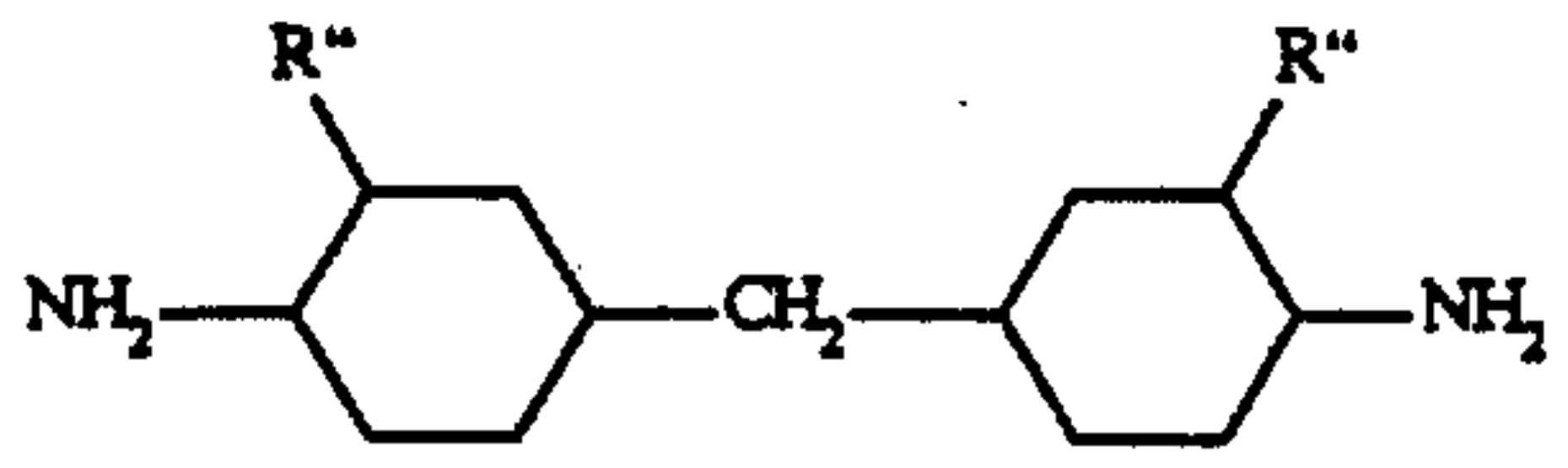


where R"' = CH_3- or H in the presence of a lithium salt.

The molar excess of toluylene diisocynate is preferably 2 - 4 mol, particularly preferably 2 - 3 mol. Preferably, the toluylene diisocyanate isomers contain a 2,4-isomer proportion of 50-80%.

After completion of the reaction of the alcohol R-OH with parts of the available diisocyanate to form the isocyanate monoadduct, the unreacted excess of the diisocyanate is removed from the reaction mixture, preferably by vacuum distillation under mild conditions.

LiCl or $LiNO_3$, but preferably $LiNO_3$, may be used as lithium salts. The solids content of the urea urethane solutions generated in this way is 5 - 80%, preferably 20 - 60%, particularly preferably 25 - 50%. The reaction of the monoadducts with the diamine takes place in a polar aprotic solvent, such as, for Example, dimethyl sulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, N-butylpyrrolidone or comparable alkylpyrrolidones.

The amount of lithium compounds is 0.2 - 2 mol, preferably 0.5 - 1.5 mol, particularly preferably 0.75 - 1.25 mol of lithium, relative to the amine equivalent of the diamine used.

The use of $LiNO_3$ in contrast to LiCl is particularly advantageous since chloride ions have a disadvantageous effect on coating compounds and promote the corrosion of the metallic bases to which the thixotropic coating compounds are applied.

The urea urethanes prepared in this way do not contain either free isocyanate groups or free amino groups. They are accordingly physiologically safe. Furthermore, no adverse side reactions occur with binders or fillers. The storage stability of these urea urethane solutions prepared in this way is extraordinarily high and is certainly 6 months or more at normal storage temperature.

<u>1. Comparison Example according to EP 0006252 (not according to the invention)</u>

1 mol (174 g) of toluylene diisocyanate (65% 2,4-isomer, referred to as T65 below) is introduced into the reaction vessel and 1 mol of butyl triglycol (mean MW: 212 g) is slowly added dropwise while stirring and the reaction is brought to an end by a known process. During this process, the temperature is kept below 40°C. The isocyanate adduct prepared in this way has a free TDI content of 7.3%, while the total NCO content is 10.9%. This reaction mixture is added to a solution of 0.5 mol of xylylenediamine (68 g) and 0.75 mol of LiCl, relative to the amine equivalent, in N-methylpyrrolidone (NMP). The solids are 50% by weight. The reaction proceeds exothermically.

The urea solution prepared in this way has a tendency to form crystals or to gel formation after a relatively short time.

2. Preparation of the monoadducts (according to the invention), Examples 1 - 8:

<u>Example 1:</u>

0.5 mol (37 g) of n-butanol is added at 30°C to 1.25 mol (217.5 g) of toluylene diisocyanate (80% 2,4-isomer, referred to as T80 below) in 2 hours. In this process, the temperature is kept below 45°C. After completion of the addition, stirring is continued for a further 2 hours until the theoretical NCO content of 33.0% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 16.9%, while the free TDI content is < 0.5%.

Example 2:

0.25 mol of butyl triglycol (53 g) (hydroxyl value: 265) is added at room temperature to 0.625 mol (108.75 g) of toluylene diisocyanate (T65) in 2 hours. In this process, the temperature is kept below 45°C. After completion of the addition, stirring is continued for a further 2.5 hours until the theoretical NCO content of 26.0% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 10.7%, while the free TDI content is < 0.5%.

Example 3:

0.3 mol of 1-decanol (47.4 g) is added at 50°C to 0.6 mol (104.4 g) of toluylene diisocyanate (T80) in 2 hours. In this process, the temperature is kept between 50°C and 55°C. After completion of the addition, stirring is continued for a further 3 hours until the theoretical NCO content of 24,9% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 12.7%, while the free TDI content is < 0.5%.

Example 4:

0.3 mol of 1-dodecanol (55.8 g) is added at 50°C to 0.6 mol (104.4 g) of toluylene diisocyanate (T80) in 2 hours. In this process, the temperature is kept between 50°C and 55°C. After completion of the addition, stirring is continued for a further 3 hours until the theoretical NCO content of 23.6% is reached. The isocyanate excess is distilled off in vacuum(0.1 mbar) at 150 - 170°C. The NCO content is 11.7%, while the free TDI content is < 0.5%.

Example 5:

0.2 mol of cyclohexanol (20 g) is added at 30°C to 0.8 mol (139.2 g) of toluylene diisocyanate (T65) in 2 hours. In this process, the temperature increases and is kept between 50°C and 55°C. After completion of the addition, stirring is continued for a further 3.5 hours until the theoretical NCO content of 36.9% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 15.4%, while the free TDI content is < 0.5%.

Example 6:

0.25 mol of isotridecanol (50 g) is added at 40°C to 0.75 mol (130.5 g) of toluylene diisocyanate (T65) in 2 hours. In this process, the temperature is kept below 60°C. After completion of the addition, stirring is continued for a further 2 hours until the theoretical NCO content of 29.1% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 11.3%, while the free TDI content is < 0.5%.

Example 7:

0.25 mol of butanol (18 g) is reacted with 0.5 mol of caprolactone (57 g) and 0.1% (0.075 g) of Dibutyl-tinlaurat at 160°C for 6 hours and then cooled to 50°C. The hydroxyester (BuCP2) (hydroxyl value 186) prepared in this way is added at 40°C to 0.75 mol of toluylene diisocyanate (130.5 g) in 2 hours. In this process, the temperature is kept below 60°C. After completion of the addition, stirring is continued for a further 2 hours until the theoretical NCO content of 25.5% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 8.9%, while the free TDI content is < 0.5%.

Example 8:

0.2 mol of methoxypoly(ethylene glycol) 350 (70 g) is added at 50°C to 0.6 mol (104.4 g) of toluylene diisocyanate (T80) in 2 hours. In this process, the temperature is kept between 50°C and 55°C After completion of the addition, stirring is continued for a further 3 hours until the theoretical NCO content of 24.1% is reached. The isocyanate excess is distilled off in vacuum (0.1 mbar) at 150 - 170°C. The NCO content is 8.0%, while the free TDI content is < 0.5%.

Table 1: Monoadducts

Example	Alcohol	NCO content	Equ. Weight	Mol ratio
1	Butanol	16,9%	248	2.5:1
2	Butyl triglycol	10.7%	392	2.5:1
3	Decanol	12.7%	330	2:1
4	Dodecanol	11.7%	358	2:1
5	Cyclohexanol	15,4%	274	4:1
6	Isotridecanol	11.3%	372	3:1
7	BuCP2	8.9%	457	3:1
8	MPEG 350	8.0%	525	3:1

2. Preparation of the urea urethanes (according to the invention), Examples 9-16

Example 9:

15.9 g of LiCl and 68 g (0.5 mol) of xylylenediamine are dissolved at 80°C in 332 g of N-methylpyrrolidone. 248 g of the monoadduct prepared in Example 1 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 50% by weight. A clear product is obtained that remains stable for a fairly long time without gel formation.

Example 10:

15.9 g of LiCl and 68 g (0.5 mol) of xylylenediamine are dissolved at 80°C in 476 g of N-methylpyrrolidone. 386 g of the monoadduct prepared in Example 2 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 50% by weight. A clear product with longterm stability is obtained.

Example 11:

25.8 g of $LiNO_3$ and 68 g (0.5 mol) of xylylenediamine are dissolved at 80°C in 424 g of dimethylformamide. 332 g of the monoadduct prepared in Example 3 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 50% by weight. The product is clear for a fairly long time interval.

Example 12:

25.8 g of $LiNO_3$ and 68 g (0.5 mol) of xylylenediamine are dissolved at 80°C in 839 g of dimethylacetamide. 360 g of the monoadduct prepared in Example 4 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 35% by weight. A clear product with longterm stability is obtained.

Example 13:

15.9 g of LiCl and 84 g (0.5 mol) of hexamethylenediamine are dissolved at 80°C in 374 g of N-methylpyrrolidone. 274 g of the monoadduct prepared in Example 5 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 50% by weight. A clear product with longterm stability is obtained.

Example 14:

12.9 g of $LiNO_3$ and 42 g (0.25 mol) of hexamethylenediamine are dissolved at 80°C in 361.5 g of dimethylformamide. 186 g of the monoadduct prepared in Example 6 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 40% by weight. A clear product with longterm stability is obtained.

Example 15:

8.0 g of LiCl and 27.2 g (0.2 mol) of xylylenediamine are dissolved at 80°C in 652 g of N-methylpyrrolidone. 191 g of the monoadduct prepared in Example 7 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 25% by weight. A clear product with longterm stability is obtained.

Example 16:

9.0 g of LiCl and 27.2 g (0.2 mol) of xylylenediamine are dissolved at 80°C in 245 g of N-methylpyrrolidone. 210 g of the monoadduct prepared in Example 8 are then added in the course of 1 hour. After completion of the addition, stirring is continued for a further 30 min and then cooling is carried out to room temperature. The urea urethane solution obtained in this way has a solids content of 50% by weight. A clear product with longterm stability is obtained.

Table 2: Urea urethanes

Example No.	**Adduct from Example No.**	**Diamine**	**Solvent**
9	1	Xylylenediamine	N-methylpyrrolidone
10	2	Xylylenediamine	N-methylpyrrolidone
11	3	Xylylenediamine	Dimethylformamide
12	4	Xylylenediamine	N-methylpyrrolidone
13	5	Hexamethylene-diamine	N-methylpyrrolidone
14	6	Hexamethylene-diamine	Dimethylformamide
15	7	Xylylenediamine	N-methylpyrrolidone
16	8	Xylylenediamine	N-methylpyrrolidone

Application Examples:

The urea urethanes according to the invention were investigated in water, solvent mixtures and in binder solutions for their ability to form gels. The achievable layer thicknesses were furthermore determined in the binders.

1:4 n-Butanol/xylene and 3:1 n-butyl acetate/methoxypropanol were used as solvent mixtures.

The following binders were used:
Desmophen VPLS 2009: hydroxyl-functional polyacrylate, 70%-solids in n-butyl acetate (Bayer AG)
Plexigum PQ 610: thermoplastic polyacrylate powder, dissolved with 60%-solids in n-butyl acetate (Röhm GmbH)

Test in the binder:
1% of the urea urethane solution was stirred into the solvent-containing binder while stirring vigorously (Dispermat, 2 m/sec).

After 24 hours, the sagging test was performed at 30 - 300 μm. For this purpose, this mixture was applied with a doctor blade with variable film thickness.

Evaluation: sagging property (thickness layer) in μm

Test in solvent or water:
To check the gel strength in water or in solvents, the urea urethanes are incorporated in the water or the solvents by simply shaking. The evaluation is made after 4 hours.
Evaluation in the water or solvent mixture: 1 = strong gel, 6 = no gel

Table 3: Application results

	Gel strength in 1:4 n-butanol/ xylene	**Gel strength in 3:1 butyl acetate/ methoxy-propanol**	**Thickness layer in Desmophen VPLS 2009**	**Thickness layer in Plexigum PQ 610**
Comparison Example	3-4	3-4	120μm/ slight seeds	90μm/ seeds
Example 9	2-3	2	150μm/no seeds	150μm/no seeds
Example 10	2	2-3	180μm/no seeds	150μm/no seeds
Example 11	2	2	150μm/no seeds	180μm/no seeds
Example 12	2	2	150μm/no seeds	210μm/no seeds
Example 13	2-3	2	150μm/no seeds	150μm/no seeds
Example 14	2	2	180μm/no seeds	150μm/no seeds
Example 15	2	2-3	150μm/no seeds	120μm/no seeds
	Gel strength in water			
Example 16	2	-	150μm/no seeds	-

Patent Claims:

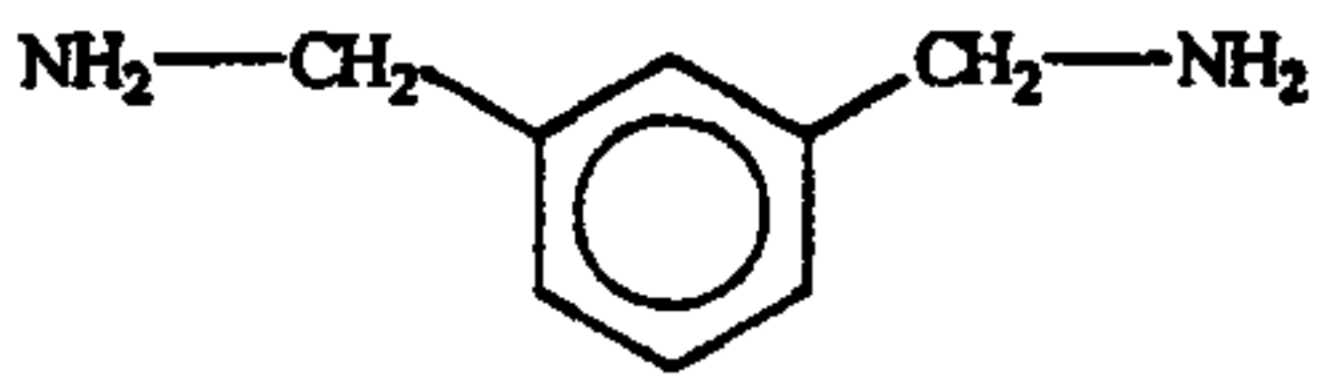
1. Process for preparing a solution that is active as a thixotropic agent and contains urea urethanes, in which monohydroxyl compounds are reacted with diisocyanate and the monoisocyanate adducts formed are further reacted with diamines in aprotic solvent in the presence of a lithium salt to form urea urethanes, characterized in that monohydroxyl compounds of the general formula (I)

$$R\text{-}OH \qquad (I)$$

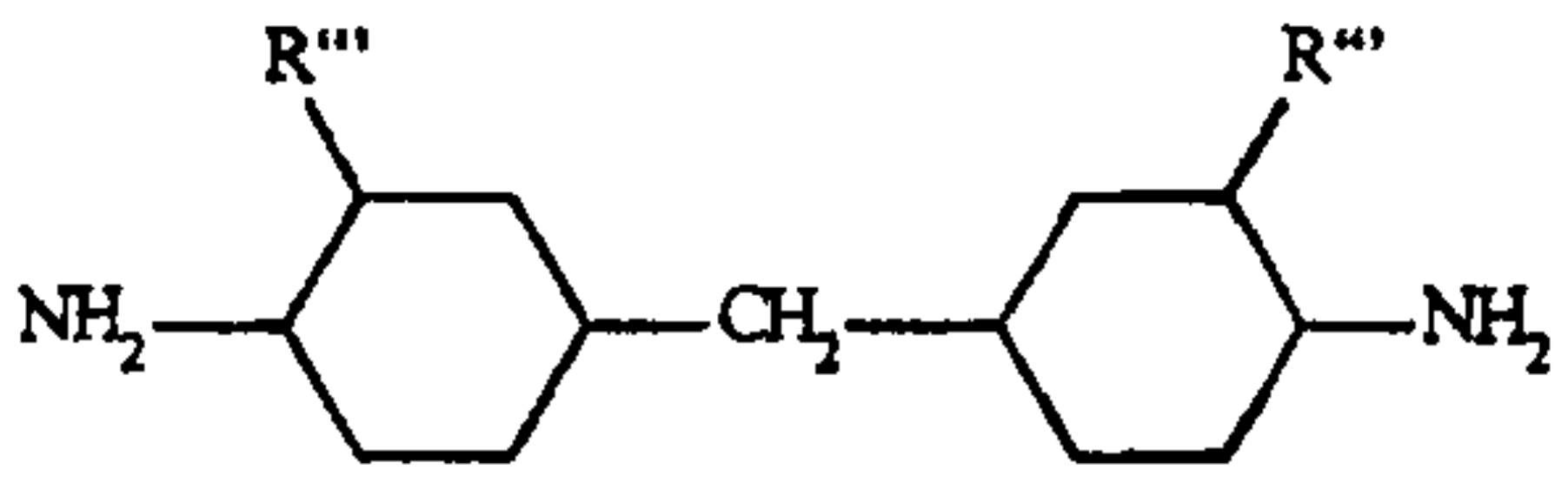
in which R is n-alkyl or isoalkyl containing 4 to 22 carbon atoms, cycloalkyl containing 6 to 12 carbon atoms, aralkyl containing 7 to 12 carbon atoms or a radical of the formula $C_mH_{2m+1}(O\text{-}C_nH_{2n})_x\text{-}$ or $C_mH_{2m+1}(OOC\text{-}C_vH_{2v})_x\text{-}$, where $m = 1 - 22$, $n = 2 - 4$, $x = 1 - 15$ and $v = 4$ or 5, are reacted with a 1.5 times to 5 times molar excess of toluylene diisocyanate, the unreacted portion of the toluylene diisocyanate is removed from the reaction mixture and the monoisocyanate adduct obtained is reacted with diamines of the general formula (II)

$$H_2N\text{-}R''\text{-}NH_2 \qquad (II)$$

where $R'' = -C_yH_{2y}$ with $y = 2\text{-}12$, with



with



where R''' = CH_3- or H,

or with mixtures thereof, in the presence of a lithium salt.

2. Process according to Claim 1, characterized in that a solution having a solids content of 5 - 80% by weight is prepared.

3. Process according to Claim 1 or 2, characterized in that the molar excess of toluylene diisocynate is 2 - 4 mol.

4. Process according to Claims 1 - 3, characterized in that the toluylene diisocyanate isomer mixture is used with a 2,4-isomer proportion of 50-80% by weight.

5. Process according to Claims 1 to 4, characterized in that 0.2 - 2 mol of lithium compound, relative to the equivalent weight of the diamine, is used.

6. Process according to Claims 1 to 5, characterized in that $LiNO_3$ is used as lithium salt.

7. Use of the solution prepared by the process according to Claims 1 to 6 for imparting thixotropic properties to coating compounds.