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(71) Demandeur/Applicant:
BAYER MATERIALSCIENCE AG, DE

(72) Inventeurs/Inventors:
LOEVENICH, CATHERINE J., DE;
HETTEL, HANS, DE;
KLESCZEWSKI, BERT, DE;
FUSSANGEL, CHRISTEL, DE

(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : PROCEDE DE PRODUCTION DE POLYOLS PIPA
(54) Title: PIPA-POLYOLE PRODUCTION METHOD

(57) Abrégé/Abstract:
The invention relates to a method for producing pyrrole-imidazole-polyamide (PIPA) polyols and the use thereof for producing polyurethane soft foam materials.

Process for the preparation of PIPA polyols

Abstract

The present invention describes a process for the preparation of PIPA polyols and their use for the production of flexible polyurethane foams.

Process for the preparation of PIPA polyols

The present invention describes a process for the preparation of PIPA polyols and their use for the production of flexible polyurethane foams.

PUR foams are obtained by reacting polyisocyanates and compounds having at least two reactive hydrogen atoms in the presence of blowing agents and other additives. A survey of the preparation of polyurethanes is given in Kunststoff-Handbuch, volume VII, "Polyurethane", 3rd edition, 1993, by Dr G. Oertel (Carl Hanser Verlag).

Highly elastic HR foams are predominantly produced with filler-modified polyols. Different types of filled polyethers are known: polymer polyols (PMPOs), polyurea dispersions (PUD polyols) and polyisocyanate polyaddition polyols (PIPA polyols). PMPOs are obtained by the free-radical copolymerization of styrene and acrylonitrile in polyols (US-A 3,304,273 and US-A 3,823,201), PUD polyols (US-A 4,093,569 and GB-A 1,501,172) are prepared by the polyaddition reaction of hydrazines or amines with mono-, di- or polyisocyanates in polyols, and PIPA polyols ("PIPA – Process for the Future", K. Picken, Urethanes Technology, 1984, pp 23-24, GB-A 2 072 204) are obtained by the polyaddition of polyisocyanates and alkanolamines (compounds having at least one hydroxyl group and at least one primary, secondary or tertiary amino group) in polyetherpolyols. In all three cases the polyetherpolyol is almost inert, but the reaction of a small proportion of the polyol with the filler stabilizes the dispersion.

Highly elastic foams are not only more elastic than standard foams, but also exhibit better burning properties. One aim of the flexible foam manufacturer is constant improvement of the burning properties of the foams. Different fire behaviour tests are used for different ultimate applications in different countries. Typical examples are "California 117A", "California 117D", "Motor Vehicle Safety System 302" and "British Standard 5852 part 2, Crib V". In particular, the last test can generally only

be passed by using a relatively high proportion of expensive flameproofing agents.

Although many PIPA polyols and their foams are known, other PIPA polyols are still being developed in order to improve specific properties of the polyols and their foams.

The stability and/or viscosity of PIPA polyols is often problematic. In EP-A 129 977 good PIPA polyols are obtained when a dispersant is used in the preparation. Without the dispersant, the products are coarse, highly viscous or solid pastes.

One aim of many developments is to increase the filler content in order to improve the properties of the foams produced with the PIPA polyol and reduce the amount of PIPA polyol to be transported. An unacceptable increase in viscosity must be avoided when increasing the filler content. EP-A 79 115 describes PIPA polyols containing 40 – 80 wt.% of filler. Part of the isocyanate is kept back and added at a later stage. If a polyol containing 50% of filler is prepared (Example 3), the ratio of triethanolamine to TDI is very important: With 26.55 parts to 23.45 parts a product is obtained which can be diluted to a filler content of 10%, whereas with 23.08 parts to 26.92 parts a viscous, lumpy product is obtained which forms aggregates when diluted to a filler content of 10%.

In US-A 4,523,025 a polyamine is reacted with alkylene oxide in the first step and the product of this reaction is reacted with a polyisocyanate in the presence of a polyol. If the polyamine is not reacted first with the alkylene oxide, the reaction mixture gels too rapidly, the solids settle out or the foams are of a poorer quality. The disadvantage of this method is that it requires an additional reaction step.

In WO 94/12553, in the preparation of PIPA polyols with a filler content of 25 – 70%, the viscosity is reduced and stabilized after production (i.e. little or no viscosity increase over time) by adding a second olamine to the reaction mixture of isocyanate and olamine in a second mixing head. Without the addition of the second

olamine, the product gels. In US-A 5,179,131 the viscosity is stabilized by adding 0.05 to 0.5 part by weight of a monocarboxylic or dicarboxylic acid.

In WO 94/20558 the viscosity and stability of PIPA dispersions are improved by using a stabilizer, which in turn is itself a PIPA polyol. In this way it is possible to prepare PIPA polyols with a filler content of 30 wt.% in which the filler does not settle out over time.

WO 00/73364 describes that the stability (and viscosity) of PIPA polyols containing 30 – 80% of filler can be improved by carrying out the preparation at 60 to 100°C and using a high shear intensity.

DE-A 198 11 471 describes a process for the preparation of stable dispersions by the addition of a monofunctional amine (e.g. di-n-butylamine). The Comparative Examples without di-n-butylamine were either incapable of being processed as flexible foam polyol, or they led to a very inhomogeneous foam structure. In US-A 4,293,470 a change in the viscosity of the filled polyol is avoided by adding 0.1 – 1.0 wt.% of a secondary amine such as dibutylamine, the storage stability thereby being improved.

It is known to use water in the preparation of PIPA or PUD polyols in order to reduce the viscosity. According to US-A 4,093,569 more than 4 wt.% (particularly preferably 10 – 25 wt.%) of water is used. The disadvantage, however, is that the large proportions of water have to be removed before foaming. Other documents of the state of the art therefore teach the use of smaller proportions of water. In US-A 4,497,913 approx. 0.1 to 0.5 wt.% of water is added in the preparation of a filled polyol from a short-chain polyol and a polyisocyanate. WO 2004/099281 describes the preparation of PIPA polyols with filler contents of 1 – 80 wt.% from a short-chain polyol and an MDI-based isocyanate in the presence of 0.1 – 5 wt.% of water.

As described in WO 00/73364, many of the processes for the preparation of PIPA polyols yield products with a high viscosity or unstable products or, in an uncontrollable reaction, produce PIPA polyols that can cause foam collapse.

PIPA polyols known from the state of the art tend towards inhomogeneity (formation of lumps or agglomerates) or instability (phase separation or viscosity change) and are therefore unsuitable for the production of foams.

One object of the present invention is to provide PIPA polyols of improved homogeneity. It has now been found that the homogeneity can be improved by adding urea in the polyol preparation.

Another object of the present invention is to provide PIPA polyols which can be used for the production of flexible polyurethane foams whose fire behaviour in respect of weight loss and burn-out time according to "British Standard 5822 part 2, Crib V" fire behaviour test is improved compared with conventional PIPA polyols.

The invention provides a process for the preparation of polyisocyanate polyaddition polyols (PIPA polyols), wherein polyisocyanates are reacted with amines or alkanolamines or mixtures thereof in a polyetherpolyol in the presence of urea and water.

The polyisocyanate used in the process according to the invention is preferably toluylene diisocyanate (TDI), particularly preferably in the form of an isomer mixture containing 80 wt.% of 2,4-TDI ('TDI 80'). In another embodiment the polyisocyanate used is diphenylmethane diisocyanate (MDI) in the form of monomeric MDI, mixtures of MDI and its higher homologues ('polymeric MDI'), or mixtures thereof.

Mono-, di- or trifunctional amines having primary, secondary or tertiary amino groups, preferably primary or secondary amino groups, can be used in the process

according to the invention. It is possible to use aliphatic, cycloaliphatic or aromatic amines. Examples of suitable amines are N-methyl-1,3-propanediamine, phenylhydrazine, 1,12-diamino-4,9-dioxadecane, 1,2-propylenediamine and 1,3-propylenediamine, α-aminodiphenylmethane, N,N-dibenzylethylenediamine, amino-terminated polyols (e.g. Jeffamine® from Huntsman ICI), N,N-bis(3-aminopropyl)methylamine, cyclohexylamine, 3-dimethylamino-1-propylamine, diethylenetriamine and aminoethylpiperazine. Preferred amines are 1,12-diamino-4,9-dioxadecane, 1,2-propylenediamine, α-aminodiphenylmethane, N,N-dibenzylethylenediamine, difunctional polyoxypropylenamine with a number-average molecular weight of 230 g/mol (Jeffamine® D230), 3-dimethylamino-1-propylamine and diethylenetriamine.

Suitable alkanolamines for the process according to the invention are diethanolamine (DEOA), 3-amino-1-propanol, aminoethylethanolamine, aminoethanol and amino-ethoxyethanol. Diethanolamine, 3-amino-1-propanol or aminoethylethanolamine is preferred. It is particularly preferable to use combinations of diethanolamine with other amines or alkanolamines. The mixing ratio of DEOA to other amines or alkanolamines is preferably 0.5:1 to 5:1. The NH number of the mixtures is typically 400 to 700. The different reactivities of primary and secondary NH groups are not taken into account here. For the purposes of calculating the formulation, it is assumed that the OH groups in alkanolamines do not react.

Suitable polyetherpolyols for the process according to the invention normally have an OH number of 28 to 56, an OH functionality of 2 to 4 and an ethylene oxide content of 15 – 20 wt.%.

An aqueous urea solution is used concomitantly in the process according to the invention. The weight ratio of urea to water is normally 1:1. The solubility of urea in water at 20°C is 1080 g/l, so highly concentrated solutions are not possible. Overall, 0.5 to 5 parts by weight, preferably 1 to 2 parts by weight, of aqueous urea solution are used concomitantly, based on the total formulation. A more dilute

solution can likewise produce homogeneous dispersions. In this case the amounts have to be adapted accordingly. Very dilute solutions are of no interest, however, if their use means that the PIPA polyols prepared therewith would contain more than approx. 3 parts of water, since 3 parts of water are typically used in foaming and an additional step (distillation to remove excess water) is undesirable.

0.1 to 2.0 parts by weight of an antioxidant, based on the total formulation, can optionally be added.

In the process according to the invention, polyisocyanate and amines or alkanolamines are used in proportions such that the ratio of isocyanate groups to isocyanate-reactive NH or NH_2 groups is 0.90 to 1.1, preferably 0.95 to 1.05 and particularly preferably 1:1. The PIPA polyols prepared by the process according to the invention have filler contents of 1 to 50 wt.% and preferably of 10 to 20 wt.%.

The process according to the invention can be carried out by first mixing polyetherpolyol, amines or alkanolamines, water and urea and then adding the polyisocyanate. Alternatively, all the components can also be mixed simultaneously in a mixing head. The process according to the invention is normally carried out at room temperature.

The PIPA polyols prepared by the process according to the invention are distinguished by a particular homogeneity and can therefore advantageously be processed further to flexible polyurethane foams.

It is assumed that urea participates chemically in the reaction in such a way as to stabilize the dispersion. As described in WO 94/20558, a polymer polyol useful for flexible polyurethane foams must be a stable dispersion of discrete polymer particles in a base polyether. The filled polyol must also exhibit good processing properties: The viscosity must be in an acceptable range so that the filled polyol can be worked in conventional foaming units. Ideally this filled polyol should also produce a foam

with a good porosity, i.e. not too much porosity, because otherwise foam collapse occurs, and not too little porosity, so as to avoid shrinkage or poor quality of the resulting foam.

Examples

In the Tables, parts and percentages are always by weight, unless indicated otherwise. The viscosities of the PIPA polyols were measured at 25°C with a Haake "Rheostress RS75" rotational viscometer at a shear rate of 50/s. To determine the hydroxyl number (OH number), a sample of the polyol in pyridine was reacted at room temperature with excess acetic anhydride under 4-dimethylaminopyridine catalysis. The excess acetic anhydride was saponified with water and the acetic acid formed was titrated with sodium hydroxide solution. The total base content was measured by potentiometric titration: the basic constituents of a sample dissolved in acetic acid were titrated potentiometrically with perchloric acid.

The following products were used in the Examples:

Polyether A:	trifunctional polyetherpolyol of OH number 35 with an EO content of 17.5 wt.%
DEOA:	diethanolamine
Desmodur® T80:	mixture of 2,4- and 2,6-TDI (80:20) with an NCO content of 48 wt.%
Irganox® 1135:	antioxidant (Ciba Speciality Chemicals)
Irganox® 68b:	antioxidant (Ciba Speciality Chemicals)
Jeffamine® D230:	polyoxypropylenamine, MW = 230 (Huntsman ICI)
Tegostab® B8681:	foam stabilizer based on polysiloxane-polyether (Goldschmidt AG)

Niax® A1: bis(2-dimethylamino)ethyl ether in dipropylene glycol (GE Speciality Chemicals)

Dabco® 33-LV: 33% triethylenediamine, 67% dipropylene glycol (Air Products)

Desmorapid® SO: tin 2-ethylhexanoate (Rhein Chemie)

Levagard PP: tris(2-chloroisopropyl) phosphate (Rhein Chemie)

Process for Examples 1 – 9

Polyether A, the amines and/or alkanolamines and an aqueous urea solution (50 wt.%) were placed in a mixing beaker at room temperature. The mixture was stirred with a Pendraulik stirrer at ~2400 rpm for two minutes. Desmodur® T80 was added all at once and the mixture was stirred at ~2400 rpm for a further 2 minutes. The mixture heated up considerably due to the exothermicity of the reaction. As soon as the dispersion had cooled to approx. 60°C, Irganox® 1135 was added.

Example		**1**	**2**	**3**	**4**	**5**
Polyether A	parts	77.82	77.81	77.80	77.80	77.81
DEOA	parts	10.93	8.12	8.21	8.12	8.12
α-Aminodiphenylmethane	parts		3.49			
N,N-dibenzylethylenediamine	parts			2.90		
Jeffamine D230	parts				2.94	
Aminoethylethanolamine	parts					1.93
Urea	parts	1.0	1.0	1.0	1.0	1.0
Water	parts	1.0	1.0	1.0	1.0	1.0
Irganox 1135	parts	0.2	0.2	0.2	0.2	0.2
Desmodur T80	parts	9.047	8.376	8.895	8.945	9.943
Filler content (%)		20	20	20	20	20
Viscosity [at 50/s and 25°C] (mPas)		1850	4390	1850	1821	1908
OH number (mg KOH/g)		148	117	119	118	127
Total base content (mg KOH/kg)		1898	1177	1398	1197	3334

Example		6	7	8	9
Polyether A	parts	77.80	77.80	77.80	88.90
DEOA	parts	8.12	8.12	5.36	4.06
Aminoethylethanolamine	parts				0.97
3-Amino-1-propanol	parts	2.39			
2-(2-Aminoethoxyethanol)	parts		2.82	5.58	
Urea	parts	1.0	1.0	1.0	0.5
Water	parts	1.0	1.0	1.0	0.5
Irganox 1135	parts	0.2	0.2	0.2	0.1
Desmodur T80	parts	9.488	9.055	9.055	4.971
Filler content (%)		20	20	20	10
Viscosity [at 50/s and 25°C] (mPas)		2001	2156	2521	1217
OH number (mg KOH/g)		135	134	119	78
Total base content (mg KOH/kg)		2361	2433	2839	1077

All the PIPA dispersions 1 – 9 were homogeneous and had viscosities of between 1800 and 4500 mPa·s (at 25°C).

In Comparative Examples 1a – 9a the PIPA preparation was carried out without urea: The aqueous urea solution was replaced with water only. A homogeneous PIPA dispersion was obtained only in the case of 6a.

Process for Comparative Examples 1a – 9a

Polyether A, the amines and/or alkanolamines and water were placed in a mixing beaker at room temperature. The mixture was stirred with a Pendraulik stirrer at ~2400 rpm for two minutes. Desmodur® T80 was added all at once and the mixture was stirred at ~2400 rpm for a further 2 minutes. The mixture heated up considerably due to the exothermicity of the reaction. As soon as the dispersion had cooled to approx. 60°C, Irganox® 1135 was added.

Example		**1a**	**2a**	**3a**	**4a**	**5a**
Polyether A	parts	78.82	78.81	78.80	78.80	78.81
DEOA	parts	10.93	8.12	8.21	8.12	8.12
α-Aminodiphenylmethane	parts		3.49			
N,N-dibenzylethylenediamine	parts			2.90		
Jeffamine D230	parts				2.94	
Aminoethylethanolamine	parts					1.93
Urea	parts	-	-	-	-	-
Water	parts	1.0	1.0	1.0	1.0	1.0
Irganox 1135	parts	0.2	0.2	0.2	0.2	0.2
Desmodur T80	parts	9.047	8.376	8.895	8.945	9.943
Filler content (%)		20	20	20	20	20
Comment		not homo-geneous	not homo-geneous	not homo-geneous	not homo-geneous	not homo-geneous : lumps

Example		**6a**	**7a**	**8a**	**9a**
Polyether A	parts	78.80	78.80	78.80	88.90
DEOA	parts	8.12	8.12	5.36	4.06
Aminoethylethanolamine	parts				0.965
3-Amino-1-propanol	parts	2.39			
2-(2-Aminoethoxyethanol)	parts		2.82	5.58	
Urea	parts	-	-	-	-
Water	parts	1.0	1.0	1.0	0.5
Irganox 1135	parts	0.2	0.2	0.2	0.1
Desmodur T80	parts	9.488	9.055	9.055	4.971
Filler content (%)		20	20	20	10
Viscosity [at 50/s and 25°C] (mPas)		1634			
OH number (mg KOH/g)		134			
Total base content (mg KOH/kg)		1497			
Comment			streaks: unstable dispersion	streaks: unstable dispersion	not homo-geneous

In Comparative Examples 1b – 9b the PIPA preparation was carried out without urea and without water. All the polyols were inhomogeneous.

Process for Comparative Examples 1b – 8b

Polyether A and the amines and/or alkanolamines were placed in a mixing beaker at

room temperature. The mixture was stirred with a Pendraulik stirrer at ~2400 rpm for two minutes. Desmodur® T80 was added all at once and the mixture was stirred at ~2400 rpm for a further 2 minutes. The mixture heated up considerably due to the exothermicity of the reaction. As soon as the dispersion had cooled to approx. 60°C, Irganox® 1135 was added.

Example		**1b**	**2b**	**3b**	**4b**	**5b**
Polyether A	parts	79.82	79.8	79.80	79.80	79.81
DEOA	parts	10.93	8.12	8.21	8.12	8.12
α-Aminodiphenylmethane	parts		3.49			
N,N-dibenzylethylenediamine	parts			2.90		
Jeffamine D230	parts				2.94	
Aminoethylethanolamine	parts					1.93
Urea	parts	-	-	-	-	-
Water	parts	-	-	-	-	-
Irganox 1135	parts	0.2	0.2	0.2	0.2	0.2
Desmodur T80	parts	9.047	8.376	8.895	8.945	9.943
Filler content (%)		20	20	20	20	20
Comment		not homo-geneous	not homo-geneous	not homo-geneous	not homo-geneous : lumps	not homo-geneous (coarse filler particles)

Example		**6b**	**7b**	**8b**	**9b**
Polyether A	parts	79.80	79.80	79.80	88.90
DEOA	parts	8.12	8.12	5.36	4.06
Aminoethylethanolamine	parts				0.965
3-Amino-1-propanol	parts	2.39			
2-(2-Aminoethoxyethanol)	parts		2.82	5.58	
Urea	parts	-	-	-	-
Water	parts	-	-	-	-
Irganox 1135	parts	0.2	0.2	0.2	0.1
Desmodur T80	parts	9.488	9.055	9.055	4.971
Filler content (%)		20	20	20	10
Comment		not homo-geneous	not homo-geneous	not homo-geneous	not homo-geneous

The homogeneous PIPA dispersions 1 – 9 and 6a were used for the production of flexible foams (Examples 10 – 19):

Examples 10 – 19

100 parts of the PIPA polyol dispersions were stirred for 20 s with water, Tegostab® B8681, DEOA, Niax® A1 and Dabco® 33-LV. After the addition of Desmorapid® SO, the mixture was stirred for a further 10 s. Desmodur® T80 was then added and the mixture was stirred for 8 to 13 s (depending on start time). The reaction mixture was poured into a mould. When the rise time had ended, the foam was cured for 20 minutes at 100 – 120°C.

Example		**10**	**11**	**12**	**13**	**14**
PIPA polyol dispersion no.		1	2	3	4	5
PIPA polyol dispersion	parts	100	100	100	100	100
Water	parts	3.0	3.0	3.0	3.0	3.0
B8681	parts	0.3	0.3	0.3	0.3	0.3
DEOA	parts	1.0	1.0	1.0	1.0	1.0
Niax A1	parts	0.05	0.05	0.05	0.05	0.05
Dabco 33LV	parts	0.15	0.15	0.15	0.15	0.15
Desmorapid SO	parts	0.25	0.25	0.25	0.25	0.18
T80	parts	38.3	38.3	38.3	38.3	38.3
Start time	s	10	9	9	10	9
Rise time	s	95	90	100	115	95
Gross density	kg/m^3	34.4	36.0	33.0	31.3	34.6
Resistance to fluid flow (water column)	mm	70	100	75	90	80
Foam structure		OK	OK	OK	OK	OK

Example		**15**	**16**	**17**	**18**	**19**
PIPA polyol dispersion no.		6	6a	7	8	9
PIPA polyol dispersion	parts	100	100	100	100	100
Water	parts	3.0	3.0	3.0	3.0	3.0
B8681	parts	0.3	0.3	0.3	0.3	0.3
DEOA	parts	1.0	1.0	1.0	1.0	1.0
Niax A1	parts	0.05	0.05	0.05	0.05	0.05
Dabco 33LV	parts	0.15	0.15	0.15	0.15	0.15
Desmorapid SO	parts	0.25	0.25	0.25	0.25	0.25
T80	parts	38.3	38.3	38.3	38.3	38.3
Start time	s	10	14	9	9	9
Rise time	s	90	120	115	120	115
Gross density	kg/m^3	33.5	32.9	35.4	34.0	31.1
Resistance to fluid flow (water column)	mm	85	90	80	55	110
Foam structure		OK	substantial shrinkage	OK	OK	OK

The start time is the period of time from the beginning of the last mixing operation to an optically perceptible change or a marked increase in the volume of the reaction mixture.

The rise time is the period of time between the beginning of mixing and the maximum vertical foam expansion. The gross density is measured by determining the volume and weight of a specimen.

The resistance to fluid flow (porosity) is determined by passing air through the specimen and measuring the resistance to this air flow with the aid of a water column on a scale of 0 to 350 mm. The apparatus used for this purpose consists of a glass cylinder with millimetre scale divisions from 0 to 350 and an inside diameter of 36 mm, and an inner tube with an inside diameter of 7 mm. This inner tube terminates at the top in a T-piece which has the air feed connected to one side and the hose with the measuring head connected to the other side. The hose for the measuring head has an inside diameter of 12 mm and a length of 1.80 m. The glass cylinder is closed at the bottom and can be filled with water through a funnel attached at the back. The test apparatus is connected to a compressed air supply via two taps, a pressure reducer and a hose of arbitrary length and diameter, the pressure reducer being set to approx. 2.0 bar. The glass container is filled with distilled water until the lower edge of the meniscus reaches the H_2O standard mark. Tap 1 is then opened and the flow rate is modified at tap 2 until the lower edge of the meniscus of the inner column reaches the 0 mm mark, thereby establishing an admission pressure of 100 mm water column. After adjustment of the admission pressure, the measuring head is placed on the sample without pressure and the height of the water column appearing in the inner tube is read off. This is equal to the resistance to fluid flow of the sample.

Dispersions 1 – 9, prepared with the aqueous urea solution, produced acceptable flexible foams. Dispersion 6a, prepared without urea, produced an unacceptable

foam with substantial shrinkage. This shows that the use of an aqueous urea solution in the preparation of the PIPA polyol not only results in an improvement in the homogeneity of the polyol, but can also have a positive influence on the foaming.

Comparative Examples 20 – 21

In Comparative Examples 20 and 21 the filled polyol was prepared with the catalyst dibutyltin dilaurate and without aqueous urea solution. Example 20 is directly comparable with Example 9. The polyols used in Examples 20 and 9 are both homogeneous, but the polyol in Example 20 causes foam collapse. The polyol in Example 21 was likewise prepared with dibutyltin dilaurate as catalyst, but the corresponding filled polyol was not homogeneous.

Example		**20**	**21**
Polyether A	parts	89.40	89.40
DEOA	parts	4.06	4.06
Aminoethylethanolamine	parts	0.97	
3-Amino-1-propanol	parts		1.20
Dibutyltin dilaurate	parts	0.03	0.03
Desmodur T80	parts	4.98	4.744
Filler content (%)		10	10
Viscosity [at 50/s and 25°C] (mPas)		1294	not homo-geneous
OH number (mg KOH/g)		82	
Total base content (mg KOH/kg)		1863	
Foaming		collapse	-

Examples 22 and 24 and Comparative Examples 23 and 25

Example 22 is a 10% PIPA prepared as in Example 9, except that in this case the PIPA polyol is prepared via a low-pressure mixing head with a mechanical stirrer. In Comparative Example 23 a standard PIPA based on TEOA and with dibutyltin dilaurate as catalyst was also prepared via a low-pressure mixing head with a mechanical stirrer. Both experiments yielded stable PIPA polyols, which were foamed on a UBT unit in Example 24 and Comparative Example 25. Although both

products pass the "Crib V" fire behaviour test (weight loss < 60 g and burning time < 10 min), the weight loss and the burn-out time for the foams with the PIPA polyols according to the invention in Example 24 are respectively lower and shorter than in Comparative Example 25. This shows that the burning properties can be improved by optimizing the polyol combinations.

Example		**22**	**23**
Polyether A	parts	88.94	89.90
DEOA	parts	4.04	
Aminoethylethanolamine	parts	0.97	
Triethanolamine	parts		4.7
Urea	parts	0.5	
Water	parts	0.5	
Irganox 68b	parts	0.1	0.1
Dibutyltin dilaurate	parts		0.03
Desmodur T80	parts	4.94	5.3
Filler content (%)		10	10
Example		**24**	**25**
PIPA polyol dispersion no.		22	23
PIPA polyol dispersion	parts	100	100
Water	parts	2.7	2.7
B8681	parts	0.35	0.35
DEOA	parts	1.2	1.2
Dabco 33LV	parts	0.2	0.2
Levagard PP	parts	8.0	8.0
Desmorapid SO	parts	0.18	0.22
T80	parts	36.8	36.8
Start time	s	13	13
Rise time	s	120	95
Gross density	kg/m^3	39.3	38.2
BS 5852 "Crib V" fire behaviour test			
Weight loss (<60 g)	g	32/29*	34/36*
Burn-out time (<10 min)	min	2.55/3.15*	3.20/3.25*
Test passed		yes	yes

* determined in duplicate

Claims

1. Process for the preparation of polyisocyanate polyaddition polyols (PIPA polyols), wherein polyisocyanates are reacted with amines or alkanolamines in a polyetherpolyol in the presence of urea and water.

2. Process according to Claim 1 wherein the polyisocyanate used is an isomer mixture of toluylene diisocyanate (TDI) containing 80 wt.% of 2,4-TDI.

3. Process according to Claim 1 or 2 wherein the alkanolamine used is diethanolamine, 3-amino-1-propanol or aminoethylethanolamine.

4. Process according to one of Claims 1 to 3 wherein mixtures of diethanolamine with amines or alkanolamines are used.

5. PIPA polyols obtainable by a process according to one of Claims 1 to 4.

6. Use of PIPA polyols according to Claim 5 for the production of flexible polyurethane foams.

Fetherstonhaugh
Ottawa, Canada
Patent Agents