

New depolymerization method for polyurethanes

The present invention relates to a new and improved process for depolymerization of polyurethanes, wherein polyether polyols and polyamines can be recovered in high yields.

Polyurethanes are materials of considerable utility in the production of rigid and flexible foams, solid and microcellular elastomers, sealants, coatings and adhesives. The versatility, relatively low cost, and superior properties of polyurethanes have resulted in the rapid growth of the polyurethane industry over the past 50 years. Currently, many thousand tons of polyurethanes are produced each year throughout the world. Unfortunately, most polyurethanes are thermoset materials which are cross-linked to one degree or another. Unlike thermoplastics such as polyethylene, polypropylene, and polystyrene, scrap or waste polyurethanes thus cannot be readily remelted or reprocessed into useful articles. Since it would be highly desirable for economic and environmental reasons to reuse or recover the large volume of scrap or waste polyurethane generated each year rather than burning it or disposing of it in landfills, considerable inventive effort has been devoted to devising processes for recovering useful chemical components from scrap polyurethane materials.

Glycolysis is used for recycling , i.e. depolymerization, of PUs (polyurethanes) waste including both rigid and flexible type products. The methods require various steps like (1) grinding, (2) step-wise addition of waste to diethylene glycol in the presence of catalyst, (3) alkoxylation, and (4) degassing and filtration for recovering polyols.

Scraps of polyurethane foam may also be recycled via ammonolysis and aminolysis methods by using ammonia, amines, or alkanolamines to retrieve monomeric polyols, which can be reused for the synthesis of PU. DE 102006036007 A1 for example describes a process wherein polyurethanes and polyureas are recycled via aminolysis.

Acidolysis has also been suggested to recycle polyols. None of these processes has been used in large industrial scale, yet. They are too complex, expensive, i.e. require high temperatures and pressures, and the quality of the recycling polyols respectively amines is bad, so that only small amounts can be used together with large amounts of virgin raw materials to produce new polyurethane foams.

Hydrolysis methods were also tested for depolymerization of polyurethanes in the prior art. Hydrolysis of a polyurethane using base catalysis to recover polyether polyols and polyamines as known in the art, however, suffers from several disadvantages. At relatively low temperatures, the hydrolysis rate is slow, respectively the hydrolysis was reported to be incomplete. At higher temperatures, the rate is faster but certain undesired side reactions may occur. US 5,208,379 for

example suggests a method to hydrolyze a polyurethane produced by reacting an active hydrogen-containing polyether and an organic polyisocyanate, which comprises contacting said polyurethane with water in the presence of an effective amount of a strong base selected from the group consisting of alkali metal oxides, alkali metal hydroxides, alkaline earth metal oxides, and alkaline earth metal hydroxides and an effective amount of an activating agent selected from the group consisting of quaternary ammonium salts containing at least 15 carbon atoms and organic sulfonates containing at least 7 carbon atoms for a time and at a temperature effective to yield the active hydrogen-containing polyether and an organic polyamine. Even though US 5,208,379 discloses in the general description that the reaction temperature may be chosen in a range of from 80 to 225 °C, example 19 shows that at 120 °C only partial hydrolysis took place and example 18 shows that at 140°C yields were only 70%. Thus, the process of US 5,208,379 cannot economically be used at lower temperatures.

Therefore, a strong need remains to provide more efficient processes for polyurethane recycling to recover polyether polyols and/or polyamines in good quality and good yield.

Subject of the present invention was to provide a new process for depolymerization of polyurethanes that overcomes the aforementioned deficiencies of prior art methods.

A specific problem of the invention was to provide a process that can be operated at lower temperatures compared to the prior art, with good yield.

A further specific problem to be solved by the invention was to provide a process that allows to obtain polyether polyols and/or polyamines in a quality very close to that of the raw materials used to produce the polyurethane to be recycled. It should be possible to use recovered polyether polyols and/or polyamines in high proportions for production of new polyurethanes.

Further problems solved by the present invention but not described before, result from the subsequent description, examples and claims.

The inventors surprisingly found out that a method of hydrolyzing a polyurethane, preferably produced by reacting an active hydrogen containing polyether and an organic polyisocyanate, which comprises contacting said polyurethane with water in the presence of a strong inorganic base having a pK_b value at 25°C of below 1 and a quaternary ammonium salt containing an ammonium cation containing 6 to 14 carbon atoms if the ammonium cation does not comprises a benzyl residue or containing 6 to 12 carbon atoms if the ammonium cation comprises a benzyl residue, allows to obtain an active hydrogen containing polyether, preferably polyether polyol, and an organic polyamine in high yields.

It was particularly surprising that, in contrast to the teaching of US 5,208,379, ammonium cations with a lower number of carbon atoms lead to higher yields at lower reaction temperatures.

Recovered active hydrogen containing polyether and/or organic polyamines of the present invention are of excellent quality and can be used in high proportions to produce new polyurethane foams. Even if 100% active hydrogen containing polyether of the present invention are used to produce new polyurethane foams high quality polyurethane foams could be obtained. Without being bound to any theory inventors believe, that the specific mild reaction conditions, the process of the invention avoids the formation of by-products which could cause problems during polyurethane production.

An embodiment of the present invention therefore is a process as defined in claim 1, the dependent claims and the description. A further embodiment is the use of recovered active hydrogen containing polyether, preferably polyether polyols, and/or organic polyamines of the invention for production of polyurethanes, in particular polyurethane foams.

Before describing the invention in more details some important terms are defined as follows: The verb "to comprise" as is used in the description, examples and the claims and its conjugation is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. "Comprising" includes "consisting of" meaning that items following the word "comprising", are included without any additional, not specifically mentioned items, as preferred embodiment.

Reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the elements is present, unless the context clearly requires that there is one and only one of the elements. The indefinite article "a" or "an" thus usually means "one or more".

The terms "catalyst" and "activating agent" are used synonymously in the present invention.

Polyurethane (PU) in the context of the present invention is especially understood to mean a product obtainable by reaction of polyisocyanates and polyols, or compounds having isocyanate-reactive groups. The polyurethanes which may be subjected to the process of the present invention are those prepared from active hydrogen-containing polyethers and polyisocyanates. Polyurethanes of this type are well known and are described, for example, in Ulrich, "Urethane Polymers", in Encyclopedia of Chemical Technology, Vol. 23, pp. 576-608(1983) and Backus et al., "Polyurethanes", in Encyclopedia of Polymer Science and Technology, Vol. 13, pp. 243-303(1988). Any known polyurethane can be used in the process of the invention.

The active hydrogen-containing polyether preferably is a polyether polyol (i.e., a polyether having primary and/or secondary end groups, preferably hydroxyl groups) but may also be an amine-

functionalized polyether (e.g., the "Jeffamine" polyoxypropylamines sold by Texaco Chemical Co.). Such materials are generally made by the catalytic ring-opening polymerization of one or more cyclic ethers such as epoxides, oxetanes, or oxolanes. Initiators having two or more active hydrogens such as polyhydric alcohols, amines, or acids may be employed to vary the functionality (number of active hydrogens) of the polyether. If more than one type of cyclic ether is used, they may be reacted either simultaneously (to yield a random-type copolymer) or sequentially (to yield a block-type copolymer). Illustrative cyclic ethers include propylene oxide, ethylene oxide, butylene oxide, tetrahydrofuran, and oxetane. Examples of suitable active hydrogen-containing polyethers include polypropylene glycol, polyethylene glycol, polytetramethylene glycol, polytrimethylene glycol, ethylene oxide-capped polypropylene glycol, random copolymers of ethylene oxide and propylene oxide.

The structure of the active hydrogen containing polyether, preferably polyether polyols, recovered in the process of the invention correlates to the structure of the polyether polyols used to prepare the polyurethane to be treated in the process of the invention.

The structure of the polyamines recovered in the process of the invention correlates to the structure of the polyisocyanates used to prepare the polyurethane to be treated in the process of the invention. "Polyamines" as used in the present invention includes diamines and preferably includes amines having two or more primary amino groups in the molecule.

The polyurethane employed in the process of this invention may be derived from any polyisocyanate reactant (i.e., an organic compound containing two or more isocyanate groups). Suitable polyisocyanates include, but are not limited to, aliphatic diisocyanates, cycloaliphatic diisocyanates, aryl alkyl diisocyanates, aromatic diisocyanates (e.g., toluene diisocyanates and diisocyanatodiphenyl methanes), aromatic triisocyanates, as well as isocyanate mixtures such as the isocyanates commonly referred to as "PMDI". Modified, masked, or blocked polyisocyanates may, of course, also be utilized.

The polyurethane used in the process of the present invention may also include any of the conventional additional reactants or additives known in the art such as for example chain extenders or curatives (relatively low molecular weight active hydrogen-containing compounds such as glycols and di- or polyamines), physical or chemical blowing agents, flame retardants, surfactants, fillers, stabilizers, anti-oxidants, colorants, polymers other than the polyurethane polymer (e.g., styrene-acrylonitrile copolymers such as are found in polymer polyols), catalysts, for example catalysts promoting the gelling reaction (isocyanate-polyol), the blowing reaction (isocyanate-water) and/or the dimerization or trimerization of the isocyanate. The polyurethane may be in solid, microcellular, or foam form and may range from a rubbery, elastomeric, flexible material to a hard, rigid substance.

To facilitate handling of the polyurethane, it is preferably desirable to chop, pulverize, grind, or otherwise comminute the polyurethane such that it is in the form of relatively small particles or granules. If the polyurethane is a foam, it may be partially or fully compressed prior to contacting with the water, strong base, and activating agent. If the polyurethane is in solid form, an initial
5 pulverization step is highly advantageous so as to maximize the surface area available for reaction (thereby reducing the reaction time required to achieve the desired level of hydrolysis).

The process of this invention will result in the effective hydrolytic cleavage of the urethane and urea bonds present in the polyurethane being treated so as to generate active hydrogen containing
10 polyether, preferably polyether polyols, polyamines, and, if the polyurethane was prepared using chain extenders or curatives, low molecular weight glycols, diols, diamines.

The bases used in the present invention are strong inorganic bases having a pK_b value at 25°C of below 1, preferably 0.5 to -2, more preferred 0.25 to -1.5 and most preferred 0 to -1. Inorganic
15 bases are bases that do not comprise CH bonds.

Particular preferred the strong base is selected from the group consisting of alkali metal hydroxides, alkali metal oxides, alkaline earth metal hydroxides, alkaline earth metal oxides and mixtures thereof. Preferred alkali metals are selected from the group consisting of Na, K and Li
20 and mixtures thereof, most preferred Na and K and mixtures thereof. Preferred alkaline earth metals are selected from the group consisting of Be, Mg, Ca, Sr, Ba and mixtures thereof, most preferred Mg and Ca and mixtures thereof. Most preferred alkali metals selected from the group consisting of potassium or sodium and mixtures thereof are used.

25 Use of the bases described before allows to run the process of the invention with higher yields at lower temperatures compared to prior art processes and thus, significantly contributes to a reduction of the operating costs.

The amount of base in the reaction mixture must be sufficient to catalyze the desired hydrolysis of
30 the polyurethane at a practicable rate. Preferably the weight ratio of base to polyurethane is from 0.01 to 25, more preferred 0.1 to 15, even more preferred 0.2 to 10 and most preferred 0.5 to 5. The base is preferably used in form of a base solution comprising a base and water. For an efficient conversion rate, it is particular preferred if the concentration of base in the base solution is higher than or equal to 5 weight %, based on the weight of the base solution, preferably 5 to 70
35 weight percent, more preferred 5 to 60 weight percent, even more preferred 10 to 50 weight percent, particular preferred 15 to 40 weight percent and most preferred 20 to 40 weight percent.

Quaternary ammonium salts are used as phase transfer catalysts in the process of the present invention. Although the addition of even trace amounts of these catalysts will accelerate the
40 hydrolysis rate, it is preferred that at least 0.5 weight percent catalyst, based on the weight of the

polyurethane be used, more preferably 0.5 to 15 weight percent, even more preferred 1 to 10 weight percent, particular preferred more 1 to 8 weight percent, especially preferred 1 to 7 and most preferred 1 to 6 weight percent.

- 5 The quaternary ammonium salts useful in the invention include those organic nitrogen-containing compounds in which the molecular structure includes a central positively-charged nitrogen atom joined to four organic (i.e., hydrocarbyl) groups, i.e. the ammonium cation, and a negatively charged anion such as halide, preferably chloride, bromide, hydrogen sulfate, alkyl sulfate, preferably methylsulfate and ethylsulfate, carbonate, hydrogen carbonate, carboxylate, preferably acetate, or hydroxide.

Quaternary ammonium salts are well known and are described, for example, in Cahn et al., "Surfactants and Defensive Systems", in Encyclopedia of Chemical Technology, Third Edition Vol. 22, pp. 383-385 (1983) and Cationic Surfactants, E. Jungermann, Ed., Marcel Dekker, New York 15 (1970), pp. 1-173. Many such compounds are commercially available at relatively low cost.

Quaternary ammonium salts containing an ammonium cation containing a total of 6 to 14 carbon atoms if the ammonium cations do not comprise a benzyl residue, respectively 6 to 12 carbon atoms if the ammonium cations comprise a benzyl residue, have been found to be most effective in 20 the process of the invention. In contrast to the teachings of US 5,208,379, the inventors found out that yields significantly decrease if for the same reaction temperature ammonium cation containing a higher number of carbon atoms are used. The same is true if the number of carbon atoms is below 6.

- 25 Catalyst that have proven to be highly efficient and thus are preferably used in the process of the present invention are quaternary ammonium salts having the general structure $R_1 R_2 R_3 R_4 NX$ wherein R_1, R_2, R_3 , and R_4 are the same or different and are hydrocarbyl groups selected from alkyl, aryl, and arylalkyl and X is selected from the group consisting of halide, preferably chloride and/or bromide, hydrogen sulfate, alkyl sulfate, preferably methylsulfate and ethylsulfate, carbonate, 30 hydrogen carbonate, carboxylate, preferably acetate, or hydroxide.

Preferably

- R_1 to R_3 are the same or different and are alkyl groups with 1 to 6, preferably 1 to 5, more preferred 1 to 4, even more preferred 1 to 3, especially preferred 1 or 2 and 35 most preferred 1 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear, saturated alkyl groups,
- R_4 is selected from the group consisting of alkyl groups with 3 to 11, preferably 3 to 10, more preferred 3 to 8, most preferred 4 to 6 carbon atoms, aryl groups with 6 to 11, preferably 6 to 10, and most preferred 6 to 8 carbon atoms, and aralkyl groups 40 with 7 to 11, preferably 7 to 10, and most preferred 7 to 9 carbon atoms, wherein the

alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear, saturated alkyl groups, and

- X is selected from the group consisting of halide, preferably chloride and/or bromide, hydrogen sulfate, alkyl sulfate, preferably methylsulfate and ethylsulfate, carbonate, hydrogene carbonate, acetate or hydroxide.

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In a first preferred embodiment the catalyst is a quaternary ammonium salt having the general structure $R_1 R_2 R_3 R_4 NX$, wherein R_4 is different from a benzyl residue and R_1 to R_4 are selected such that the sum of carbon atoms in the quaternary ammonium cation is 6 to 14, preferably 7 to 14, more preferred 8 to 13.

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In a second preferred embodiment the catalyst is a quaternary ammonium salt having the general structure $R_1 R_2 R_3 R_4 NX$ wherein R_4 is a benzyl residue and R_1 to R_3 are selected such that the sum of carbon atoms in the quaternary ammonium cation is 6 to 12, preferably 7 to 12, more preferred 8 to 11.

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Most preferred quaternary ammonium salts appropriate for use as the activating agent in the process of this invention include benzyltrimethylammonium chloride, tributyl methyl ammonium chloride.

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Preferably the polyurethane is reacted with water, the base and the catalyst in the process of the invention at a temperature of from 80°C to 200°C, preferably 90°C to 180°C, more preferred 95°C to 170°C and most preferred 100°C to 160°C. If the temperature is too low, the yields are insufficient. Too high temperatures are inefficient from an economic point of view and might cause side reactions, forming unwanted by-products.

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Preferably the polyurethane is reacted with water, the base and the catalyst for 1 minute to 14 hours, preferably 1 minute to 12 hours, more preferred 5 minutes to 12 hours, even more preferred 10 minutes to 11 hours, particularly preferred 20 minutes to 10 hours, especially preferred 20 minutes to 8 hours and most preferred 20 minutes to 7 hours.

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While water functions as a reactant in the desired polyurethane hydrolysis reaction and thus does not need to be present in stoichiometric excess relative to the urethane functional groups in the polymer to be hydrolyzed, it will generally be desirable to utilize a substantial quantity of water in order that it may conveniently serve as a reaction medium and solvent or carrier for the strong base and activating agent. For these reasons, the water is preferably present in condensed (liquid) form. Typically, the weight ratio of polyurethane to water is from 3:1 to 1:15.

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The hydrolysis is preferably conducted at atmospheric pressure, although superatmospheric pressures may be employed, if desired. Optionally, a water-miscible or water-immiscible solvent

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such as alcohol, ketone, ester, ether, amide, sulfoxide, halogenated hydrocarbon, aliphatic hydrocarbon, or aromatic hydrocarbon may be present in the reaction mixture to facilitate the hydrolysis process or to aid in recovering the reaction products.

- 5 The hydrolysis reaction may be carried out in a batch, continuous, or semi-continuous manner in any appropriate vessel or other apparatus (for example, a stirred tank reactor or screw extruder) whereby the polyurethane may be contacted with water in the presence of the base and activating agent. It will generally be preferred to agitate or stir the reaction components so as to assure intimate contact, rapid hydrolysis rates, and adequate temperature control.

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The active hydrogen containing polyether, preferably polyether polyols, organic polyamines, chain extenders, and curatives produced in the hydrolysis may be separated and recovered from the crude reaction mixture using any suitable method or combination of methods known in the art such as for example extraction (using water-immiscible organic solvents as the extractant, for example),
15 distillation, precipitation, filtration.

The recovered active hydrogen containing polyether, preferably polyether polyols, obtained in the process of the present invention are of excellent quality. The inventors found out that they can be used to produce polyurethane foams of high quality even without addition of virgin polyether polyol.

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This is a significant improvement compared to the polyurethane depolymerization processes of the prior art.

The recovered polyamines can be converted to organic polyisocyanates by conventional processes and similarly employed as components of polyurethanes.

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Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention of its fullest extent. The following examples, therefore, are to be considered as merely illustrative and not limitative of the claims or remainder of the disclosure in any.

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EXAMPLE 1 – 5 and Comparative Examples CE 1 - 6

- A reactor from Parr instrumental company equipped with a PTFE liner and a mechanical stirrer, was charged with 25g of compressed polyurethane foam pieces (ca. 1cm x 1 cm) and 75g of an aqueous base solution was added. Thereafter catalyst was added, the reactor closed and heated
35 to the operating temperature. After the desired reaction time was over the mixture was allowed to cool down, the reactor was opened and the reaction mixture was transferred into a round-bottom flask.

Water was removed and the remaining solid was extracted with cyclohexane. The cyclohexane solution was washed with 1N aqueous HCl solution, dried over magnesium sulfate and the solvent was removed. The solid was extracted with warm toluene to obtain the amine after drying and removal of solvent.

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The used base solution and catalyst, their amounts, reaction time and temperature as well as yields of the recovered polyether polyol and amine are given in Table 1.

Table 1

Example	Base	Concentration of base in solution	catalyst	Amount of catalyst [wt. %]	Reaction Temperature [°C]	Reaction time [hours]	Yield Polyetherpolyol [%]	Yield Polyamine [%]
1 (T31)	NaOH	20% in H ₂ O	TBMAC	5	100	14	63	Not determined
CE1	NaOH	20% in H ₂ O	TBAHS	5	100	14	42	Not determined
2 (T41)	NaOH	20% in H ₂ O	TBMAC	2,5	130	14	81,85	86
CE 2	NaOH	20% in H ₂ O	TBAHS	2,5	130	14	50	Not determined
3 (T14)	NaOH	20% in H ₂ O	BnTMAC	5	130	14	92,59	Not determined
CE 3	NaOH	20% in H ₂ O	TBAHS	5	130	14	87	Not determined
CE 4	NaOH	20% in H ₂ O	Variquat K1215	5	130	14	38	Not determined
CE 5	NaOH	20% in H ₂ O	Varisoft 137-90	5	130	14	43	Not determined
CE 6	NaOH	20% in H ₂ O	Adogen 432 CG	5	130	14	39	Not determined
4 (T39)	NaOH	20% in H ₂ O	TBMAC	2,5	150	14	79,7	Not determined
5 (T40)	NaOH	20% in H ₂ O	BnTMAC	2,5	150	14	73,5	Not determined

TBMAC = Tributylmethylammonium chloride (C = 13)

BnTMAC = Benzyltrimethylammoniumchloride (C = 10)

TBAHS = Tetrabutylammoniumhydrogensulfat (C = 16)

Variquat K1215 = Methyl bis(polyethoxyethanol)cocoammonium chloride (C > 37)

Varisoft 137-90 = Dimethyl di (C₁₄ – C₁₈ alkyl)ammonium methylsulfate (C > 30)

Adogen 432 CG = Dihexadecyl dimethyl ammonium chlorid (C = 34)

All Comparative Examples CE1 to 6 fulfill the requirements of US 5,208,379, i.e. have a number of carbon atoms of the ammonium cation larger than 15. In contrast thereto in inventive examples 1 to 5 the number of carbon atoms in the ammonium cation is 10 respectively 13, i.e. below 15 and thus, out of the scope of US 5,208,379. The examples and comparative examples show, that under all reaction conditions the process of the invention leads to better yields than the process of US 5,208,379.

Performance tests

Production of hot-cure flexible PU foams (flexible slabstock foam)

For the performance testing of the recycled polyols, the hot-cure flexible PU foam formulations specified in Table 2 were used.

Table 2: Formulations for hot-cure flexible PU foam production.

Formulation 1	Parts by mass (pphp)
Polyol ¹⁾	100 parts
Water	4.00 parts
KOSMOS® T9 ²⁾	0.20 parts
DABCO® DMEA ³⁾	0.15 parts
TEGOSTAB® BF2370 ⁴⁾	1.0 part
Desmodur® T 80 ⁵⁾	Variable, Constant Index of 105
Formulation 2	Parts by mass (pphp)
Polyol ¹⁾	100 parts
Water	3.00 parts
KOSMOS® EF ⁶⁾	0.60 parts
DABCO® NE1050 ⁷⁾	0.15 parts
TEGOSTAB® BF 2370LC ⁸⁾	1.0 part
Desmodur® T 80 ⁵⁾	Variable, Constant Index of 110

¹⁾Polyol 1: Standard virgin polyol Arcol® 1104 available from Covestro, this is a glycerol-based polyether polyol having an OH number of 56 mg KOH/g and an average molar mass of 3000 g/mol or inventive recycled polyol or non-inventive recycled polyol. The recycled polyol is obtained by chemical recycling from flexible polyurethane foams. The inventive recycled polyol of Example 2 was used.

²⁾ KOSMOS® T9, available from Evonik Industries: tin(II) salt of 2-ethylhexanoic acid.

- 3) DABCO® DMEA: dimethylethanolamine, available from Evonik Industries. Amine catalyst for production of polyurethane foams.
- 4) Polyether-modified polysiloxane, available from Evonik Industries.
- 5) Tolyene diisocyanate T 80 (80% 2,4 isomer, 20% 2,6 isomer) from Covestro, 3 mPa·s, 48% NCO, functionality 2.
- 6) KOSMOS® EF, emission free metal catalyst, available from Evonik Industries: tin(II) salt of ricinoleic acid
- 7) DABCO® NE1050: low emission amine catalyst, available from Evonik Industries.
- 8) Low emission polyether-modified polysiloxane with < 0.03 wt% of total cyclic siloxanes, available from Evonik Industries.

Production of Recycled Polyols

15 Recycled Polyol 1 (non-inventive)

The non-inventive recycled polyol 1 was produced following a procedure published by H&S Anlagentechnik in 2012: <https://www.dbu.de/OPAC/ab/DBU-Abschlussbericht-AZ-29395.pdf>

- 20 A Reactor from Parr instrumental company equipped with a glass in liner and a mechanical stirrer, was charged with 300.2 g of compressed polyurethane foam pieces (ca. 1 cm x 1 cm). The used polyurethane foam was produced according to Formulation 1, Table 2 by using the conventional polyol Arcol®1104.

- 25 152.64 g of the polyol Arcol®1104, 75.63 g phthalic acid and 11.97 g hydrogen peroxide (30wt% in water) were added to the foam pieces. The reaction mixture was heated to 250°C inner-temperature. The reaction was kept under this condition for 5 hours at an inner-temperature between 237°C and 256°C. After the heating was stopped the second portion of 140,63 g Arcol®1104 was added at 160°C under nitrogen atmosphere. At 80°C the reaction mixture was decanted and then cooled down to room temperature. The cooled and decanted reaction mixture
- 30 was used as non-inventive recycled polyol 1. The process was repeated to generate a sufficient quantity recycled polyol for the foaming experiments.

Recycled Polyol 2 (inventive)

- 35 The inventive recycled polyol of Example 2 was used.

General Procedure for Production of the Foam Samples

For each foaming test 300 g of polyol was used; the other formulation constituents were recalculated accordingly. 1.00 part of a component denoted 1.00 g of this substance per 100 g of polyol for example.

- 5 The foaming was carried out in the so-called manual mixing process. Formulation 1 or formulation 2 as specified in Table 2 were used. To this end, a paper cup was charged with the different polyols, the respective amine catalyst, the tin catalyst tin(II) 2-ethylhexanoate, water and a foam stabilizer, and the contents were mixed at 1000 rpm for 60 seconds with a disc stirrer. After the first stirring the isocyanate (TDI) was added to the reaction mixture and stirred at 2500 rpm for 7 s and
10 then the reaction mixture was immediately transferred into a paper-lined box (30 cm × 30 cm base area and 30 cm height). After being poured in, the foam rose in the foaming box. In the ideal case, the foam blew off on attainment of the maximum rise height and then fell back slightly. This opened the cell membranes of the foam bubbles and an open-pore cell structure of the foam was obtained. Defined foam bodies were cut out of the resulting hot-cure flexible PU foam blocks and were
15 analyzed further.

Characterization of the flexible PU foams:

- The flexible polyurethane foams produced were assessed according to the following foam
20 properties a) to l):
- a) Fallback of the foam after the end of the rise phase (= settling): The settling, or the further rise, is found from the difference of the foam height after direct blow-off and after 3 minutes after foam blow-off. The foam height is measured at the maximum in the middle of the foam crest
25 by means of a needle secured to a centimeter scale. A positive value here describes the settling of the foam after blow-off; a negative value correspondingly describes further rise of the foam.
 - b) Foam height: The height of the freely risen foam formed after 3 minutes. Foam height is reported in centimeters (cm).
 - 30 c) Rise time: The period of time between the end of mixing of the reaction components and the blow-off of the polyurethane foam. The rise time is reported in seconds (s).
 - d) Porosity by dynamic pressure measurement: The gas permeability of the foam was determined in accordance with DIN EN ISO 4638:1993-07 by a dynamic pressure measurement on the foam. The dynamic pressure measured was reported in mm water
35 column, and lower dynamic pressure values characterize a more open foam. The values were measured in the range from 0 – 300 mm water column. The dynamic pressure was measured by means of an apparatus comprising a nitrogen source, reducing valve with pressure gauge, flow regulating screw, wash bottle, flow meter, T-piece, applicator nozzle and a graduated glass tube filled with water. The applicator nozzle has an edge length of 100 × 100 mm, a

- weight of 800 g, an internal diameter of the outlet opening of 5 mm, an internal diameter of the lower applicator ring of 20 mm and an external diameter of the lower applicator ring of 30 mm. The measurement is carried out by setting the nitrogen admission pressure to 1 bar by means of the reducing valve and setting the flow rate to 480 l/h. The amount of water in the graduated glass tube is set so that no pressure difference is built up and none can be read off. For measurement on the test specimen having dimensions of 250 × 250 × 50 mm, the applicator nozzle is laid onto the corners of the test specimen, flush with the edges, and also once onto the (estimated) middle of the test specimen (in each case on the side having the greatest surface area). The result is read off when a constant dynamic pressure has been established. The final result is calculated by forming the average of the five measurements obtained.
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- e) Number of cells per cm (cell number): This is determined visually on a cut surface (measured to DIN EN 15702).
- f) Compression hardness CLD, 40 % to DIN EN ISO 33861:1997 + A1:2010. The measured values are reported in kilopascals (kPa).
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- g) Constant Deflection Compression Set (also commonly called compression set)
Five test specimens each of size 5 cm x 5 cm x 2.5cm were cut out of the finished foams. The starting thickness was measured. Compression set was measured no earlier than 72 h after production in accordance with DIN EN ISO1856 2018. The test specimens were placed between the plates of the deforming device and were compressed by 90 % of their thickness (i.e. to 2.5 mm). Within 15 minutes, the test specimens were placed into an oven at 70°C and left therein for 22 h. After this time, the apparatus was removed from the oven, the test specimens were removed from the apparatus within 1 min, and they were placed on a wood surface. After relaxation for 30 min, the thickness was measured again and the compression set was calculated and results are reported as a percentage of the original thickness:
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- $$DVR = (d_0 - d_r) / d_0 \times 100\%$$
- h) Tensile strength and elongation at break to DIN EN ISO1798:2008. The measurements of tensile strength are reported in kilopascals (kPa), and those of elongation at break in percent (%).
- i) Rebound resilience to DIN EN ISO 8307: 2007. The measurements are reported in percent (%).
- 30
- j) Emission profile at room temperature according to DIN EN ISO 16000-9:2008-04. The materials are characterized here with regard to the type and the amount of the organic substances emitting therefrom. The analysis method serves to ascertain emissions from materials that are used in furniture and mattresses. This is done by using test chambers to measure the emissions at room temperature.
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- Analysis
- Test specimen: sample preparation, sampling and specimen dimensions
- The reaction mixture is transferred into a box (30 cm × 30 cm base area and 30 cm height) which is covered by a PE plastic bag which is open at the top. After being poured in, the foam

- rose in the foaming box. In the ideal case, the foam blew off on attainment of the maximum rise height and then fell back slightly. This opened the cell membranes of the foam bubbles and an open-pore cell structure of the foam was obtained. After the foam has risen and blown off, the PE bag is closed 3 min after the blow-off. The foam is stored in this way at room
- 5 temperature for 12 hours in order to enable complete reaction, but simultaneously in order to prevent premature escape of VOCs. Subsequently, the PE bag is opened, and a 7 cm x 7 cm x 7 cm cube is taken from the centre of the foam block and immediately wrapped in aluminium foil and sealed airtight in a PE bag. It was then transported to the analytical laboratory, and the foam cube was introduced into a cleaned 30 l glass test chamber. The conditions in the test
- 10 chamber were controlled climatic conditions (temperature 21°C, air humidity 50%). Half the volume of the test chamber is exchanged per hour. After 24 hours, samples are taken from the test chamber air. Tenax adsorption tubes serve to absorb the VOCs. The Tenax tube is then heated, and the volatile substances released are cryofocused in a cold trap of a temperature-programmable evaporator with the aid of an inert gas stream. After the heating phase and
- 15 cryofocusing has ended, the cold trap is rapidly heated to 280°C and the focused substances are evaporated. They are subsequently separated in the gas chromatography separation column and detected by mass spectrometry. Calibration with reference substances permits a semi-quantitative estimate of the emission, expressed in "µg/m³". The quantitative reference substance used for the VOC analysis (VOC value) is toluene. Signal peaks can be assigned to
- 20 substances using their mass spectra and retention indices. The following equipment is used for the analysis: Gerstel, D-45473 Mühlheim an der Ruhr, Eberhard-Gerstel-Platz 1, Germany, TDS-3 / KAS-4, Tenax® desorption tubes, Agilent Technologies 7890A (GC) / 5975C (MS), column: HP Ultra2 (50 m, 0.32 mm, 0.52 µm), carrier gas: helium. More specific procedural instructions can be taken from DIN EN ISO 16000-9:2008-04.
- 25 k) Odor testing of the resulting foams. The finished foams were packed in odor - neutral plastic bags and stored under airtight conditions. For the odor assessment of the foam, cubes measuring 10 cm x 10 cm x 10 cm were cut out and transferred to jars with a volume of 1 L, from which the samples were smelled. The jars were closed with a screw lid. The odor test took place after storing the jars for 24 hours at 22°C. The odor test was assessed by a panel
- 30 of 13 trained odor testers. They were questioned here about the intensity of the odor, a low odor level was rated +, moderate odor ++, and high odor +++.
- l) Emission of aldehydes according to VDA 275
- 35 In the method, test specimens having a certain mass and size are secured above distilled water in a closed 1 L glass bottle and stored for a defined period at constant temperature. The bottles are subsequently cooled down and the absorbed aldehydes are determined in the distilled water. The amount of aldehydes determined is based on the dry weight of the foam sample (mg / kg).
- After the foams have been taken out of the foaming box, they are stored at 21 ° C and about 50 % relative humidity for 24 hours. Samples of the foam blocks are then taken at suitable and

representative sites distributed uniformly across the width of the (cooled) foam block. The foam samples are then wrapped in aluminum foil and sealed in a polyethylene bag. The samples each have a size of 100 x 40 x 40 mm thickness (about 9 g). For each foam block, 3 test specimens are taken for the determination of aldehydes.

- 5 The sealed samples are sent for direct determination immediately after receipt. The samples are weighed on an analytical balance to an accuracy of 0.001 g before analysis. A 50 ml quantity of distilled water is pipetted into each of the glass bottles used. The samples are introduced into the glass bottle, and the vessel is sealed and kept at a constant temperature of 60°C in a thermal cabinet for 3 hours. The vessels are removed from the thermal cabinet after
- 10 the test period. After standing at room temperature for 60 minutes, the samples are removed from the test bottle. This is followed by derivatization by the DNPH method (dinitrophenylhydrazine). For this, 900 µl of the aqueous phase is admixed with 100 µl of a DNPH solution. The DNPH solution is prepared as follows: 50 mg of DNPH in 40 ml of MeCN (acetonitrile) is acidulated with 250 µl of dilute HCl (1:10) and made up to 50 ml with MeCN.
- 15 On completion of derivatization, a sample is analyzed by means of HPLC. Separation into the individual aldehyde homologues is effected.

HPLC Instrument Parameters

The following instrument is used for the analysis:

Agilent Technologies 1260

- 20 Chromatography column: Phenomenex Luna250 * 4.6 mm C18, 5µ particle size
Eluent: water acetonitrile gradient
Detection: UV 365 nm

25 Results of the foaming experiments

The results of the influence of the recycled polyols according to the invention on foaming process and foam physical properties of the resulting hot-cure flexible PU foams are compiled in the tables below. Hot-cure flexible PU foams were produced following Formulation 1, Table 2 with a standard virgin polyol, recycled polyol not inventive and with the inventive recycled polyol 2

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Table 3: Foaming results and foam physical properties of the foams with use of different types of polyols according to Formulation 1, Table 2.

Foam Sample	#6	#7	#8
Arcol®1104, OHN 56, Reference	100		
Recycled Polyol 1 (non-inventive), OHN 82		100	
Recycled Polyol 2 (inventive), OHN 54			100

Index	105	105	105
Rise time (s)	117	-	122
Rise height (cm)	24,0	-	24,1
Settling (cm)	0,2	-	0,2
Cells (per cm)	14	-	14
Porosity (mm water column)	15	-	10
Hardness CLD 40% compression (kPa)	3,4	-	3,5
Elongation (%)	160	-	150
Tensile Strength (kPa)	113	-	116
Ball Rebound (%)	43	-	43
Compression Set 90% 22h at 70°C (%)	5	-	7
Remarks	Standard foam	Collapse	Standard foam

- The foaming results in Table 3 show that replacing the standard virgin polyol Arcol®1104 by the inventive recycled polyol 2 (foam # 8) allows to produce flexible PU foam with comparable foaming processing characteristics to the reference foam (#6). Furthermore, all foam physical properties are comparable to the reference foam. On the contrary it was not possible to produce any reasonable foam by using 100 pphp of the non-inventive recycled polyol 1, this foam was collapsing (foam #7).

- The results of the influence of the recycled polyols according to the invention on foam emissions at room temperature are compiled in Table 4. Hot-cure flexible PU foams were produced following Formulation 2, Table 2 by using a standard virgin polyol, a recycled polyol 1 (not inventive) and the inventive recycled polyol 2.

Table 4: Emission and odor testing results of the foams with use of different polyol types according to Formulation 2, Table 2

Foam Sample	#9	#10	#11
Arcol®1104, OHN 56, Reference	100		
Recycled Polyol 1 (non-inventive), OHN 82		100	
Recycled Polyol 2 (inventive), OHN 54			100
Index	110	110	110
Emissions according to DIN EN ISO 16000-9:2008-04 [$\mu\text{g}/\text{m}^3$]	50		125
Odor	++	-	++

Emission of aldehydes according to VDA 275, Formaldehyde [ppm]	0,2	-	0,2
Emission of aldehydes according to VDA 275, Acetaldehyde [ppm]	0,3	-	0,3
Emission of aldehydes according to VDA 275, Propionaldehyde [ppm]	0,3	-	0,2
Remarks	Standard Foam	No foam	Standard Foam

- The hot-cure flexible PU foams according to the invention are found to have low emissions if emissions-optimized additives are used. This can be seen in the VOC tests according to DIN EN ISO 16000-9:2008-04. Even though the total emissions are slightly increased when using 100 pphp of the inventive recycled polyol 2 (from 50 $\mu\text{g}/\text{m}^3$ for foam#9 to 125 $\mu\text{g}/\text{m}^3$ for foam#11), the emissions are still well below the typical limits for TVOC of 500 $\mu\text{g}/\text{m}^3$. The inventive recycled polyol 2 is thus suitable for low-emissions formulations. On the contrary it was not possible to produce any reasonable foam by using 100 pphp of the non-inventive recycled polyol 1.
- 10 The results in Table 4 show that replacing the standard virgin polyol Arcol®1104 by the inventive recycled polyol 2 allows to produce flexible PU foam with comparable odor characteristics as well as aldehyde emissions. The emissions of formaldehyde, acetaldehyde and propionaldehyde, measured according to VDA275, are in a comparable range for foam #9 and foam #11.

Claims:

1. A method of hydrolyzing a polyurethane, preferably produced by reacting an active
5 hydrogen containing polyether and an organic polyisocyanate, which comprises contacting
said polyurethane with water in the presence of a strong inorganic base having a pK_b value
at 25°C of below 1, preferably 0.5 to -2, more preferred 0.25 to -1.5 and most preferred 0 to
-1 and as catalyst a quaternary ammonium salt containing an ammonium cation containing
10 6 to 14 carbon atoms if the ammonium cation does not comprises a benzyl residue or
containing 6 to 12 carbon atoms if the ammonium cation comprises a benzyl residue to
yield an active hydrogen containing polyether, preferably polyether polyol, and an organic
polyamine.
2. The method of claim 1 wherein the strong base is selected from the group consisting of
15 alkali metal hydroxides, alkali metal oxides, alkaline earth metal hydroxides, alkaline earth
metal oxides and mixtures thereof.
3. The method of claim 2 wherein the alkali metals are selected from the group consisting of
Na, K and Li and mixtures thereof, most preferred Na and K and mixtures thereof and/or
20 the alkaline earth metals are selected from the group consisting of Be, Mg, Ca, Sr, Ba and
mixtures thereof, preferably Mg and Ca and mixtures thereof.
4. The method of any one of claim 1 to 3 wherein the catalyst is a quaternary ammonium salt
having the general structure $R_1 R_2 R_3 R_4 NX$ wherein R_1, R_2, R_3 , and R_4 are the same or
25 different and are hydrocarbyl groups selected from alkyl, aryl, and arylalkyl and X is
selected from the group consisting of halide, preferably chloride and/or bromide, hydrogen
sulfate, alkyl sulfate, preferably methylsulfate and ethylsulfate, carbonate, hydrogen
carbonate, carboxylate, preferably acetate, or hydroxide.
- 30 5. The method of claim 4, wherein
 - R_1 to R_3 are the same or different and are alkyl groups with 1 to 6, preferably 1 to 5,
more preferred 1 to 4, even more preferred 1 to 3, especially preferred 1 or 2 and
most preferred 1 carbon atoms, wherein the alkyl groups may be linear, branched,
35 cyclic, saturated or unsaturated, most preferred are linear, saturated alkyl groups,
 - R_4 is selected from the group consisting of alkyl groups with 3 to 11, preferably 3 to
10, more preferred 3 to 8, most preferred 4 to 6 carbon atoms, aryl groups with 6 to
11, preferably 6 to 10, and most preferred 6 to 8 carbon atoms, and aralkyl groups
with 7 to 11, preferably 7 to 10, and most preferred 7 to 9 carbon atoms, wherein the

- alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear, saturated alkyl groups, and
- 5 - X is selected from the group consisting of halide, preferably chloride and/or bromide, hydrogen sulfate, alkyl sulfate, preferably methylsulfate and ethylsulfate, carbonate, hydrogene carbonate, acetate or hydroxide.
6. The method of claim 4 or 5, wherein R₄ is different from a benzyl residue and R₁ to R₄ are selected such that the sum of carbon atoms in the quaternary ammonium cation is 6 to 14, preferably 7 to 14, more preferred 8 to 13.
- 10 7. The method of claims 4 or 5, wherein R₄ is a benzyl residue, R₁ to R₃ are selected such that the sum of carbon atoms in the quaternary ammonium cation is 6 to 12, preferably 7 to 12, more preferred 8 to 11.
- 15 8. The method of any one of claims 1 to 7 comprising the additional steps of separating and recovering the organic polyamine and/or an active hydrogen containing polyether, preferably polyether polyol.
- 20 9. The method of any one of claims 1 to 8 wherein the polyurethane is foamed.
- 25 10. The method of any one of claims 1 to 9, wherein the polyurethane is reacted with water, the base and the catalyst,
at a temperature of from 80°C to 200°C, preferably 90°C to 180°C, more preferred 95°C to 170°C and most preferred 100°C to 160°C
and/or
for 1 minute to 14 hours, preferably 1 minute to 12 hours, more preferred 5 minutes to 12 hours, even more preferred 10 minutes to 11 hours, particular preferred 20 minutes to 10 hours, especially preferred 20 minutes to 8 hours and most preferred 20 minutes to 7 hours
30 and/or
at atmospheric pressure.
- 35 11. The method of any one of claims 1 to 10 wherein at least 0.5 weight percent catalyst, based on the weight of the polyurethane, is used, more preferably 0.5 to 15 weight percent, even more preferred 1 to 10 weight percent, particular preferred more 1 to 8 weight percent, especially preferred 1 to 7 and most preferred 2 to 6 weight percent.

12. The method of any one of claims 1 to 11 wherein the weight ratio of base to polyurethane is from 0.01 to 25, preferably 0.1 to 15, more preferred 0.2 to 10, even more 0.5 to 5.
- 5 13. The method of any one of claims 1 to 12 wherein a base solution comprising a base and water is used, preferably a base solution wherein the concentration of base, based on the weight of the base solution, is higher than or equal to 5 weight %, preferably 5 to 70 weight percent, more preferred 5 to 60 weight percent, even more preferred 10 to 50 weight percent, particular preferred 15 to 40 weight percent and most preferred 20 to 40 weight percent.
- 10 14. Use of an active hydrogen containing polyether, preferably polyether polyol, and/or organic polyamine obtained with the process according to any one of claims 1 to 13 for production of polyurethanes, in particular polyurethane foams.
- 15