

Improved Process for the Depolymerization of Polyurethane

The present invention relates to an improved process for producing recycled polyols (" P_{PU} ") and recycled amines (" A_{PU} ") from polyurethane (" PU "), in particular polyurethane waste. PU is hydrolyzed, and a raw product (" R_H ") comprising an organic phase (" P_O "), which typically comprises the main part of the polyols P_{PU} and amines A_{PU} that result from the hydrolysis of the PU , and an aqueous phase (" P_W ") are obtained. At least a part of P_O (" P_{O1} ") is then separated from R_H . Residual water W and amines A_{PU} are separated from P_{O1} by distillation to obtain water vapor V and an amine fraction F_A . At least a part P_{O3} of the remaining organic phase P_{O2} , which typically contains the main fraction of the polyols P_{PU} , is then further purified by stripping, wherein the water vapor V is used as countercurrent stripping gas. Preferably, the distillation of water from P_{O1} and the stripping step are carried out in the same column K_1 .

The process according to the present invention is highly energy and resource efficient. In particular, it reduces the number of necessary distillation devices by combining a distillation and stripping device, thus simplifying the overall device outlay.

Background of the Invention

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 effort has been devoted to devising processes for recovering useful chemical components from scrap polyurethane materials.

WO 2023/083968 A1 discloses a process for cleaving of PU with a reagent comprising a primary or secondary organic amine and/or an amino alcohol and water along with a catalyst. The obtained products may be recovered by distillation and/or stripping.

WO 2023/072985 A1 gives a general overview over the most important PU recycling processes, namely hydrolysis, glycolysis, and a mixed form ("hydroglycolysis"). It also stresses the challenges of PU recycling on a large scale, in particular with respect to resource efficiency and technical demands of PU recycling equipment. In particular, there is a demand in the art for a process which allows for efficient separation, purification and recycling of the typical cleavage products that are obtained during PU depolymerization, i.e. the amines and polyols that are the basic building blocks of any PU polymer.

Therefore, the problem underlying the present invention was to provide a process for recycling of **PU**, i.e. for producing recycled polyols and recycled amines from **PU**, which is procedurally simple, resource efficient, and allows for simplified installation engineering.

Short Description of the Invention

5

Surprisingly, a process for producing recycled polyols and recycled amines from **PU** that solves the above-described problems was now found.

The process according to the present invention is a process for production of at least one recycled polyol **P_{PU}** and at least one recycled amine **A_{PU}** from at least one polyurethane **PU**, wherein the at least one polyurethane **PU** is preferably provided as a **PU** foam, more preferably as a flexible **PU** foam.

10

The process according to the invention comprises the following steps:

15

- a. at least partial hydrolysis of the **PU** by contacting the **PU** with water **W** and at least one base **B**,

to give a raw product **R_H** comprising polyols **P_{PU}**, amines **A_{PU}**, water **W**, at least one base **B**, and optionally solids **S**,

20

wherein the raw product **R_H** comprises an organic phase **P_O** and an aqueous phase **P_W**,

25

- b. separating at least a part **P_{O1}** of the organic phase **P_O** from the raw product **R_H**, wherein **P_{O1}** comprises polyols **P_{PU}**, amines **A_{PU}**, water **W**,
- c. separating at least a part of the water **W** and at least a part of the amines **A_{PU}** from **P_{O1}** by distillation

30

to obtain

- water vapor **V**,
- a fraction **F_A** comprising amines **A_{PU}**,
- an organic phase **P_{O2}** comprising polyols **P_{PU}**, optionally amines **A_{PU}** and optionally water **W**,

35

- d. purifying at least a part **P_{O3}** of the organic phase **P_{O2}** by stripping,

characterized in that

40

in step d., water vapor **V** is used as stripping gas in countercurrent flow to **P_{O3}**.

The process according to the present invention thus allows to efficiently use water vapor that is obtained during distillation of the organic phase, thus saving on resources and facilitating the overall process.

Figure

5

- The Figure shows a preferred embodiment of the process according to the invention. The organic phase P_{O1} <1> of a hydrolytic raw product R_H is fed into an evaporator <2> that is connected to a distillation column K_1 <4>. The raw product R_H is obtained after PU hydrolysis using a base B and optionally a quaternary ammonium salt Q as phase transfer catalyst. The organic phase P_{O1} <1> comprises polyols P_{PU} , amines A_{PU} , residual water W , and at least one of quaternary ammonium salt Q , aminic decomposition products of Q . In the evaporator <2>, water and optionally other components comprised by P_{O1} <1>, such as amines A_{PU} , is/are evaporated from P_{O1} <1>. Hence, a stream of water vapor V <3> is obtained and conducted into column K_1 <4> to free it from other impurities that are dragged along. The residues <5> of this distillation step are then conducted to a further purification step, which typically is carried out in a short path evaporator or thin film evaporator or a further distillation column K_2 . In this additional purification step, the polyols P_{PU} and the amines A_{PU} are further separated from each other, preferably by distillation. The polyol fraction <6> obtained in this further purification is then conducted into the column K_1 <4> and may optionally be heated via heat exchanger <10>.
- Within column K_1 <4>, water vapor V <3> passes a packing <41>. Above packing <41>, column K_1 <4> may contain an optional condenser <42>, which is used to condensate and remove impurities by partial condensation, such as aminic decomposition products of Q and/or other hydrolysis products such as amines A_{PU} , that are dragged along with water vapor V <3>. These compounds are removed as condensate via piping <7>. Optionally, in case additional water vapor is needed for stripping polyol P_{PU} , additional liquid water may be fed to column K_1 <4> via piping <8>. Such additional water may be heated via heat exchanger <9>. Optionally, the condensate removed via piping <7> may partially or fully be used as reflux into column K_1 <4> and in this case may be mixed via piping <14> with additional water that is fed to column K_1 <4> via piping <8>.
- Water vapor V <3> rises to the upper part of column K_1 <4> and may be additionally heated by a heat exchanger <43> integrated in the column K_1 <4> or outside of column K_1 <4>. Water vapor V <3> then passes a second packing <44> from the bottom and contacts the polyol fraction <6> fed from the top of column K_1 <4>. By means of such countercurrent of water vapor V <3> and the polyol fraction <6>, the latter is stripped from impurities, and a purified polyol fraction <11> is obtained in liquid collector <45> where it is withdrawn from column K_1 <4>. The water vapor obtained after stripping contains aminic decomposition products of Q and/or other hydrolysis products such as amines A_{PU} . It is withdrawn from the head of column K_1 <4> and condensed in condenser <12>. The resulting condensed stream <13> may then be further processed, e.g. in a further distillation to recycle water, which may then be recycled to column K_1 <4> via piping <8> to be used for stripping again and/or isolate the desired amines A_{PU} . Alternatively, the water may be

recycled to the reaction step to create more hydrolytic raw product R_H and therewith more organic phase $P_{O1} <1>$.

Detailed Description of the Invention

5 In the process according to the present invention, at least one recycled polyol P_{PU} and at least one recycled amine A_{PU} are obtained from at least one polyurethane PU . "Recycled" in the context of this invention means that the decomposition products that P_{PU} and A_{PU} that are that are obtained in the process according to the invention, i.e. a process comprising a hydrolysis step of the PU may
10 be reused, for example in the synthesis of further PU , in particular PU foam, preferably flexible PU foam.

The polyol P_{PU} , the amine A_{PU} , and the at least one polyurethane PU that may be used in the process according to the invention are further described below.

15

1. Polyol P_{PU}

"Polyol P_{PU} " encompasses any organic compound that has two or more isocyanate-reactive groups, preferably two or more OH groups. Such polyols are for example described in JP H04-
20 136017 A, WO 2022/042909 A1, WO 2022/042910 A1, WO 2023/072985, WO 2023/078802 A1.

The structure of the polyol P_{PU} recovered in the process of the invention correlates with the structure of the polyols used to prepare the polyurethane PU treated in the process of the invention.

25

Preferably, the at least one polyol P_{PU} is selected from the group consisting of

- polyether polyols;
- polyester polyols;
- hydroxyl-containing aliphatic polycarbonates, in particular polyether polycarbonate polyols;
- 30 - natural oil-based polyols (NOPs);
- polymeric polyols (filled polyols);
- prepolymer polyols;
- autocatalytic polyols.

35 More preferably, the at least one polyol P_{PU} is selected from the group consisting of polyether polyols, polyester polyols, even more preferably the at least one polyol P_{PU} is selected from polyether polyols.

The at least one polyol P_{PU} preferably has an average functionality of 2 to 6, more preferably 2 to 3,
40 most preferably 2.

"Functionality" means the number of isocyanate-reactive groups, preferably OH groups, per molecule.

In a mixture M_P of more than one polyols P_{PU} , "average functionality" refers to the number of all isocyanate-reactive groups, preferably all OH groups, in the mixture M_P divided by the amount of substance (mol) of all polyols P_{PU} in the mixture M_P .

The at least one polyol P_{PU} preferably has an average number molecular weight in the range of from 500 to 15000 g/mol. The average number molecular weights are typically determined by gel permeation chromatography ("GPC"), in particular using polypropylene glycol as reference and tetrahydrofuran ("THF") as eluent.

The at least one polyol P_{PU} preferably has an OH number in the range from 10 to 1200 mg KOH/g. The OH numbers are determined, in particular, in accordance with the DIN standard DIN 53240:1971-12.

15

1.1 Polyether polyols

Polyether polyols, from which the at least one polyol P_{PU} is preferably selected, are known to the skilled person and preferably are a polyether having primary and/or secondary end groups, preferably hydroxyl groups. Amine-functionalized polyethers (e.g., the "Jeffamine" polyoxypropylamines sold by Texaco Chemical Co.) may also be used. It is preferred to use polyether polyols with hydroxyl end groups.

Polyether polyols, from which the at least one polyol P_{PU} is preferably selected, are obtainable by known methods. 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 polyether polyols include polypropylene glycol, polyethylene glycol, polytetramethylene glycol, polytrimethylene glycol, ethylene oxide-capped polypropylene glycol, random copolymers of ethylene oxide and propylene oxide.

Polyether polyols, from which the at least one polyol P_{PU} is preferably selected, may also be obtained by anionic polymerization of alkylene oxides ("AO") in presence of alkali metal hydroxides, alkali metal alkoxides or amines as catalysts and by addition of at least one starter molecule ("SM"), which preferably contains two or three reactive hydrogen atoms in banded form, or by cationic polymerization of AO in the presence of Lewis acids, such as, for example, antimony pentachloride or boron trifluoride etherate, or by double meta cyanide catalysis.

Suitable **AO** contain from two to four carbon atoms. Examples are tetrahydrofuran, 1,3-propylene oxide, 1,2-propylene oxide, 1,2-butylene oxide and 2,3-butylene oxide. Ethylene oxide and 1,2-propylene oxide are preferably used. The alkylene oxides can be used individually, cumulatively, in blocks, in alternation or as mixtures.

5

Starter molecules **SM** used may especially be compounds having at least two, preferably two to eight, hydroxyl groups, or having at least two primary amino groups in the molecule.

Preferred starter molecules **SM** are selected from the group consisting of

- water;
- 10 - di-, tri- or tetrahydric alcohols, in particular selected from ethylene glycol, propane-1,2-diol, propane-1,3-diol, diethylene glycol, dipropylene glycol, glycerol, trimethylolpropane, pentaerythritol;
- fatty acid triglycerides, wherein at least two of the fatty acids carry at least one -OH group, preferably castor oil, which is a triglyceride, wherein at least two, preferably each of the
- 15 three fatty acid residues are 12-hydroxy-9-octadecenoic acid (known as "ricinoleic acid");
- higher polyfunctional polyols, especially sugar compounds, for example glucose, sorbitol, mannitol and sucrose;
- polyhydric phenols, resols, for example oligomeric condensation products of phenol and formaldehyde, and Mannich condensates of phenols, formaldehyde and dialkanolamines,
- 20 and melamine, or amines such as aniline, ethylene diamine ("**EDA**"), toluene diamine ("**TDA**"), diphenylmethane diamine ("**MDA**", which is preferably diphenylmethane 2,4'-diamine or diphenylmethane 2,2'-diamine), 1,5-pentamethylene diamine ("**PMDA**").

The choice of the suitable starter molecule **SM** depends on the particular field of use of the resulting polyether polyol in the polyurethane production (for example, polyols used for production of flexible **PU** foams are different from those used in the production of rigid **PU** foams).

Polyether polyols, from which the polyol **P_{PU}** is preferably selected, may also be obtained from natural sources. Such polyether polyols and their preparation from biological sources are described by H. Sardon, D. Mecerreyes, A. Basterretxea, L. Avérous, C. Jehanno, *ACS Sustainable Chem. Eng.* **2021**, 9, 10664–10677 (hereinafter "Sardon *et al.*").

1.2 Polyester polyols

35 Polyester polyols, which is another group of polyols from which the polyol **P_{PU}** is preferably selected, are based on esters of polybasic aliphatic or aromatic carboxylic acids, preferably having two to twelve carbon atoms.

Examples of aliphatic carboxylic acids are succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid. Examples of aromatic carboxylic acids are phthalic acid, isophthalic acid, terephthalic acid and the isomeric naphthalenedicarboxylic acids. The polyester polyols are obtained by condensation of these

40

polybasic carboxylic acids with polyhydric alcohols, preferably of diols or triols having two to twelve, more preferably two to six, carbon atoms, preferably trimethylolpropane and glycerol.

Polyester polyols, from which the polyol **P_{PU}** is preferably selected, may also be obtained from natural sources. Such polyester polyols and their preparation from biological sources are described by Sardon *et al.*

1.3 Hydroxyl-containing aliphatic polycarbonates

Hydroxyl-containing aliphatic polycarbonates, which is another group of polyols from which the polyol **P_{PU}** is preferably selected, are polyols containing carbon dioxide bound in the form of carbonate [-O-C(=O)-O]. Since carbon dioxide forms as a by-product in large volumes in many processes in the chemical industry, the use of carbon dioxide as comonomer in alkylene oxide polymerizations is of particular interest from a commercial point of view. Partial replacement of alkylene oxides in polyols with carbon dioxide has the potential to distinctly lower the costs for the production of polyols. Moreover, the use of CO₂ as co-monomer is very advantageous in environmental terms since this reaction constitutes the conversion of a greenhouse gas to a polymer. Such polyols are described for example by J. Xu, E. Feng, J. Song, *J Appl Polym Sci.* **2014**, 131: 10.1002/app.39822. The preparation of these polyols by addition of alkylene oxides and carbon dioxide onto H-functional starter substances by use of catalysts is well known. Various catalyst systems can be used here: The first generation was that of heterogeneous zinc or aluminium salts, as described, for example, in US 3,900,424 A or US 3,953,383 A. In addition, mono- and binuclear metal complexes have been used successfully for copolymerization of CO₂ and alkylene oxides (WO 2010/028362 A1, WO 2009/130470 A1, WO 2013/022932 A1 or WO 2011/163133 A1). The most important class of catalyst systems for the copolymerization of carbon dioxide and alkylene oxides is that of double metal cyanide catalysts, also referred to as “**DMC catalysts**” (US 4,500,704 A, WO 2008/058913 A1). Suitable alkylene oxides and H-functional starter substances are those also used for preparing carbonate-free polyether polyols, as described above.

1.4 Natural oil-based polyols (**NOPs**)

A further group of polyols from which the polyol **P_{PU}** is preferably selected are polyols that are based on renewable raw materials, namely natural oil-based polyols (**NOPs**). Use of **NOPs** for production of **PU** foams are of increasing interest with regard to the long-term limits in the availability of fossil resources, namely oil, coal and gas, and against the background of rising crude oil prices. **NOPs** have already been described many times in such applications (WO 2005/033167 A2, US 2006/0293400 A1, WO 2006/094227 A2, WO 2004/096882 A1, US 2002/0103091 A1, WO 2006/116456 A1 and WO 2005/033167 A2). **NOPs** are now available on the market from various manufacturers (US 2006/0167125 A1, US 2006/0229375 A1, WO 2009/058367 A1). Depending on the base raw material, e.g. soya bean oil, palm oil or castor oil (described in Figure 2 B. of Sardon *et al.*), and the subsequent workup, polyols with different

properties are obtained. It is possible here to distinguish essentially between two groups: a) polyols based on renewable raw materials which are modified such that they can be used to an extent of 100 % for production of polyurethanes (US 2006/0167125 A1, US 2006/0229375 A1); b) polyols based on renewable raw materials which, because of the processing and properties thereof, can replace the petrochemical-based polyol only in a certain proportion (WO 2009/058367 A1). As described above, polyether polyols, polyester polyols and other polyols from which the polyol **P_{PU}** may be selected, may also be obtained from natural sources (see Sardon *et al.*).

1.5 Polymeric polyols (filled polyols)

10

A further class of polyols from which the polyol **P_{PU}** is preferably selected are the so-called polymeric polyols (filled polyols). A key characteristic of these polyols is that they contain dispersed solid organic fillers up to a solids content of 40 % or more. There are different types of polymeric polyols available: **SAN**, **PUD** and **PIPA** polyols. **SAN** polyols are highly reactive polyols containing a dispersed copolymer based on styrene-acrylonitrile ("**SAN**"). **PUD** ("poly-urea-dispersion") polyols are highly reactive polyols containing polyurea, likewise in dispersed form. **PIPA** ("poly isocyanate poly addition") polyols are highly reactive polyols containing a dispersed polyurethane, for example formed by in situ reaction of an isocyanate with an alkanolamine in a conventional polyol.

Depending on the application, the preferred solid content is typically between 5 weight-% ("weight-%" = "wt.-%") and 40 wt.-% based on the polyol. The solid content of the polymeric polyols supports improved cell opening, which results in a more controlled foaming process, especially when **TDI** ("toluene di-isocyanate") is used, so that no shrinkage of the foams occurs. The solids content thus acts as an essential processing aid. A further function is to control the foam hardness via the solids content in the foam formulation, since higher solid contents result in higher foam hardness. The formulations with polymeric polyols are distinctly less self-stable and therefore tend to require additional physical stabilization to the chemical stabilization coming from the crosslinking reaction. Depending on the solid contents of the polyols, they can be used alone or in a blend with the abovementioned unfilled polyols.

1.6 Prepolymer polyols

A further class of polyols from which the polyol **P_{PU}** is preferably selected are obtained as prepolymers via reaction of polyol with isocyanate in a molar ratio of 100 : 1 to 5 : 1, preferably 50 : 1 to 10 : 1. Such prepolymers are preferably made up in the form of a solution in polymer, and the polyol preferably corresponds to the polyol used for preparing the prepolymers.

1.7 Autocatalytic polyols

A further class of polyols from which the polyol **P_{PU}** is preferably selected are the so-called autocatalytic polyols, especially autocatalytic polyether polyols. Polyols of this kind are based, for example, on polyether blocks, preferably on ethylene oxide and/or propylene oxide blocks, and

40

additionally include catalytically active functional groups, for example nitrogen-containing functional groups, especially amino groups, preferably tertiary amine functions, urea groups and/or heterocycles containing nitrogen atoms. By using such autocatalytic polyols in the production of **PU** foams, preferably flexible **PU** foams, it is possible to reduce the required catalyst amount used in addition, depending on application, and/or to match it to specific desired foam properties. Suitable polyols are described, for example, in WO 0158976 A1, WO 2005/063841 A1, WO 02/22702 A1, WO 2006/055396 A1, WO 03/029320 A1, WO 01/58976 A1, US 6,924,321 B2, US 6,762,274 B2, WO 2008/079614 A1, WO 2004/060956 A1 or WO 2013/102053 A1 and can be purchased, for example, under the Voractiv™ and/or SpecFlex™ Activ trade names from Dow.

10

Depending on the required properties of the resulting foams, it is advantageously possible to use appropriate polyols, as described for example in: US 2007/0072951 A1, WO 2007/111828 A2, US 2007/0238800 A1, US 6,359,022 B2 or WO 96/12759 A2. Further polyols are known to those skilled in the art and can be found, for example, in EP 0 380 993 A2 or US 3,346,557 A1, to which reference is made in full.

15

1.8 Preferred polyols

1.8.1) More preferably the at least one polyol **P_{PU}** has the general structure according to formula (I):
 $HX^2-V^1-X^1H$, wherein the residue **V¹** is a divalent hydrocarbon residue, which optionally contains at least one group selected from an ester group, an ether group, a thioether group, an amine group, a cyano group, a hydroxy group.

20

V¹ preferably is selected from the group consisting of alkylene, alkenylene, alkynylene, aromatic hydrocarbon residue, wherein optionally the alkylene, alkenylene, alkynylene and/or aromatic hydrocarbon residue comprises at least one group selected from an ester group, an ether group, a thioether group, an amine group, cyano group, hydroxy group.

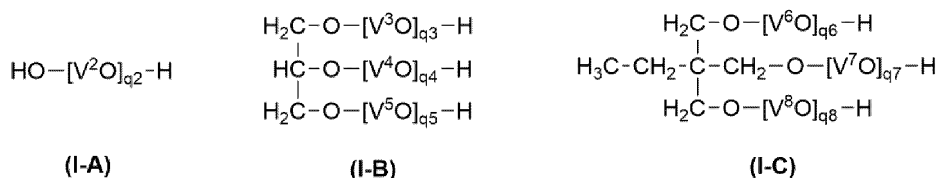
25

X¹, **X²** are independently each selected from the group consisting of -O-, -NH-, -N(R')-, -S-, wherein **R'** is an alkyl group, preferably an alkyl group with 1 to 6 carbon atoms.
 Preferably, **X¹** = -O- and **X²** = -O-.

30

1.8.2) The polyol **P_{PU}** of the formula (I) preferably has a general structure that is selected from the group consisting of formulae (I-A), (I-B), (I-C), even more preferably formula (I-A):

35



wherein $q_2, q_3, q_4, q_5, q_6, q_7, q_8$ each independently is an integer ≥ 2 , preferably in the range of from 2 to 1000, more preferably in the range of from 5 to 500, even more preferably in the range of from 10 to 200,

wherein $V^2, V^3, V^4, V^5, V^6, V^7, V^8$ each independently is a group with the formula $-C_nH_{2n}-$, wherein n is an integer and $n = 1$ to 100, preferably $n = 2$ to 50, more preferably $n = 2$ to 10, even more preferably $n = 2$ to 6, even more preferably $n = 2$ to 4, even more preferably $n = 2$ to 3,

preferably $V^2, V^3, V^4, V^5, V^6, V^7, V^8$ each independently is selected from the group consisting of, $-CH_2CH_2-$, $-CH_2-CH(CH_3)-$, $-CH(CH_3)-CH_2-$, $-CH_2CH_2CH_2-$,

10

and wherein the residues V^2 in the polyol P_{PU} according to the general structure (I-A) are the same or different,

and wherein the residues V^3 in the polyol P_{PU} according to the general structure (I-B) are the same or different,

15 and wherein the residues V^4 in the polyol P_{PU} according to the general structure (I-B) are the same or different,

and wherein the residues V^5 in the polyol P_{PU} according to the general structure (I-B) are the same or different,

20 and wherein the residues V^6 in the polyol P_{PU} according to the general structure (I-C) are the same or different,

and wherein the residues V^7 in the polyol P_{PU} according to the general structure (I-C) are the same or different,

and wherein the residues V^8 in the polyol P_{PU} according to the general structure (I-C) are the same or different.

25

According to the present invention “ $-C_nH_{2n}-$ ” comprises linear and branched alkylene residues, preferably selected from the group consisting of methylene, ethylene, *n*-propylene, *iso*-propylene, more preferably selected from the group consisting of ethylene, *n*-propylene, *iso*-propylene.

30 Polyols P_{PU} of the formulae (I-A), (I-B), (I-C) are polyether polyols.

2. Amine A_{PU}

35 The structure of the amines A_{PU} correlates to the structure of the polyisocyanates comprised by the polyurethane PU that is subjected to the process of the invention. “Amines A_{PU} ” as used in the present invention includes amines with two or more amine groups, preferably includes amines having two or more primary amino groups in the molecule.

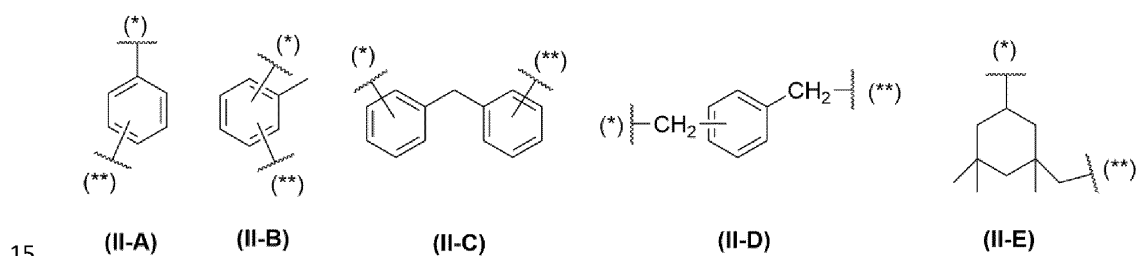
40 In a preferred embodiment, the at least one amine A_{PU} has the general structure according to formula (II): $H_2N-W^1-NH_2$, wherein the residue W^1 is a divalent hydrocarbon residue, which optionally contains at least one group selected from an ester group, ether group, a thioether group, an amine group, a cyano group, a hydroxy group, amino group.

W¹ preferably is selected from the group consisting of alkylene, alkenylene, alkynylene, aromatic hydrocarbon residue, wherein optionally the alkylene, alkenylene, alkynylene and/or aromatic hydrocarbon residue comprises at least one group selected from an ester group, ether group, an amine group, a thioether group, hydroxy group, cyano group, amino group.

W¹ more preferably is selected from the group consisting of alkylene, aromatic hydrocarbon residue, wherein optionally the alkylene and/or aromatic hydrocarbon residue comprises at least one group selected from hydroxy group, amino group.

10

2.1) Even more preferably, W¹ in formula (II) is selected from the group consisting of C₁-C₆ alkylene and formulae (II-A), (II-B), (II-C), (II-D), (II-E), even more preferably from the group consisting of C₅-alkylene, C₆-alkylene, formulae (II-A), (II-B), (II-C), (II-D), (II-E), wherein



where the bond identified by “(*)” in formulae (II-A), (II-B), (II-C), (II-D), (II-E) denotes the bond to one of the amino groups in formula (II) and the bond identified by “(**)” in formulae (II-A), (II-B), (II-C), (II-D), (II-E) denotes the bond to the other amino group in formula (II).

20

In formula (II-A), it is preferred that the two bonds identified by “(*)” and “(**)”, respectively, are in *para*-position at the aromatic ring with respect to each other.

In formula (II-B), it is preferred that the two bonds identified by “(*)” and “(**)”, respectively, are in 2,4-position or 2,6-position at the aromatic ring with respect to the methyl group.

25

In formula (II-C), the aromatic carbon atoms that are not linked to one of the bonds identified by “(*)” or “(**)”, i.e. the aromatic carbons atoms that carry a hydrogen in formula (II-C), may be substituted by a group selected from amino group, an alkyl group, wherein the alkyl group is preferably methyl. More preferably, all of the aromatic carbon atoms in formula (II-C) that are not linked to one of the bonds identified by “(*)” or “(**)” each carry a hydrogen.

30

In formula (II-D), it is preferred that the two residues carrying the bonds identified by “(*)” and “(**)”, respectively, are in *para*-position at the aromatic ring with respect to each other.

35

2.2) In an even more preferred embodiment, the at least one amine **A_{PU}** is selected from the group consisting of phenylene diamine, toluene diamine ("**TDA**"), di- and polyamines of diphenyl methanes ("**MDA**"), 1,5-pentane diamine ("**PDA**"), 1,6-hexamethylene diamine ("**HDA**"), isophorone diamine ("**IPDA**"), xylylene diamine ("**XDA**"). Most preferred is that the at least one amine **A_{PU}** is

5 **TDA**.

In **TDA**, the two amino groups are preferably in 2,4-position or 2,6-position at the aromatic ring with respect to the methyl group.

10

3. Polyurethane **PU**

In step a. of the process according to the present invention, polyurethane (**PU**) is used. This **PU** is then subjected to the partial or full hydrolysis according to step a.

15 One of the advantages of the method according to the present invention is its applicability to a broad range of **PU**. Hence, the **PU** to be subjected to step a. of the process of the present invention is not especially limited, and any known polyurethane **PU** can be used in the process of the invention. Preferably the polyurethane **PU** subjected to step a. is polyurethane waste.

The **PU** subjected to step a. of the present invention is preferably provided as a **PU** foam, more

20 preferably as a flexible **PU** foam.

In particular, the polyurethanes **PU** which may be subjected to the process of the present invention are those prepared from active hydrogen-containing polyols, preferably polyethers, and polyisocyanates. Polyurethanes of this type are well known and are described, for example, in

25 US 5,208,379 A, 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).

Typically, the polyurethane subjected to step a. of the process according to the invention is a polymer, in which at least two OH-groups of a polyol **P_{PU}** are each linked to a NH-group of an amine **A_{PU}** via a urethane functionality and at least two NH-groups of an amine **A_{PU}** are each linked

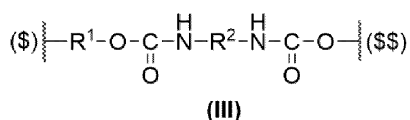
30 to a OH-group of a polyol **P_{PU}** via a urethane functionality.

The **PU** 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

35 methanes), aromatic triisocyanates, as well as isocyanate mixtures such as the isocyanates commonly referred to as polymeric diphenyl methane diisocyanate ("**PMDI**"). Modified, masked, or blocked polyisocyanates may, of course, also be utilized. The **PU** subjected to the process according to the present invention may also comprise groups selected from allophanate groups, isocyanurate groups, urea groups. If one or more of these groups is present, at least a part of these

groups may be cleaved during step a. The **PU** subjected to 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 **PU** 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.

In particular, the at least one **PU** subjected to step a. of the present invention comprises at least one polymer strand **PU_s**, where **PU_s** has m mutually linked repeat units of the chemical structure (III) with



15

where m is an integer ≥ 4 , preferably 4 to 10^6 , even more preferably 10 to 10^5 , even more preferably 100 to 10^4 ,

where the repeat units of the chemical structure (III) within **PU_s** are the same or at least partly different from one another,

where the repeat units of the chemical structure (III) within **PU_s** are joined to one another in such a way that the bond identified by “(\$)” in a particular repeat unit is joined by the bond identified by “(\$\$)” in the adjacent repeat unit,

wherein **R¹** is a divalent hydrocarbon residue which optionally contains at least one group selected from ester group, ether group, hydroxy group, cyano group, amine group, thioether group, wherein **R²** is a divalent hydrocarbon residue preferably comprising aromatic carbon atoms,

wherein in those cases where **PU** comprises more than one polymer strand **PU_s**, one or more residues **R¹** of a first polymer strand **PU_s** may be covalently bonded to one or more other residue(s) **R¹** of the same or a second polymer strand **PU_s**.

In particular, the **PU** subjected to step a. according to the process of the present invention comprises the polyol **P_{PU}** and the amine **A_{PU}** that are, from a formal point of view, mutually linked to each other via urethane bonds that connect a hydroxy group of the **P_{PU}** to the amino group of the **A_{PU}**. Upon hydrolysis of the **PU** in step a., the urethane groups are cleaved, thus releasing the **P_{PU}** and **A_{PU}**.

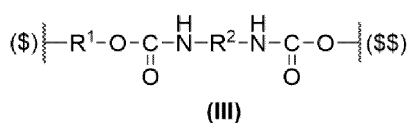
In line with this, in a preferred embodiment according to the present invention (hereinafter abbreviated as “preferred embodiment **Θ**”), the polyol **P_{PU}** has a general structure that is selected

from the group consisting of formulae **(I-A)**, **(I-B)**, **(I-C)** as defined under point 1.8.2), even more preferably formula **(I-A)** as defined under point 1.8.2),

and the at least one amine **A_{PU}** has the general structure according to formula **(II)**: H₂N-W¹-NH₂, wherein the residue W¹ is as defined under point 2.1), even more preferred the at least one amine

5 **A_{PU}** is as defined under point 2.2),

and the at least one **PU** subjected to step a. of the present invention comprises at least one polymer strand **PU_s**, where **PU_s** has m mutually linked repeat units of the chemical structure **(III)** with



10

where m is an integer ≥ 4 , preferably 4 to 10⁶, even more preferably 10 to 10⁵, even more preferably 100 to 10⁴,

where the repeat units of the chemical structure **(III)** within **PU_s** are the same or at least partly different from one another,

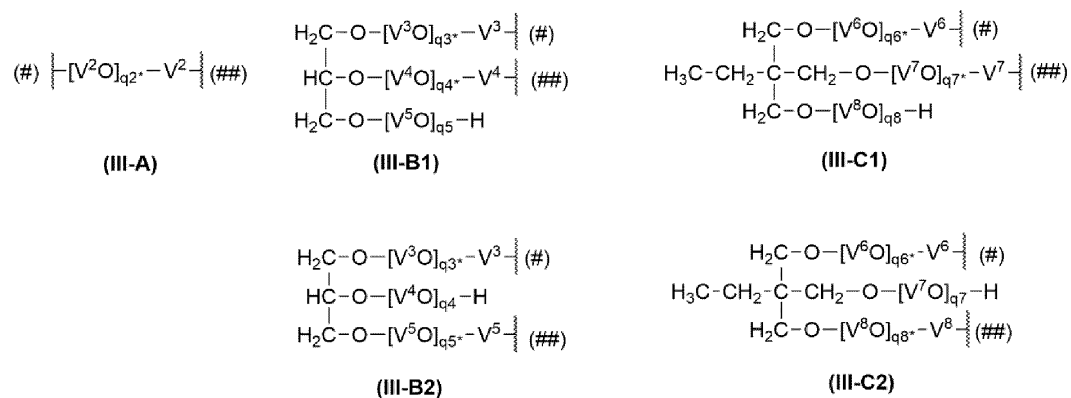
15

where the repeat units of the chemical structure **(III)** within **PU_s** are joined to one another in such a way that the bond identified by “(\$)” in a particular repeat unit is joined by the bond identified by “(\$\$)” in the adjacent repeat unit,

wherein R¹ is selected from one of the divalent residues according to formulae **(III-A)**, **(III-B1)**, **(III-**

20

B2), **(III-C1)**, **(III-C2)**



wherein V², V³, V⁴, V⁵, V⁶, V⁷, V⁸ are as defined for formulae **(I-A)**, **(I-B)**, **(I-C)** under point 1.8.2,

wherein q2* in formula **(III-A)** is dependent on q2 as defined for formula **(I-A)** by the following relation $q2 = 1 + q2^*$;

25 wherein q3* in formulae **(III-B1)** and **(III-B2)** is dependent on q3 as defined for formula **(I-B)** by the following relation $q3 = 1 + q3^*$;

wherein $q4^*$ in formula (III-B1) is dependent on $q4$ as defined for formula (I-B) by the following relation $q4 = 1 + q4^*$;

wherein $q5$ in formula (III-B1) is as defined for formula (I-B);

wherein $q4$ in formula (III-B2) is as defined for formula (I-B);

- 5 wherein $q5^*$ in formula (III-B2) is dependent on $q5$ as defined for formula (I-B) by the following relation $q5 = 1 + q5^*$;

wherein $q6^*$ in formulae (III-C1) and (III-C2) is dependent on $q6$ as defined for formula (I-C) by the following relation $q6 = 1 + q6^*$;

- 10 wherein $q7^*$ in formula (III-C1) is dependent on $q7$ as defined for formula (I-C) by the following relation $q7 = 1 + q7^*$;

wherein $q8$ in formula (III-C1) is as defined for formula (I-C);

wherein $q7$ in formula (III-C2) is as defined for formula (I-C);

wherein $q8^*$ in formula (III-C2) is dependent on $q8$ as defined for formula (I-C) by the following relation $q8 = 1 + q8^*$;

- 15 wherein the bond identified by “(#)” in formulae (III-A), (III-B1), (III-B2), (III-C1), (III-C2) corresponds to the bond identified by “(\$)” in formula (III) and wherein the bond identified by “(##)” in formulae (III-A), (III-B1), (III-B2), (III-C1), (III-C2) corresponds to the bond from R^1 to the oxygen atom in formula (III), i.e. the bond from R^1 that is different from the bond identified by “(\$)” in formula (III)

- 20 and where R^2 is selected from the group consisting of C_1 - C_6 alkylene and formulae (II-A), (II-B), (II-C), (II-D), (II-E), even more preferably selected from the group consisting of C_5 -alkylene, C_6 -alkylene, formulae (II-A), (II-B), (II-C), (II-D), (II-E) as defined above under item 2.1, where in the context of formula (III), the bond identified by “(*)” in formulae (II-A), (II-B), (II-C), (II-D), (II-E)
- 25 denotes the bond to a nitrogen of one of the urethane functions in formula (III) and the bond identified by “(**)” in formulae (II-A), (II-B), (II-C), (II-D), (II-E) denotes the bond to the nitrogen of the other urethane function in formula (III).

- 30 The **PU** subjected to step a. of the process according to the invention, and in particular the polymer strand **PU_s** in embodiment **Θ**, may contain further repeat units that are different from the residues R^1 and R^2 as defined above. For example, it may contain further repeat units that are derived from at least one unit selected from the group consisting of

- polyether polyols, in particular as defined under point 1.1 above;
- polyester polyols, in particular as defined under point 1.2 above;
- 35 - hydroxyl-containing aliphatic polycarbonates, in particular polyether polycarbonate polyols, in particular as defined under point 1.3 above;
- natural oil-based polyols (**NOPs**), in particular as defined under point 1.4 above;
- polymeric polyols (filled polyols), in particular as defined under point 1.5 above;

- prepolymer polyols, in particular as defined under point 1.6 above;
- autocatalytic polyols, in particular as defined under point 1.7 above.

4. Step a.

5

In step a. of the process according to the invention, **PU** is at least partially hydrolyzed by contacting the **PU** with water and at least one base **B**.

Such hydrolysis reactions of **PU** are known to the skilled person and are described for example in WO 2023/083968 A1, WO 2023/072985 A1. These documents compare hydrolysis to other
10 reactions for cleaving **PU** such as glycolysis.

US 5,208,379 A also discloses typical hydrolysis conditions.

“Hydrolysis” means in the context of this invention the cleavage of at least a part of the urethane groups in the **PU** with water molecules (as nucleophiles) to obtain the respective amines and polyols.

15

4.1 Base **B**

The at least one base **B** that is employed in step a. may be chosen by the skilled person according to his knowledge.

20 Preferably, the at least one base **B** is selected from the group consisting of alkali metal phosphates, alkali earth metal phosphates, alkali metal hydrogen phosphates, alkali earth metal hydrogen phosphates, alkali metal carbonates, alkali earth metal carbonates, alkali metal silicates, alkali earth metal silicates, alkali metal hydrogen carbonates, alkali earth metal hydrogen carbonates, alkali metal carboxylates, in particular alkali metal acetates, alkali earth metal
25 carboxylates, in particular alkali earth metal acetates, alkali metal sulfites, alkali earth metal sulfites, ammonium hydroxide, alkali metal hydroxides, alkali metal oxides, alkali earth metal hydroxides, alkali earth metal oxides.

More preferably, the at least one base **B** is selected from the group consisting of alkali metal phosphates, alkali metal hydrogen phosphates, alkali metal carbonates, alkali metal silicates, alkali
30 metal hydrogen carbonates, alkali metal carboxylates, wherein the carboxylate is in particular acetate, alkali metal sulfites, ammonium hydroxide, alkali metal hydroxides, alkali metal oxides, alkali earth metal hydroxides, alkali earth metal oxides.

The alkali metal comprised by base **B** is preferably selected from the group consisting of potassium, sodium, lithium, more preferably selected from the group consisting of potassium,
35 sodium.

The alkali earth metal comprised by base **B** is preferably selected from the group consisting of beryllium, magnesium, calcium, strontium, barium, more preferably selected from the group consisting of magnesium, calcium.

5 Even more preferably, the at least one base **B** is selected from the group consisting of potassium carbonate, sodium carbonate.

In a preferred embodiment, the ratio of the total weight of all bases **B** used in step a. relative to the total weight of all **PU** subjected to step a. is in the range of 50 : 1 to 1 : 1, preferably 10 : 1 to 2 : 1, most preferably 4 : 1.

10

4.2 Phase transfer catalyst

In a further preferred embodiment, the hydrolysis in step a. is catalyzed with at least one phase transfer catalyst selected from the group consisting of quaternary ammonium salts **Q**, organic sulfonates, preferably at least one phase transfer catalyst selected from the group consisting of quaternary ammonium salts **Q**.

20 The quaternary ammonium salt **Q** preferably has the general structure $R^1R^2R^3R^4NX$, wherein R^1 , R^2 , R^3 , and R^4 are the same or different and each is a hydrocarbyl groups selected from alkyl, aryl, arylalkyl, and X is selected from the group consisting of hydroxide, carbonate, hydrogen carbonate, hydrogen sulfate, carboxylate, wherein the carboxylate is preferably acetate, halide, wherein the halide is preferably selected from chloride and bromide, alkyl sulfate, wherein the alkyl sulfate is preferably selected from methylsulfate, ethylsulfate. Preferably, X = hydroxide, hydrogen sulfate. Most preferably, X = hydroxide.

25 The quaternary ammonium salt **Q** preferably contains an ammonium cation with 6 to 30 carbon atoms.

The organic sulfonate preferably contains at least 7 carbon atoms.

In a preferred embodiment, the hydrolysis in step a. is catalyzed with at least one quaternary ammonium salt **Q**, and even more preferably the at least one quaternary ammonium salt **Q** comprises a cation selected from the group consisting of tetrabutylammonium cation, benzyltrimethylammonium cation. Even more preferably, the at least one quaternary ammonium salt **Q** is selected from the group consisting of tetrabutylammonium hydroxide, benzyltrimethylammonium hydroxide, tetrabutylammonium hydrogen sulfate.

35 In those cases in which at least one quaternary ammonium salt **Q**, is used in step a., it is further preferred that the weight of all quaternary ammonium salt **Q** used in step a. is at least 0.5 weight percent (= "wt.-%"), based on the total weight of the **PU** subjected to step a., more preferably in the range of from 0.5 to 15 wt.-%, even more preferred in the range of from 0.75 to 10 wt.-%, particular

preferred in the range of from 0.90 to 8 wt.-%, especially preferred in the range of from 1.0 to 7 wt.-%.

In an alternative embodiment of the process according to the invention, the at least partial hydrolysis according to step a. is carried out without addition of a phase transfer catalyst.

5 4.3 Base-catalyst combinations

In a preferred embodiment of the process of the present invention, the at least one base **B** is used in a "base-catalyst-combination" with at least one quaternary ammonium salt **Q** or an organic sulfonate in step a. Even more preferred, the at least one base **B** is used in a "base-catalyst-combination" with at least one quaternary ammonium salt **Q** in step a.

Even more preferred, the base-catalyst combination is selected from the group consisting of **BCC**₁, **BCC**₂, **BCC**₃, in particular selected from the group consisting of **BCC**₁, **BCC**₂.

BCC₁ comprises base **B**₁ and quaternary ammonium ion **Q**₁ or base **B**₁ and an organic sulfonate **S**₁, preferably **BCC**₁ comprises base **B**₁ and quaternary ammonium ion **Q**₁,

wherein **B**₁ comprises an alkali metal cation and/or an ammonium cation and has a pK_b value at 25 °C of from 1 to 10, and wherein **Q**₁ contains an ammonium cation containing 6 to 30 carbon atoms and wherein **S**₁ contains at least 7 carbon atoms.

More preferably, **Q**₁ has the general structure R¹R²R³R⁴NX, wherein

- R¹ and R² are the same or different and are alkyl groups with 1 to 12, preferably 1 to 10, more preferred 1 to 7, even more preferred 1 to 6, especially preferred 1 to 5 and most preferred 1 to 4 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear, saturated alkyl groups,

- R³ is selected from the group consisting of alkyl groups with 1 to 12, preferably 1 to 10, more preferred 1 to 7, even more preferred 1 to 6, especially preferred 1 to 5 and most preferred 1 to 4 carbon atoms, aryl groups with 6 to 14, preferably 6 to 12, and most preferred 6 to 10 carbon atoms, and aralkyl groups with 7 to 14, preferably 7 to 12, and most preferred 7 to 10 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred linear and saturated, and

- R⁴ is selected from the group consisting of alkyl groups with 3 to 12, preferably 3 to 10, more preferred 3 to 7, most preferred 4 to 6 carbon atoms, aryl groups with 6 to 14, preferably 6 to 12, and most preferred 6 to 10 carbon atoms, and aralkyl groups with 7 to 14, preferably 7 to 12, and most preferred 7 to 10 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred linear and saturated, and

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

- 5 Even more preferably, **Q₁** has the general structure $R^1R^2R^3R^4NX$, wherein 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
or
 R^1 to R^4 are selected such that the sum of carbon atoms in the quaternary ammonium cation is 15
10 to 30, preferably 15 to 28, more preferred 15 to 24, even more preferred 16 to 22 and most preferred 16 to 20.

- BCC₂** comprises base **B₂** and quaternary ammonium ion **Q₂**, wherein **B₂** has a pK_b value at 25 °C
15 of < 1, and wherein **Q₂** contains an ammonium cation containing 6 to 14 carbon atoms, preferably 7 to 12 carbon atoms if the ammonium cation comprises a benzyl residue.

- More preferably, **Q₂** has the general structure $R^1R^2R^3R^4NX$, wherein
- R^1 to R^3 are the same or different and are alkyl groups with 1 to 6, preferably 1 to 5, more
20 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, 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,
25 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
- X is selected from the group consisting of hydrogen carbonate, carbonate, acetate, hydroxide, halide, wherein the halide is preferably selected from chloride and bromide, hydrogen sulfate, alkyl
30 sulfate, wherein the alkyl sulfate is preferably selected from methylsulfate and ethylsulfate.

- Even more preferably, **Q₂** has the general structure $R^1R^2R^3R^4NX$, 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
35 or
 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.

- BCC₃** comprises base **B₃** and quaternary ammonium ion **Q₃**, wherein base **B₃** has pK_b value at
40 25 °C of < 1, and wherein **Q₃** contains an ammonium cation containing 15 to 30 carbon atoms, preferably 15 to 28, more preferred 15 to 24, even more preferred 16 to 22 and most preferred 16 to 20.

More preferably, Q_3 has the general structure $R^1R^2R^3R^4NX$, wherein

- 5 - R^1 and R^2 are the same or different and are alkyl groups with 1 to 12, preferably 1 to 10, more preferred 1 to 7, even more preferred 1 to 6, especially preferred 1 to 5 and most preferred 1 to 4 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear, saturated alkyl groups,
- 10 - R^3 is selected from the group consisting of alkyl groups with 1 to 12, preferably 1 to 10, more preferred 1 to 7, even more preferred 1 to 6, especially preferred 1 to 5 and most preferred 1 to 4 carbon atoms, aryl groups with 6 to 14, preferably 6 to 12, and most preferred 6 to 10 carbon atoms, and aralkyl groups with 7 to 14, preferably 7 to 12, and most preferred 7 to 10 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear and saturated alkyl groups, and,
- 15 - R^4 is selected from the group consisting of alkyl groups with 3 to 12, preferably 3 to 10, more preferred 3 to 7, most preferred 4 to 6 carbon atoms, aryl groups with 6 to 14, preferably 6 to 12, and most preferred 6 to 10 carbon atoms, and aralkyl groups with 7 to 14, preferably 7 to 12, and most preferred 7 to 10 carbon atoms, wherein the alkyl groups may be linear, branched, cyclic, saturated or unsaturated, most preferred are linear and saturated alkyl groups, and
- 20 - X is selected from the group consisting of carbonate, hydrogen carbonate, acetate, hydroxide, halide, wherein the halide is preferably selected from chloride and bromide, hydrogen sulfate, alkyl sulfate, wherein the alkyl sulfate is preferably selected from methylsulfate and ethylsulfate.
- 25

4.4 Raw product R_H

As a result of step a., a raw product R_H comprising polyols P_{PU} , amines A_{PU} , water W , at least one base B is obtained.

30

The hydrolytic raw product R_H comprises an organic phase P_O and an aqueous phase P_W .

In a preferred embodiment, the organic phase P_O comprises the main part of the polyols P_{PU} that are formed during step a. as part of the raw product R_H and the main part of the amines A_{PU} that are formed during step a. as part of the raw product R_H .

35

"Main part of the polyols P_{PU} that are formed during step a. as part of the raw product R_H " in particular means > 50 molar percent (= "mol.-%"), preferably at least 60 mol.-%, more preferably at least 70 mol.-%, more preferably at least 80 mol.-%, more preferably at least 90 mol.-%, more

preferably at least 99 mol.-%, even more preferably essentially all of the polyols **P_{PU}** that are formed during step a. as part of the raw product **R_H**.

“Main part of the amines **A_{PU}** that are formed during step a. as part of the raw product **R_H**” in particular means > 50 molar percent (= “mol.-%”), preferably at least 60 mol.-%, more preferably at least 70 mol.-%, more preferably at least 80 mol.-%, more preferably at least 90 mol.-%, more preferably at least 99 mol.-%, even more preferably essentially all of the amines **A_{PU}** that are formed during step a. as part of the raw product **R_H**.

The aqueous phase **P_W** is essentially formed by the water **W** and the base **B** comprised by the raw product **R_H** after step a., although the organic phase **P_O** typically also contains water **W** and base **B** to some extent due to the Nernst distribution law according to which any compound will always distribute between two immiscible phases.

In particular, at least 75 wt.-%, preferably at least 95 wt.-%, of the water **W** contained by the raw product **R_H** after step a. form part of the aqueous phase **P_W**, while the organic phase **P_O** also comprises water **W** and comprises 25 wt.-% or less, preferably 5 wt.-% or less, of the water **W** contained by the raw product **R_H** after step a.

In particular, at least 75 wt.-% of the base **B** contained by the raw product **R_H** after step a. form part of the aqueous phase **P_W**, while the organic phase **P_O** comprises 25 wt.-% or less, preferably 5 wt.-% or less, of the base **B** contained by the raw product **R_H** after step a.

In those cases, in which a phase transfer catalyst is employed in step a., and in particular if at least one quaternary ammonium salt **Q** is used in step a., the organic phase **P_O** in particular also comprises at least a part of the quaternary ammonium salt **Q** or decomposition products **D_Q** formed from **Q** during the reaction according to step a.

In particular, the aqueous phase **P_W** comprises the main part of the base **B** that is comprised by the raw product **R_H** after step a.

The process of this invention will result in the effective hydrolytic cleavage of the urethane and urea bonds present in the **PU** being treated so as to generate amines **A_{PU}** and polyols **P_{PU}**, wherein **P_{PU}** preferably are polyether polyols. In particular in those cases where the **PU** was prepared using chain extenders or curatives, further products such as low molecular weight glycols, diols which are different from the polyols **P_{PU}**, diamines which are different from the amines **A_{PU}** may also be obtained.

Likewise, since the process according to the present invention may be applied for recycling of **PU** from a wide range of sources and wastes, the **PU** subjected to the process according to the present invention may contain further additives and processing aids that are then found in the hydrolytic raw product **R_H** and in particular in the organic phase **P_O** and the aqueous phase **P_W** comprised by the raw product **R_H** that is obtained after step a.

In a particular embodiment of the present invention, the raw product **R_H** obtained after step a. hence contains at least one component **C**, wherein **C** is selected from the group consisting of foam catalysts, inorganic fillers, polymeric fillers, flame retardants, carboxylates such as formiate,

acetate, polydimethylsiloxane, organic pigments, polymeric fillers, which are preferably **SAN** polymers.

Typically, foam catalysts, inorganic fillers, polymeric fillers, organic pigments are found in the organic phase **P_O**, while carboxylates such as formiate, acetate, polydimethylsiloxane, inorganic
5 fillers, polymeric fillers, preferably **SAN** polymers, flame retardants are found in the aqueous phase **P_W**.

Hence, in a preferred embodiment, (i) the organic phase **P_O** comprised by the raw product **R_H** that is obtained after step a., further comprises one or more components **C_O** selected from the group consisting of foam catalysts, inorganic fillers, polymeric fillers, organic pigments, antioxidants, dyes,
10 and/or

(ii) the aqueous phase **P_W** comprised by the raw product **R_H** that is obtained after step a., further comprises one or more components **C_W** selected from the group consisting of dyes,
15 polydimethylsiloxane, polymeric fillers, inorganic fillers, flame retardants, carboxylates, wherein the carboxylates are preferably at least one of formiate, acetate.

In case of the preferred embodiment (ii), it is even more preferred that at least a part, preferably all, of the components **C_W** are separated from the aqueous phase **P_W** before, during or after, even
20 more preferably before or after, **P_{O1}** is separated from **R_H** according to step b., so that the amount of components **C_W** in **P_W** is minimized, preferably **P_W** is essentially free of components **C_W**.

In case of the preferred embodiment (i), it is even more preferred that at least a part, preferably all, of the components **C_O** are separated from the organic phase **P_O** before, during or after, even more preferably before or after, **P_{O1}** is separated from **R_H** according to step b., so that the amount of
25 components **C_O** in **P_{O1}** is minimized, preferably **P_{O1}** is essentially free of components **C_O**.

In some embodiments, in particular in those cases where the **PU** subjected to step a. is only partially hydrolyzed in step a., the raw product may also comprise solids **S**. These solids **S** may be particles of only partially hydrolyzed **PU**, or additional polymer fillers (such as styrene-acrylonitril polymers, abbreviated as "**SAN** polymers"), for example in those cases where the **PU** is composed
30 of polyol, in particular polyether polyol, building blocks that contain such polymers (**SAN** polymers), in dispersed or covalently bound form.

Hence, the raw product **R_H** that is obtained after step a. optionally comprises solids **S**.

In a preferred embodiment, the composition of the raw product **R_H** is as follows:

In this preferred embodiment, the organic phase **P_O** in the raw product **R_H** obtained after step a. comprises,
35

(α) more than 40 wt.-%, preferably 45 to 90 wt.-%, more preferred 50 to 80 wt.-%, even more preferred 55 to 80 wt.-% and even more preferred 60 to 75 wt.-%, most preferred 65 wt.-%, by weight of the organic phase **P_O**, of polyols **P_{PU}**,

- (β) 10 to 40 wt.-%, preferably 15 to 35 wt.-%, more preferred 20 to 30 wt.-% and most preferred 22 to 27 wt.-%, by weight of the organic phase **P_O**, of amines **A_{PU}**,
- (γ) water **W** in an amount of less than 20 wt.-%, preferably 0.1 to 15 wt.-%, more preferred 1 to 10 wt.-%, even more preferred 3 to 8 wt.-%, most preferred 5 wt.-%, by weight of the organic phase **P_O**,
- (δ) less than 15 wt.-%, preferably 0.1 to 10 wt.-%, more preferred 0.5 to 8 wt.-% and most preferred 1 to 5 wt.-%, by weight of the organic phase **P_O**, of the inorganic base **B**,
- (ε) in those cases where at least one quaternary ammonium salt **Q** was used in step a. as phase transfer catalyst, in sum < 15 wt.-%, preferably 0 to 10 wt.-%, more preferred 0.01 to 6 wt.-%, even more preferred 0.05 to 6 wt.-%, particularly preferred 0.5 to 4 wt.-% and most preferred 1 to 2.5 wt.-%, by weight of the organic phase **P_O**, are constituted by the sum of quaternary ammonium salt **Q** and decomposition products **D_Q** of the quaternary ammonium salt **Q**, wherein **D_Q** are the corresponding amine **A_Q** and the corresponding alcohols **P_Q**,
- (ζ) in those cases where the **PU** subjected to step a. contained the respective compound **C_O**, the compounds **C_O** in a total amount of less than 15 wt.-%, preferably 0.1 to 10 wt.-%, more preferred 0.5 to 8 wt.-% and most preferred 1 to 5 wt.-% by weight of the organic phase **P_O**, wherein the compound **C_O** is selected from the group consisting of foam catalysts, inorganic fillers, polymeric fillers, organic pigments, antioxidants, dyes,
- wherein the amounts of components (α) to (ζ) plus optionally further components comprised sum up to a maximum of 100 wt.-% of the organic phase **P_O**.

- Alternatively or additionally, preferably additionally, the aqueous phase **P_W** in the raw product **R_H** obtained after step a. comprises,
- (η) less than 4 wt.-%, preferably 0 to 2 wt.-%, more preferred 0 to 1 wt.-% and most preferred 0 to 0.1 wt.-%, by weight of the aqueous phase **P_W**, of polyols **P_{PU}**,
- (θ) 0 to 3 wt.-%, preferably 0 to 2 wt.-%, more preferred 0.001 to 1 wt.-%, even more preferred 0.001 to 0.5 wt.-% and most preferred 0.01 to 0.1 wt.-%, by weight of the aqueous phase **P_W**, of amines **A_{PU}**,
- (i) 40 to 80 wt.-%, preferably 45 to 70 wt.-%, more preferred 50 to 60 wt.-% and most preferred 55 to 65 wt.-%, by weight of the aqueous phase **P_W**, of the water **W**,
- (κ) 20 to 60 wt.-%, preferably 25 to 50 wt.-%, more preferred 30 to 40 wt.-% and most preferred 35 to 45 wt.-%, by weight of the aqueous phase **P_W**, of the inorganic base **B**,
- (λ) in those cases where at least one quaternary ammonium salt **Q** was used in step a. as phase transfer catalyst, in sum 0 to 3 wt.-%, preferably 0 to 2 wt.-%, more preferred 0.001 to 1 wt.-%, even more preferred 0.001 to 0.5 wt.-% and most preferred 0.01 to 0.1 wt.-%, by weight of the aqueous phase **P_W** are constituted by the sum of quaternary ammonium salts **Q** and decomposition products **D_Q** of the quaternary ammonium salt **Q**, wherein **D_Q** are the corresponding amine **A_Q** and the corresponding alcohols **P_Q**,
- (μ) in those cases where the **PU** subjected to step a. contained the respective compound **C_W**, the compounds **C_W** in a total amount of less than 15 wt.-%, preferably 0.1 to 10 wt.-%, more preferred

0.5 to 8 wt.-% and most preferred 1 to 5 wt.-% by weight of the aqueous phase **P_W**, wherein the compound **C_W** is selected from the group consisting of carboxylates (such as formiate, acetate), polydimethylsiloxane, polymeric fillers, preferably SAN polymers, flame retardants, dyes, inorganic fillers,

5

wherein the amounts of components (η) to (μ) plus optionally further components sum up to a maximum of 100 wt.-% of the aqueous phase **P_W**.

10 In those cases where the quaternary ammonium salt **Q** has the general structure $R^1R^2R^3R^4NX$, the corresponding amine **A_Q** is preferably a compound selected from the group consisting of $R^1R^2R^3N$, $R^1R^3R^4N$, $R^1R^2R^4N$, $R^2R^3R^4N$, R^1R^2NH , R^1R^3NH , R^1R^4NH , R^2R^3NH , R^2R^4NH , R^3R^4NH , R^1-NH_2 , R^2-NH_2 , R^3-NH_2 , R^4-NH_2 , and the corresponding alcohols **P_Q** is preferably a compound selected from the group consisting of R^1-OH , R^2-OH , R^3-OH , R^4-OH .

15 4.5 Reaction conditions in step a.

According to the invention, step a. is carried out by contacting water **W**, at least one base **B**, and the **PU** that is subjected to the hydrolysis reaction. This contacting is, in particular, carried out in a reactor, in which the respective reaction components are mixed and reacted with each other. Such reactor is in particular selected from a continuous stirred-tank reactor, autoclave.

20 Step a. may, in an alternative embodiment, also be carried out in a reactor that is specifically designed for continuous processing, such as an extruder (e.g. screw extruder, planetary-gear extruder), kneader, etc.

The reaction conditions applied in step a. are known to the skilled person.

25 It is preferred that the at least partial hydrolysis according to step a. is carried out at a temperature of from 90 °C to 220 °C, preferably 100 °C to 200 °C, more preferred 110 °C to 200 °C even more preferred 120 °C to 200 °C, and most preferred 140 °C to 200 °C.

30 It is further preferred that the hydrolysis according to step a. is carried out for 30 minutes to 20 hours, preferably 30 minutes to 16 hours, more preferred 30 minutes to 14 hours, even more preferred 45 minutes to 10 hours, particular preferred 60 minutes to 8 hours, even more preferred 60 minutes to 6 hours.

35 It is further preferred that that hydrolysis according to step a. is carried out at atmospheric pressure or under elevated pressure, in particular under a pressure of from 1 to 30 bar abs., preferably 2 to 20 bar abs., more preferred 3 to 15 bar abs.

4.6 Comminuting step (optional)

To facilitate handling of the **PU** in step a., it is preferable to carry out a preceding step (i.e. before step a.) in which the **PU** is subjected to at least one pretreatment by which the **PU** is comminuted. This comminution is even more preferably selected from the group consisting of chopping, pulverizing, grinding. By this preferred pretreatment step, **PU** is obtained that is in the form of relatively small particles or granules. This pretreatment step is in particular advantageous, if the **PU** that is subjected to the process of the present invention is in solid form. In this case, the initial 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.

In a further preferred embodiment of the present invention, and in particular if the **PU** that is subjected to the process according to the invention is a foam, the **PU** may be partially or fully compressed prior to subjecting it to step a.

The progress of the hydrolysis of **PU** in step a. may be monitored by nuclear magnetic resonance ("NMR") or infrared ("IR") spectroscopy. In particular, these methods may be used to monitor the amount of urethane groups in the **PU** employed in step a. and the amount of urethane groups in the **PU** after the reaction has progressed.

In a preferred embodiment, step a. is carried out until the amount of urethane groups in the **PU** initially subjected to step a. has decreased by at least 10 %, more preferably by at least 25 %, more preferably by at least 40 %, more preferably by at least 51 %, more preferably by at least 75 %, more preferably by at least 85 %, more preferably by at least 92 %, more preferably by at least 99 %.

Even more preferred, step a. is carried out until essentially no **PU** groups may be detected any more.

5. Step b.

According to step b. of the process of the invention, at least a part **P_{O1}** of the organic phase **P_O** is separated from the raw product **R_H**, wherein **P_{O1}** comprises polyols **P_{PU}**, amines **A_{PU}**, water **W**.

In Step b., "separating at least a part **P_{O1}** from **R_H**" also comprises an embodiment where essentially the complete organic phase **P_O** is separated from the complete aqueous phase **P_W** that is comprised by the raw product **R_H**. In this embodiment, **P_{O1}** is essentially identical to **P_O**.

After step b., an organic phase **P_{O1}** is obtained that is not in direct contact with the rest of the raw product **R_H** that was obtained after step a. In other words, the organic phase **P_{O1}** is separated from at least a part of the aqueous phase **P_W** obtained after step a.

The separation of the at least a part **P_{O1}** of the organic phase **P_O** from the raw product **R_H** according to step b. may be carried out according to the skilled person's knowledge.

In particular, the separation may be carried out in a separation funnel and or via centrifugation or via decantation in step b.

In those cases where the raw product R_H contains solids S , it is preferred to separate at least a part of the solids S comprised by the raw product R_H from the raw product R_H , in particular from at least one phase selected from the organic phase P_O and the aqueous phase P_W , preferably from the organic phase P_O , before or after the at least part P_{O1} of P_O is separated from R_H .

This preferred separation of the solids S from R_H , in particular from at least one phase selected from the organic phase P_O and the aqueous phase P_W , may be carried out according to the skilled person's knowledge, in particular by at least one method selected from filtration, decantation, centrifugation.

After step b., the at least part P_{O1} of the organic phase P_O that is separated from the rest of the raw product R_H is obtained. The aqueous phase that is still comprised by the raw product R_H after step b. is abbreviated as " P_{W1} " herein.

In particular, the composition of the thus obtained organic phase P_{O1} corresponds to the composition of the organic phase P_O as it is comprised by the raw product R_H that is obtained after step a.

Hence, in a preferred embodiment, the composition of the organic phase P_{O1} obtained after step b. comprises,

- (α_1) more than 40 wt.-%, preferably 45 to 90 wt.-%, more preferred 50 to 80 wt.-%, even more preferred 55 to 80 wt.-% and even more preferred 60 to 75 wt.-%, most preferred 65 wt.-%, by weight of the organic phase P_{O1} , of polyols P_{PU} ,
- (β_1) 10 to 40 wt.-%, preferably 15 to 35 wt.-%, more preferred 20 to 30 wt.-% and most preferred 22 to 27 wt.-%, by weight of the organic phase P_{O1} , of amines A_{PU} ,
- (γ_1) water W in an amount of less than 20 wt.-%, preferably 0.1 to 15 wt.-%, more preferred 1 to 10 wt.-%, even more preferred 3 to 8 wt.-%, most preferred 5 wt.-%, by weight of the organic phase P_{O1} ,
- (δ_1) less than 15 wt.-%, preferably 0.1 to 10 wt.-%, more preferred 0.5 to 8 wt.-% and most preferred 1 to 5 wt.-%, by weight of the organic phase P_{O1} , of the inorganic base B ,
- (ϵ_1) in those cases where at least one quaternary ammonium salt Q was used in step a. as phase transfer catalyst, in sum < 15 wt.-%, preferably 0 to 10 wt.-%, more preferred 0.01 to 6 wt.-%, even more preferred 0.05 to 6 wt.-%, particularly preferred 0.5 to 4 wt.-% and most preferred 1 to 2.5 wt.-%, by weight of the organic phase P_{O1} , are constituted by the sum of quaternary ammonium salt Q and decomposition products D_Q of the quaternary ammonium salt Q , wherein D_Q are the corresponding amine A_Q and the corresponding alcohols P_Q ,
- (ζ_1) in those cases where the PU subjected to step a. contained the respective compound C_O , the compounds C_O in a total amount of less than 15 wt.-%, preferably 0.1 to 10 wt.-%, more preferred 0.5 to 8 wt.-% and most preferred 1 to 5 wt.-% by weight of the organic phase P_{O1} , wherein the compound C_O is selected from the group consisting of foam catalysts, inorganic fillers, polymeric fillers, organic pigments, antioxidants, dyes,

wherein the amounts of components (α_1) to (ζ_1) plus optionally further components comprised sum up to a maximum of 100 wt.-% of the organic phase P_{O1} .

It is essential that P_{O1} as obtained after step b. still comprises water. This logically means that, accordingly, P_O that is obtained after step a. as part of the raw product R_H , necessarily also comprises water. This is due to the Nernst distribution law according to which, although naturally the main part of the water in R_H forms the aqueous phase P_W , water is also be found in the organic phase P_O .

In addition, water (and base B) comprised by P_{O1} after step b. may also result from the fact that, during phase separation, they are carried over from the aqueous phase P_W , and thus result from an inaccurate separation method. Such slight inaccuracies in phase separation can be minimized, but not always be avoided completely, although it is preferred that a clear and exact separation of P_{O1} from R_H is achieved in step a.

Preferably, the separation is carried out by at least one separation method selected from the group consisting of centrifugation, filtration, decantation, membrane process.

The process of the present invention is advantageous under several aspects, one of them being its resource efficiency. To further improve this resource efficiency, the process according to the invention, in a preferred aspect, is characterized in that, after the separation of P_{O1} from R_H according to step b., at least a part of the aqueous phase P_W comprised by R_H is used in the hydrolysis according to step a.

In particular, at least a part of the water and/or at least a part of the base B comprised by the aqueous phase P_{W1} that is obtained after P_{O1} is separated from R_H in step b., is used in the hydrolysis in step a.

For example, at least a part of the aqueous phase P_{W1} comprised by R_H that is obtained after P_{O1} is separated from R_H in step b., may be fed into the hydrolysis reaction mixture in which the hydrolysis according to step a. is carried out.

In an alternative embodiment to recycle water and base B from P_{W1} , this aqueous phase may also be subjected to a distillation and the thus distilled water be fed into the hydrolysis of step a., and/or the base B comprised by P_{W1} may be obtained by crystallizing from the respective phase P_{W1} . By this, a separate recovery of water and base B from P_{W1} is achieved, which allows to feed water and base B , respectively, separately from each other into the reaction mixture according to step a., and also allows to gauge the amount of either compound independently of the other.

6. Step c.

According to step c. of the process of the invention, at least a part of the water W and at least a part of the amines A_{PU} are separated from P_{O1} by distillation.

In a preferred embodiment of step c., a part of the amines A_{PU} and at least a part of the water W are separated from P_{O1} by distillation.

After carrying out step c., water vapor V , a fraction F_A comprising amines A_{PU} , and an organic phase P_{O2} comprising polyols P_{PU} , optionally amines A_{PU} and optionally water W , are obtained.
 “Organic phase P_{O2} comprising polyols P_{PU} , optionally amines A_{PU} and optionally water W ” is to be understood that the organic phase P_{O2} comprises polyols P_{PU} , that the organic phase P_{O2} optionally comprises amines A_{PU} and that the organic phase P_{O2} optionally comprises water W .

10 Preferably, P_{O2} comprises polyols P_{PU} , amines A_{PU} and optionally water W .

The distillation step c. may be carried out according to the skilled person's knowledge. The essential requirement is that after step c., water vapor V , the fraction F_A , and the organic phase P_{O2} are obtained as separate phases, i.e. not in direct contact with each other.

15

In a preferred embodiment, step c. comprises at least two distillation steps $c1.$ and $c2.$, where in step $c1.$, at least part of the water W is separated by distillation from P_{O1} to obtain water vapor V and a residual organic phase P_{O1*} , and where in step $c2.$, at least a part, preferably a part, of the amines A_{PU} is separated from P_{O1*} by distillation to obtain fraction F_A and the residual organic phase P_{O2} .

20

In step c and in particular in step $c1.$, “water vapor V ” is obtained. Hence, water preferably has a lower boiling point than the at least one amine A_{PU} . Preferably, the distillation according to step $c1.$ is carried out at a temperature $T_{c1} \leq 220$ °C, preferably $T_{c1} \leq 200$ °C and a pressure $p_{c1} \leq 1$ bar abs., preferably $0 < p_{c1} \leq 1000$ mbar abs., more preferably $1 \leq p_{c1} \leq 500$ mbar abs., most preferred $20 \leq p_{c1} \leq 300$ mbar abs..

25

Alternatively or additionally, preferably additionally, it is preferred that in step c and in particular in step $c2.$, the fraction F_A containing the amines A_{PU} is obtained. Hence, the at least one amine A_{PU} preferably has a lower boiling point than the at least one polyol P_{PU} . Preferably, the distillation according to step $c2.$ is carried out at a temperature $T_{c2} \leq 220$ °C, preferably $T_{c2} \leq 200$ °C and a pressure $p_{c2} \leq 1$ bar abs., preferably $0 < p_{c2} \leq 1000$ mbar abs., more preferably $0 \leq p_{c2} \leq 100$ mbar abs., most preferred $0 \leq p_{c2} \leq 20$ mbar abs.

30

During step $c2.$, it is preferred that the temperature of distillation is higher than the temperature of distillation during step $c1.$ and that the pressure of distillation during step $c2.$ is equal or lower than the pressure of distillation during step $c1.$, hence: it is preferred that $T_{c1} < T_{c2}$ and $p_{c1} \geq p_{c2}$.

35

These conditions are especially advantageous in those cases where the at least one amine A_{PU} has the general structure according to formula (II): $H_2N-W^1-NH_2$, wherein W^1 has the above-mentioned structure (II-B), preferably where the at least one amine A_{PU} is toluene diamine (“TDA”).

40

The composition of the residual organic phase P_{O1^*} , that is obtained after step c1. and subjected to step c2., in particular, corresponds to the composition of P_{O1} that is subjected to step c1., wherein the amount of water comprised by P_{O1^*} is lower than the amount of water comprised by P_{O1} .

- 5 Optionally, the amount of amines A_{PU} comprised by P_{O1^*} is lower than the amount of amines A_{PU} comprised by P_{O1} .

The composition of the residual organic phase P_{O2} , that is obtained after step c2. and subjected to step d., in particular, corresponds to the composition of P_{O1^*} that is subjected to step c2., wherein the amount of amines A_{PU} comprised by P_{O2} is lower than the amount of amines A_{PU} comprised by

- 10 P_{O1^*} . Optionally, the amount of water comprised by P_{O2} is lower than the amount of water comprised by P_{O1^*} .

In particular, step c1. is at least partly carried out in a distillation column K_1 .

- 15 Any desired distillation column known to those skilled in the art may be used as distillation column K_1 (or as distillation column K_2 described hereinafter) in this preferred embodiment of step c. of the process. The distillation columns K_1 and K_2 preferably contain internals. Suitable internals are, for example, trays, unstructured packings or structured packings. Trays used are typically bubble-cap trays, sieve trays, valve trays, tunnel-cap trays or slotted trays. Unstructured packings are generally
- 20 beds of random packing elements. Random packing elements used are typically Raschig rings, Pall rings, Berl saddles or Intalox® saddles. Structured packings are sold, for example, under the Sulzer Mellapak® trade name. Apart from the internals mentioned, further suitable internals are known to a person skilled in the art and can likewise be used.

- In a further preferred embodiment, step c2., is at least partially carried out in at least one device
- 25 selected from short path evaporator, thin film evaporator, distillation column K_2 , wherein distillation column K_2 is different from distillation column K_1 .

- In a preferred embodiment, the boiling point of the at least one amine A_{PU} is above the boiling point of water, and the boiling point of the at least one polyol P_{PU} is above the boiling point of the at least
- 30 one amine A_{PU} .

- In those embodiments where P_{O1} comprises quaternary ammonium salt Q and / or decomposition products D_Q of the quaternary ammonium salt Q , it is preferred that these are separated from P_{O1} in an additional distillation step and/or together with the water vapor W . In particular, in those
- 35 embodiments where P_{O1} comprises quaternary ammonium salt Q and / or decomposition products D_Q of the quaternary ammonium salts Q , and where steps c1. and c2. are carried out, it is preferred that at least a part of the quaternary ammonium salt Q and / or of the decomposition products D_Q of the quaternary ammonium salts Q , more preferred the decomposition products D_Q of the quaternary ammonium salts Q , is separated by distillation during step c1., i.e. subsequently or
- 40 simultaneously with the water vapor V .

In those cases where the water vapor **V** obtained after step c1. is contaminated with quaternary ammonium salts **Q** and / or the decomposition products **D_Q** of the quaternary ammonium salts **Q**, it is preferably subjected to an additional distillation step before it is used as stripping gas in step d.

- 5 Preferably, at least a part of step c., in particular at least step c2., is carried out under an atmosphere having an oxygen content of 0 to 21 vol.-%, preferably 0 to 8 vol.-%, more preferred 0 to 1 vol.-% and most preferred 0 to 0.1 vol.-%, preferably an atmosphere comprising solely product vapors and one or more inert gases.
- 10 This further improves the purity of the recycled amines **A_{PU}** and the recycled polyols **P_{PU}**, which makes them especially useful to be recycled for the production of **PU**.

7. Step d.

15

According to step d. of the process of the invention, at least a part **P_{O3}** of the organic phase **P_{O2}** is purified by stripping. It is characteristic for the process of the present invention, that in step d., water vapor **V** is used as stripping gas in countercurrent flow to **P_{O3}**.

- 20 Due to this procedure, the water isolated from **P_{O1}** may be used, and no additional water needs to be added in order to carry out the stripping step d.

This stripping step d. is advantageous as it further purifies at least the part **P_{O3}** of the organic phase **P_{O2}** which is obtained after step c., in particular after step c2. In a preferred embodiment, this phase **P_{O2}** still comprises amines **A_{PU}** and/or quaternary ammonium salts **Q** and/or decomposition products **D_Q**. In particular, **P_{O2}** still comprises amines **A_{PU}**. These impurities in **P_{O2}** are at least partially, preferably completely, removed in step d.

- "Stripping" is a physical separation process known to those skilled in the art which is used in many fields in the prior art for purifying liquids (described for example in M. Kriebel: "Absorption, 2. Design of Systems and Equipment", Ullmann's Encyclopedia of Industrial Chemistry, Electronic Release, chap. 3, Wiley VCH, Weinheim October 2008).

In the context of the present invention, a gas phase, i.e. the water vapor **V**, is contacted in countercurrent flow with the phase to be purified, i.e. **P_{O3}**, or the phase to be purified, i.e. **P_{O3}**, is contacted at reduced pressure of less than 1 bar with the water vapor **V** in countercurrent flow. In accordance with the invention, this contacting occurs, in particular in a distillation column, more preferably in column **K₁** in those cases where column **K₁** is used in step c.

- In the present invention, the stripping is preferably conducted at a reduced pressure of < 1 bar. Optionally, in addition to the water vapor **V**, a further inert stripping gas may be used in countercurrent flow. This further inert stripping gas is preferably selected from the group consisting of noble gases, nitrogen. Likewise, in addition to the water vapor **V** obtained in step c., additional water vapor may be used in step d. to further improve the purification of **P_{O3}**.

The temperature of the stripping can be adjusted by setting an appropriate negative pressure in the column in a routine manner by those skilled in the art.

The pressure in step d. according to the invention is preferably < 1 bar abs., is in particular in the range of 1 - 500 mbar abs., more preferably in the range of 20 - 300 mbar abs.

- 5 Step d., preferably, is carried out at a temperature ≤ 250 °C, preferably ≤ 200 °C.

In particular, the organic phase P_{O3} is employed in step d. with a temperature of ≤ 200 °C, preferably 150 °C to 200 °C, while the water vapor V is employed in step d. with a temperature of ≤ 250 °C, preferably 180 °C to 200 °C.

- 10 The purification of P_{O3} in step d. can be improved by increasing the surface area of the column K_1 in the section of column K_1 where P_{O3} and water vapor V are contacted during stripping. Preferably, for this purpose, the P_{O3} in step d. of the method according to the invention is passed at least partially over a bed of packing elements or over a structured packing within column K_1 . Of suitability for this purpose are all packing elements and structured packings which are known to the person skilled in the art from the prior art for distillations and for absorption processes.
- 15 Alternatively, the stripping can be carried out in a falling-film or thin-film evaporator. These apparatuses are known from the prior art to those skilled in the art.

It is preferred, that step d. and at least a part of step c. are carried out in the same distillation column K_1 . In those embodiments where step c. comprises steps c1. and c2., it is further preferred that step c1. and step d. are carried out in the same distillation column K_1 .

- 20 In this preferred embodiment, the resource efficiency is even more improved, as only one column K_1 is used in two steps c. and d. In addition, the water vapor obtained in step c. can, within column K_1 , be conducted towards the head of column K_1 , so that there is no need to condensate and evaporate water vapor V . P_{O3} that is subjected to step d. is then preferably fed from the head of column K_1 .
- 25 In those cases where the organic phase P_{O3} that is subjected to step d. comprises at least one amine A^* selected from amine A_{PU} , amine decomposition products D_Q , the amount of all amines A^* in P_{O3} is reduced during step d. to < 5 wt. %, preferably < 1 wt. %, more preferred < 0.5 wt. %, even more preferred < 0.3 wt. %, and most preferred < 0.1 wt. %.

30 8. Optional purification steps

In a preferred embodiment, the process according to the present invention comprises at least one further step e. in which fraction F_A that is obtained after step c. is further purified and/or organic phase P_{O3} that is obtained after step d. is further purified.

- 35 Optional step e. is preferably selected from the group consisting of filtration, fractional distillation, crystallization, membrane processes, solvent extraction.

In particular, in step e., at least one impurity selected from water, polyols and lighter alcohols, catalyst decomposition products, amine oxidation products, fillers, additives, preferably pigments and coloring agents, and impurities from the **PU** foam production is removed from **F_A** and/or **P_{O3}**, respectively.

5

9. Recycling steps

The process according to the present invention is a resource efficient process that gives polyol **P_{PU}** and amine **A_{PU}** in a high purity degree. Hence, either compound obtained in the process is efficiently recycled and may be used for the synthesis of **PU**.

Preferably, at least one of these compounds selected from polyol **P_{PU}** and amine **A_{PU}** is then used to produce new **PU**, preferably **PU** foam. Hence, in a preferred embodiment of the present process, amine **A_{PU}**, which is obtained in the process of the invention from fraction **F_A** in step c., is, in an additional step f., subjected to a reaction in which the amino groups of amine **A_{PU}** are converted into isocyanate groups, preferably via phosgenation. Such phosgenation is known to the skilled person and for example described in R.J. Slocombe, E.E. Hardy, J.H. Saunders, R.L. Jenkins, *J. Am. Chem. Soc.* **1950**, 72, 1888-1891 & H.J. Twitchett, *Chem. Soc. Rev.* **1974**, 3, 209-230.

A further preferred aspect of the present invention is the use of the polyol **P_{PU}** obtained in the process according to the invention (in particular step d.) and/or the isocyanates obtained in step f. to produce polyurethane, in particular polyurethane foam.

Even more preferred, is the use of the polyol **P_{PU}** obtained in the process according to the invention (in particular step d.) and the isocyanates obtained in step f. to produce polyurethane, in particular polyurethane foam. In this even more preferred embodiment, it is most preferred that the polyol **P_{PU}** obtained in the process according to the invention (in particular step d.) and the isocyanates obtained in step f. are polymerized with each other to produce polyurethane, in particular polyurethane foam.

30

Examples

1. Hydrolysis reaction

5 **PU** waste containing polymers of 2,4- and 2,6-toluene diisocyanate with polyether polyols, that are polymers of ethylene oxide and 1,2- as well as 1,3-propylene oxide, is comminuted in a shredder.

10 10 kg of these **PU** particles are then mixed with 97.3 kg of a 40 wt.-% aqueous solution of K_2CO_3 , and 0.956 kg of tetrabutylammonium hydrogen sulfate in a steel kettle. The resulting mixture is heated to 150 °C and stirred for 4 hours. The thus obtained raw product is left to stand to cool to room temperature. It contains solids, an aqueous phase and an organic phase. The organic phase is left to settle in the reactor and is then separated from the aqueous phase and the solids.

The organic phase contains ~ 5 wt.-% water, ~ 22 wt.-% **TDA** and ~ 65 wt.-% polyether polyol.

2. Work-up of the organic phase

15

The organic phase is worked-up by distillation in a device as shown in the Figure.

In particular, the organic phase is supplied as stream <1> to an evaporator <2> that is connected to a distillation column <4>. The distillation column <4> contains two packings <41>, <44> and a liquid collector <45> at the bottom of the upper packing <44>.

20 In the evaporator <2>, the organic phase is heated up to 200 °C, while the pressure in the column <4> is 50 to 200 mbar abs. In the column <4>, water vapors <3> pass the lower packing <41> and are partially condensed in a condenser <42> within the column <4> so that impurities in the water vapor, especially lower boilers and higher boiling compounds such as **TDA** or aminic decomposition products of the phase transfer catalyst (such as tributyl amine, "**TriBA**"), are
25 separated from the water vapor by condensation and led off via piping <7>. Additionally, part of the condensate is recycled via feed <14> into column <4> via heater <9>. Additional water may be supplied to this reflux via piping <8>. The water vapor <3> is optionally heated (for example by a heating means <43> in the column <4>) and passes the upper packing <44>.

30 The liquid distillation residue <5> that remains in the evaporator <2> is then conducted to a short film evaporator (not shown in the Figure), where **TDA** is removed from <5> by distillation at 190 °C and 4 mbar abs.

The liquid distillation residue <6> that remains from this second distillation in the short film evaporator comprises mainly polyol. It is fed to the top of column <4> after it is heated to 160 °C in pre-heater <10>. In the upper part of column <4>, the organic phase <6> is stripped in
35 countercurrent with water vapor <3>. This final stripping step essentially removes impurities from polyol phase <6>, such as aminic compounds, in particular **TDA** and **TriBA**. The highly pure polyol <11> is then obtained. The water vapor containing impurities from the polyol phase <6> is then led

off as stream <13> at the top of column <4>. It is possible to condensate this water vapor via condensator <12> and feed it into column <4> via piping <8>, preferably after further cleaning it from impurities.

5 3. Advantages compared to prior art processes

The procedure provides several advantages compared to the prior art processes, where distillation of water/ amine such as **TDA**/ stripping of the polyol phase are carried out separately or are not even described in any specific detail. In the process according to the present invention, the final
10 purification step, i.e. the stripping, which is necessary to obtain a highly purified polyol phase, is carried out in a resource efficient manner. The thus obtained polyol phase is so pure that the polyol may be directly used in polymerization with isocyanates to obtain polyurethanes **PU**.

3.1) The water that is evaporated from the organic phase <1> is used directly for stripping of organic phase <6>. It is hence not necessary to provide additional water to the process. The
15 feed <8> is completely optional and not necessary to achieve the advantageous effect.

3.2) The water vapor <3> obtained in the first distillation step may be used directly for stripping of the organic phase <6>, as it is already in the "correct" aggregate state, namely gaseous.
Hence, the present process does not require energy for condensation/ evaporation of water.

3.3) This process can be conducted in one column, which makes it even more advantageous, as it
20 also saves on equipment, since only one column <4> may be used for two distillation steps.

Claims

1. Process for production of at least one recycled polyol P_{PU} and at least one recycled amine A_{PU} from at least one polyurethane PU ,
- 5 comprising the following steps:
- a. at least partial hydrolysis of the PU by contacting the PU with water W and at least one base B ,
- 10 to give a raw product R_H comprising polyols P_{PU} , amines A_{PU} , water W , at least one base B , and optionally solids S ,
- wherein the raw product R_H comprises an organic phase P_O and an aqueous phase P_W ,
- 15 b. separating at least a part P_{O1} of the organic phase P_O from the raw product R_H , wherein P_{O1} comprises polyols P_{PU} , amines A_{PU} , water W ,
- c. separating at least a part of the water W and at least a part of the amines A_{PU} from P_{O1} by distillation
- 20 to obtain
- water vapor V ,
 - a fraction F_A comprising amines A_{PU} ,
 - an organic phase P_{O2} comprising polyols P_{PU} , optionally amines A_{PU} and optionally water W ,
- 25 d. purifying at least a part P_{O3} of the organic phase P_{O2} by stripping,
- 30 **characterized in that**
- in step d., water vapor V is used as stripping gas in countercurrent flow to P_{O3} .
- 35 2. Process according to claim 1, characterized in that the at least one base B is selected from the group consisting of alkali metal phosphates, alkali earth metal phosphates, alkali metal hydrogen phosphates, alkali earth metal hydrogen phosphates, alkali metal carbonates, alkali earth metal carbonates, alkali metal silicates, alkali earth metal silicates, alkali metal hydrogen carbonates, alkali earth metal hydrogen carbonates, alkali metal carboxylates, alkali earth metal carboxylates, alkali metal sulfites, alkali earth metal sulfites, ammonium hydroxide, alkali metal hydroxides, alkali metal oxides, alkali earth metal oxides, alkali earth metal hydroxides.
- 40

3. The process according to claim 1 or 2, characterized in that the hydrolysis in step a. is catalyzed with at least one phase transfer catalyst selected from the group consisting of quaternary ammonium salts **Q**, organic sulfonates,
- wherein preferably the quaternary ammonium salt **Q** has the general structure $R^1R^2R^3R^4NX$, wherein R^1 , R^2 , R^3 , and R^4 are the same or different and each is a hydrocarbyl group selected from alkyl, aryl, arylalkyl, and X is selected from the group consisting of hydroxide, carbonate, hydrogen carbonate, hydrogen sulfate, carboxylate, halide, alkyl sulfate.
4. The process according to one of claims 1 to 3, characterized in that, after the separation of **P_{O1}** from **R_H** according to step b., at least a part of the aqueous phase **P_W** comprised by **R_H** is used in the hydrolysis according to step a.
5. The process according to one of claims 1 to 4, characterized in that
- (i) the organic phase **P_O** comprised by the raw product **R_H** further comprises one or more components **C_O** selected from the group consisting of foam catalysts, inorganic fillers, polymeric fillers, organic pigments, antioxidants, dyes,
- and/or
- (ii) the aqueous phase **P_W** comprised by the raw product **R_H** further comprises one or more components **C_W** selected from the group consisting of carboxylates, polydimethylsiloxane, inorganic fillers, polymeric fillers, flame retardants, dyes.
6. Process according to one of claims 1 to 5, characterized in that step c. comprises at least two distillation steps c1. and c2., where in step c1., at least a part of the water **W** is separated by distillation from **P_{O1}** to obtain water vapor **V** and a residual organic phase **P_{O1*}**, and where in step c2., at least a part of the amines **A_{PU}** is separated from **P_{O1*}** by distillation to obtain fraction **F_A** and the residual organic phase **P_{O2}**.
7. Process according to claim 6, characterized in that step c1. is at least partially carried out in a distillation column **K₁**.
8. Process according to claim 6 or 7, characterized in that step c2. is at least partially carried out in at least one device selected from short path evaporator, thin film evaporator, distillation column **K₂**, wherein the distillation column **K₂** is different from the distillation column **K₁**.

9. The process according to one of claims 6 to 8, characterized in that

- the distillation according to step c1. is carried out at a temperature $T_{c1} \leq 220\text{ }^{\circ}\text{C}$, preferably $T_{c1} \leq 200\text{ }^{\circ}\text{C}$ and a pressure $p_{c1} \leq 1\text{ bar abs.}$, preferably
5 $0 < p_{c1} \leq 1000\text{ mbar abs.}$, more preferably $1 \leq p_{c1} \leq 500\text{ mbar abs.}$, most preferred $20 \leq p_{c1} \leq 300\text{ mbar abs.}$,

and

- 10 - the distillation according to step c2. is carried out at a temperature $T_{c2} \leq 220\text{ }^{\circ}\text{C}$, preferably $T_{c2} \leq 200\text{ }^{\circ}\text{C}$ and a pressure $p_{c2} \leq 1\text{ bar abs.}$, preferably
 $0 < p_{c2} \leq 1000\text{ mbar abs.}$, more preferably $0 \leq p_{c2} \leq 100\text{ mbar abs.}$, most preferred $0 \leq p_{c2} \leq 20\text{ mbar abs.}$,

15 and where preferably $T_{c1} < T_{c2}$ and $p_{c1} \geq p_{c2}$.

- 10. The process according to any one of claims 1 to 9, characterized in that at least a part of step c., preferably step c.2, is carried out in an atmosphere having an oxygen content of 0 to 21 vol.-%, preferably 0 to 8 vol.-%, more preferred 0 to 1 vol.-% and most preferred
20 0 to 0.1 vol.-%, preferably an atmosphere comprising solely product vapors and one or more inert gases.

- 11. The process according to any one of claims 1 to 10, characterized in that at least a part of step d. and at least a part of step c, preferably step c.1, are carried out in the same
25 distillation column K_1 .

- 12. The process according to any one of claims 1 to 11, characterized in that the at least partial hydrolysis according to step a. is carried out

30 at a temperature of from $90\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$, preferably $100\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$, more preferred $120\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$, and most preferred $140\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$,

and/or

35 for 30 minutes to 20 hours, preferably 30 minutes to 16 hours, more preferred 30 minutes to 14 hours, even more preferred 45 minutes to 10 hours, particular preferred 60 minutes to 8 hours, and most preferred 60 minutes to 6 hours,

and/or

40

at atmospheric pressure or under elevated pressure, in particular under a pressure of from 1 to 30 bar abs., preferably 2 to 20 bar abs., more preferred 3 to 15 bar abs.

13. The process according to one of claims 1 to 12, characterized in that it comprises at least one further step e. in which fraction F_A that is obtained after step c. is further purified and/or purified organic phase P_{O3} that is obtained after step d. is further purified, wherein step e. is preferably selected from the group consisting of filtration, fractional distillation, crystallization, membrane processes, solvent extraction.
14. The process according to one of claims 1 to 13, characterized in that, in a step f., amine A_{PU} from fraction F_A , is subjected to a reaction in which the amino groups of the amine A_{PU} are converted into isocyanate groups, preferably via phosgenation.
15. Process for production of polyurethane, in particular a polyurethane foam, from at least one recycled polyol P_{PU} comprising the steps:
- (1) producing at least one recycled polyol P_{PU} according to a process according to any of the claims 1 to 13,
 - (2) optionally producing an isocyanate according to a process according to claim 14,
 - (3) reacting the at least one recycled polyol P_{PU} with an isocyanate, preferably the isocyanate from step (2).