

Process for producing polyether polyols having primary hydroxyl end groups

The present invention relates to a process for producing polyether polyols having primary hydroxyl end groups, comprising the steps of reacting a starter compound containing active hydrogen atoms with an epoxide under double metal cyanide catalysis, reacting the resulting product with a cyclic carboxylic anhydride and reacting this resulting product with ethylene oxide in the presence of a catalyst containing at least one nitrogen atom per molecule, excluding non-cyclic, identically substituted tertiary amines. The invention further relates to polyether polyols obtainable by this process, compositions containing said polyols and polyurethane polymers based on said polyols.

Long-chain polyether polyols produced by double metal cyanide catalysis (DMC catalysis) are also known as IMPACT polyethers. The nature of the system is such that they contain predominantly secondary hydroxyl end groups. The use of ethylene/propylene oxide mixes (EO/PO) is possible only up to a certain proportion of EO; for that reason it is not possible to obtain long-chain polyether polyols containing predominantly primary hydroxyl end groups by the impact method. Instead such polyethers are obtained either by catalysing exclusively with conventional base catalysis (for example KOH) or in a two-stage procedure by polymerising an EO end block onto an IMPACT PO polyether obtained by DMC catalysis, optionally a PO/EO mixed polyether or a polyether having PO/EO mixed end blocks, under KOH catalysis.

The KOH method generally has the disadvantage that this catalyst has to be separated off by laborious means, for example by neutralisation and filtration. Furthermore, in the case of long-chain polyethers in particular, undesired olefinic end groups are formed as secondary products. Such olefinic end groups or allyl ether end groups reduce the functionality of these polyethers and make them more difficult to use in certain applications. They also lead to polyurethane (PUR) products, which are of a poorer quality.

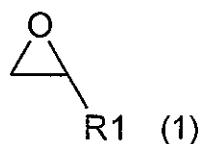
US 4,487,853 discloses a process for producing a polyether ester polyol with a high content of primary hydroxyl groups. In this process a) the reaction product of a

condensate of a polyol with an alkylene oxide is reacted with a cyclic carboxylic acid and b) ethylene oxide at a temperature of 50°C to 125°C. The condensate is obtained from a polyol having 2 to 8 hydroxyl groups and an equivalent weight of 30 to 45 and an alkylene oxide having 2 to 4 carbon atoms and mixtures thereof. The
5 condensate has an equivalent weight of 500 to 10,000. Following reaction with the cyclic carboxylic anhydride a semiester is obtained. The reaction of a) with ethylene oxide takes place in the presence of an effective amount of an amine, oxide or divalent metal catalyst. The ratio of equivalents of the anhydride to equivalents of the condensate is in the range from approximately 1:1 to approximately 1:2 and the
10 molar ratio of ethylene oxide to anhydride is in the range from approximately 2:1 to approximately 1.5:1. A polyurethane from the reaction of an organic polyisocyanate with such polyols is also disclosed.

However, US 4,487,853 does not describe how polyether polyols produced under DMC catalysis can be converted into polyols having primary hydroxyl end groups
15 with as little processing effort as possible. There is consequently still a need for alternative production processes for polyether polyols having primary hydroxyl end groups and in particular for such processes which convert polyethers produced with DMC catalysis.

The invention provides a process for producing polyether polyols having primary
20 hydroxyl end groups, comprising the following steps:

1. Reacting a starter compound containing active hydrogen atoms with an epoxide of the general formula (1):



in which R1 denotes hydrogen, an alkyl radical or an aryl radical and
25 with the proviso that ≥ 0 wt.% to ≤ 30 wt.%, relative to the total amount of the epoxide (1) used, are ethylene oxide,
the reaction being performed in the presence of a double metal cyanide catalyst and the crude product of this reaction undergoing no further purification other than a possible distillation step;

2. Reacting the product obtained in step 1 with a cyclic carboxylic anhydride; and
3. Reacting the product obtained in step 2 with ethylene oxide in the presence of a catalyst containing at least one nitrogen atom per molecule, excluding non-cyclic, identically substituted tertiary amines.

Where the present invention refers to the production of polyether polyols as the end product, the term naturally encompasses such polyether polyols which as a consequence of the process according to the invention also contain ester units.

- 10 One advantage of the process according to the invention is that polyethers produced under DMC catalysis which even with high average molecular masses exhibit no difference or only a technically insignificant difference between the actual and the ideal OH functionality, react to form polyols having a relatively high proportion of primary OH groups. The overall process is simplified by the fact that removal of the catalyst after the first step is dispensed with.

Compounds having (number-average) molecular weights of ≥ 18 g/mol to ≤ 2000 g/mol and ≥ 1 to ≤ 8 hydroxyl groups are preferably used as starter compounds containing active hydrogen atoms in step 1. Examples thereof are ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, 1,4-butanediol, hexamethylene glycol, bisphenol A, bisphenol F, trimethylolpropane, glycerol, castor oil, pentaerythritol, sorbitol, cane sugar, degraded starch and/or water.

Such starter compounds containing active hydrogen atoms can moreover also be used which were produced by for example conventional alkali catalysis from the aforementioned low-molecular-weight starter compounds and which are oligomeric alkoxylation products having (number-average) molecular weights of ≥ 200 g/mol to ≤ 2000 g/mol.

The epoxide of the general formula (1) is a terminal epoxide with a substituent R1, which can be hydrogen, an alkyl radical or an aryl radical. In the context of the

overall invention the term "alkyl" generally encompasses substituents from the group comprising n-alkyl such as methyl, ethyl or propyl, branched alkyl and/or cycloalkyl. In the context of the overall invention the term "aryl" generally encompasses substituents from the group comprising mononuclear carboaryl or heteroaryl substituents such as phenyl and/or polynuclear carboaryl or heteroaryl substituents. It is also possible for mixtures of various epoxides to be used in the process according to the invention, provided that the constituents of the epoxide mixture all fall under the general formula (1). If mixtures of various epoxides are used, it is also possible for the mixing ratio of the epoxides to be altered incrementally or continuously during metering.

The double metal cyanide catalysts that are suitable for step 1 of the process according to the invention preferably have the general formula $M^1_a[M^2(CN)_b(A)_c]_d \cdot f M^1_g X_z \cdot h (H_2O) \cdot e L$.

M^1 here is a metal ion selected from the group containing Zn^{2+} , Fe^{2+} , Co^{3+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Sn^{2+} , Pb^{2+} , Mo^{4+} , Mo^{6+} , Al^{3+} , V^{4+} , V^{5+} , Sr^{2+} , W^{4+} , W^{6+} , Cr^{2+} , Cr^{3+} and/or Cd^{2+} . M^2 denotes a metal ion selected from the group containing Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , Mn^{2+} , Mn^{3+} , V^{4+} , V^{5+} , Cr^{2+} , Cr^{3+} , Rh^{3+} , Ru^{2+} and/or Ir^{3+} . M^1 and M^2 are identical or different.

A is an anion selected from the group containing halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and/or nitrate. X is an anion selected from the group containing halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and/or nitrate. L is a water-miscible ligand selected from the group containing alcohols, aldehydes, ketones, ethers, polyethers, esters, ureas, amides, nitriles and/or sulfides.

The counting variables a, b, c, d, g and z are selected so as to ensure the electroneutrality of the compound. Furthermore, e denotes the coordination number of the ligand, f a fraction or integer greater than or equal to 0 and h a fraction or integer greater than or equal to 0.

The DMC catalysts that are suitable for step 1 of the process according to the invention are known in principle from the prior art (US 3,404,109, US 3,829,505, US 3,941,849 and US 5,158,922). Improved, highly active DMC catalysts, which are described for example in US 5,470,813, EP 0 700 949 A2, EP 0 743 093 A1, 5 EP 0 761 708 A2, WO 97/40086 A1, WO 98/16310 A1 and WO 00/47649 A1, are preferably used. They have an exceptionally high activity and allow polyether polyols to be produced with very low catalyst concentrations. The highly active DMC catalysts described in EP 0 700 949 A2, which in addition to a double metal cyanide compound such as zinc hexacyanocobaltate(III) and an organic complex 10 ligand such as tert-butanol also contain a polyether having a number-average molecular weight of greater than 500 g/mol, are a typical example.

The DMC catalyst in step 1 is preferably obtained in accordance with the teaching from EP 0 700 949 A2, to which reference is made in full extent. The catalyst can contain as components a double metal cyanide compound, in other words a reaction 15 product of a water-soluble metal salt and a water-soluble metal cyanide salt, also an organic complexing agent L and ≥ 5 wt.% to ≤ 80 wt.%, relative to the amount of catalyst, of a polyether having a number-average molecular mass of ≥ 500 g/mol.

The catalyst can be used in a proportion of, for example, ≥ 1 ppm to ≤ 100 ppm and preferably ≥ 10 ppm to ≤ 50 ppm, relative to the total mass of starter compound and 20 epoxide (1) used.

The DMC-catalysed reaction between the starter compound and the epoxide (1) in step 1 generally takes place at temperatures of $\geq 20^{\circ}\text{C}$ to $\leq 200^{\circ}\text{C}$, preferably in the range from $\geq 40^{\circ}\text{C}$ to $\leq 180^{\circ}\text{C}$, particularly preferably at temperatures from $\geq 50^{\circ}\text{C}$ to $\leq 150^{\circ}\text{C}$. The reaction can be performed at total pressures of 0.0001 to 20 bar.

25 The (number-average) molecular weights of the polyether polyols produced in step 1 of the process according to the invention can be ≥ 500 g/mol to $\leq 100,000$ g/mol, preferably ≥ 1000 g/mol to $\leq 50,000$ g/mol, particularly preferably ≥ 2000 g/mol to $\leq 20,000$ g/mol.

The reaction in step 1 can be performed continuously or discontinuously, for example in a batch or semi-batch process.

In the process according to the invention it is provided that in step 1 the epoxide (1) contains at most 30 wt.% of ethylene oxide. It has been found that with higher
5 ethylene oxide contents no satisfactory reaction products are obtained for further processing in the subsequent steps of the process.

Within the context of the present invention it is provided that the crude product of the reaction from step 1 undergoes no further purification other than a possible distillation step. This distillation step is thus optional. The distillation step can
10 remove unreacted epoxide (1), for example, from the resulting polyol. Purification steps which are not used on the product would include filtration, solvent extraction or chromatographic purification. This is an advantage of the process according to the invention, as costly purification steps for polyether polyols produced by the KOH
15 metal cyanide catalysts can remain in the crude product without disrupting the subsequent reactions and because they are needed in only small quantities.

In step 2 of the process according to the invention the product from step 1, which has been purified only by distillation if at all, is reacted further. In this step terminal hydroxyl groups of the polyether polyol obtained are reacted with a cyclic carboxylic
20 anhydride. Opening the anhydride group results in an ester bond to the polyether polyol and a further free carboxyl group. The reaction is optionally performed in the presence of a catalyst containing at least one nitrogen atom per molecule. This is preferably an organic molecule, so the catalyst is an organic amine. Non-cyclic, identically substituted tertiary amines are excluded, however. An example of one
25 such unsuitable amine is triethylamine. If a catalyst is used it is advantageously the same catalyst as in the subsequent step 3.

The amount of nitrogen-containing catalyst, relative to the total mass of the reaction batch in step 2, can be for example ≥ 10 ppm to $\leq 10,000$ ppm, preferably ≥ 50 ppm to ≤ 5000 ppm and more preferably ≥ 100 ppm to ≤ 2000 ppm. The reaction
30 temperature in step 2 can be $\geq 70^{\circ}\text{C}$ to $\leq 150^{\circ}\text{C}$ and preferably $\geq 80^{\circ}\text{C}$ to $\leq 135^{\circ}\text{C}$.

Step 3 of the process according to the invention relates to the reaction of the product obtained in step 2 with ethylene oxide. Reacting the carboxyl groups of the polyether by means of a ring-opening reaction produces hydroxyalkyl groups. Preferably $\geq 80\%$, $\geq 90\%$ or $\geq 95\%$ of the carboxyl groups react with the epoxide, and a
5 proportion of primary hydroxyl groups of ≥ 50 mol% to ≤ 100 mol% or ≥ 60 mol% to ≤ 85 mol% is obtained.

It is provided according to the invention that this reaction is performed in the presence of a catalyst containing at least one nitrogen atom per molecule. This is preferably an organic molecule, so the catalyst is an organic amine. Non-cyclic,
10 identically substituted tertiary amines are however excluded according to the invention. An example of one such unsuitable amine is triethylamine.

The amount of nitrogen-containing catalyst, relative to the total mass of the reaction batch in step 3, can be for example ≥ 10 ppm to $\leq 10,000$ ppm, preferably ≥ 50 ppm to ≤ 5000 ppm and more preferably ≥ 100 ppm to ≤ 2000 ppm. The reaction
15 temperature in step 3 can be $\geq 70^\circ\text{C}$ to $\leq 150^\circ\text{C}$ and preferably $\geq 80^\circ\text{C}$ to $\leq 135^\circ\text{C}$.

This step advantageously follows immediately after step 2, such that the ethylene oxide is added to the reaction batch from step 2 on completion of the reaction with the cyclic carboxylic anhydride.

In one embodiment of the process according to the invention the starter compound
20 used in step 1 is a poly(oxyalkylene) polyol with an average functionality of ≥ 2.0 to ≤ 5.0 , a number-average molecular mass of ≥ 62 g/mol to ≤ 1000 g/mol and an OH value of ≥ 100 mg KOH/g to ≤ 1860 mg KOH/g. The average functionality can also be ≥ 2.3 to ≤ 4.0 , the number-average molecular mass ≥ 100 g/mol to ≤ 500 g/mol and the OH value 200 mg KOH/g to ≤ 300 mg KOH/g. The OH value can be
25 determined in accordance with the standard DIN 53240.

In a further embodiment of the process according to the invention R1 in the epoxide of the general formula (1) is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, cyclohexyl and/or phenyl. R1 is preferably methyl. Then the epoxide used is propylene oxide. Mixtures of propylene oxide and ethylene

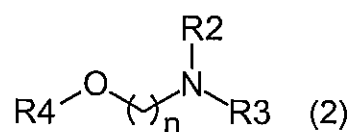
oxide are likewise preferred, resulting in mixed polyether blocks. A plurality of mixtures of propylene oxide and ethylene oxide with various mixing ratios can also be used in succession.

In a further embodiment of the process according to the invention the double metal
 5 cyanide catalyst in step 1 comprises zinc, cobalt and tert-butanol. This catalyst preferably also comprises ≥ 5 wt.% to ≤ 80 wt.%, relative to the amount of catalyst, of a polyether with a number-average molecular mass of ≥ 500 g/mol. The proportion of polyether can also be ≥ 10 wt.% to ≤ 70 wt.% and particularly preferably ≥ 15 wt.% to ≤ 60 wt.%. Particularly suitable polyethers are for example
 10 polyether polyols with an average OH functionality of 2 to 8 and a number-average molecular mass of ≥ 1000 g/mol to $\leq 10,000$ g/mol and preferably ≥ 1000 g/mol to ≤ 5000 g/mol. Poly(oxypropylene) polyols, in particular diols and/or triols, with a number-average molecular mass of ≥ 1000 g/mol to ≤ 4000 g/mol are cited by way of example.

15 In a further embodiment of the process according to the invention the cyclic carboxylic anhydride used in step 2 is selected from the group comprising phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride and/or maleic anhydride.

In a further embodiment of the process according to the invention the catalyst used
 20 in step 3 is selected from the group comprising:

(A) Amines of the general formula (2):



25 in which:

R₂ and R₃ are independently of each other hydrogen, alkyl or aryl; or

R₂ and R₃ together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

n is a whole number from 1 to 10;

R4 is hydrogen, alkyl or aryl; or

R4 denotes $-(CH_2)_x-N(R41)(R42)$, in which:

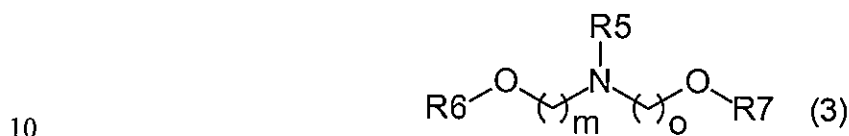
R41 and R42 are independently of each other hydrogen, alkyl or aryl;

5 or

R41 and R42 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

x is a whole number from 1 to 10;

(B) Amines of the general formula (3):



in which:

R5 is hydrogen, alkyl or aryl;

R6 and R7 are independently of each other hydrogen, alkyl or aryl;

m and o are independently of each other a whole number from 1 to 10;

15 and/or:

(C) Diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene, dialkylbenzylamine, dimethylpiperazine, 2,2'-dimorpholinyldiethyl ether and/or pyridine.

20 The catalyst which can optionally be used in step 2 of the process can likewise be selected from groups (A), (B) and/or (C) described above.

Amines of the general formula (2) can be described in the broadest sense as amino alcohols or ethers thereof. If R4 is hydrogen then the catalysts can be incorporated into a polyurethane matrix if the polyether polyol is reacted with a polyisocyanate. This is advantageous as a means of preventing the escape of catalyst, which in the case of amines can be associated with disadvantageous odour problems, to the

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polyurethane surface, a phenomenon known as the fogging or VOC (volatile organic compounds) problem.

Amines of the general formula (3) can be described in the broadest sense as amino (bis)alcohols or ethers thereof. If R6 or R7 is hydrogen then these catalysts can
5 likewise be incorporated into a polyurethane matrix.

It is preferred that in the amine of the general formula (2) R2 and R3 are methyl, R4 is hydrogen and $n = 2$ or that R2 and R3 are methyl, R4 is $-(CH_2)_2-N(CH_3)_2$ and $n = 2$. This therefore results overall in either N,N-dimethylethanolamine or bis(2-(dimethylamino)ethyl) ether.

10 It is further preferred that in the amine of the general formula (3) R5 is methyl, R6 and R7 are hydrogen, $m = 2$ and $o = 2$. This therefore results overall in N-methyldiethanolamine.

In a further embodiment of the process according to the invention the molar ratio in step 2 of cyclic anhydride to hydroxyl groups in the product obtained in step 1 is
15 $\geq 0.75 : 1$ to $\leq 1.3 : 1$. The ratio is preferably $\geq 0.95 : 1$ to $\leq 1.25 : 1$, more preferably $\geq 1.02 : 1$ to $\leq 1.15 : 1$.

In a further embodiment of the process according to the invention the catalyst containing at least one nitrogen atom per molecule is present in step 3 in a proportion of ≥ 500 ppm to ≤ 1500 ppm relative to the total mass of the reaction
20 batch in step 3. The proportion of catalyst can also be ≥ 750 ppm to ≤ 1250 ppm. The same applies correspondingly if such a catalyst is used in step 2 too.

In a further embodiment of the process according to the invention the molar ratio in step 3 of ethylene oxide to hydroxyl groups in the product obtained in step 1 is
25 $\geq 0.90 : 1$ to $\leq 5.0 : 1$. The ratio can also be $\geq 1.0 : 1$ to $\leq 2.0 : 1$ or preferably $\geq 1.05 : 1$ to $\leq 1.2 : 1$.

The present invention also provides a polyether polyol having primary hydroxyl end groups, obtainable by a process according to the invention and comprising a polyether block, a terminal hydroxyethyl group and a diester unit linking the

polyether block and the terminal hydroxyethyl group and wherein the molar proportion of terminal double bonds, relative to all end groups of the polyether polyol, is ≥ 0 milliequivalents per kg to ≤ 10 milliequivalents per kg. The polyether polyol is obtainable by a process according to the invention and in particular is
5 obtained in this way. For that reason reference is made to the embodiments of the process in regard to details of its synthesis.

Without being limited thereto, the polyether block can for example be an ethylene oxide block, propylene oxide block, ethylene oxide/propylene oxide mixed block and/or any sequence of these blocks, started on a di-, tri-, tetra- or pentafunctional
10 alcohol. The number of monomer units in the polyether block, in other words for example the number of ethylene oxide or propylene oxide units, can be in a range from ≥ 10 monomer units to ≤ 5000 monomer units, preferably ≥ 50 monomer units to ≤ 1000 monomer units.

A diester unit which can be attributed to the product of the reaction of an OH end
15 group of the polyether block with a cyclic carboxylic anhydride is connected to the polyether block. In a ring-opening reaction a semiester is initially formed which then reacts with ethylene oxide to form the hydroxyethyl end group. Examples of the cyclic carboxylic anhydride are phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride and/or maleic anhydride.

20 The polyether polyol according to the invention is characterised in that the proportion of terminal double bonds, relative to all end groups of the polyether polyol (meaning the total number of polyether polyol molecules), is in the range from ≥ 0 to ≤ 10 milliequivalents per kg, regardless of the molar mass. For all practical purposes it is therefore free from unsaturated end groups. These end groups
25 would reduce the functionality of the polyether and bring about corresponding disadvantages in the production of polyurethane polymers. Terminal double bonds are avoided for example by polymerising the polyether block onto the starter alcohol by means of DMC catalysis. The polyether polyol according to the invention can be checked for the absence of unsaturated end groups by $^1\text{H-NMR}$ spectroscopy.
30 Another common method is the determination of terminal double bonds using

mercury acetate in accordance with ISO 17710. The content can also be ≥ 0 milliequivalents per kg to ≤ 5 milliequivalents per kg. Polyether polyols according to the invention can furthermore have functionalities in the range from ≥ 2 to ≤ 6 and molar masses in the range from ≥ 1800 Da to $\leq 20,000$ Da.

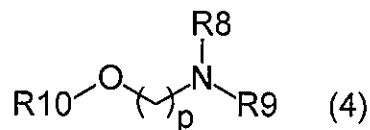
- 5 In one embodiment of the polyether polyol according to the invention the molar proportion of primary hydroxyl groups is ≥ 50 mol% to ≤ 100 mol%. This is understood to be the molar proportion of primary hydroxyl groups as compared with secondary hydroxyl groups in the polyether polyol overall, in other words not relative to a single molecule. This can be determined by $^1\text{H-NMR}$ spectroscopy, for
 10 example. The proportion can also be in a range from ≥ 55 mol% to ≤ 90 mol% or from ≥ 60 mol% to ≤ 85 mol%.

In a further embodiment of the polyether polyol according to the invention it has an OH value of ≥ 10 mg KOH/g to ≤ 100 mg KOH/g. The hydroxyl value can be determined by reference to the standard DIN 53240 and can also be ≥ 15 mg KOH/g
 15 to ≤ 80 mg KOH/g or ≥ 20 mg KOH/g to ≤ 50 mg KOH/g.

In a further embodiment of the polyether polyol according to the invention it has an acid value of ≥ 0.01 mg KOH/g to ≤ 5 mg KOH/g. The acid value can be determined by reference to the standard DIN 53402 and can also be ≥ 0.02 mg KOH/g to ≤ 4.9 mg KOH/g or ≥ 0.02 mg KOH/g to ≤ 4.8 mg KOH/g.

- 20 The present invention also provides a polyether polyol composition comprising a polyether polyol according to the invention and additionally:

(A) Amines of the general formula (4):



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in which:

R8 and R9 are independently of each other hydrogen, alkyl or aryl; or

R8 and R9 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

p is a whole number from 1 to 10, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

R10 is hydrogen, alkyl or aryl; or

5 R10 denotes $-(CH_2)_y-N(R11)(R12)$, in which:

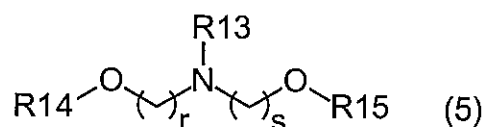
R11 and R12 are independently of each other hydrogen, alkyl or aryl;

or

R11 and R12 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

10 y is a whole number from 1 to 10, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

(B) Amines of the general formula (5):



in which:

R13 is hydrogen, alkyl or aryl;

15 R14 and R15 are independently of each other hydrogen, alkyl or aryl;

r and s are independently of each other a whole number from 1 to 10, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

and/or:

(C) Diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene,
20 dialkylbenzylamine, dimethylpiperazine, 2,2'-dimorpholinyl diethyl ether
and/or pyridine.

In certain variants such compounds can also be used as blowing catalysts, which means that they preferentially catalyse the reaction of the isocyanate groups with water to form carbon dioxide and to a lesser extent also their reaction with hydroxyl
25 groups to form urethane groups. For that reason this composition can be used directly in the production of polyurethanes. If Zerewitinoff-active hydrogen atoms

are present, these catalysts can be incorporated into a polyurethane matrix. This reduces the content of volatile organic compounds in the polyurethane. N,N-Dimethylethanolamine, bis(2-(dimethylamino)ethyl) ether or N-methyldiethanolamine are preferred.

- 5 The proportion of these compounds (A), (B) and/or (C) relative to the polyol according to the invention can be for example ≥ 10 ppm to $\leq 10,000$ ppm, preferably ≥ 50 ppm to ≤ 5000 ppm and more preferably ≥ 100 ppm to ≤ 2000 ppm.

The present invention also provides a polyurethane polymer, obtainable from the reaction of a polyisocyanate with a polyether polyol according to the invention or a
 10 polyether polyol composition according to the invention. Also included according to the invention under the term "polyurethane polymer" are prepolymers obtainable from the reaction of a polyisocyanate with a polyether according to the invention or a polyether polyol composition according to the invention.

The present invention is illustrated in more detail by the examples below. The
 15 meanings and sources of the materials and abbreviations used are as follows:

2,2,2-Diazabicyclooctane (DABCO):	Aldrich
N,N-Dimethylethanolamine (DMEA):	Aldrich
Bis(2-(dimethylamino)ethyl) ether (DMAEE):	Alfa Aesar
Triethylamine:	Aldrich
20 Tetrahydrophthalic anhydride (THPA):	Aldrich

The analyses were performed as follows:

Viscosity: MCR 51 rheometer from Anton Paar

Determination of the molar proportion of primary OH groups: by ^1H -NMR (Bruker DPX 400, deuteriochloroform)

25 Hydroxyl value: by reference to DIN 53240

Acid value: by reference to DIN 53402

1. Production of the DMC-catalysed precursors:

Precursor A:

117.6 g of a poly(oxypropylene) triol with an OH value of 238 mg KOH/g and 0.024 g of DMC catalyst (produced in accordance with EP 0 700 949 A2) were
5 placed in a 1-litre stainless steel pressure reactor under nitrogen, heated to 130°C and then stripped for 30 minutes at 0.1 bar while passing nitrogen through the reactor. Then 682 g of propylene oxide were added at 130°C within 3 hours. Following a post-reaction time at 130°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes
10 and the reaction mixture was then cooled to room temperature. The OH value of the product was 34.1 mg KOH/g at a viscosity (25°C) of 967 mPas.

Precursor B:

117.6 g of a poly(oxypropylene) triol with an OH value of 238 mg KOH/g and 0.024 g of DMC catalyst (produced in accordance with EP 0 700 949 A2) were
15 placed in a 1-litre stainless steel pressure reactor under nitrogen, heated to 130°C and then stripped for 30 minutes at 0.1 bar while passing nitrogen through the reactor. Then a mixture of 504 g of propylene oxide and 38 g of ethylene oxide, followed by a mixture of 53 g of propylene oxide and 17 g of ethylene oxide and finally a mixture of 35 g of propylene oxide and 35 g of ethylene oxide were added
20 at 130°C within 3 hours. Following a post-reaction time at 130°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature. The OH value of the product was 34.6 mg KOH/g at a viscosity (25°C) of 954 mPas.

25 Precursor C:

117.6 g of a poly(oxypropylene) triol with an OH value of 238 mg KOH/g and 0.024 g of DMC catalyst (produced in accordance with EP 0 700 949 A2) were
placed in a 1-litre stainless steel pressure reactor under nitrogen, heated to 130°C and then stripped for 30 minutes at 0.1 bar while passing nitrogen through the
30 reactor. Then a mixture of 439 g of propylene oxide and 33 g of ethylene oxide,

followed by a mixture of 53 g of propylene oxide and 17 g of ethylene oxide, then a mixture of 35 g of propylene oxide and 35 g of ethylene oxide and finally a mixture of 21 g of propylene oxide and 49 g of ethylene oxide were added at 130°C within 3 hours. Following a post-reaction time at 130°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature. The OH value of the product was 35.3 mg KOH/g at a viscosity (25°C) of 916 mPas.

Table 1 below summarises the data for precursors A, B and C.

		Precursor A	Precursor B	Precursor C
Polyoxypropylene triol	[g]	117.6	117.6	117.6
DMC catalyst	[g]	0.024	0.024	0.024
Propylene/ethylene oxide	[g / g]	682 / 0	504 / 38	439 / 33
Propylene/ethylene oxide	[g / g]		53 / 17	53 / 17
Propylene/ethylene oxide	[g / g]		35 / 35	35 / 35
Propylene/ethylene oxide	[g / g]			21 / 49
Proportion of ethylene oxide in total epoxide used	[wt.%]	0	15	24
OH value	[mg KOH/g]	34.1	34.6	35.3
Viscosity	[mPas, 25°C]	967	954	916

2. Reaction of DMC-catalysed precursors with cyclic anhydrides and ethylene oxide under amine catalysis:

Example 1 (comparative example):

- 400 g of the DMC-catalysed precursor A, 40.66 g of tetrahydrophthalic anhydride and 0.462 g (1000 ppm, relative to the complete batch) of triethylamine were placed in a 1-litre stainless steel pressure reactor under nitrogen. The molar ratio of

anhydride to the hydroxyl groups in precursor A was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.42 g of ethylene oxide were metered into the reactor at 125°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor A was 2 : 1. Following a
5 post-reaction time at 125°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature. The acid value of the product was 23.6 mg KOH/g at a viscosity (25°C) of 4140 mPas. The very high acid value shows that only a small conversion with ethylene oxide occurred.

10 Example 2:

400 g of the DMC-catalysed precursor A, 40.66 g of tetrahydrophthalic anhydride and 0.462 g (1000 ppm, relative to the complete batch) of DABCO (triethylenediamine) were placed in a 1-litre stainless steel pressure reactor under nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor A was
15 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.42 g of ethylene oxide were metered into the reactor at 125°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor A was 2 : 1. Following a post-reaction time at 125°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum
20 at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

OH value: 28.2 mg KOH/g
Acid value: 2.58 mg KOH/g
25 Viscosity (25°C): 3035 mPas
Primary OH groups: 65%

Example 3:

400 g of the DMC-catalysed precursor A, 40.66 g of tetrahydrophthalic anhydride and 0.462 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl)
30 ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The

molar ratio of anhydride to the hydroxyl groups in precursor A was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.42 g of ethylene oxide were metered into the reactor at 125°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor A
5 was 2 : 1. Following a post-reaction time at 125°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

OH value: 32.8 mg KOH/g
10 Acid value: 0.04 mg KOH/g
Viscosity (25°C): 2685 mPas
Primary OH groups: 69%

Example 4:

400 g of the DMC-catalysed precursor B, 37.54 g of tetrahydrophthalic anhydride
15 and 0.459 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl) ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor B was 1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.74 g of ethylene oxide were metered into the reactor at 105°C over a period of
20 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor B was 2 : 1. Following a post-reaction time at 105°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

25 Product characteristics:

OH value: 32.8 mg KOH/g
Acid value: 0.05 mg KOH/g
Viscosity (25°C): 2437 mPas
Primary OH groups: 73%

Example 5:

400 g of the DMC-catalysed precursor B, 37.54 g of tetrahydrophthalic anhydride and 0.459 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl) ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The
5 molar ratio of anhydride to the hydroxyl groups in precursor B was 1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.74 g of ethylene oxide were metered into the reactor at 145°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor B was 2 : 1. Following a post-reaction time at 145°C to establish constant pressure in
10 the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

OH value: 32.1 mg KOH/g
Acid value: 0.66 mg KOH/g
15 Viscosity (25°C): 2229 mPas
Primary OH groups: 69%

Example 6:

400 g of the DMC-catalysed precursor B, 41.29 g of tetrahydrophthalic anhydride and 0.463 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl)
20 ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor B was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.74 g of ethylene oxide were metered into the reactor at 105°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor B
25 was 2 : 1. Following a post-reaction time at 105°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

OH value: 32.2 mg KOH/g

Acid value: 0.53 mg KOH/g

Viscosity (25°C): 2750 mPas

5 Primary OH groups: 74%

Example 7:

400 g of the DMC-catalysed precursor B, 41.29 g of tetrahydrophthalic anhydride and 0.463 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl) ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The
10 molar ratio of anhydride to the hydroxyl groups in precursor B was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.74 g of ethylene oxide were metered into the reactor at 145°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor B was 2 : 1. Following a post-reaction time at 145°C to establish constant pressure in
15 the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

OH value: 28.3 mg KOH/g

Acid value: 2.84 mg KOH/g

20 Viscosity (25°C): 2525 mPas

Primary OH groups: 66%

Example 8:

400 g of the DMC-catalysed precursor B, 41.29 g of tetrahydrophthalic anhydride and 0.463 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl)
25 ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor B was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 21.74 g of ethylene oxide were metered into the reactor at 90°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor B
30 was 2 : 1. Following a post-reaction time at 90°C to establish constant pressure in

the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

- OH value: 28.2 mg KOH/g
5 Acid value: 2.41 mg KOH/g
Viscosity (25°C): 3074 mPas
Primary OH groups: 75%

Example 9:

- 200 g of the DMC-catalysed precursor B, 20.64 g of tetrahydrophthalic anhydride
10 and 0.232 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl)
ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The
molar ratio of anhydride to the hydroxyl groups in precursor B was 1.1 : 1. Then the
mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 6.0 g
of ethylene oxide were metered into the reactor at 125°C over a period of
15 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor B
was 1.1 : 1. Following a post-reaction time at 125°C to establish constant pressure in
the reactor, highly volatile components were distilled off under vacuum at 90°C for
30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

- 20 OH value: 24.1 mg KOH/g
Acid value: 4.75 mg KOH/g
Viscosity (25°C): 2578 mPas
Primary OH groups: 63%

Example 10:

- 25 300 g of the DMC-catalysed precursor C, 31.59 g of tetrahydrophthalic anhydride
and 0.348 g (1000 ppm, relative to the complete batch) of DABCO
(triethylenediamine) were placed in a 1-litre stainless steel pressure reactor under
nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor C was
1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for
30 3 hours. Then 16.63 g of ethylene oxide were metered into the reactor at 125°C over

a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor C was 2 : 1. Following a post-reaction time at 125°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room
5 temperature.

Product characteristics:

OH value: 33.7 mg KOH/g

Acid value: 0.23 mg KOH/g

Viscosity (25°C): 2760 mPas

10 Primary OH groups: 76%

Example 11:

300 g of the DMC-catalysed precursor C, 31.59 g of tetrahydrophthalic anhydride and 0.348 g (1000 ppm, relative to the complete batch) of N,N-dimethylethanolamine were placed in a 1-litre stainless steel pressure reactor under
15 nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor C was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 16.63 g of ethylene oxide were metered into the reactor at 125°C over a period of 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor C was 2 : 1. Following a post-reaction time at 125°C to establish constant
20 pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

OH value: 34.3 mg KOH/g

25 Acid value: 0.12 mg KOH/g

Viscosity (25°C): 2274 mPas

Primary OH groups: 65%

Example 12:

300 g of the DMC-catalysed precursor C, 31.59 g of tetrahydrophthalic anhydride
30 and 0.348 g (1000 ppm, relative to the complete batch) of bis(2-dimethylaminoethyl)

ether were placed in a 1-litre stainless steel pressure reactor under nitrogen. The molar ratio of anhydride to the hydroxyl groups in precursor C was 1.1 : 1. Then the mixture was heated to 125°C and stirred at this temperature for 3 hours. Then 16.63 g of ethylene oxide were metered into the reactor at 125°C over a period of 5 30 minutes. The molar ratio of ethylene oxide to the hydroxyl groups in precursor C was 2 : 1. Following a post-reaction time at 125°C to establish constant pressure in the reactor, highly volatile components were distilled off under vacuum at 90°C for 30 minutes and the reaction mixture was then cooled to room temperature.

Product characteristics:

- 10 OH value: 34.6 mg KOH/g
Acid value: 0.06 mg KOH/g
Viscosity (25°C): 2535 mPas
Primary OH groups: 70%

Tables 2 below summarises the data for Examples 1 to 12:

Example		1 (*)	2	3	4
Polyether polyol from precursor	Type	A	A	A	B
	[g]	400	400	400	400
Cyclic carboxylic anhydride	Type	THPA	THPA	THPA	THPA
	[g]	40.66	40.66	40.66	37.54
Molar ratio of anhydride to hydroxyl groups in polyether polyol	[mol / mol]	1.1 : 1	1.1 : 1	1.1 : 1	1 : 1
Catalyst	Type	NEt ₃	DABCO	DMAEE	DMAEE
	[g]	0.462	0.462	0.462	0.459
Ethylene oxide	[g]	21.42	21.42	21.42	21.74
Molar ratio of ethylene oxide to hydroxyl groups in polyether polyol	[mol / mol]	2 : 1	2 : 1	2 : 1	2 : 1
Metering time for ethylene oxide	[min]	30	30	30	30
Metering temperature	[°C]	125	125	125	105
Hydroxyl value	[mg KOH/g]	n.d.	28.2	32.8	32.8
Acid value	[mg KOH/g]	23.6	2.58	0.04	0.05
Viscosity	[mPas, 25°C]	4140	3035	2685	2437
Hydroxyl groups, primary	[mol%]	n.d.	65	69	73

(*): Comparative example

Example		5	6	7	8
Polyether polyol from precursor	Type	B	B	B	B
	[g]	400	400	400	400
Cyclic carboxylic anhydride	Type	THPA	THPA	THPA	THPA
	[g]	37.54	41.29	41.29	41.29
Molar ratio of anhydride to hydroxyl groups in polyether polyol	[mol / mol]	1 : 1	1.1 : 1	1.1 : 1	1.1 : 1
Catalyst	Type	DMAEE	DMAEE	DMAEE	DMAEE
	[g]	0.459	0.463	0.459	0.463
Ethylene oxide	[g]	21.74	21.74	21.74	21.74
Molar ratio of ethylene oxide to hydroxyl groups in polyether polyol	[mol / mol]	2 : 1	2 : 1	2 : 1	2 : 1
Metering time for ethylene oxide	[min]	30	30	30	30
Metering temperature	[°C]	145	105	145	90
Hydroxyl value	[mg KOH/g]	32.1	32.2	28.3	28.2
Acid value	[mg KOH/g]	0.66	0.53	2.84	2.41
Viscosity	[mPas, 25°C]	2229	2750	2525	3074
Hydroxyl groups, primary	[mol%]	69	74	66	75

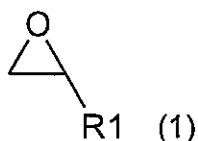
Example		9	10	11	12
Polyether polyol from precursor	Type	B	C	C	C
	[g]	200	300	300	300
Cyclic carboxylic anhydride	Type	THPA	THPA	THPA	THPA
	[g]	20.64	31.59	31.59	31.59
Molar ratio of anhydride to hydroxyl groups in polyether polyol	[mol / mol]	1.1 : 1	1.1 : 1	1.1 : 1	1.1 : 1
Catalyst	Type	DMAEE	DABCO	DMEA	DMAEE
	[g]	0.232	0.348	0.348	0.348
Ethylene oxide	[g]	6	16.63	16.63	16.63
Molar ratio of ethylene oxide to hydroxyl groups in polyether polyol	[mol / mol]	1.1 : 1	2 : 1	2 : 1	2 : 1
Metering time for ethylene oxide	[min]	30	30	30	30
Metering temperature	[°C]	125	125	125	125
Hydroxyl value	[mg KOH/g]	24.1	33.7	34.3	34.6
Acid value	[mg KOH/g]	4.75	0.23	0.12	0.06
Viscosity	[mPas, 25°C]	2578	2760	2274	2535
Hydroxyl groups, primary	[mol%]	63	76	65	70

It is clear from the very low acid values in the end products of the examples according to the invention that scarcely any free carboxyl groups which form after the opening of the cyclic anhydride did not react with ethylene oxide. Furthermore, a comparison of the hydroxyl values of the end products and of the precursor polyethers A, B and C used at the start shows that only a slight increase in the molecular weights of precursors A, B and C occurred as a result of the process according to the invention. Finally the results show that primary end groups were obtained in each case in a proportion of over 50%.

Claims

1. Process for producing polyether polyols having primary hydroxyl end groups, comprising the following steps:

1. Reacting a starter compound containing active hydrogen atoms with
5 an epoxide of the general formula (1):



- in which R1 denotes hydrogen, an alkyl radical or an aryl radical and with the proviso that ≥ 0 wt.% to ≤ 30 wt.%, relative to the total amount of the epoxide (1) used, are ethylene oxide,
10 the reaction being performed in the presence of a double metal cyanide catalyst and the crude product of this reaction undergoing no further purification other than a possible distillation step;
2. Reacting the product obtained in step 1 with a cyclic carboxylic anhydride; and
- 15 3. Reacting the product obtained in step 2 with ethylene oxide in the presence of a catalyst containing at least one nitrogen atom per molecule, excluding non-cyclic, identically substituted tertiary amines.

2. Process according to claim 1, wherein the starter compound used in step 1 is
20 a poly(oxyalkylene) polyol with an average functionality of ≥ 2.0 to ≤ 5.0 , a number-average molecular mass of ≥ 62 g/mol to ≤ 1000 g/mol and an OH value of ≥ 100 mg KOH/g to ≤ 1860 mg KOH/g.

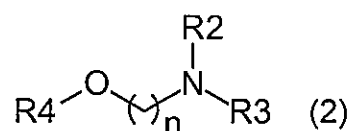
3. Process according to claim 1, wherein R1 in the epoxide of the general formula (1) is hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl,
25 isobutyl, tert-butyl, cyclohexyl and/or phenyl.

4. Process according to claim 1, wherein the double metal cyanide catalyst in step 1 comprises zinc, cobalt and tert-butanol.

5. Process according to claim 1, wherein the cyclic carboxylic anhydride used in step 2 is selected from the group comprising phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride and/or maleic anhydride.

6. Process according to claim 1, wherein the catalyst used in step 3 is selected from the group comprising:

(A) Amines of the general formula (2):



10 in which:

R2 and R3 are independently of each other hydrogen, alkyl or aryl; or

R2 and R3 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

n is a whole number from 1 to 10;

15 R4 is hydrogen, alkyl or aryl; or

R4 denotes $-(\text{CH}_2)_x-\text{N}(\text{R41})(\text{R42})$, in which:

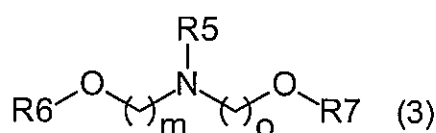
R41 and R42 are independently of each other hydrogen, alkyl or aryl;

or

R41 and R42 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

x is a whole number from 1 to 10;

(B) Amines of the general formula (3):



in which:

25 R5 is hydrogen, alkyl or aryl;

R6 and R7 are independently of each other hydrogen, alkyl or aryl;
m and o are independently of each other a whole number from 1 to 10;

and/or:

- 5 (C) Diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene, dialkylbenzyl-amine, dimethylpiperazine, 2,2'-dimorpholinyldiethyl ether and/or pyridine.

7. Process according to claim 1, wherein the molar ratio in step 2 of cyclic anhydride to hydroxyl groups in the product obtained in step 1 is $\geq 0.75 : 1$ to $\leq 1.3 : 1$.

8. Process according to claim 1, wherein the catalyst containing at least one
10 nitrogen atom per molecule is present in step 3 in a proportion of ≥ 500 ppm to ≤ 1500 ppm relative to the total mass of the reaction batch in steps 2 and 3.

9. Process according to claim 1, wherein the molar ratio in step 3 of ethylene oxide to hydroxyl groups in the product obtained in step 1 is $\geq 0.90 : 1$ to $\leq 5.0 : 1$.

10. Polyether polyol having primary hydroxyl end groups, obtainable by a
15 process according to claim 1, comprising a polyether block, a terminal hydroxyethyl group and a diester unit linking the polyether block and the terminal hydroxyethyl group and wherein the molar proportion of terminal double bonds, relative to all end groups of the polyether polyol, is ≥ 0 milliequivalents per kg to ≤ 10 milliequivalents per kg.

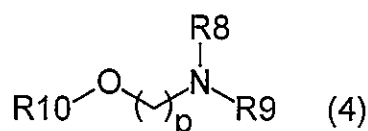
- 20 11. Polyether polyol according to claim 10, wherein the molar proportion of primary hydroxyl groups is ≥ 50 mol% to ≤ 100 mol%.

12. Polyether polyol according to claim 10 with an OH value of ≥ 10 mg KOH/g to ≤ 100 mg KOH/g.

13. Polyether polyol according to claim 10 with an acid value of ≥ 0.01 mg
25 KOH/g to ≤ 5 mg KOH/g.

14. Polyether polyol composition comprising a polyether polyol according to claim 10 and additionally:

(A) Amines of the general formula (4):



in which:

R8 and R9 are independently of each other hydrogen, alkyl or aryl; or

R8 and R9 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

p is a whole number from 1 to 10, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

R10 is hydrogen, alkyl or aryl; or

R10 denotes $-(\text{CH}_2)_y-\text{N}(\text{R11})(\text{R12})$, in which:

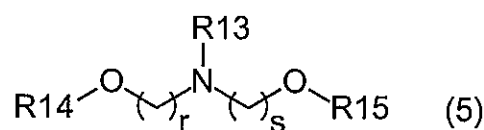
R11 and R12 are independently of each other hydrogen, alkyl or aryl;

or

R11 and R12 together with the N-atom bearing them form an aliphatic, unsaturated or aromatic heterocycle;

y is a whole number from 1 to 10, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

(B) Amines of the general formula (5):



in which:

R13 is hydrogen, alkyl or aryl;

R14 and R15 are independently of each other hydrogen, alkyl or aryl;

r and s are independently of each other a whole number from 1 to 10, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

and/or:

- (C) Diazabicyclo[2.2.2]octane, diazabicyclo[5.4.0]undec-7-ene,
dialkylbenzylamine, dimethylpiperazine, 2,2'-dimorpholinyl diethyl ether
and/or pyridine.
- 5 15. Polyurethane polymer obtainable from the reaction of a polyisocyanate with a
polyether polyol according to claim 10 or a polyether polyol composition according
to claim 14.