

Polyether alcohols

The present invention relates to polyetherols, their preparation
5 and their use for producing polyurethanes.

Polyether alcohols are used in large quantities for producing
polyurethanes. They are usually prepared by catalytic addition of
lower alkylene oxides, in particular ethylene oxide and propylene
10 oxide, onto H-functional initiator molecules. The catalysts used
are usually basic metal hydroxides or salts, with potassium
hydroxide having the greatest industrial importance.

In the synthesis of polyether alcohols having long chains and
15 hydroxyl numbers of from about 26 to about 60 mg KOH/g, as are
used especially for the production of flexible polyurethane
foams, secondary reactions occur as chain growth progresses and
these lead to malfunctions in the buildup of the chains. The
by-products are referred to as unsaturated constituents and have
20 an adverse effect on the properties of the resulting polyurethane
materials. In particular these unsaturated constituents, which
have an OH functionality of 1, have the following consequences:

- Owing to their sometimes very low molecular weight, they are
25 volatile and thus increase the total content of volatile
constituents in the polyether polyol and in the polyurethanes
produced therefrom, in particular flexible polyurethane
foams.
- 30 - They act as chain terminators in the production of the
polyurethane because they delay or reduce the crosslinking of
the polyurethane or the buildup of the molecular weight of
the polyurethane.

35 It is therefore very desirable in industry to avoid the
unsaturated constituents as far as possible.

One way of preparing polyether alcohols having a low content of
unsaturated constituents is the use of multimetal cyanide
40 catalysts, usually zinc hexacyanometalates, as alkoxylation
catalysts. There is a large number of documents in which the
preparation of polyether alcohols by means of such catalysts is
described. Thus, DD-A-203 735 and DD-A-203 734 describe the
preparation of polyether alcohols using zinc hexacyanocobaltate.
45 The use of multimetal cyanide catalysts can reduce the content of
unsaturated constituents in the polyether polyol to about
0.003-0.009 meq/g - in the case of conventional catalysis using

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potassium hydroxide, about 10 times these amounts are found (about 0.03-0.08 meq/g).

The preparation of the multimetal cyanide catalysts is also known. These catalysts are usually prepared by reacting solutions of metal salts such as zinc chloride with solutions of alkali metal or alkaline earth metal cyanometalates, e.g. potassium hexacyanocobaltate. A water-miscible, heteroatom-containing component is generally added to the resulting suspension immediately after the precipitation process. This component can also be present beforehand in one or both starting solutions. This water-miscible, heteroatom-containing component can be, for example, an ether, polyether, alcohol, ketone or a mixture thereof. Such processes are described, for example, in US 3,278,457, US 3,278,458, US 3,278,459, US 3,427,256, US 3,427,334 and US 3,404,109.

A problem when using polyether alcohols which have been prepared by means of multimetal cyanide catalysts is that these polyols behave differently in the production of polyurethanes than do polyether alcohols which have been prepared from the same starting materials but using alkali metal hydroxides as catalysts. These effects show up particularly in polyether alcohols whose chains are made up of two or more alkylene oxides.

Thus, it has been found that polyether alcohols having a random end block of propylene oxide and ethylene oxide which have been prepared by means of multimetal cyanides as catalysts have a significantly higher reactivity than polyether alcohols of the same composition which have been prepared by means of potassium hydroxide as catalyst. This increased reactivity, which is attributable to a higher primary hydroxyl group content, causes considerable problems in most applications of such polyether alcohols.

Thus, WO 97/27,236 (EP 876,416) describes a polyether alcohol for use in high-elasticity flexible foams, which polyether alcohol comprises an inner propylene oxide block which makes up not more than 35% by weight of the total amount of alkylene oxide and one or more external blocks of ethylene oxide and propylene oxide containing at least 2% by weight of ethylene oxide, and the inner block is catalyzed at least partly and the external blocks completely by means of multimetal cyanide catalysts. However, such polyether alcohols are, as mentioned above, significantly more reactive than commercial base-catalyzed polyether alcohols

and can thus not be readily incorporated into polyurethane systems.

The problems indicated show up particularly in polyurethane
5 foams, in particular flexible foams, and most clearly in the case of flexible slabstock foams. In particular, crack formation occurs in the foam and the mechanical properties of the foams are impaired.

- 10 A possible way of alleviating this deficiency is to change the proportions of the alkylene oxides used in the preparation of the polyether alcohols. However, the variations possible here are only small, since such a change would cause problems in setting the foam properties, which is usually undesirable. Changes in the
15 formulation of the polyurethanes which would be able to compensate for the altered reactivity of the polyether alcohols are usually associated with adverse effects on the foam properties.
- 20 A further possible way of alleviating this deficiency is proposed in EP-A-654 056, in which alkali metal oxides and hydroxides and/or alkaline earth metal oxides and hydroxides are added in an amount of from 0.5 to 10 ppm to the polyether alcohols prepared by means of multimetal cyanide catalysts after removal of the
25 catalyst.

However, it has been found that polyether alcohols which have been prepared by means of multimetal cyanide catalysts and to which the compounds described in EP-A-654 056 have been added
30 cannot be used for producing flexible polyurethane foams. In particular, foams produced in this way displayed poor curing behavior with pronounced crack formation. In addition, such flexible foams have an insufficient open cell content.

- 35 It has now surprisingly been found that polyether alcohols prepared by means of multimetal cyanide catalysts have the same reactivity as polyether alcohols which have the same proportions of ethylene oxide and propylene oxide in the polymer chain but have been catalyzed using potassium hydroxide if a propylene
40 oxide block is incorporated at the end of the polyether chain of the polyether alcohols prepared by means of multimetal cyanide catalysts.

The present invention accordingly provides polyether alcohols
45 which can be prepared by catalytic molecular addition of ethylene oxide and propylene oxide, wherein at least one multimetal

cyanide compound is used as catalyst and a block of propylene oxide units is added on at the end of the chain.

The present invention further provides a process for preparing
5 polyether alcohols by catalytic molecular addition of ethylene oxide and propylene oxide, wherein at least one multimetal cyanide compound is used as catalyst and a block of an alkylene oxide having at least three carbon atoms, in particular propylene oxide, is added on at the end of the chain.

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The invention further provides a process for producing polyurethanes, preferably flexible polyurethane foams, in particular flexible slabstock foam, by reacting polyisocyanates with the polyether alcohols of the present invention, and also
15 provides the polyurethanes produced by this process.

In a preferred embodiment of the present invention, the end block of an alkylene oxide having at least three carbon atoms, in particular propylene oxide, makes up from 2 to 50% by weight,
20 preferably from 2 to 20% by weight and particularly preferably from 5 to 15% by weight, of the total mass of the polyether alcohol.

In the polyether alcohols of the present invention, preferably at
25 least 80%, particularly preferably at least 90% and in particular at least 95%, of the total number of hydroxyl groups are secondary hydroxyl groups. The content of unsaturated constituents is preferably less than 0.015 meq/g. The value was determined titrimetrically by means of the iodine number
30 measured in accordance with the BASF Schwarzheide GmbH standard test method PPU 00/03-12.

The molecular addition of the end block of alkylene oxides having at least three carbon atoms, in particular propylene oxide, can
35 be carried out in various possible ways. Thus, it is possible to prepare polyether alcohols having a purely blockwise arrangement of the alkylene oxides. In this process variant, only one alkylene oxide is metered in at a time, followed by the next, and so forth. According to the present invention, a pure propylene
40 oxide block is added on as last block.

In a further preferred variant, a pure alkylene oxide block, preferably propylene oxide, is, if desired, first added onto the initiator substance, followed by metered addition of a mixture of
45 ethylene oxide and propylene oxide, with the ratio of ethylene oxide to propylene oxide being able to vary over the time of metered addition or preferably remaining constant, and, at the

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end of the metered addition of alkylene oxide, a pure propylene oxide block is added on as specified according to the present invention.

5 In a further preferred variant, firstly, if desired, a pure alkylene oxide block, preferably propylene oxide, is likewise preferably added on and then a mixture of ethylene oxide and propylene oxide is likewise added on, with the proportion of ethylene oxide in the mixture being reduced during the course of
10 the metered addition until only propylene oxide is being metered in at the end of the metered addition.

It is also possible to add small amounts of ethylene oxide to the end block of at least one alkylene oxide having at least three
15 carbon atoms provided that this does not adversely affect the properties of the polyether alcohols of the present invention. Here, small amounts means a proportion of not more than 5% by weight, preferably not more than 2% by weight, in each case based on the weight of the end block.

20 As alkylene oxide having at most [sic] 3 carbon atoms, particular preference is given to using propylene oxide. Further preferred compounds are butylene oxide, styrene oxide or epoxidized fatty oils such as epoxidized soybean oil. The compounds mentioned can
25 be used individually or in the form of any mixtures with one another.

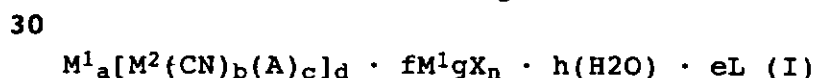
The polyether alcohols of the present invention usually have a functionality of from 2 to 8, preferably from 2 to 4 and in
30 particular from 2 to 3, and an equivalent weight of greater than 500 g/mol. Initiator substances used may be relatively high functionality initiator substances, in particular sugar alcohols such as sorbitol, hexitol and sucrose, but are usually bifunctional and/or trifunctional alcohols or water, either as
35 the individual substance or as a mixture of at least two of the initiator substances mentioned. Examples of bifunctional initiator substances are ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol and 1,5-pentanediol. Examples of trifunctional initiator substances
40 are trimethylolpropane, pentaerythritol and, in particular, glycerol. The initiator substances can also be used in the form of alkoxylates, in particular those having a molecular weight M_w in the range from 62 to 15,000 g/mol. These alkoxylates can be prepared in a separate process step, and it is also possible to
45 use catalysts other than multimetal cyanide compounds, for example alkali metal hydroxides, for preparing them. When using alkali metal hydroxides for preparing the alkoxylates, it is

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necessary to remove virtually all of the catalyst since alkali metal hydroxides can deactivate the multimetal cyanide catalysts. The advantage of using alkoxylates as initiator substances is faster starting of the reaction, but disadvantages are the
 5 introduction of an additional process step and, as mentioned above, possibly the complicated purification of the alkoxylate.

At the beginning of the reaction, the initiator substance is placed in a reaction vessel and, if necessary, water and other
 10 volatile compounds are removed. This is usually carried out by means of distillation, preferably under reduced pressure. The catalyst may already be present in the initiator substance, but it is also possible to add the catalyst only after the treatment of the initiator substance. In the latter variant, the catalyst
 15 is subject to less thermal stress. Prior to metering in the alkylene oxides, it is customary to make the reactor inert in order to avoid undesirable reactions of the alkylene oxides with oxygen. The alkylene oxides are then metered in and the molecular addition is carried out in the manner described above. The
 20 molecular addition of the alkylene oxides is usually carried out at from 50 to 200°C, preferably from 90 to 150°C, and pressures in the range from 0.01 bar to 10 bar. It has been found that the rate at which the alkylene oxides are metered in likewise has an influence on the reactivity of the polyether alcohols formed. The
 25 faster the alkylene oxides are metered in, the higher the reactivity of the resulting polyether alcohols.

The multimetal cyanide catalysts used in the process of the present invention usually have the formula (I)



where

35 M^1 is a metal ion selected from the group consisting of 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+} , Cd^{2+} ,

M^2 is a metal ion selected from the group consisting of Fe^{2+} ,
 40 Fe^{3+} , Co^{2+} , Co^{3+} , Mn^{2+} , Mn^{3+} , V^{4+} , V^{5+} , Cr^{2+} , Cr^{3+} , Rh^{3+} , Ru^{2+} , Ir^{3+}

and M^1 and M^2 are identical or different,

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- A is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and nitrate,
- 5 X is an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate and nitrate,
- 10 L is a water-miscible ligand selected from the group consisting of alcohols, aldehydes, ketones, ethers, polyethers, esters, ureas, amides, nitriles and sulfides,
- and
- 15 a, b, c, d, g and n are chosen so that the compound is electrically neutral, and
- e is the coordination number of the ligand,
- 20 f is a fraction or an integer greater than or equal to 0 and
- h is a fraction or an integer greater than or equal to 0.

These compounds are prepared by generally known methods by
25 combining the aqueous solution of a water-soluble metal salt with the aqueous solution of a hexacyanometalate compound, in particular a salt or an acid, and adding a water-soluble ligand thereto either during or after the mixing of the two solutions.

30 The catalyst is usually used in an amount of less than 1% by weight, preferably in an amount of less than 0.5% by weight, particularly preferably in an amount of less than 1000 ppm and in particular in an amount of less than 500 ppm, in each case based on the weight of the polyether alcohol.

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The process of the present invention is preferably carried out using multimetal cyanide catalysts prepared by combining a metal salt and a cyanometallic acid as described in EP-A-862,947. Preference is also given to multimetal cyanide catalysts which
40 contain acetate, formate or propionate and display an X-ray diffraction pattern as described in DE 97,42,978 or crystallize in a monoclinic system.

These multimetal cyanide catalysts are crystalline and have, if
45 they can be prepared as a single phase, a strict stoichiometry in respect of the metal salt and the cyanometallic component. Thus, a multimetal cyanide catalyst which is prepared as described in

DE 197,42,978 and contains acetate and crystallizes in a monoclinic system always has a zinc:cobalt ratio of 2:1.

Among these crystalline multimetal cyanide catalysts, preference
5 is given to those which have a platelet-like morphology. In this context, the term platelet-like refers to a particle whose width and length are more than five times the thickness of the particle.

10 Compared to the use of amorphous and nonstoichiometric multimetal cyanide catalysts, the use of crystalline and stoichiometric multimetal cyanide catalysts has the advantage that tailoring of the solid state structure and surface structure makes it possible
15 to avoid undesirable polymerization-active centers which can lead, for example, to the formation of high molecular weight polyols.

The reaction can be carried out continuously or batchwise. After the reaction is complete, the unreacted monomers and volatile
20 compounds are removed from the reaction mixture, usually by means of distillation. The catalyst may remain in the polyether alcohol, but it is usually removed, for example by means of filtration.

25 As mentioned above, the polyether alcohols of the present invention are preferably reacted with polyisocyanates to give polyurethanes, preferably polyurethane foams and thermoplastic polyurethanes, in particular flexible polyurethane foams. Here, the polyether alcohols of the present invention can be used
30 individually, as a mixture of at least two polyether alcohols according to the present invention or in admixture with other compounds containing at least two active hydrogen atoms.

Polyisocyanates which can be used here are all isocyanates having
35 two or more isocyanate groups in the molecule. It is possible to use either aliphatic isocyanates such as hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI), or preferably aromatic isocyanates such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) or mixtures of
40 diphenylmethane diisocyanate and polyphenylpolymethylene polyisocyanates (crude MDI). It is also possible to use isocyanates which have been modified by incorporation of urethane, uretdione, isocyanurate, allophanate, uretonimine and other groups, referred to as modified isocyanates.

As compounds which contain at least two isocyanate-reactive groups and can be used in admixture with the polyether alcohols of the present invention, it is possible to use amines, mercaptans and preferably polyols. Among the polyols, polyether
5 polyols and polyester polyols have the greatest industrial importance. The polyether polyols used for producing polyurethanes are usually prepared by base-catalyzed addition of alkylene oxides, in particular ethylene oxide and/or propylene oxide, onto H-functional initiator substances. Polyester polyols
10 are usually prepared by esterification of polyfunctional carboxylic acids with polyfunctional alcohols.

The compounds containing at least two groups which are reactive toward isocyanate groups also include chain extenders and/or
15 crosslinkers which may be employed if desired. These are at least bifunctional amines and/or alcohols having molecular weights in the range from 60 to 400.

As blowing agents, use is usually made of water and/or compounds
20 which are gaseous at the reaction temperature of the urethane reaction and are inert toward the starting materials for the polyurethanes, known as physically acting blowing agents, and also mixtures thereof. Physically acting blowing agents used are hydrocarbons having from 2 to 6 carbon atoms, halogenated
25 hydrocarbons having from 2 to 6 carbon atoms, ketones, acetals, ethers, inert gases such as carbon dioxide and/or noble gases.

Catalysts used are, in particular, amine compounds and/or metal compounds, in particular heavy metal salts and/or organic metal
30 compounds. In particular, known tertiary amines and/or organic metal compounds are used as catalysts. Suitable organic metal compounds are, for example, tin compounds such as tin(II) salts of organic carboxylic acids, e.g. tin(II) acetate, tin(II) octoate, tin(II) ethylhexanoate and tin(II) laurate, and the
35 dialkyltin(IV) salts of organic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate. Examples of organic amines customary for this purpose are: triethylamine, 1,4-diazabicyclo[2.2.2]octane, tributylamine, dimethylbenzylamine,
40 N,N,N',N'-tetramethylethylenediamine,
N,N,N',N'-tetramethyl-butanediamine,
N,N,N',N'-tetramethylhexane-1,6-diamine, dimethylcyclohexylamine, pentamethyldipropylenetriamine, pentamethyldiethylenetriamine, 3-methyl-6-dimethylamino-3-azapentol, dimethylaminopropylamine,
45 1,3-bis(dimethylamino)butane, bis(2-dimethylaminoethyl) ether, N-ethylmorpholine, N-methylmorpholine, N-cyclohexylmorpholine, 2-dimethylaminoethoxyethanol, dimethylethanolamine,

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- tetramethylhexamethylenediamine,
 dimethylamino-N-methylethanolamine, N-methylimidazole,
 N-formyl-N,N'-dimethylbutylenediamine,
 N-dimethylaminoethylmorpholine,
- 5 3,3'-bis(dimethylamino)di-n-propylamine and/or
 bis(2-piperazinoisopropyl) ether, diazabicyclo[2.2.2]octane,
 dimethylpiperazine, N,N'-bis(3-aminopropyl)ethylenediamine and/or
 tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine,
 4-chloro-2,5-dimethyl-1-(N-methylaminoethyl)imidazole,
- 10 2-aminopropyl-4,5-dimethoxy-1-methylimidazole,
 1-aminopropyl-2,4,5-tributylimidazole,
 1-aminoethyl-4-hexylimidazole,
 1-aminobutyl-2,5-dimethylimidazole,
 1-(3-aminopropyl)-2-ethyl-4-methylimidazole,
- 15 1-(3-aminopropyl)imidazole and/or
 1-(3-aminopropyl)-2-methylimidazole, preferably
 1,4-diazabicyclo[2.2.2]octane and/or imidazoles, particularly
 preferably 1-(3-aminopropyl)imidazole,
 1-(3-aminopropyl)-2-methylimidazole and/or
- 20 1,4-diazabicyclo[2.2.2]octane. The catalysts described can be
 used individually or in the form of mixtures.

Auxiliaries and/or additives used are, for example, mold release
 agents, flame retardants, colorants, fillers and/or reinforcing
 25 materials.

It is customary in industry to mix all starting materials with
 the exception of the polyisocyanates to form a polyol component
 and to react this with the polyisocyanates to give the
 30 polyurethane.

The polyurethanes can be produced by the one-shot method or by
 the prepolymer method. The flexible polyurethane foams may be
 either slabstock foams or molded foams.

35 An overview of the starting materials for producing polyurethanes
 and the processes employed for this purpose may be found, for
 example, in the *Kunststoffhandbuch*, Volume 7, "Polyurethane",
 Carl-Hanser-Verlag, Munich, Vienna, 1st edition 1966, 2nd edition
 40 1983 and 3rd edition 1993.

It has surprisingly been found that, in the polyurethane systems,
 the polyether alcohols of the present invention behave like
 conventional polyether alcohols catalyzed by means of alkali
 45 metal hydroxides.

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The processability of polyols which have been prepared by means of multimetal cyanide catalysts and have no propylene oxide end block is, particularly when these polyols are used for producing flexible polyurethane foams, especially in the production of flexible slabstock foams, very restricted. The high reactivity of these polyols does not allow crack-free and 100% open-celled foams, in particular flexible slabstock foams, to be obtained. Increasing the catalysis, in particular tin catalysis, in foam production leads to a reduction in crack formation but the open cell content of the foams decreases greatly at the same time, so that the foams shrink. These polyols are therefore unsuitable for the production of flexible slabstock foams. These disadvantages are completely overcome when using the polyether alcohols of the present invention.

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The invention is illustrated by the following examples.

Example 1 (comparison)

20 The synthesis was carried out in a cleaned and dried 10 l stirring autoclave. At 50°C, 211.6 g of a propoxylate of glycerol and propylene oxide having a molecular weight M_w of 400 g/mol were placed in the stirring autoclave and admixed with 0.8 g of a multimetal cyanide catalyst. The contents of the autoclave were made inert using nitrogen and treated at 110°C under reduced pressure for a total of 1.5 hours. At 125°C, 3.5 bar of nitrogen were introduced and a mixture of 2018.1 g of propylene oxide and 297.4 g of ethylene oxide were subsequently metered in over a period of 5 hours 15 minutes. The mixture was stirred for a further 30 minutes and degassed at 105°C and 9 mbar. The polyether alcohol was worked up by filtration. The resulting polyether alcohol had the following properties:

Hydroxyl number: 35.2 mg KOH/g;
Viscosity at 25°C: 934 mPas;

35 Zn/Co content: 3/6 ppm;
Primary hydroxyl group content: 10% (determined in accordance with BASF Schwarzheide test method PFO/A 00/22-28)

Example 2

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The synthesis was carried out in a cleaned and dried 10 l stirring autoclave. At 50°C, 437.9 g of propoxylated glycerol having a molecular weight M_w of 400 g/mol were placed in the stirring autoclave and admixed with 1.5 g of a multimetal cyanide catalyst. The contents of the autoclave were made inert using nitrogen and treated at 110°C under reduced pressure for a total of 1.5 hours. At 125°C, 3.5 bar of nitrogen were introduced and a

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mixture of 3462.2 g of propylene oxide and 585.4 g of ethylene oxide were subsequently metered in over a period of 2 hours 44 minutes. After a 10 minute pause, 487.8 g of propylene oxide were metered in. The mixture was stirred for a further 30 minutes and
5 degassed at 105°C and 9 mbar. The polyether alcohol was worked up by filtration. The resulting polyether alcohol had the following properties:

Hydroxyl number: 34.2 mg KOH/g;

Viscosity at 25°C: 880 mPas;

10 Zn/Co content: 4/9 ppm;

Primary hydroxyl group content: 5% (determined in accordance with BASF Schwarzheide test method PFO/A 00/22-28)

Example 3 (comparison)

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The synthesis was carried out in a cleaned and dried 20 l stirring autoclave. 2.0 kg of propoxylated glycerol having a molecular weight M_w of 400 g/mol (L3300) and 0.196 g of propoxylated ethylene glycol having a molar mass of 250 g/mol
20 were placed in the stirring autoclave and admixed with 19.2 g of multimetal cyanide catalyst. The contents of the autoclave were made inert using nitrogen and treated at 110°C under reduced pressure for a total of 1.5 hours. At 115°C, 3.5 bar of nitrogen were introduced and subsequently, over a period of 3.5 hours,
25 firstly 3.45 kg of propylene oxide then 12.37 kg of a mixture of 10.5 kg of propylene oxide and 1.87 kg of ethylene oxide were metered in. The mixture was stirred for a further 0.6 hour and degassed at 115°C and 9 mbar. The polyether alcohol was worked up by filtration. The resulting polyether alcohol had the following
30 properties:

Hydroxyl number: 47.4 mg KOH/g;

Viscosity at 25°C: 536 mPas;

Zn/Co content: 4/9 ppm;

Primary hydroxyl group content: 10 % (determined in accordance
35 with BASF Schwarzheide test method PFO/A 00/22-28)

Example 4

The synthesis was carried out in a cleaned and dried 20 l
40 stirring autoclave. 2.0 kg of propoxylated glycerol having a molecular weight M_w of 400 and 0.196 g of propoxylated ethylene glycol having a molar mass of 250 g/mol were placed in the stirring autoclave and admixed with 19 g of multimetal cyanide catalyst. The contents of the autoclave were made inert using
45 nitrogen and treated at 110°C under reduced pressure for a total of 1.5 hours. At 115°C, 3.5 bar of nitrogen were introduced and subsequently, over a period of 3.5 hours, firstly 3.45 kg of

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propylene oxide then 12.1 kg of a mixture of 10.2 kg of propylene oxide and 1.9 kg of ethylene oxide were metered in. 2.0 kg of propylene oxide were subsequently added on. The mixture was stirred for a further 0.6 hour and degassed at 115°C and 9 mbar.

- 5 The product was worked up by filtration. The resulting polyether alcohol had the following properties:

Hydroxyl number: 47.4 mg KOH/g;

Viscosity at 25°C: 578 mPas;

Zn/Co content: 22/55 ppm;

- 10 Primary hydroxyl group content: 5% (determined in accordance with BASF Schwarzheide test method PFO/A 00/22-28)

To determine the primary hydroxyl group content, the hydroxyl groups of the polyether alcohol are reacted with trichloroacetyl isocyanate and this reaction product is examined by NMR

- 15 spectroscopy. The measurement was carried out using a Bruker DPX 250 NMR spectrometer. In the spectrum, primary and secondary hydroxyl groups appear as different peaks.

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Table 1

Example		Comparative example 5	Comparative example 6	Example 7	Example 8	Example 9
A-Component	OHN[mgKOH /g]	Amount [g]	Amount [g]	Amount [g]	Amount [g]	Amount [g]
Polyol A	48.3	1000	1000			
Polyol B	47.2			1000	1000	1000
Water	6233	38	38	38	38	38
BF 2370	0	10	10	10	10	10
N201:N206 - 3:1	526	3.2	3.2	3.2	3.2	3.2
K 29	0	2.0	2.5	2.0	2.5	3.4
Total		1053.2	1053.7	1053.2	1053.7	1054.6
B-Component	NCO [%]	Amount [g]	Amount [g]	Amount [g]	Amount [g]	Amount [g]
Lupranat® T80 A	48.3	489.1	489.1	487.1	487.1	487.1
Index		110	110	110	110	110
Test data	Unit					
Cream time	[s]	9	9	9	9	9
Fiber time	[s]	65	65	65	70	65
Rise time	[s]	70	70	70	75	70
Rise height	[mm]	275	280	280	280	280

Rise height after 5 min	[mm]	270	275	275	275	275
Foam density	[kg/m ³]	24.6	24.0	24.7	24.5	24.2
Compressive strength at 40 %	[kPa]	X	X	3.8	3.9	4.1
Tensile strength	[kPa]	X	X	67	71	78
Elongation	[%]	X	X	128	124	120
Compressive set after 50% compression	[%]	X	X	2.4	2.5	2.7
Rebound resilience	[N]	X	X	47	49	49
Indentation hardness	[%]	X	X	200	221	230
Air permeability	[mmWs]	10	10	10	10	30
Appearance		Sn cracks	Sn cracks	Homogeneous, fine-celled foam	Homogeneous, fine-celled foam	Homogeneous, fine-celled foam

X - values could not be determined

Examples 5 to 7

Production of the polyisocyanate polyaddition products

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The starting materials indicated in Table 1 apart from the isocyanate Lupranat® T80 A (BASF Aktiengesellschaft) were intensively mixed. The Lupranat® T80 A was then added while stirring and the reaction mixture was poured into an open mold
 10 (400 x 400 x 400 mm) in which it foamed to give the polyurethane foam. The foaming data and the properties of the resulting polyurethane foams are likewise shown in Table 1.

Polyol A: Polyetherol prepared as described in Example 3
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Polyol B: Polyetherol prepared as described in Example 4

Lupragen® N201: 1,4-Diazabicyclo[2.2.2]octane (33%) in
 20 dipropylene glycol (67%) (BASF Aktiengesellschaft)

Lupragen® N206: Bis(2-dimethylaminoethyl) ether (70%) in
 25 dipropylene glycol (30%) (BASF Aktiengesellschaft)

Kosmus® 29: Tin(II) salt of ethylhexanoic acid
 (Goldschmidt AG)

Tegostab® BF 2370: Silicone stabilizer
 30 (Goldschmidt AG)

Lupranat® T80: 2,4-/2,6-tolylene diisocyanate mixture
 (BASF Aktiengesellschaft)

35	Test	Standard
	Foam density	DIN 53420
	Tensile test -tensile strength -elongation	DIN 53571
	Compressive set	DIN 53572
40	Rebound resilience	DIN 53573
	Indentation hardness	DIN 53576
	Compressive strength	DIN 53577

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We claim:

1. A process for preparing polyether alcohols with an equivalent weight of greater than 500 g/mol by catalytic addition of ethylene oxide and propylene oxide onto H-functional initiator substances, wherein at least one multimetal cyanide compound is used as catalyst and a block of an alkylene oxide having at least three carbon atoms in the molecule is added on at the end of the chain.
2. A process as claimed in claim 1, wherein the block of an alkylene oxide having at least three carbon atoms in the molecule makes up from 2 to 50% by weight of the total mass of the polyether alcohol.
3. A process as claimed in claim 1, wherein the block of an alkylene oxide having at least three carbon atoms in the molecule makes up from 2 to 20% by weight of the total mass of the polyether alcohol.
4. A process as claimed in claim 1, wherein the block of an alkylene oxide having at least three carbon atoms in the molecule makes up from 5 to 15% by weight of the total mass of the polyether alcohol.
5. A process as claimed in claim 1, wherein the alkylene oxide having at least three carbon atoms in the molecule is propylene oxide.
6. A process as claimed in claim 1, wherein at least 80% of the total number of hydroxyl groups present in the polyether alcohol are secondary hydroxyl groups.
7. A process as claimed in claim 1, wherein at least 90% of the total number of hydroxyl groups present in the polyether alcohol are secondary hydroxyl groups.
8. A process as claimed in claim 1, wherein at least 95% of the total number of hydroxyl groups present in the polyether alcohol are secondary hydroxyl groups.
9. A process as claimed in claim 1, wherein firstly a block of propylene oxide units, then a mixture of ethylene oxide and propylene oxide and then, at the end of the chain, a block of propylene oxide units are added onto the initiator substance.

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10. A process as claimed in claim 1, wherein the proportion of ethylene oxide in the mixture of ethylene oxide and propylene oxide is reduced during the course of the metered addition until pure propylene oxide is being introduced at the end of the metered addition.
11. A polyether alcohol which can be prepared as claimed in any of claims 1 to 10.
12. A process for producing polyurethanes by reacting polyisocyanates with compounds containing at least two hydrogen atoms which are reactive toward isocyanate groups, wherein the compounds containing at least two hydrogen atoms which are reactive toward isocyanate groups comprise at least one polyether alcohol as claimed in claim 11.
13. The use of polyether alcohols as claimed in claim 11 for producing polyurethanes.
14. A polyurethane, in particular a flexible polyurethane foam, which can be produced as claimed in claim 12.