

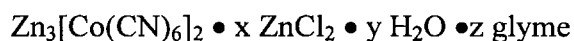
Process for the preparation of DMC catalysts

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The invention relates to an improved process for the preparation of double metal cyanide (DMC) catalysts for the preparation of polyether polyols by polyaddition of alkylene oxides on to starter compounds containing active hydrogen atoms.

- 5 Double metal cyanide (DMC) catalysts for the polyaddition of alkylene oxides on to starter compounds containing active hydrogen atoms have been known for a long time (see, for example, US-A 3 404 109, US-A 3 829 505, US-A 3 941 849 and US-A 5 158 922). The use of these DMC catalysts for the preparation of polyether polyols has the effect, in particular, of a reduction in the content of monofunctional
- 10 polyethers with terminal double bonds, so-called mono-ols, compared with the conventional preparation of polyether polyols by means of alkali metal catalysts, such as alkali metal hydroxides. The polyether polyols obtained in this way can be processed to high-quality polyurethanes (e.g. elastomers, foams and coatings).

- DMC catalysts are usually obtained by reacting an aqueous solution of a metal salt
- 15 with the aqueous solution of a metal cyanide salt in the presence of an organic complexing ligand, e.g. an ether. In a typical catalyst preparation, for example, aqueous solutions of zinc chloride (in excess) and potassium hexacyanocobaltate are mixed and dimethoxyethane (glyme) is then added to the dispersion formed. After filtration and washing of the catalyst with aqueous glyme solution, an active catalyst
- 20 of the general formula



is obtained (see e.g. EP-A 700 949).

- According to the prior art, DMC catalysts are prepared e.g. by mixing aqueous solutions of a metal salt (preferably of a zinc salt, such as e.g. zinc chloride) and a
- 25 metal cyanide salt (e.g. potassium hexacyanocobaltate) in the presence of an organic complexing ligand (preferably tert-butanol) and optionally further ligands in a stirred tank to form a dispersion. The catalyst is isolated from the dispersion by known techniques, preferably by centrifugation or filtration. To achieve a sufficiently high



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- 2 -

catalyst activity it is necessary subsequently to wash the catalyst with an aqueous ligand solution. Water-soluble by-products, such as e.g. potassium chloride, which can reduce the activity of the catalyst, are removed from the catalyst by this washing step. According to the prior art this washing step is carried out by redispersing the catalyst in an aqueous ligand solution, e.g. in a stirred tank, with subsequent renewed isolation of the solid by e.g. centrifugation or filtration. To obtain highly active DMC catalysts it is in general necessary to wash the catalyst at least once more, non-aqueous ligand solutions preferably being used for the further washing operations. According to the prior art the further washing steps are also carried out by redispersing with subsequent isolation of the catalyst. Finally, the DMC catalyst must be dried. This form of catalyst preparation is exceptionally time-consuming and cost-intensive. Process times of more than 100 hours are required for preparation of DMC catalysts on a commercial scale (see e.g. US-A 5 900 384). Because of the high catalyst costs, the profitability of the DMC-catalysed process of polyether polyol preparation is therefore considerably impaired.

It has now been found that highly active DMC catalysts can be obtained by a considerably simplified process in which aqueous solutions of a metal salt and a metal cyanide salt are first reacted in the presence of an organic complexing ligand a) and optionally one or more further complex-forming components b) to form a DMC catalyst dispersion, this dispersion is then filtered, the filter cake is subsequently washed by a filter cake washing and the washed filter cake is finally dried, after optional pressing out or mechanical removal of moisture.

This improved process for the preparation of catalysts avoids the several redispersions of the catalyst, with subsequent isolation, required according to the prior art to date for the preparation of highly active DMC catalysts and therefore leads to a considerable shortening of the process times for preparation of DMC catalysts. DMC catalysts which are prepared by the new, improved process have a comparable activity to DMC catalysts which are prepared in a significantly more expensive manner according to the prior art to date.

- 3 -

The present invention therefore provides an improved process for the preparation of double metal cyanide (DMC) catalysts, in which aqueous solutions of a metal salt and a metal cyanide salt are first reacted in the presence of an organic complexing ligand a) and optionally one or more further complex-forming components b) to form a DMC catalyst dispersion, this dispersion is then filtered, the filter cake is subsequently washed with one or more aqueous or non-aqueous solutions of the organic complexing ligand a) and optionally one or more further complex-forming components b) by a filter cake washing and the washed filter cake is finally dried, after an optional pressing out or mechanical removal of moisture.

The double metal cyanide compounds contained in the DMC catalysts which are suitable for the process according to the invention are the reaction products of water-soluble metal salts and water-soluble metal cyanide salts.

Water-soluble metal salts which are suitable for the preparation of the double metal cyanide compounds preferably have the general formula (I)

$$M(X)_n \text{ (I),}$$

wherein M is chosen from the metals Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II) and Cr(III). Zn(II), Fe(II), Co(II) and Ni(II) are particularly preferred. The X are identical or different, preferably identical anions, preferably chosen from the group consisting of halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates or nitrates. The value for n is 1, 2 or 3.

Examples of suitable water-soluble metals salts are zinc chloride, zinc bromide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, iron(II) chloride, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) nitrate. Mixtures of different water-soluble metal salts can also be employed.

- 4 -

Water-soluble metal cyanide salts which are suitable for the preparation of the double metal cyanide compounds preferably have the general formula (II)



wherein M' is chosen from the metals Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III),
 5 Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV) and V(V). M' is particularly preferably chosen from the metals Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II). The water-soluble metal cyanide salt can comprise one or more of these metals. The Y are identical or different, preferably identical alkali metal cations or alkaline earth metal cations. The A are identical or different, preferably identical
 10 anions chosen from the group consisting of halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates or nitrates. Both a, and b and c are integers, the values for a, b and c being chosen such that electroneutrality of the metal cyanide salt exists; a is preferably 1, 2, 3 or 4; b is preferably 4, 5 or 6; c preferably has the value 0. Examples of suitable water-soluble
 15 metal cyanide salts are potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III) and lithium hexacyanocobaltate(III).

Preferred double metal cyanide compounds contained in the DMC catalysts are compounds of the general formula (III)



wherein M is as defined in formula (I) and M' is as defined in formula (II), and x, x', y and z are integers and are chosen such that electroneutrality of the double metal cyanide compound exists. Preferably, x = 3, x' = 1, y = 6 and z = 2, M = Zn(II), Fe(II), Co(II) or Ni(II) and M' = Co(III), Fe(III), Cr(III) or Ir(III).

25 Examples of suitable double metal cyanide compounds are zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III) and

- 5 -

cobalt(II) hexacyanocobaltate(III). Further examples of suitable double metal cyanide compounds are to be found e.g. in US-A 5 158 922. Zinc hexacyanocobaltate(II) is particularly preferably used.

Organic complexing ligands a) which can be employed in the process according to the invention are water-soluble organic compounds with heteroatoms, such as oxygen, nitrogen, phosphorus or sulfur, which can form complexes with the double metal cyanide compound. Suitable organic complexing ligands are e.g. alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides and mixtures thereof. Preferred organic complexing ligands are water-soluble aliphatic alcohols, such as ethanol, isopropanol, n-butanol, iso-butanol, sec-butanol and tert-butanol. tert-Butanol is particularly preferred.

The organic complexing ligand a) is added either during the preparation of the catalyst or directly after formation of the dispersion of the double metal cyanide compound. The organic complexing ligand a) is usually employed in excess.

DMC catalysts which are preferred for the process according to the invention are those which, in addition to the organic complexing ligands a) mentioned above, also comprise one or more further organic complex-forming components b). This component b) can be chosen from the same classes of compounds as complexing ligand a). Component b) is preferably a polyether, polyester, polycarbonate, glycidyl ether, glycoside, carboxylic acid ester of polyhydric alcohols, polyalkylene glycol sorbitan ester, a bile acid or salt, ester or amide thereof, a cyclodextrin, organic phosphate, phosphite, phosphonate, phosphonite, phosphinate or phosphinite, an ionic surface- or interface-active compound or an α,β -unsaturated carboxylic acid ester. DMC catalysts with such ligand combinations are described e.g. in EP-A 700 949, EP-A 761 708, WO 97/40086, WO 98/08073, WO 98/16310, WO 99/01203, WO 99/19062, WO 99/19063 or German Patent Application 19905611.0.

- 6 -

The DMC catalysts which are suitable for the process according to the invention can optionally also comprise water and/or one or more water-soluble metal salts of the formula (I) from the preparation of the double metal cyanide compound.

5 The DMC catalysts according to the invention are conventionally prepared in aqueous solution by reaction of metal salts, in particular of the formula (I), with metal cyanide salts, in particular of the formula (II), organic complexing ligands a) and optionally one or more further complex-forming components b).

10 The aqueous solutions of the metal salt (e.g. zinc chloride, employed in stoichiometric excess (at least 50 mol%, based on the metal cyanide salt)) and of the metal cyanide salt (e.g. potassium hexacyanocobaltate) are preferably first reacted here in the presence of the organic complexing ligand a) (e.g. tert-butanol), a dispersion forming.

15 The organic complexing ligand a) can be present here in the aqueous solution of the metal salt and/or other metal cyanide salt, or it is added directly to the dispersion obtained after precipitation of the double metal cyanide compound.

Preferably, the dispersion formed is then also treated with one or more further complex-forming components b). The further complex-forming component b) is preferably employed here in a mixture with water and organic complexing ligand a).

20 The DMC catalyst dispersion can be prepared e.g. in a stirred tank, optionally by the process variant described in US-A 5 891 818, in which some of the catalyst dispersion prepared in a stirred reactor is circulated and sprayed into the reactor headspace and the circulating stream here is passed through a "high shear in-line mixer".

25 However, the DMC catalyst dispersion is preferably prepared using a mixing nozzle (e.g. a smooth jet nozzle, Levos nozzle, Bosch nozzle and the like), particularly

- 7 -

preferably a jet disperser, such as is described in German Patent Application 199 58 355.2.

In a smooth jet nozzle a first educt stream is first accelerated in a nozzle and atomized at a high flow rate into a slowly flowing second educt stream. Mixing of the two educt streams then takes place via the turbulent disintegration of the resulting jet into eddies of different size (eddy cascade). Compared with the stirred tank, concentration differences can be broken down significantly faster in this manner, since significantly higher and more homogeneous output densities can be achieved.

However, a jet disperser should preferably be employed for the process according to the invention. The jet disperser can be constructed such that two nozzles are arranged in series. A first educt stream is first accelerated to high degree in the first nozzle due to the narrowing in cross-section. The accelerated jet sucks up the second component here because of the high flow rate. The resulting jet is then passed from the mixing chamber through further nozzles arranged perpendicular to the direction of the first educt stream. The distance between the nozzles will preferably be chosen such that because of the short residence time, only seed formation but not crystal growth takes place in the mixing chamber. The rate of seed formation of the solid is thus decisive for the optimum design of the jet disperser. A residence time of 0.0001 s to 0.15 s, preferably 0.001 s to 0.1 s is favourably established. The crystal growth takes place only in the outflow. The diameter of the further nozzles should preferably be chosen such that further acceleration of the partly mixed educt streams takes place there. Because of the shear forces which additionally occur in the further nozzles as a result, the state of homogeneous mixing is achieved by a faster eddy disintegration in a shorter time compared with a smooth jet nozzle. As a result, even in precipitation reactions with a very high rate of seed formation it is possible to achieve the state of ideal mixing of the educts, so that it is possible to establish defined stoichiometric compositions during the precipitation reaction. Nozzle diameters of 5,000 μm to 50 μm , preferably 2,000 μm to 200 μm

- 8 -

have proved favourable at pressure losses in the nozzle of 0.1 bar to 1,000 bar or output densities in the range from $1 \cdot 10^7 \text{ W/m}^3$ to $1 \cdot 10^{13} \text{ W/m}^3$.

n nozzles (where $n = 1 - 5$) can be arranged in succession, depending on the desired particle size, so that a multi-stage jet disperser is obtained. The additional advantage
5 of further dispersers is that particles which have already formed can be comminuted mechanically by the high shear forces in the nozzles. It is possible in this manner to prepare particles with diameters of 20 μm to 0.1 μm . Instead of having several nozzles arranged in series, however, the comminution can also be achieved by circulating the dispersion.

10 Other mixing organs for the preparation of dispersions, such as are described in EP-A 101 007, WO 95/30476 or German Patent Application 199 28 123.8, or combinations of these mixing organs can also be employed.

Heating of the dispersion may occur due to the energy dissipation in the nozzles and the crystallization enthalpy. Since the temperature can have a considerable influence
15 on the crystal formation process, a heat exchanger can be installed downstream of the mixing organ for an isothermal process procedure.

Problem-free scale-up is possible, for example, by the use of a relatively large number of bores, arrangement of several mixing organs in parallel or enlargement of the free nozzle area. However, the latter is not achieved by increasing the nozzle
20 diameter, since the possibility of emergence of a core stream exists in this manner, the result of which is a deterioration in the mixing result. Slits with an appropriate area are therefore preferably to be employed in the case of nozzles with large free nozzle areas.

The catalyst dispersion is now subjected to a working up process, the aims of which
25 are separating off of the catalyst particles, washing, mechanical removal of moisture and thermal drying of the catalyst. A large number of processes and apparatus conversions exist for each of the individual process steps. A single apparatus in

- 9 -

which the steps mentioned can be carried out in their entirety is preferably employed in the process according to the invention.

To separate off the catalyst particles from the dispersion, all the known processes for filtration or sedimentation can be employed, such as are described e.g. in "Ullmann's Encyclopedia of Industrial Chemistry", vol. B2, chapter 9 and 10, VCH, Weinheim 1988 and in "Handbuch der industriellen Fest-Flüssig-Trennung", eds.: H. Gasper, D. Oechsle and E. Pongratz, Wiley-VCH-Verlag, Weinheim, 2000. The driving potential for the separating off can be applied by mass forces (centrifugal force, force of gravity), electrical forces of pressure differences (gas pressure difference, hydraulic pressure, mechanical pressure). The apparatuses here can operate continuously or batchwise.

Apparatuses which operate batchwise or by sedimentation are, for example, tube centrifuges with or without inserts in the centrifuge chamber. Continuously operating variants are separators with a high thickening effect. Apparatuses which operate batchwise by filtration are, for example, suction filters (vacuum or pressure suction filters), plate pressure filters, candle filters or filter presses (frame, chamber, membrane filter presses, "Autopress" from BHS Sonthofen GmbH, D-87527 Sonthofen (see GB-A 2282977), press filter machines) and also paring or reversing filter centrifuges. Apparatuses which operate continuously by filtration are, for example, vacuum belt filters, drum filters (pressure or vacuum), disc filters (pressure or vacuum), cross-flow filters or dynamic filters, and also decanting centrifuges.

Discontinuously operating filters or filtering centrifuges are preferably employed. Membrane filter presses have proved to be particularly favourable. For the separating off, charging of the membrane filter press with a fine-pored filter medium, preferably multi-thread fabrics based on polypropylene, since these are resistant to solvents, such as tert-butanol, is required.

- 10 -

The separating off is in general carried out at temperatures of 10°C to 80°C. The pressure differences applied can be 0.001 bar to 200 bar, preferably 0.1 bar to 100 bar, particularly preferably 0.1 bar to 25 bar, the pressure difference employed depending on the device employed. This results in filtration times of a few minutes to several hours. The moist filter cake usually has a residual moisture content of 30% to 95%.

In the following process step the catalyst which has been separated off but is still contaminated by water-soluble by-products is washed. A mash or a filter cake washing (= displacement washing) or a combination of the two is possible in principle for this purpose. In the process according to the invention a displacement washing is preferably carried out with one or more aqueous solutions of the complexing ligand a) and optionally one or more further complexing components b).

The moist filter cake is particularly preferably first washed with an aqueous solution of the organic complexing ligand a) (e.g. tert-butanol). Water-soluble by-products, such as e.g. potassium chloride, can be removed from the catalyst in this manner. The amount of organic complexing ligand a) in the aqueous wash solution here is preferably 40 to 80 wt.%, based on the total solution. It is furthermore preferable to add to the aqueous wash solution an amount of further complexing component b), particularly preferably 0.5 to 5 wt.%, based on the total solution.

Flow-through washing in the filter apparatus offers advantages in respect of the time required for the working up compared with mash washing. In addition, the filter cake to which solvent adheres does not have to be removed from the filter and transferred into another apparatus, as with mash washing.

Variants of flow-through washing on the membrane filter press preferably employed are gap washing and washing through the entire cake. In gap washing, the chambers of the filter press are not filled completely with filter cake, so that a gap remains between the two halves of filter cake in the filter chamber. The wash liquid is added via the suspension channel under a sufficiently high pressure, is distributed in the

- 11 -

gap, flows through the filter cake and leaves the filter press through the filtrate channels. In the case of displacement washing through the entire cake, after the filtration the two halves of the cake are brought together by pumping up the membranes of the membrane filter press. Compaction of the filter cake takes place,
5 depending on the membrane pressing pressure applied. The membrane pressing pressure is maintained during the washing. The wash liquid pressure is preferably to be chosen lower than the membrane pressing pressure.

Gap washing is preferably employed in the process according to the invention, since it requires less time and gives particularly homogeneous catalysts of high quality.

10 An amount of wash liquid which has the effect of as complete as possible an exchange of the amount of liquid in the original filter cake is employed in the washing. The volume of wash liquid employed, based on the filter cake volume, is in general 0.5/1 to 1,000/1, preferably 1/1 to 500/1, particularly preferably 1/1 to 50/1.

15 The gap washing is in general carried out at temperatures of 10°C to 80°C, preferably at 15°C to 60°C. The pressure differences applied can be 0.001 bar to 200 bar, preferably 0.1 bar to 100 bar, particularly preferably 0.1 bar to 25 bar. The washing times are as a rule a few minutes to some hours.

This first washing step can be followed by further washing steps with aqueous or
20 non-aqueous solutions of the organic complexing ligand a) and optionally one or more further complexing components b), which are likewise carried out according to the invention as filter cake washing. The activity of the catalyst can be increased further by this means. However, it has been found that as a rule a single washing of the filter cake with an aqueous solution of the organic complexing ligand a) and
25 optionally one or more further complexing components b) by filter cake washing is already sufficient to obtain DMC catalysts with an exceptionally high activity.

A significant reduction in the total amount of wash solution to be employed is often possible in the process according to the invention compared with the processes of the prior art, so that the process according to the invention also leads to a reduction in the material costs of the DMC catalyst preparation.

- 5 For substantial removal of the wash liquid from the filter cakes for the purpose of improving the purity and reducing the energy consumption during later thermal drying, the liquid content of the filter cake is reduced in a further process step.

For this there are the possibilities of reducing the pore volume of the filter cakes by pressing out by means of pressing rams or membranes, or of removing the moisture
10 from the filter cakes by a gas pressure difference or by centrifugal forces. This can take place in the same apparatus as the prior working up (for example reversing filter centrifuge or membrane filter press) or in an additional apparatus (for example extruder press or tubular filter press). The liquid escapes through a suitable filter medium.

- 15 A membrane filter press is preferably employed in the process according to the invention. Pressing out in the membrane filter press with membrane pressing pressures of between 0.5 bar and 200 bar, preferably under the highest possible pressures, has proved to be advantageous. This can be followed by a removal of moisture by a gas pressure difference under the membrane pressing pressure applied.
20 The gas pressure can be chosen lower than the membrane pressing pressure.

The DMC catalyst is then dried at temperatures of about 20 to 120°C and under pressures of about 0.1 mbar to normal pressure (1013 mbar). Contact dryers (for example paddle dryers) and convection dryers (for example belt dryers) and also spray dryers are suitable for this purpose. Drying can also be carried out directly in
25 the devices for mechanical separating off of liquid. The latter is preferred in the process according to the invention for safety and industrial hygiene reasons.

- 13 -

Examples of filter apparatuses in which products can be dried by convection are candle, plate pressure, drum, disc or belt filters. Suitable filter centrifuges are centrifuge dryers or reversing filter centrifuges.

5 Examples of combined filter apparatuses and contact dryers are stirred pressure suction filters and candle filters, in which the cakes are thrown on to a heated base and mixed thoroughly there before drying by the candle.

10 A heatable filter press is preferably employed in the process. This is constructed like a conventional filter press with a membrane package. The membrane sheets to be used differ constructionally from conventional membrane sheets in that a heating medium can flow through the space behind the membrane. Liquid-tight (so-called "drip-" or "gas-tight") membrane filter sheets are preferably employed.

15 The heated heating medium flows on to the reverse of the pressing membranes, completely separated from the filter cake through the pressing membrane and the filter medium, past the filter cakes and thereby heats these. The pressing medium is under a sufficiently high pressure here to ensure contact of the membranes with the filter cakes. The filter cakes can be heated on one or both sides. Heating on both sides is favourable in respect of the duration of the drying.

20 To assist the drying process, a vacuum is applied on the filtrate side. This vacuum can be generated, for example, by a liquid ring pump. The stream of vapours sucked off is cooled before the vacuum pump in order to condense out the volatile constituents (e.g. tert-butanol and water). The measurement and control parameters are the amount condensed out, the pressure in the filtrate system of the press and the filter cake temperature.

25 In the process described, the membrane pressing pressures are preferably 0.1 bar to 10 bar. Temperatures of the pressing and heating medium are 30°C to 80°C, preferably 40°C to 60°C. The pressure on the filtrate side is preferably less than 100 mbar. The flow rate of the heating medium here is to be chosen high enough for

- 14 -

a good heat transfer to take place between the heating medium and product. Drying times are in general some minutes to several hours, conventionally one to ten hours. Residual moisture contents below the specification limit of approx. 5% are reliably achieved with this type of drying.

- 5 The product isolated and freed from secondary components in this manner can be ground and packaged in further process steps.

10 A significant shortening of the process times of the preparation of DMC catalysts compared with the prior art is possible by this improved preparation process for DMC catalysts. Since DMC catalysts which are prepared by the new, improved process have a comparable activity in the preparation of polyether polyols to that of DMC catalysts which are prepared in a considerably more expensive manner by the prior art to date, this leads to a considerably increased profitability of the DMC-catalysed process for the preparation of polyether polyols.

15 The present invention also provides the use of the DMC catalysts prepared by the process according to the invention in a process for the preparation of polyether polyols by polyaddition of alkylene oxides on to starter compounds containing active hydrogen atoms.

20 Because of their exceptionally high activity, the DMC catalysts prepared by the process according to the invention can often be employed in very low concentrations (25 ppm and less, based on the amount of polyether polyol to be prepared). If the polyether polyols prepared in the presence of the DMC catalysts prepared by the process according to the invention are used for the preparation of polyurethanes, removal of the catalyst from the polyether polyol can be omitted without the product qualities of the polyurethane obtained being adversely influenced.

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Examples

Preparation of the catalyst

Example 1 (comparison example): Catalyst A

(Preparation of the catalyst with a single washing of the filter cake by redispersing with subsequent filtration)

5 A solution of 81.25 g zinc chloride in 810 g distilled water was circulated at 45°C in a loop reactor which comprises a jet disperser (1 bore of diameter 0.7 mm). A solution of 26 g potassium hexacyanocobaltate in 200 g distilled water was metered into this solution. The pressure loss in the jet disperser here was 2.5 bar. Directly
10 after the precipitation a mixture of 325 g tert-butanol and 325 g distilled water was metered in and the dispersion was circulated for 80 min at 45°C under a pressure loss in the jet disperser of 2.5 bar. A mixture of 6.5 g cholic acid sodium salt, 6.5 g tert-butanol and 650 g distilled water was then metered in and the dispersion was subsequently circulated for 20 min under a pressure loss in the jet disperser of
15 2.5 bar. The solid was isolated by filtration over a vacuum suction filter. The moist filter cake was then washed with a mixture of 13 g cholic acid sodium salt, 455 g tert-butanol and 195 g distilled water by circulation in the loop reactor for 20 min at 45°C under a pressure loss in the jet disperser of 2.5 bar. The solid was filtered again over a vacuum suction filter and the moist filter cake was then dried at 100°C
20 for 5 h under a high vacuum.

Example 2 (comparison example): Catalyst B

(Preparation of the catalyst with washing of the filter cake twice by redispersing with subsequent filtration)

25 A solution of 81.25 g zinc chloride in 810 g distilled water is circulated at 45°C in a loop reactor which comprises a jet disperser (1 bore of diameter 0.7 mm). A solution of 26 g potassium hexacyanocobaltate in 200 g distilled water was metered into this solution. The pressure loss in the jet disperser here was 2.5 bar. Directly after the precipitation a mixture of 325 g tert-butanol and 325 g distilled water was

- 16 -

metered in and the dispersion was circulated for 80 min at 45°C under a pressure loss in the jet disperser of 2.5 bar. A mixture of 6.5 g cholic acid sodium salt, 6.5 g tert-butanol and 650 g distilled water was then metered in and the dispersion was subsequently circulated for 20 min under a pressure loss in the jet disperser of 2.5 bar. The solid was isolated by filtration over a vacuum suction filter. The moist filter cake was then washed with a mixture of 13 g cholic acid sodium salt, 455 g tert-butanol and 195 g distilled water by circulation in the loop reactor for 20 min at 45°C under a pressure loss in the jet disperser of 2.5 bar. The solid was filtered again over a vacuum suction filter and the moist filter cake was finally washed once again with a mixture of 4.8 g cholic acid sodium salt, 650 g tert-butanol and 65 g distilled water by circulating in the loop reactor for 20 min at 45°C under a pressure loss in the jet disperser of 2.5 bar. After renewed filtration over a vacuum suction filter, the washed, moist filter cake was dried at 100°C for 5 h under a high vacuum.

Example 3: Catalyst C

(Preparation of the catalyst with a single filter cake washing)

A solution of 81.25 g zinc chloride in 810 g distilled water was circulated at 45°C in a loop reactor which comprises a jet disperser (1 bore of diameter 0.7 mm). A solution of 26 g potassium hexacyanocobaltate in 200 g distilled water was metered into this solution. The pressure loss in the jet disperser here was 2.5 bar. Directly after the precipitation a mixture of 325 g tert-butanol and 325 g distilled water was metered in and the dispersion was circulated for 80 min at 45°C under a pressure loss in the jet disperser of 2.5 bar. A mixture of 6.5 g cholic acid sodium salt, 6.5 g tert-butanol and 650 g distilled water was then metered in and the dispersion was subsequently circulated for 20 min under a pressure loss in the jet disperser of 2.5 bar. 350 g of this dispersion were filtered in a pressure suction filter under an increased pressure of 2.0 bar. The moist filter cake in the pressure suction filter was then washed under an increased pressure of 3.0 bar with a mixture of 2 g cholic acid sodium salt, 70 g tert-butanol and 30 g distilled water by a filter cake washing. The washed, moist filter cake was dried at 100°C for 5 h under a high vacuum.

Example 4 (comparison example): Catalyst D

(Preparation of the catalyst with washing of the filter cake twice by redispersing with subsequent filtration)

A solution of 1.625 kg zinc chloride in 16.2 kg distilled water was circulated at 35°C
5 in a loop reactor which comprises a jet disperser (110 bores of diameter 0.7 mm). A
solution of 0.52 kg potassium hexacyanocobaltate in 4.0 kg distilled water was
metered into this solution. The pressure loss in the jet disperser here was 1.2 bar.
Directly after the precipitation a mixture of 6.5 kg tert-butanol and 6.5 kg distilled
water was metered in and the dispersion was circulated for 20 min at 35°C under a
10 pressure loss in the jet disperser of 1.2 bar. A mixture of 0.13 kg cholic acid sodium
salt, 0.13 kg tert-butanol and 13.0 kg distilled water was then metered in and the
dispersion was subsequently circulated for 10 min under a pressure loss in the jet
disperser of 0.1 bar. The solid was filtered in a membrane filter press under an
increased pressure of 2.0 bar and pressed out under 4.0 bar. The moist, pressed-out
15 filter cake was then washed with a mixture of 0.26 kg cholic acid sodium salt, 9.1 kg
tert-butanol and 3.9 kg distilled water by circulating in the loop reactor for 20 min at
35°C under a pressure loss in the jet disperser of 1.8 bar. The solid was filtered
again in a membrane filter press under an increased pressure of 2.0 bar and pressed
out under 4.0 bar, and the moist, pressed-out filter cake was finally washed once
20 again with a mixture of 0.096 kg cholic acid sodium salt, 13 kg tert-butanol and
1.3 kg distilled water by circulating in the loop reactor for 20 min at 35°C under a
pressure loss in the jet disperser of 1.8 bar. After renewed filtration in a membrane
filter press under 2.0 bar and pressing out of the filter cake under 4.0 bar, the moist,
pressed-out filter cake was dried at 100°C for 5 h under a high vacuum.

25 **Example 5: Catalyst E**

(Preparation of the catalyst with a single filter cake washing)

A solution of 1.625 kg zinc chloride in 16.2 kg distilled water was circulated at 35°C
in a loop reactor which comprises a jet disperser (110 bores of diameter 0.7 mm). A
solution of 0.52 kg potassium hexacyanocobaltate in 4.0 kg distilled water was
30 metered into this solution. The pressure loss in the jet disperser here was 1.2 bar.

- 18 -

Directly after the precipitation a mixture of 6.5 kg tert-butanol and 6.5 kg distilled water was metered in and the dispersion was circulated for 20 min at 35°C under a pressure loss in the jet disperser of 1.2 bar. A mixture of 0.13 kg cholic acid sodium salt, 0.13 kg tert-butanol and 13.0 kg distilled water was then metered in and the dispersion was subsequently circulated for 10 min under a pressure loss in the jet disperser of 0.1 bar. The solid was filtered in a membrane filter press under an increased pressure of 2.0 bar. The moist filter cake in the membrane filter press was then washed under an increased pressure of 2.5 bar with a mixture of 0.22 kg cholic acid sodium salt, 8.0 kg tert-butanol and 3.4 kg distilled water by a filter cake washing and the washed filter cake was then pressed out under an increased pressure of 5.0 bar. The moist, pressed-out filter cake was dried at 100°C for 5 h under a high vacuum.

Example 6: Catalyst F

(Preparation of the catalyst with a single filter cake washing using a "hot filter press")

A solution of 6.485 kg zinc chloride in 23.9 kg distilled water and 3.4 kg tert-butanol was circulated at 50°C in a loop reactor which comprises a jet disperser (28 bores of diameter 0.7 mm). A solution of 0.65 kg potassium hexacyanocobaltate in 8.0 kg distilled water was metered into this solution. The pressure loss in the jet disperser here was 2.5 bar. Directly after the precipitation a mixture of 0.144 kg tert-butanol, 0.685 kg polypropylene glycol 1000 and 3.98 kg distilled water was metered in under a pressure loss in the jet disperser of 0.1 bar. The dispersion was then circulated for a further 90 min at 50°C under a pressure loss in the jet disperser of 2.5 bar.

58 kg of this dispersion were filtered in a membrane filter press (two chambers, filter area 0.6 m²) with a constant pressure difference of 1 bar (20 min). The filtration phase was followed by gap washing with a wash liquid pressure of 1 bar (30 min). 44 kg wash solution (65 wt.% tert-butanol, 33.7 wt.% water, 1.3 wt.% polypropylene glycol 1000) were employed for this. The filter cakes were then pressed out with a membrane pressing pressure of 16 bar for one hour. The cakes were now dried in

- 19 -

the membrane filter press. The membrane pressing pressure was adjusted to 1 bar. The heating and pressing medium was water with a temperature of 60°C. A pressure of initially 50 mbar and towards the end of the drying 30 mbar was applied on the filtrate side. After a drying time of 5.5 seconds, the residual moisture content of the filter cake was approx. 3%.

Preparation of polyether polyols

General procedure

50 g polypropylene glycol starter (molecular weight = 1,000 g/mol) and 3-5 mg catalyst (15-25 ppm, based on the amount of polyether polyol to be prepared) were initially introduced into a 500 ml pressure reactor under an inert gas (argon) and were heated up to 105°C, while stirring. 10 g propylene oxide were then metered in all at once. Further propylene oxide was only metered in again when an accelerated drop in pressure in the reactor was observed. This accelerated drop in pressure indicates that the catalyst is activated. The remaining propylene oxide (140 g) was then metered in continuously under a constant overall pressure of 2.5 bar. When metering of the propylene oxide was complete and after an after-reaction time of 2 hours at 105°C, volatile contents were distilled off at 90°C (1 mbar) and the reaction mixture was then cooled to room temperature.

The resulting polyether polyols were characterized by determination of the OH numbers, the double bond contents and the viscosities.

The course of the reaction was monitored with the aid of time/conversion curves (propylene oxide consumption [g] v. reaction time [min]). The induction time was determined from the point of intersection of the tangent at the steepest point of the time/conversion curve with the extended base line of the curve. The propoxylation times, which are decisive for the catalyst activity, correspond to the period of time between activation of the catalyst (end of the induction period) and the end of metering of the propylene oxide.

Example 7 (comparison): Preparation of polyether polyol with catalyst A (25 ppm)

	Propoxylation time:	31 min
	Polyether polyol: OH number (mg KOH/g):	28.7
	Double bond content (mmol/kg):	6
5	Viscosity 25°C (mPas):	882

Example 8 (comparison): Preparation of polyether polyol with catalyst B (25 ppm)

	Propoxylation time:	20 min
	Polyether polyol: OH number (mg KOH/g):	28.9
	Double bond content (mmol/kg):	5
10	Viscosity 25°C (mPas):	893

Example 9: Preparation of polyether polyol with catalyst C (25 ppm)

	Propoxylation time:	19 min
	Polyether polyol: OH number (mg KOH/g):	29.3
	Double bond content (mmol/kg):	5
15	Viscosity 25°C (mPas):	887

Example 10 (comparison): Preparation of polyether polyol with catalyst D (25 ppm)

	Propoxylation time:	19 min
	Polyether polyol: OH number (mg KOH/g):	29.2
20	Double bond content (mmol/kg):	6
	Viscosity 25°C (mPas):	832

Example 11: Preparation of polyether polyol with catalyst E (25 ppm)

	Propoxylation time:	20 min
	Polyether polyol: OH number (mg KOH/g):	28.9
25	Double bond content (mmol/kg):	6
	Viscosity 25°C (mPas):	869

- 21 -

Example 12: Preparation of polyether polyol with catalyst F (25 ppm)

	Propoxylation time:	14 min
	Polyether polyol: OH number (mg KOH/g):	30.0
	Double bond content (mmol/kg):	6
5	Viscosity 25°C (mPas):	809

Example 13: Preparation of polyether polyol with catalyst F (15 ppm)

	Propoxylation time:	23 min
	Polyether polyol: OH number (mg KOH/g):	29.3
	Double bond content (mmol/kg):	5
10	Viscosity 25°C (mPas):	881

Patent claims

1. Process for the preparation of DMC catalysts, in which
 - A) aqueous solutions of metal salts are reacted with aqueous solutions of metal cyanide salts in the presence of organic complexing ligands to form a DMC catalyst dispersion,
 - B) the dispersion formed is filtered,
 - C) the filter cake obtained is washed with solutions of organic complexing ligands by a filter cake washing and
 - D) the washed filter cake is dried.
2. Process according to claim 1, in which step A) is carried out in the presence of an organic complexing ligand a) and one or more further complexing ligands b) which differ from a).
3. Process according to claim 1 or 2, in which in step C) the filter cake is washed with an aqueous solution of an organic complexing ligand a) and optionally one or more further complexing ligands b) which differ from a).
4. Process according to claim 1 or 2, in which in step C) the filter cake is washed with a non-aqueous solution of an organic complexing ligand a) and optionally one or more further complexing ligands b) which differ from a).
5. Process according to one of claims 1 to 4, in which the filter cake washing is carried out as a flow-through washing.
6. Process according to one of claims 1 to 5, in which the washed filter cake is pressed out or subjected to mechanical removal of moisture before the drying.

- 23 -

7. Process according to one of claims 1 to 6, in which steps B) and C) are carried out using a filter press.
8. Process according to claim 7, in which steps B), C) and D) are carried out using a heatable filter press.
- 5 9. Process according to one of claims 1 to 8, in which step A) is carried out using a mixing nozzle.
10. Process according to claim 9, in which the mixing nozzle is a jet disperser.
11. DMC catalyst, obtainable according to one of claims 1 to 109 [sic].
12. Use of a DMC catalyst prepared according to one of claims 1 to 109 [sic] for
10 the preparation of polyether polyols.