

Description

This invention relates to a process for the purification of polyols for use in the preparation of polyurethanes.

5 The preparation of polyols by the polymerization of alkylene oxides using catalysts of the double metal cyanide complex class is known. Also known is that the catalyst residues present in such polyols if not removed cause certain undesirable reactions forming volatile by-products which cause odor and other storage problems. U.S.-A-4,355,188 teaches that the removal of double metal cyanide catalyst residue can be accomplished by adding a strong base selected from potassium hydroxide, sodium hydroxide, potassium metal, and sodium metal.

10 The present invention provides another method for removing double metal cyanide complex catalyst residue from polyols involving the use of an alkali metal hydride.

According to this invention, there is provided a method for removing double metal cyanide complex catalyst residue from polyols which comprises after polyol formation the steps of: (a) incorporating into the catalyst residue-containing polyol an effective amount of an alkali metal hydride to convert the double metal cyanide complex catalyst into an insoluble ionic metal species separable from the polyol wherein the polyol hydroxyl groups are also converted to alkoxide groups; and (b) separating the insoluble ionic metal species from the polyol.

High molecular weight polyols suitable for use in the practice of this invention are typically prepared by polymerizing an alkylene oxide onto an initiator or telogen having at least one hydroxyl group using a double metal cyanide complex catalyst.

Any suitable telogen and alkylene oxide can be used. Suitable telogens for use to produce polyols usable in the invention include diols such as ethylene glycol, triols such as trimethylolpropane and glycerine, polyols such as pentaerythritol and various sugars. The preferred alkylene oxides are propylene oxide, 1,2-butylene oxide, and ethylene oxide.

The double metal cyanide complex class catalysts suitable for use and their preparation are described in U.S.-A-4,472,560 and 4,477,589 to Shell Chemical Company and U.S.-A-3,941,849 and 4,335,188 to General Tire & Rubber Company.

One double metal cyanide complex catalyst found particularly suitable for use is a zinc hexacyanomethylate of formula



wherein M may be Co(III), or Cr(III); x, y, and z may be fractional numbers, integers, or zero and vary depending on the exact method of preparation of the complex.

In one embodiment of the invention after the incorporation of the alkali metal hydride but before the insoluble ionic metal species is separated from the polyol, ethylene oxide is added to the mixture and the mixture is heated to convert the secondary hydroxyl groups of the polyol to primary hydroxyl groups.

Any suitable alkali metal hydride can be employed in the practice of the invention. Preferred alkali metal hydrides are sodium hydride, potassium hydride, and lithium hydride. The amount of hydride employed is that amount effective to convert the double metal cyanide complex catalyst residue into an insoluble ionic metal species. Broadly, molar ratios of hydroxyl groups on the polyol to alkali metal hydride of from 1:1 to 500:1 are contemplated. Although not required, in order to enhance the speed at which the insoluble ionic metal species forms it is desirable to heat the mixture. Heating at a temperature within the range of from 40°C to 100°C for up to five hours has been found advantageous.

Likewise, in the above-mentioned embodiment involving the additional step of end capping with ethylene oxide, heating the mixture serves to facilitate the reaction.

After the double metal cyanide complex catalyst residue has been converted to the insoluble ionic metal species, it can be separated from the polyol by conventional methods such as filtration using, for example, diatomaceous earth, or passing through an acidic ion exchange resin as taught in U.S.-A-4,355,188.

In yet another embodiment of this invention, it has been found that the insoluble ionic metal species can be easily separated from the polyol by filtration if a minor amount of magnesium silicate, aluminum silicate, or mixtures thereof, is incorporated into the mixture prior to separation. The silicate can be used alone or in combination with conventional filter aids such as diatomaceous earth. In addition to facilitating separation, it has been discovered that treatment with silicate also converts polyol alkoxide groups to hydroxyl groups and absorbs the resulting alkali metal hydroxide.

Typically, the amount of silicate added will be from about 1 to about 5 parts by weight per each 100 parts by weight of the polyol containing catalyst residue mixture and the mixture will be heated for 1 to 12 hours at a temperature of from 80°C to 150°C before filtration. It is preferred that the silicate be finely divided and have a high surface area. The addition of a small amount of water (0.1-3%) has been found to provide more reliable and quantitative catalyst removal.

The following examples further demonstrate the method of the invention.

EXAMPLE 1

10 A. Double Metal Cyanide Complex Catalyst Preparation

A solution of 4.15 g (12.5 mmole) potassium hexacyanocobaltate in 100 ml water was added slowly with good mixing to a mixture of 3.82 g (28.0 mmole) zinc chloride and 25.0 g 100-200 mesh alumina (United Catalysts SAHT-99) in 40 ml water. After addition was completed, 25 ml glyme was added and the mixture stirred for one hour. The catalyst was collected by filtration in a 6.5 cm diameter fritted filter funnel, washed 3 times with 70 ml 30% glyme and twice with 70 ml 90% glyme. Filtration required approximately 50 minutes and the filtrate was only slightly cloudy. The filter cake was air-dried, crushed, and dried 18 hours at 0.1 mm pressure at 25°C.

20 B. Polymerization

A one-liter stirred autoclave was charged with 2.23 g catalyst from A above, 21.5 g propoxylated trimethylolpropane (470 MW), 110 ml tetrahydrofuran (THF), and 32 g propylene oxide (PO). A pressure drop was observed shortly after heating the mixture to 90°C. Another 523 g of PO was added over 6 hours. Propylene oxide triols of approximately 10,000 molecular weight were prepared by this polymerization.

C. Catalyst Conversion

The reaction mixture obtained from B was cooled to 30-40°C and then treated with 0.62 g sodium hydride (NaH) for 3 hours at 75°C to convert the catalyst to insoluble ionic species.

D. Ethoxylation

To the mixture from C was added 43 g ethylene oxide (EO) over a period of 5 hours at 75°C, and the mixture was allowed to react an additional 6 hours at 95°C to ensure complete ethoxylation of the secondary hydroxyl groups to primary hydroxyl groups.

E. Purification of the Product Polyols

After removing the unreacted EO from the mixture from D, 50 ml THF and 17 g magnesium silicate were added to the reactor and the whole heated to 110°C for 8 hours. The reaction products were then washed out of the reactor with THF and filtered. The small amounts of EO homopolymer formed were removed by stripping off the THF, diluting with hexane, and refiltering. The analysis of the final product is shown in Table I, Example 1.

EXAMPLE 2

The reaction mixture from Example 1B was cooled to 40°C and then treated with 0.63 g potassium hydride (KH) for 1 hour at 75°C. Over the next 2.5 hours, 64 g EO was added at 75°C and the mixture was allowed to react an additional 4 hours at 95°C. While removing the excess EO from the mixture, 50 ml THF and 17 g magnesium silicate were added to the reactor and heated to 110°C for 8 hours. The product was worked up as in Example 1E, and the analysis of the final product is shown in Table I, Example 2.

EXAMPLE 3 (comparative)

To illustrate that the purification of the polyol by removal of the ionic species from the catalyst residues by treatment with magnesium silicate is equally applicable to the known reactions using alkali metal dispersions to reduce the catalyst, the following was done.

The reaction mixture from Example 1B was cooled to 40°C and then treated with 0.61 g sodium dispersion (Na) for 3 hours at 75°C. Over the next 4.5 hours, 43 g EO was added at 75°C and the mixture was allowed to react an additional 9 hours at 95°C. After removing the excess EO from the mixture, 50 ml THF and 17.5 g magnesium silicate were added to the reactor and heated to 110°C for 8 hours. The product was worked up as in example 1E, and the analysis of the final product is shown in Table I, Example 3.

TABLE I

Example No:	1	2	3
Metal used	NaH	KH	Na
M _n , Calc.	12,400	12,100	11,700
M _n , GPC	8,200	8,870	9,620
Hydroxyl No.	16	17	17
Unsat., meq/g	<0.01	0.004	-
Wt. % EO	5.6	5.5	3.6
% Primary OH	84	65	71
Co, ppm	<1	6	<1
Zn, ppm	<0.5	5	0.5
Na, ppm	0.99	-	1.8
K, ppm	-	4.2	-

Claims

1. A method for removing double metal cyanide complex catalyst residue from polyols which comprises after polyol formation the steps of:
 - (a) incorporating into the catalyst residue-containing polyol an effective amount of an alkali metal hydride to convert the double metal cyanide complex catalyst into an insoluble ionic metal species separable from the polyol wherein the polyol hydroxyl groups are also converted to alkoxide groups; and
 - (b) separating the insoluble ionic metal species from the polyol.
2. The method of claim 1 in which said separating is accomplished by filtration.
3. The method of claim 1 in which said separating is accomplished by passing the mixture of catalyst residue-containing polyol and alkali metal hydride through an ion exchange resin.
4. The method of any one of claims 1 to 3 in which said alkali metal hydride is one or more of sodium hydride and potassium hydride.
5. The method of any preceding claim in which said alkali metal hydride is employed in a molar ratio of alkali metal hydride to hydroxyl groups on the polyol of from 1:1 to 1:500.



The reaction mixture from Example 1B was cooled to 40°C and then treated with 0.61 g sodium dispersion (Na) for 3 hours at 75°C. Over the next 4.5 hours, 43 g EO was added at 75°C and the mixture was allowed to react an additional 9 hours at 95°C. After removing the excess EO from the mixture, 50 ml THF and 17.5 g magnesium silicate were added to the reactor and heated to 110°C for 8 hours. The product was worked up as in example 1E, and the analysis of the final product is shown in Table I, Example 3.

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Wt. % EO	5.6	5.5	3.6
% Primary OH	84	65	71
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Zn, ppm	<0.5	5	0.5
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 50 residue-containing polyol and alkali metal hydride through an ion exchange resin.
4. The method of any one of claims 1 to 3 in which said alkali metal hydride is one or more of sodium hydride and potassium hydride.
- 55 5. The method of any preceding claim in which said alkali metal hydride is employed in a molar ratio of alkali metal hydride to hydroxyl groups on the polyol of from 1:1 to 1:500.



6. The method of any preceding claim wherein the mixture of catalyst residue-containing polyol and alkali metal hydride prepared in step (a) is heated to enhance the speed at which the insoluble ionic metal species forms.
- 5 7. The method of any preceding claim comprising after step (a) and before step (b) the step of incorporating an effective amount of ethylene oxide into the catalyst residue-containing polyol/alkali metal hydride mixture to convert any secondary hydroxyl groups of the polyol to primary hydroxyl groups.
- 10 8. The method of any preceding claim wherein a minor amount of one or more of magnesium-silicate and aluminum-silicate is introduced into the mixture and the insoluble ionic metal species is separated from the polyol in step (b) by filtration.

Patentansprüche

- 15 1. Verfahren zur Entfernung eines Doppelmetallcyanidkomplex-Katalysatorrückstands aus Polyolen, bei dem man nach der Polyolbildung
 - (a) in das den Katalysatorrückstand enthaltene Polyol eine wirksame Menge eines Alkalimetallhydrids inkorporiert, um den Doppelmetallcyanidkomplex-Katalysator in eine unlösliche ionische
 - 20 Metallspezies umzuwandeln, die von dem Polyol abtrennbar ist, wobei die Polyolhydroxylgruppen auch zu Alkoxidgruppen umgewandelt werden und
 - (b) die unlösliche ionische Metallspezies aus dem Polyol abtrennt.
2. Verfahren nach Anspruch 1, bei dem die Abtrennung durch Filtration erfolgt.
- 25 3. Verfahren nach Anspruch 1, bei dem die Abtrennung erfolgt, indem man die Mischung aus einem einen Katalysatorrückstand enthaltenden Polyol und Alkalimetallhydrid durch ein Ionenaustauschharz leitet.
4. Verfahren nach Anspruch 1 bis 3, bei dem das Alkalimetallhydrid Natriumhydrid und/oder Kaliumhydrid
- 30 ist.
5. Verfahren nach einem der vorstehenden Ansprüche, bei dem das Alkalimetallhydrid in einem Molverhältnis von Alkalimetallhydrid zu Hydroxylgruppen auf dem Polyol von 1 : 1 bis 1 : 500 eingesetzt wird.
- 35 6. Verfahren nach einem der vorstehenden Ansprüche, bei dem die in Schritt (a) hergestellte Mischung aus einem Katalysatorrückstand enthaltendem Polyol und Alkalimetallhydrid erhitzt wird, um die Geschwindigkeit zu erhöhen, mit der sich die unlösliche ionische Metallspezies bildet.
7. Verfahren nach einem der vorstehenden Ansprüche, bei dem nach Schritt (a) und vor Schritt (b) eine
- 40 wirksame Menge Ethylenoxid in die Mischung aus einem einen Katalysatorrückstand enthaltenden Polyol und Alkalimetallhydrid inkorporiert wird, um alle sekundären Hydroxylgruppen des Polyols zu primären Hydroxylgruppen umzuwandeln.
8. Verfahren nach einem der vorstehenden Ansprüche, bei dem eine kleinere Menge Magnesiumsilicat
- 45 und/oder Aluminiumsilicat in die Mischung eingearbeitet und die unlösliche ionische Metallspezies in Schritt (b) durch Filtration von dem Polyol abgetrennt wird.

Revendications

- 50 1. Procédé pour éliminer un résidu de catalyseur du type complexe de cyanures bimétalliques des polyols, qui comprend, après la formation d'un polyol, les étapes suivantes :
 - (a) l'incorporation dans le polyol contenant le résidu catalytique, d'une quantité efficace d'un hydrure de métal alcalin pour convertir le catalyseur du type complexe de cyanures bimétalliques en une
 - 55 espèce métallique ionique insoluble pouvant être séparée du polyol, les groupes hydroxy du polyol étant aussi convertis en groupes alcoolates; et
 - (b) la séparation de l'espèce métallique ionique insoluble du polyol.
2. Procédé suivant la revendication 1, dans lequel cette séparation est accomplie par filtration.



3. Procédé suivant la revendication 1, dans lequel cette séparation est accomplie par passage du mélange de polyol contenant un résidu catalytique et d'hydruure de métal alcalin à travers une résine d'échange d'ions.
- 5 4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel cet hydruure de métal alcalin est l'hydruure de sodium et/ou l'hydruure de potassium.
5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel cet hydruure de métal alcalin est employé selon un rapport molaire de l'hydruure de métal alcalin aux groupes hydroxy sur le polyol
- 10 compris entre 1:1 et 1:500.
6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel ce mélange de polyol contenant le résidu catalytique et d'hydruure de métal alcalin préparé dans l'étape (a) est chauffé pour augmenter la vitesse de formation de l'espèce métallique ionique insoluble.
- 15 7. Procédé suivant l'une quelconque des revendications 1 à 6, comprenant après l'étape (a) et avant l'étape (b), l'étape d'incorporation d'une quantité efficace d'oxyde d'éthylène dans le mélange de polyol contenant le résidu catalytique et d'hydruure de métal alcalin, pour convertir d'éventuels groupes hydroxy secondaires du polyol en groupes hydroxy primaires.
- 20 8. Procédé suivant l'une quelconque des revendications 1 à 7, dans lequel une quantité mineure de silicate de magnésium et/ou de silicate d'aluminium est introduite dans le mélange et l'espèce métallique ionique insoluble est séparée du polyol dans l'étape (b) par filtration.

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