

Process for producing polyetherester polyols based on natural oils and use thereof in rigid polyurethane foams

Description

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The present application relates to a method for preparing polyetherester polyols based on natural oils and use thereof in rigid polyurethane foams.

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Polyetherester polyols are an important raw material for the preparation of polyurethane (PU) plastics. The tolerability of the polyols for nonpolar propellants, such as pentane or cyclopentane, is an important factor in the preparation of polyurethanes.

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However, particularly polyols which are used for rigid PU foams – i.e. polyols having a relatively high OH number, such as sugar (sucrose)-based polyols –, usually have a rather low propellant compatibility or pentane compatibility due to their high proportion of polar functional groups. Polyols which comprise triglycerides as hydrophobic units, in addition to polyfunctional starters such as sugar or glycerol, may offer a solution to this problem for polyols for rigid PU foams. Natural raw materials, such as fats or oils, may also be used as building block for polyols and thus ultimately for rigid PU foams.

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The preparation of polyetherester polyols is known in principle and is described, *inter alia*, in EP1923417.

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EP 1923417A1 describes, for example, the synthesis and use of polyetherester polyols based on sorbitol/glycerol and/or sucrose/glycerol mixtures with fatty acid esters. In this case, 5-85%, preferably 20-60% of fatty acid esters are used for the synthesis of the polyols according to the invention. The use of fatty acid esters increases the capacity of these polyols for hydrophobic substances such as cyclopentane. The document discloses polyols having hydroxyl values less than 400 mg/KOH and a functionality < 4.1 for soybean oil contents of 23%, 37% and 52%.

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These polyols show an increased capacity for hydrophobic substances such as cyclopentane. The OH number of the polyetherester polyols described in the examples in this document is from ca. 50 mg KOH/g (*inter alia* in Ex. I) up to less than 460 mg KOH/g (Ex. H).

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WO 2012/084760 describes a method for preparing polyetherester polyols based on renewable raw materials with the emphasis on soybean oil and using basic catalysts with the emphasis on KOH. The polyols are neutralized with sulfuric acid after the alkoxylation step and the salt formed therefrom remains in the product. A subsequent further reaction with alkylene oxides using the DMC catalyst is also described; the use of the polyols thus prepared in flexible PU foams is also disclosed. The OH number of the polyetherester polyols described in the examples section of this document is ca. 50 to 60 mg KOH/g (see Ex. 1 to 4).

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It was therefore the object to provide, as far as possible, propellant-compatible polyols for rigid PU foam applications; the polyols should therefore have an OH number of at least 460 mg KOH/g, preferably at least 480 mg KOH/g. The viscosity of the polyols should nevertheless be in a justifiable range, i.e. not be excessively high, in order to ensure the processability.

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It has been found, surprisingly, during investigations of the dependence of the compatibility of polyetherester polyols for rigid foam applications (having an OH number of at least 460 mg KOH/g, preferably at least 480 mg KOH/g) with hydrophobic propellants such as cyclopentane as a function of the amount of fatty acid ester used, that surprisingly no linear dependence of the amount of triglyceride to the pentane compatibility existed, as would be expected by those skilled in the art. In fact, we found a defined concentration of the amount of triglyceride, which is between 2 and 23%, at which the capacity for hydrophobic substances is at a maximum.

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The present invention therefore relates to a polyetherester polyol, preferably a homogeneous polyetherester polyol, having an OH number of 460 to 580 mg KOH/g, preferably 480 to 580 mg KOH/g, particularly preferably 480 to 570 mg KOH/g, especially preferably 480 to 550 mg KOH/g, comprising the reaction product of

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- a1) 5 to 63% by weight, preferably 21 to 50% by weight, based on the total weight of the end product, of one or more compound(s) having at least two OH groups and/or compound(s) having at least two NH groups or mixtures thereof, having an average functionality of 2.5 to 8, preferably 4 to 6.5, preferably 4 to 6.0, particularly preferably 4.2 to 5.5,
- a2) 2 to 23% by weight, based on the total weight of the end product, preferably 10-22% by weight, of one or more fatty acid triglycerides comprising fatty acids having 10 to 22 carbon atoms which do not have free OH groups,
- a3) 25 to 70% by weight, preferably 33% to 65% by weight, based on the total weight of the end product, of one or more alkylene oxides having 2 to 4 carbon atoms.

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The present invention further relates to a method for preparing a polyetherester polyol, preferably a homogeneous polyetherester polyol, having an OH number of 460 to 580 mg KOH/g, preferably 480 to 580 mg KOH/g, particularly preferably 480 to 570 mg KOH/g, especially preferably 480 to 550 mg KOH/g, wherein

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- a1) 5 to 63% by weight, preferably 21 to 50% by weight, based on the total weight of the end product, of one or more compound(s) having at least two OH groups and/or compound(s) having at least two NH groups or mixtures thereof, having an average functionality of 2.5 to 8, preferably 4 to 6.5, preferably 4 to 6.0, particularly preferably 4.2 to 5.5, with
 - a2) 2 to 23% by weight, based on the total weight of the end product, preferably 10-22% by weight, of one or more fatty acid triglycerides comprising fatty acids having 10 to 22 carbon atoms which do not have free OH groups, and
 - a3) 25 to 70% by weight, preferably 33% to 65% by weight, based on the total weight of the end product, of one or more alkylene oxides having 2 to 4 carbon atoms,
- are reacted using a basic catalyst.

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Here, the OH number is in each case determined according to DIN 53240 (DIN = "deutsche Industrienorm [German Industry Standard]").

5 In addition, the present invention further relates to a method for preparing a polyurethane, wherein the polyetherester polyol according to the invention or a polyetherester polyol which can be prepared by the method according to the invention is reacted with at least one isocyanate, optionally using at least one propellant.

10 In a preferred embodiment, the polyols or polyamines of component a1) in the polyetheresterol according to the invention are selected from the group consisting of sugars, pentaerythritol, sorbitol, trimethylolpropane, glycerol, tolylenediamine, ethylenediamine, ethylene glycol, propylene glycol, water and mixtures thereof.

15 In a further preferred embodiment, component a1) comprises a mixture of glycerol and sucrose, preferably in a mixing ratio of sucrose to glycerol in the range of 9:1 to 1:1, particularly preferably sucrose to glycerol of 4:1 to 1:1, based on the percentage by weight.

20 In a further preferred embodiment, component a2) is selected from the group consisting of soybean oil, rapeseed oil, palm oil, olive oil, sunflower oil, tallow, fish oil and mixtures thereof, preferably mixtures comprising soybean oil, rapeseed oil and/or palm oil, particularly preferably soybean oil.

25 In a further preferred embodiment, the alkylene oxide of component a3) is selected from the group comprising ethylene oxide, propylene oxide, butylene oxide and mixtures thereof, preferably mixtures comprising propylene oxide and ethylene oxide, particularly preferably propylene oxide.

30 In a further preferred embodiment, the polyetherester polyol according to the invention has a functionality of 2.5 to 8, preferably 4 to 6.5.

In a further preferred embodiment, the polyetherester polyol according to the invention has an acid number of less than or equal to 0.5 mg KOH/g, determined according to DIN 53402.

35 In a further preferred embodiment, the polyetherester polyol according to the invention can be prepared using an amine catalyst.

40 In a preferred embodiment of the method according to the invention, the basic catalyst is selected from the group comprising KOH and aminic compounds, preferably aminic compounds, particularly preferably imidazole.

In a further preferred embodiment of the method according to the invention, the method is carried out in one process step, i.e. one stage.

In a further preferred embodiment of the method according to the invention, the polyols or polyamines of component a1) are selected from the group consisting of sugars, pentaerythritol, sorbitol, trimethylolpropane, glycerol, tolylenediamine, ethylenediamine, ethylene glycol, propylene glycol, water and mixtures thereof.

In a further preferred embodiment of the method according to the invention, component a1) comprises a mixture of glycerol and sucrose, preferably in a mixing ratio of sucrose to glycerol in the range of 9:1 to 1:1, particularly preferably sucrose to glycerol of 4:1 to 1:1, based on the percentage by weight.

In a further preferred embodiment of the method according to the invention, component a2) is selected from the group consisting of soybean oil, rapeseed oil, palm oil, olive oil, sunflower oil, tallow, fish oil and mixtures thereof, preferably mixtures comprising soybean oil, rapeseed oil and/or palm oil, particularly preferably soybean oil.

In a further preferred embodiment of the method according to the invention, the alkylene oxide of component a3) is selected from the group comprising ethylene oxide, propylene oxide, butylene oxide and mixtures thereof, preferably mixtures comprising propylene oxide and ethylene oxide, particularly preferably propylene oxide.

In a further preferred embodiment of the method according to the invention, the polyetherester polyol has a functionality of 2.5 to 8, preferably 4 to 6.5.

In a further preferred embodiment of the method according to the invention, the polyetherester polyol has an acid number of less than or equal to 0.5 mg KOH/g.

Figure 1 describes the pentane compatibility of the polyol obtained as a function of the proportion of soybean oil used (results of the example experiments).

Examples

Some examples to illustrate the invention are given below. The examples are for illustrative purposes only and shall on no account restrict the scope of the claims.

The pentane solubility was determined by adding pentane stepwise to the component to be measured. Pentane was added, according to the pentane solubility expected, to exactly 100 g of the component to be investigated and was mixed. If the mixture was neither cloudy nor biphasic, then further pentane had to be added and be further mixed. If the mixture was biphasic, the glass vessel was left open at room temperature until the excess pentane evaporated and the remaining solution was clear, and the dissolved amount of pentane was then reweighed. If the mixture was cloudy, the glass vessel was sealed and left to stand at room

temperature until two phases had formed. Following this, the evaporation and reweighing were carried out.

The viscosity was determined according to DIN 53018 at 25°C. The OH number was determined according to DIN 53240.

Example 1: Preparation of a polyetherester with glycerol, sucrose and soybean oil

30.4 g of glycerol, 0.1 g of imidazole, 49.1 g of sucrose and 12.0 g of soybean oil were placed in a reactor at 25°C. The reactor was then inertized with nitrogen. The tank was heated to 130°C and 148.4 g of propylene oxide were added. After a reaction time of 7 h, the tank was evacuated for 40 minutes under high vacuum at 100°C and was subsequently cooled to 25°C. 208.8 g of product were obtained.

The polyetherester obtained had the following characteristics:

OH number: 522.4 mg KOH/g

Viscosity (25°C): 11 957 mPas

Cyclopentane compatibility: 14%

Example 2: Preparation of a polyetherester with glycerol, sucrose and soybean oil

30.4 g of glycerol, 0.1 g of imidazole, 49.1 g of sucrose and 24.0 g of soybean oil were placed in a reactor at 25°C. The reactor was then inertized with nitrogen. The tank was heated to 130°C and 136.4 g of propylene oxide were added. After a reaction time of 5 h, the tank was evacuated for 40 minutes under high vacuum at 100°C and was subsequently cooled to 25°C. 211.4 g of product were obtained.

The polyetherester obtained had the following characteristics:

OH number: 512.6 mg KOH/g

Viscosity (25°C): 10 465 mPas

Cyclopentane compatibility: 25%

Example 3: Preparation of a polyetherester with glycerol, sucrose and soybean oil

30.4 g of glycerol, 0.1 g of imidazole, 49.1 g of sucrose and 36.0 g of soybean oil were placed in a reactor at 25°C. The reactor was then inertized with nitrogen. The tank was heated to 130°C and 124.4 g of propylene oxide were added. After a reaction time of 4 h, the tank was evacuated for 40 minutes under high vacuum at 100°C and was subsequently cooled to 25°C. 205.6 g of product were obtained.

The polyetherester obtained had the following characteristics:

OH number: 526.9 mg KOH/g

Viscosity (25°C): 11 294 mPas

Cyclopentane compatibility: 35%

Example 4: Preparation of a polyetherester with glycerol, sucrose and soybean oil

30.4 g of glycerol, 0.1 g of imidazole, 49.1 g of sucrose and 60.0 g of soybean oil were placed in a reactor at 25°C. The reactor was then inertized with nitrogen. The tank was heated to 130°C and 100.4 g of propylene oxide were added. After a reaction time of 8 h, the tank was evacuated for 40 minutes under high vacuum at 100°C and was subsequently cooled to 25°C. 220.3 g of product were obtained.

The polyetherester obtained had the following characteristics:

OH number: 512.8 mg KOH/g

Viscosity (25°C): 9639 mPas

Cyclopentane compatibility: 32%

Example 5: Preparation of a polyetherester with glycerol, sucrose and soybean oil

30.4 g of glycerol, 0.1 g of imidazole, 49.1 g of sucrose and 84.0 g of soybean oil were placed in a reactor at 25°C. The reactor was then inertized with nitrogen. The tank was heated to 130°C and 76.4 g of propylene oxide were added. After a reaction time of 7 h, the tank was evacuated for 40 minutes under high vacuum at 100°C and was subsequently cooled to 25°C. 225.6 g of product were obtained.

The polyetherester obtained had the following characteristics:

OH number: 505.5 mg KOH/g

Viscosity (25°C): 9243 mPas

Cyclopentane compatibility: 16%

Claims

1. A polyetherester polyol having an OH number of 480 to 580 mg KOH/g, determined according to DIN 53240, comprising the reaction product of
 - a1) 5 to 63% by weight, preferably 21 to 50% by weight, based on the total weight of the end product, of one or more compound(s) having at least two OH groups and/or compound(s) having at least two NH groups or mixtures thereof, having an average functionality of 2.5 to 8, preferably 4 to 6.5, particularly preferably 4 to 6.0, especially preferably 4.2 to 5.5,
 - a2) 10-22% by weight, based on the total weight of the end product, of one or more fatty acid triglycerides comprising fatty acids having 10 to 22 carbon atoms which do not have free OH groups,
 - a3) 25 to 70% by weight, preferably 33% to 65% by weight, based on the total weight of the end product, of one or more alkylene oxides having 2 to 4 carbon atoms.
2. The polyetherester polyol according to claim 1, wherein the polyols or polyamines of component a1) are selected from the group consisting of sugars, pentaerythritol, sorbitol, trimethylolpropane, glycerol, tolylenediamine, ethylenediamine, ethylene glycol, propylene glycol, water and mixtures thereof.
3. The polyetherester polyol according to claim 2, wherein component a1) comprises a mixture of glycerol and saccharose, preferably in a mixing ratio of saccharose to glycerol in the range of 9:1 to 1:1, particularly preferably saccharose to glycerol of 4:1 to 1:1, based on the percentage by weight.
4. The polyetherester polyol according to claim 2 or 3, wherein component a2) is selected from the group consisting of soybean oil, rapeseed oil, palm oil, olive oil, sunflower oil, tallow, fish oil and mixtures thereof, preferably mixtures comprising soybean oil, rapeseed oil and/or palm oil, particularly preferably soybean oil.
5. The polyetherester polyol according to any of claims 1 to 4, wherein the alkylene oxide of component a3) is selected from the group comprising ethylene oxide, propylene oxide, butylene oxide and mixtures thereof, preferably mixtures comprising propylene oxide and ethylene oxide, particularly preferably propylene oxide.
6. The polyetherester polyol according to any of claims 1 to 5, wherein said polyetherester polyol has a functionality of 2.5 to 8, preferably 4 to 6.5.
7. The polyetherester polyol according to any of claims 1 to 6, wherein said polyetherester polyol has an acid number of less than or equal to 0.5 mg KOH/g, determined according to DIN 53402.

8. The polyetherester polyol according to any of claims 1 to 7, wherein the polyetherester has been prepared using an amine catalyst, preferably an imidazole.
- 5 9. A method for preparing a polyetherester polyol having an OH number of 480 to 580 mg KOH/g, determined according to DIN 53240, wherein
- 10 a1) 5 to 63% by weight, preferably 21 to 50% by weight, based on the total weight of the end product, of one or more compound(s) having at least two OH groups and/or compound(s) having at least two NH groups or mixtures thereof, having an average functionality of 2.5 to 8, preferably 4 to 6.5, particularly preferably 4 to 6.0, especially preferably 4.2 to 5.5, with
- 15 a2) 10-22% by weight, based on the total weight of the end product, of one or more fatty acid triglycerides comprising fatty acids having 10 to 22 carbon atoms which do not have free OH groups, and
- 15 a3) 25 to 70% by weight, preferably 33% to 65% by weight, based on the total weight of the end product, of one or more alkylene oxides having 2 to 4 carbon atoms, are reacted using a basic catalyst.
- 20 10. The method for preparing a polyetherester polyol according to claim 9, wherein the basic catalyst is selected from the group comprising KOH and aminic compounds, preferably aminic compounds, particularly preferably imidazole.
- 25 11. The method for preparing a polyetherester polyol according to claim 9 or 10, wherein the method is carried out in one process step.
- 30 12. The method for preparing a polyetherester polyol according to any of claims 9 to 11, wherein the polyols or polyamines of component a1) are selected from the group consisting of sugars, pentaerythritol, sorbitol, trimethylolpropane, glycerol, tolylenediamine, ethylenediamine, ethylene glycol, propylene glycol, water and mixtures thereof.
- 35 13. The method for preparing a polyetherester polyol according to any of claims 9 to 12, wherein component a1) comprises a mixture of glycerol and saccharose, preferably in a mixing ratio of saccharose to glycerol in the range of 9:1 to 1:1, particularly preferably saccharose to glycerol of 4:1 to 1:1, based on the percentage by weight.
- 40 14. The method for preparing a polyetherester polyol according to any of claims 9 to 13, wherein component a2) is selected from the group consisting of soybean oil, rapeseed oil, palm oil, olive oil, sunflower oil, tallow, fish oil and mixtures thereof, preferably mixtures comprising soybean oil, rapeseed oil and/or palm oil, particularly preferably soybean oil.

15. The method for preparing a polyetherester polyol according to any of claims 9 to 14, wherein the alkylene oxide of component a3) is selected from the group comprising ethylene oxide, propylene oxide, butylene oxide and mixtures thereof, preferably mixtures comprising propylene oxide and ethylene oxide, particularly preferably propylene oxide.
- 5 16. The method for preparing a polyetherester polyol according to any of claims 9 to 15, wherein the polyetherester polyol has a functionality of 2.5 to 8, preferably 4 to 6.5.
- 10 17. The method for preparing a polyetherester polyol according to any of claims 9 to 16, wherein the polyetherester polyol has an acid number of less than or equal to 0.5 mg KOH/g, determined according to DIN 53402.
- 15 18. A method for preparing a polyurethane, wherein the polyetherester polyol according to any of claims 1 to 8 or a polyetherester polyol which can be prepared by the method of any of claims 9 to 17 is reacted with at least one isocyanate, optionally using at least one propellant.