catalyst residues that remain in the polyol after the polymerization reaction do not need to be removed. When KOH is used as the polymerization catalyst, it is necessary to neutralize the product to convert the O^-K^+ end groups to hydroxyl groups, and then to remove the catalyst residues to very low levels. This adds processing steps and increases production cost.

Polyols for high resiliency foams are made almost exclusively using potassium hydroxide as the polymerization catalyst, despite the potential advantages of using DMC catalysts. There are two main reasons for this. First, DMC catalysts are unable to catalyze the ethylene oxide polymerization reaction needed to produce polyols with high primary hydroxyl contents. Therefore, at least the ethylene oxide capping step must be performed using KOH as the catalyst. The costs of neutralization and removal of the catalyst residues therefore are incurred, which defeats a major advantage of using the DMC catalyst in the first place. In view of this, it is less expensive industrially to perform the entire polymerization using the KOH catalyst. Second, DMC catalysts produce a very small but significant high molecular weight fraction when used to polymerize propylene oxide and ethylene oxide. This high molecular weight fraction is a powerful defoamer, which works in opposition to the foam-stabilizing surfactant present in the foam formulation. This high molecular weight fraction can be tolerated when conventional foams are made, because the formulations are more stable during the foaming process. However, the high molecular weight fraction causes great difficulty in high resiliency foam formulations, which are already difficult to stabilize.

SUMMARY

The present disclosure provides a method for making a polyurethane foam having a resiliency of at least 50% on the ASTM 3574 ball rebound test and/or a hysteresis loss of no greater than 30% according to ISO 3386, a foam density of 24 to 80 kg/m^3 and a hard segment content of 22 to 40% by weight, comprising reacting, in one or more steps and in the presence of at least one foam-stabilizing surfactant and at least one catalyst for the reaction of an alcohol group with an isocyanate group, polyurethane-forming reactants comprising one or more polyol(s) having a hydroxyl equivalent weight of at least 1000 grams per equivalent, at least one crosslinker, at least one polyisocyanate and water, wherein (I) the polyol(s) having a hydroxyl equivalent weight of at least 1000 constitute at least 55% by weight of the polyurethane-forming reactants, and (II) at least 20% by weight of said polyol(s) having a hydroxyl equivalent weight of at least 1000 is one or more random copolymer(s) formed by polymerizing a mixture of 70 to 95% by weight propylene oxide and 5 to 30% by weight ethylene oxide onto an initiator

compound, the random copolymer(s) having a nominal hydroxyl functionality of at least 5, a hydroxyl equivalent weight of at least 1500 g/equivalent, no more than 0.01 milliequivalents per gram of terminal unsaturation, wherein the randomly polymerized propylene oxide and ethylene oxide constitute at least 80% of the total weight of the random copolymer and further wherein at least 70% of the hydroxyl groups of the random copolymer(s) are secondary hydroxyls.

In one aspect, there is provided a method for making a polyurethane foam comprising reacting, in one or more steps and in the presence of at least one foam-stabilizing surfactant and at least one catalyst for the reaction of an alcohol group with an isocyanate group, polyurethane-forming reactants comprising one or more polyol(s) having a hydroxyl equivalent weight of at least 1000 grams per equivalent, at least one crosslinker, at least one polyisocyanate and water, wherein (I) the polyol(s) having a hydroxyl equivalent weight of at least 1000 constitute at least 55% by weight of the polyurethane-forming reactants, and (II) at least 20% by weight of said polyol(s) having a hydroxyl equivalent weight of at least 1000 is one or more random copolymer(s) formed by polymerizing a mixture of 70 to 95% by weight propylene oxide and 5 to 30% by weight ethylene oxide onto an initiator compound, the random copolymer(s) having a nominal hydroxyl functionality of at least 5, a hydroxyl equivalent weight of at least 1500 g/equivalent, no more than 0.01 milliequivalents per gram of terminal unsaturation, wherein the randomly polymerized propylene oxide and ethylene oxide constitute at least 80% of the total weight of the random copolymer and further wherein at least 70% of the hydroxyl groups of the random copolymer(s) are secondary hydroxyls.

In another aspect, there is provided a polyurethane foam made by the method as described herein.

In another aspect, there is provided a random copolymer formed by polymerizing a mixture of 70 to 95% by weight propylene oxide and 5 to 30% by weight ethylene oxide onto an initiator compound, the random copolymer(s) having a nominal hydroxyl functionality of at least 5, a hydroxyl equivalent weight of at least 1500 grams/equivalent, no more than 0.01 milliequivalent of terminal unsaturation per gram, wherein the randomly polymerized propylene oxide and ethylene oxide constitute at least 80% of the total weight of the random copolymer and further wherein at least 70% of the hydroxyl groups of the random copolymer(s) are secondary hydroxyls.

In another aspect, there is also provided a process for producing the random copolymer as defined herein, comprising establishing steady-state polymerization conditions in a continuous reactor, continuously feeding to the continuous reactor under

reaction conditions an initiator compound having at least 5 hydroxyl groups or a mixture of initiator compounds including at least one initiator having at least 5 hydroxyl groups, a double metal cyanide catalyst complex and a mixture of 70 to 95% by weight propylene oxide and correspondingly 5 to 30% by weight ethylene oxide and continuously withdrawing the random copolymer from the continuous reactor, while maintaining said steady-state polymerization conditions in the continuous reactor.

Surprisingly, the foaming process proceeds well despite the inclusion of a significant quantity of polyol terminated mainly in secondary hydroxyl groups. The foam formulation is not prone to collapse, which is also unexpected because the polyol of the disclosure does not have a block structure and is not believed to play a significant role in compatibilizing the reactants or stabilizing the foaming reaction mixture as it cures.

Another advantage is that the polyol of the disclosure is easily made using double metal cyanide catalysts, and the benefits of using DMC catalyst technology, including low polyol manufacturing costs, can be realized in the manufacture of polyols for high resiliency foam.

DETAILED DESCRIPTION

The random copolymer contains randomly distributed propylene oxide and ethylene oxide units, where propylene oxide units have the structure $-CH_2-CH(CH_3)-O-$ and the ethylene oxide units have the structure $-CH_2-CH_2-O-$. The randomly polymerized propylene oxide and ethylene oxide should constitute at least 80 weight-%, preferably at least 85 weight-% of all the polymerized alkylene oxides in the random copolymer, and may constitute up to 100 weight-% or up to 95 weight-% thereof. The randomly polymerized propylene oxide and ethylene oxide should constitute at least 75%, preferably at least 80% and more preferably at least 85% by weight of the random copolymer, and may constitute as much as 99.5% by weight thereof. The random copolymer may contain internal blocks of homopolymerized propylene oxide that

WHAT IS CLAIMED IS:

1. A method for making a polyurethane foam comprising reacting, in one or more steps and in the presence of at least one foam-stabilizing surfactant and at least one catalyst for the reaction of an alcohol group with an isocyanate group, polyurethane-forming reactants comprising one or more polyol(s) having a hydroxyl equivalent weight of at least 1000 grams per equivalent, at least one crosslinker, at least one polyisocyanate and water, wherein (I) the polyol(s) having a hydroxyl equivalent weight of at least 1000 constitute at least 55% by weight of the polyurethane-forming reactants, and (II) at least 20% by weight of said polyol(s) having a hydroxyl equivalent weight of at least 1000 is one or more random copolymer(s) formed by polymerizing a mixture of 70 to 95% by weight propylene oxide and 5 to 30% by weight ethylene oxide onto an initiator compound, the random copolymer(s) having a nominal hydroxyl functionality of at least 5, a hydroxyl equivalent weight of at least 1500 g/equivalent, no more than 0.01 milliequivalents per gram of terminal unsaturation, wherein the randomly polymerized propylene oxide and ethylene oxide constitute at least 80% of the total weight of the random copolymer and further wherein at least 70% of the hydroxyl groups of the random copolymer(s) are secondary hydroxyls.

2. The method of claim 1 wherein the random copolymer has a nominal hydroxyl functionality of 6 to 8.

3. The method of claim 1 or 2 wherein the initiator compound is sorbitol.

4. The method of any preceding claim wherein the random copolymer has a hydroxyl equivalent weight of 1500 to 2300 g/equivalent.

5. The method of any preceding claim wherein the random copolymer contains no more than 0.007 milliequivalents per gram of terminal unsaturation.

6. The method of any preceding claim wherein the random copolymer contains internal blocks of homopolymerized propylene oxide formed by homopolymerizing in one or more steps 1 to 4 moles of propylene oxide per hydroxyl equivalent of the initiator prior to performing the random polymerization.

7. The method of any preceding claim wherein the random copolymer constitutes at least 30% by weight of said polyol(s) having a hydroxyl equivalent weight of at least 1000.

8. The method of any preceding claim wherein the random copolymer constitutes 40 to 95% by weight of said polyol(s) having a hydroxyl equivalent weight of at least 1000.

9. The method of any preceding claim wherein the foam density is 24 to 60 kg/m^3.

10. The method of any preceding claim wherein the polyol(s) having a hydroxyl equivalent weight of at least 1000 include at least one of: a) a polymer of ethylene oxide or a mixture of at least 50% by weight ethylene oxide and up to 50% by weight 1,2-propylene oxide and b) a polymer of at least 70% by weight 1,2-propylene oxide and up to 30% by weight ethylene oxide, in which at least 50% of the hydroxyl groups are primary.

11. The method of any preceding claim wherein the foam has a hard segment content of 30 to 40% by weight.

12. A polyurethane foam made in accordance with any of claims 1-11.

13. A random copolymer formed by polymerizing a mixture of 70 to 95% by weight propylene oxide and 5 to 30% by weight ethylene oxide onto an initiator compound, the random copolymer having a nominal hydroxyl functionality of at least 5, a hydroxyl equivalent weight of at least 1500 grams per equivalent and no more than 0.01 meq/g of terminal unsaturation, wherein the randomly polymerized propylene oxide