catalysis, are not suitable for current rigid formulations that are based mainly on secondary hydroxyl capped polyols. Reactivity of primary hydroxyls towards isocyanates is, on the average, 3.3 times higher versus that of the secondary hydroxyls. This would result in the need to reformulate the whole formulation or at least to adjust the catalyst package. Another issue with superacidic catalysis is cyclic volatile by-product formation. Volatile impurities formed include significant amounts of toxic and highly odored aldehydes, substituted dioxanes and dioxolanes.

There exists a need for a process to prepare short-chain polyfunctional polyether polyols having an improved (e.g., reduced) cycle time as compared to conventional semi-batch base-catalyzed processes. Further, there is a need for a semi-batch and/or continuously fed process to prepare short chain polyfunctional polyether polyols which does not require a finishing step.

SUMMARY ~~OF THE INVENTION~~

The present ~~invention~~disclosure accordingly provides such a method for the production of short-chain polyfunctional polyether polyols with improved cycle time comprising the steps of: (i) obtaining at least one oligomeric alkoxylated starter compound by reacting: (i.a) at least one starter compound comprising from 3 to 9 hydroxyl groups wherein said starter compound has a hydroxy equivalent weight (HEW) of from 22 to 90 Da; (i.b) at least one alkylene oxide in the presence of; (i.c) a superacid catalyst in an amount of from 5 to 500 ppm relative to the amount of oligomeric alkoxylated starter compound to be produced; and (i.d) at a reaction temperature of from 60°C to 180°C; wherein the resulting oligomeric alkoxylated starter compound has a HEW of from 60 to 200 Da; and (ii) converting said oligomeric alkoxylated starter compound into a short-chain polyether polyol without removal of the superacid catalyst by reacting: (ii.a) the oligomeric alkoxylated starter compound with; (ii.b) at least one alkylene oxide in the presence of; (ii.c) at least one double-metal cyanide (DMC) catalyst, wherein the concentration of the DMC catalyst is from 10 to 10,000 ppm relative to the amount of short-chain polyether polyol to be produced; and (ii.d) at a reaction temperature of from 90°C to 180°C; wherein the resulting short-chain polyether polyol has a HEW of from 90 to 400 Da.

In one aspect, there is provided a method for producing a short-chain polyether polyol comprising the steps of:

(i) obtaining at least one oligomeric alkoxylated starter compound by reacting:

(i.a) at least one low molecular weight starter compound comprising from 3 to 9 hydroxyl groups wherein said starter compound has a hydroxy equivalent weight (HEW) of from 22 to 90 Da;

(i.b) at least one alkylene oxide in the presence of;

(i.c) a superacid catalyst present in a concentration of from 5 to 500 ppm relative to the amount of oligomeric alkoxylated starter compound to be produced; and

(i.d) at a reaction temperature of from 60°C to 180°C;

wherein the oligomeric alkoxylated starter compound has a HEW of from 60 to 200 Da;

and

(ii) converting the resulting alkoxylated starter compound into a short-chain polyether polyol without removal of the superacid catalyst by reacting:

(ii.a) said oligomeric alkoxylated starter compound with;

(ii.b) at least one alkylene oxide in the presence of;

(ii.c) at least one double-metal cyanide (DMC) catalyst, wherein the concentration of the DMC catalyst is from 10 to 10,000 ppm relative to the amount of short-chain polyether polyol to be produced; and

(ii.d) at a reaction temperature of from 90°C to 180°C;

wherein the resulting short-chain polyether polyol has a HEW of from 90 to 400 Da; and

wherein the superacid is fluorinated sulfonic acid, a perfluoroalkylsulfonic acid, fluoroantimonic acid ($HSbF_6$), carborane superacid ($HCHB_{11}Cl_{11}$), perchloric acid ($HClO_4$), tetrafluoroboric acid (HBF_4), hexafluorophosphoric acid (HPF_6), boron trifluoride (BF_3), antimony pentafluoride (SbF_5), phosphorous pentafluoride (PF_5), or mixtures thereof;

or

wherein the superacid is trifluoromethanesulfonic (triflic) acid (CF_3SO_3H), fluorosulfonic acid (HSO_3F), fluoroantimonic acid, Magic acid (FSO_3H-SbF_5), or mixtures thereof.

In a preferred embodiment of the method described herein above, the starter compound is trimethylolpropane, glycerol, polyglycerol, pentaerythritol, erythritol, xylitol, sorbitol, maltitol, sucrose, dextrose, invert sugar, degraded starch, degraded cellulose,

A is chloride, bromide, iodide, nitrate, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, perchlorate, isothiocyanate, an alkanesulfonate such as methanesulfonate, an arylenesulfonate such as p-toluenesulfonate, trifluoromethanesulfonate (triflate) or a C_{1-4} carboxylate;

r is 4, 5 or 6; and

t is 0 or 1.

A particularly preferred double-meteal cyanide catalyst is a zinc hexacyanocobaltate catalyst complexed with t-butanol.

Another embodiment of the present ~~invention~~disclosure is a polyurethane polymer foam prepared from a formulation comprising a short-chain polyether polyol prepared by the method described herein above, preferably a rigid polyurethane insulation foam.

DETAILED DESCRIPTION OF THE EMBODIMENTS

The primary starting material for the inventive process is a low molecular weight polyfunctional starter compound. Suitable low molecular weight starter compounds have from 3 to 9 hydroxyl groups, preferably 3 to 8 hydroxyl groups and a hydroxy equivalent weight (HEW) of from 22 to 90 Da, preferably 27 to 42 Da. Examples of suitable low molecular weight starter compounds are polyfuntional polyols such as: trimethylolpropane, glycerol, polyglycerol, pentaerythritol, erythritol, xylitol, sorbitol, maltitol, sucrose, dextrose, invert sugar, degraded starch / cellulose, hydrogenated starch hydrolysates or aromatic Mannich polycondensates. The low molecular weight starter compounds may be used individually or as a mixture of two or more.

The second starting material, i.e., the alkoxylation agent which is herein termed the epoxide component, may be selected from epoxide compounds, or combinations of such compounds, that are capable of reacting with a low molecular weight starter compound, to form oligomeric alkoxylated starter compounds. Suitable oligomeric alkoxylated starter compounds for use in the present invention are short chain polyfunctional polyether polyols with functionality in the range from 3 to 9 and hydroxyl equivalent weights in the range from 60 to 200 Da. In certain embodiments the epoxide component is selected from ethylene oxide (EO), propylene oxide (PO), butylene oxide, 1-octene oxide, cyclohexene oxide, styrene oxide, glycidyl ether, and combinations thereof. Higher epoxides, having carbon atoms numbering, for example, from 9 to 16, may be used as well in this reaction.