Abstract:
A process to convert a secondary hydroxyl-capped polyl to a primary hydroxyl-capped polyl comprises reacting a polylether polyl, polylether-polyester polyl or polylether-ester polyl with an anhydride of a polycarboxylic acid, to form a half acid ester. The half acid ester is reacted with a secondary hydroxyl-capped polyl to form a polyester polyl or a polylether-polyester polyl. Both steps are carried out in the presence of an amine catalyst and a double metal cyanide complex catalyst. The process offers higher primary hydroxyl functionality (for example, up to 95 percent, based on total functionality) with low amounts of ethylene oxide as a reactant (for example, less than 5 percent by weight).
ETHYLENE OXIDE CAPPING OF SECONDARY HYDROXYL POLYOLS

[0001] The invention relates to a conversion of secondary hydroxyl compounds to primary hydroxyl compounds. In particular, it relates to a process for converting secondary hydroxyl compounds to half acid esters and subsequently to primary hydroxyl alkoxo ester compounds while concurrently capping with ethylene oxide.

[0002] It is well known in the polyurethane art that certain characteristics of starting polyols may contribute to, or detract from, desired properties of a final polyurethane. Secondary hydroxyl group-containing polyols may be used in some polyurethane formulations, but are often less desired than primary hydroxyl group-containing compounds, particularly for certain specialized polyurethane applications. For example, in comparison with primary hydroxyl group-containing compounds, secondary hydroxyl group-containing compounds are not as reactive as primary hydroxyl group-containing compounds, and their use in slabstock or molded flexible foam polyurethane formulations often results in foam densification or unacceptably long cycle times, making them frequently unsuitable for such applications. The secondary hydroxyl group-containing compounds may also increase costs by requiring higher catalyst levels, and may be undesirably hydrophobic, poorly miscible in formulations with other polyols and/or additives, produce foams with poorer insulation and thermal properties, and decrease fire retardancy capability. In view of these drawbacks, researchers have sought methods of efficiently converting secondary chain ends to primary chain ends.

[0003] Alkoxylation of secondary hydroxyl group-containing compounds, resulting in conversion of a portion of such end-groups to primary hydroxyl groups, is well known in the art. Use of potassium hydroxide as a catalyst while capping with ethylene oxide is one such method. For example, using 20 percent ethylene oxide, based on the weight of the secondary hydroxyl group-containing compound, may result in capping of 80 percent of the secondary groups, which means that 80 percent are thereby converted to primary hydroxyl end groups. In another method, using the same amount of ethylene oxide in the presence of a double metal cyanide catalyst may result in a reduced conversion, of less than 50 percent, due to homopolymerization of the ethylene oxide. Still other methods have included, for example, a process disclosed in U.S.
Patent 4,487,853, wherein a 2- to 8-functional polyether polyol having an equivalent weight from 500 Da to 10,000 Da is reacted with a cyclic organic acid anhydride to form a half acid ester, and ethylene oxide is then added in the presence of an amine or oxide or salt of a divalent metal catalyst. U.S. Patent 4,582,926 describes a process of reacting a secondary hydroxyl capped polyol with a carboxylic acid anhydride to form a carboxylic acid half ester in the presence of an amine catalyst, then oxyalkylating the carboxylic acid half ester with alkylene oxide in the presence of a phosphine catalyst. In another process, described in U.S. Patents 3,931,092; 4,014,846; 4,093,573; and 4,144,395, an alkylene oxide is reacted with a half acid ester obtained by the reaction of a secondary hydroxyl capped polyol with an unsaturated acid anhydride. This reaction is either uncatalyzed or trialkylamine catalyzed. U.S. Patent 5,145,883 discloses polyester ether polyol obtained by co-polymerizing poly-carboxylic-acid anhydride and alkylene oxide with an initiator in presence of a double metal cyanide catalyst. The content of poly-carboxylic-acid anhydride in the polyester ether polyol is from 10 to 50 weight percent. The initiator is a secondary hydroxyl-capped polyether polyol with a hydroxyl number of not more than 160.

[0004] The problem with all of these methods is that the capping level may be less than desired, with the result that products may contain a higher than desired level of uncapped acid and/or include a significant amount of transterification by-products, including cyclic esters, uncapped secondary hydroxyls, and fully-esterified chain-ends resulting in higher number average molecular weights (Mn) and reduced polyol functionality. Another problem may be broader than desired polydispersities and functionality distributions, and the amount of ethylene oxide required may be higher than desired and/or lead to an increase in overall polyol hydrophilicity. All of these problems may tend to reduce certain properties of a final polyurethane prepared therefrom. Such properties may include, for example, cure rate, wet compression set, flame lamination properties, thermal insulation, demold expansion, polyol miscibility, thermal stability, and flame retardancy. Thus, it is desirable in the art to discern new methods of converting secondary hydroxyl-capped polyether polyols to primary hydroxyl-capped polyols that has the potential for greater selectivity and higher conversion, while using less ethylene oxide. An additional advantage would enable
application of such method or methods particularly to DMC-catalyzed polyether polyols.

[0005] In one embodiment, the invention provides a process for preparing a polyol having primary hydroxyl functionality, comprising the steps of (a) reacting a polyether polyl, a polyester polyl, polyether-ester polyl or a polyether-polyester polyl, having predominantly secondary hydroxyl functionality, with a cyclic anhydride of a polycarboxylic acid, under conditions such that a half acid ester is formed; and (b) reacting the half acid ester with ethylene oxide, under conditions such that a polyether-ester polyl, a polyester polyl or a polyether-polyester polyl, having primary hydroxyl functionality, is formed; provided that both steps are carried out in the presence of an amine catalyst and a double metal cyanide catalyst.

[0006] In another embodiment, the invention provides a polyol having primary hydroxyl functionality prepared by a process comprising the steps of (a) reacting a polyether polyl, a polyester polyl, polyether-ester polyl or a polyether-polyester polyl, having predominantly secondary hydroxyl functionality, with a cyclic anhydride of a polycarboxylic acid, under conditions such that a half acid ester is formed; and (b) reacting the half acid ester with ethylene oxide, under conditions such that a polyether-ester polyl, a polyester polyl or a polyether-polyester polyl, having primary hydroxyl functionality, is formed; provided that both steps are carried out in the presence of an amine catalyst and a double metal cyanide catalyst.

[0007] In yet another embodiment, the invention provides a polyurethane product prepared by a process comprising reacting an organic polysisocyanate and a polyol having primary hydroxyl functionality prepared by a process including the steps of (a) reacting a polyether polyl, a polyester polyl, polyether-ester polyl or a polyether-polyester polyl, having predominantly secondary hydroxyl functionality, with a cyclic anhydride of a polycarboxylic acid, under conditions such that a half acid ester is formed; and (b) reacting the half acid ester with ethylene oxide, under conditions such that a polyether-ester polyl, a polyester polyl or a polyether-polyester polyl, having primary hydroxyl functionality, is formed; provided that both steps are carried out in the presence of an amine catalyst and a double metal cyanide catalyst.

[0008] The present invention provides a method of converting a secondary hydroxyl capped polyl into a polyether-ester polyl having a desired level of primary
hydroxyl capping. Such capping may, in certain non-limiting embodiments, range from 10 percent to 95 percent, based on the weight of the starting secondary hydroxyl capped polyol. The method is one which requires less ethylene oxide than prior art methods, thereby producing a product which, when used to formulate polyurethanes, may contribute to desirable improvements in several properties of those polyurethanes while being less expensive to produce. In particular, the polyols produced by the present invention are well suited for the production of flexible polyurethane foam.

[0009] The starting material for the inventive method may include any polyether polyol, polyester polyol, or polyether-ester polyol or polyether-polyester polyol which comprises one or more secondary hydroxyl end-groups per molecule, provided that such secondary hydroxyl end-groups predominate. By "predominate" and "predominantly" are meant herein that more than 50 percent of the end-groups per molecule are secondary hydroxyls, while the remaining portion, if any, may be primary hydroxyl groups and/or other types of terminal isocyanate reactive groups, such as carboxyl groups, that do not interfere with the inventive process.

[0010] Such starting polyol may be selected from, for example, any polyols conventionally employed in the production of polyurethanes, and blends thereof, which preferably have an equivalent weight ranging from 50 daltons (Da) to 10,000 Da. In certain particular embodiments the equivalent weight ranges from 200 to 8,000 Da, and in other particular embodiments it ranges from 500 Da to 3,000 Da. Preparation of such predominantly secondary hydroxyl capped polyols may be by, for example, KOH catalyzed propoxylation of a polyhydric alcohol with 1 to 9 hydroxy groups, an organic amine or aminoalcohol with from 1 to 9 active hydrogen atoms; double metal cyanide complex (DMC) catalyzed propoxylation of a polyol derived from natural resources, such as castor oil, that are epoxidized and/or maleated ring-opened with a functional compound natural oil, or any other natural oil modified to introduce active hydrogen containing moieties, suitable for further alkoxylation; or a mono- or polycarboxylic acid, an alkoxo ester, or a half acid ester prepared from a polyhydric alcohol with from 0 to 8 carboxy groups and/or from 1 to 9 hydroxy groups. Such polymerizations may be carried out by methods well-known to those skilled in the art, generally in the presence of one or more polymerization catalysts and at elevated temperatures in order to facilitate the reaction. Another method of preparation of the starting polyol is by
polymerization of other epoxides in addition to propylene oxide, such as butylene oxide, styrene oxide or ethylene oxide, in the presence of a catalyst, such as a DMC complex catalyst, with an active hydrogen-containing compound as the polyl initiator.

[0011] DMC compounds are well known as catalysts for epoxide polymerization. These catalysts are often highly active, have relatively high surface areas, typically within the range of from 50 to 200 square meters per gram (m²/g), and may produce polyether polyols, in particular, that have lower unsaturation when compared with otherwise similar polyols made using basic (KOH) catalysis. The catalysts can be used to make a variety of polymer products, including polyether, polyester, and polyether-ester polyols.

[0012] In some embodiments, a DMC compound may comprise a reaction product of a water-soluble metal salt and a water-soluble metal cyanide salt. A water-soluble metal salt may have the general formula

\[ \text{M(X)} \]  

(Formula 1)

in which M is a metal and X is an anion. M may be selected from 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(V), W(VI), Cu(II), and Cr(III). It may be desirable in some embodiments for M to be selected from Zn(II), Fe(II), Co(II), and Ni(II). X may be an anion selected from the group including halide, hydroxide, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate, and nitrate. The value of n may be from 1 to 3 and satisfy the valence state of M. Examples of a suitable metal salt may include, without limitation, zinc chloride, zinc bromide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) formate, nickel(II) nitrate, and combinations thereof.

[0013] A water-soluble metal cyanide salt may have the general formula

\[ (Y)_a \text{M'(CN)}_b (A) \]  

(Formula 2)

in which M' may be selected from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV), V(V), and combinations thereof, and CN is cyanide. It may be desirable in some embodiments for M' to be selected from Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III), Ni(II), and combinations thereof. It
may also be desirable that Y be an alkali metal ion or alkaline earth metal ion, while A may be an ion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate, and nitrate. Both a and b are integers equal to or greater than 1. In addition, the sum of the charges of a, b, and c balances the charge of M'. Examples of a suitable metal cyanide salt may include, without limitation, potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III), lithium hexacyano-cobaltate(III), and combinations thereof.

[0014] A solid DMC catalyst that is useful for epoxide polymerizations generally may include an organic complexing agent, often of a relatively low molecular weight and often containing a heteroatom. In some non-limiting embodiments it may be desirable or necessary for a complexing agent to be soluble in water. The complexing agent may be added during preparation and/or immediately following precipitation of the catalyst, and is frequently employed in excess. Examples of some suitable complexing agents are described in greater detail in U.S. Patents 5,158,922; 3,427,256; 3,427,334; and 3,278,459; which are incorporated herein by reference in their entireties. Such complexing agents may include alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides, polyether polyols and combinations thereof. In alternative embodiments the complexing agent may include, without limitation, a water-soluble aliphatic alcohol selected from ethanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, and tert-butyl alcohol, and tert-butyl alcohol (t-butanol) may be preferred in certain applications. In another embodiment, the selected complexing agent may be an ether, such as glyme (dimethoxyethane) or diglyme. In one conventional preparation, aqueous solutions of zinc chloride (in excess amount) and potassium hexacyanocobaltate may be combined by simple mixing. The resulting precipitate of zinc hexacyanocobaltate is then mixed with aqueous glyme. The active DMC catalyst obtained has the formula:

\[ \text{Zn}_3\text{[Co(CN)\text{6}]}_2\times \text{ZnCl}_2\cdot \text{yH}_\text{2O}\cdot \text{zGlyme} \]

(Formula 3)

[0015] DMC compounds prepared in the absence of a complexing agent are highly crystalline, as shown by X-ray diffraction analysis, and are inactive for expoxide polymerization, but may still be, along with the highly crystalline DMC compounds
prepared with a complexing agent, useful in the process of the present invention. Some researchers have shown that conventional DMC catalysts include both crystalline and amorphous components. Typically, these DMC catalysts, which are generally prepared by simple mixing, still contain at least 35 weight percent of highly crystalline DMC compound. However, there are some conventional DMC compounds, useful for epoxide polymerizations, which contain less than 30 weight percent of the highly crystalline component. These may be prepared by a method wherein aqueous solutions of a water-soluble metal salt and a water-soluble metal cyanide salt are intimately combined in the presence of the complexing agent, such as is disclosed in U.S. Patent 5,731,407, which is incorporated herein by reference in its entirety.

Examples of DMC compounds useful both in epoxide polymerizations, to prepare the starting secondary hydroxyl group-containing compound and in the conversion process of the present invention, may include zinc hexacyanocobaltate(III), zinc hexacyanoferrate(III), zinc hexacyanoferrate(III)zinc hexacyanoferrate(II), nickel(II) hexacyanoferrate(II), cobalt(II) hexacyano-cobaltate(III), and the like. In certain embodiments, it may be particularly desirable to use zinc hexacyanocobaltate(III). Further examples are listed in U.S. Patent 5,158,922, which is incorporated herein by reference in its entirety.

In some embodiments, a solid DMC catalyst may include from 5 to 80 weight percent, based on the total amount of catalyst, of a polyether. For example, it may be desirable to include from 10 to 70 weight percent of the polyether. In other embodiments it may be desirable to include from 15 to 60 weight percent of the polyether.

Such polyether may, in some embodiments, have an average of from 1 to 9 hydroxyl functionalities. In some embodiments, a polyether polyol may have a number average molecular weight of from 200 to 10,000. A polyether polyol may be made by polymerizing an epoxide in the presence of an active hydrogen-containing initiator and a basic, acidic, or organometallic catalyst (for example, a DMC catalyst), in some embodiments. Examples of a polyether polyol may include, without limitation, poly(propylene glycol)s, poly(ethylene glycol)s, ethylene oxide-capped poly(oxypropylene) polyols, mixed ethylene oxide/propylene oxide polyols, butylene oxide polymers, butylene oxide copolymers with ethylene oxide and/or propylene
oxide, polytetramethylene ether glycols, and combinations thereof. Examples of a polyether polyol may include, without limitation, tripropylene glycol, triethylene glycol, tetrapropylene glycol, tetraethylene glycol, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, monoalkyl and dialkyl ethers of glycols and poly(alkylene glycol)s, and combinations thereof. In some embodiments, poly(propylene glycol)s and poly(ethylene glycol)s having number average molecular weights within the range of from 150 to 500 may be used. An organic complexing agent and a polyether, according to some embodiments, may be used in a double metal cyanide catalyst.

Thus, a DMC catalyst may be fully described, in some embodiments, by the following formula:

$$M^1_{\text{d}}[M^2(CN)_b(A)_c]_dF^iM^1_nX_hH_2O_eL^kP$$

(Formula 4)

wherein

- $M^1_{\text{d}}$ is at least one metal ion selected from the group consisting of $\text{Zn}^{2+}$, $\text{Fe}^{3+}$, $\text{Fe}^{2+}$, $\text{Ni}^{2+}$, $\text{Mn}^{2+}$, $\text{Co}^{2+}$, $\text{Sn}^{2+}$, $\text{Pb}^{2+}$, $\text{Mo}^{6+}$, $\text{Mo}^{5+}$, $\text{Al}^{3+}$, $\text{V}^{4+}$, $\text{V}^{5+}$, $\text{Sr}^{2+}$, $\text{W}^{4+}$, $\text{W}^{6+}$, $\text{Cr}^{3+}$, $\text{Cr}^{2+}$, $\text{Cd}^{2+}$, $\text{Hg}^{2+}$, $\text{Pd}^{2+}$, $\text{Pt}^{2+}$, $\text{V}^{2+}$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, $\text{Cu}^{2+}$, $\text{La}^{3+}$, $\text{Ce}^{3+}$, $\text{Ce}^{4+}$, $\text{Eu}^{3+}$, $\text{Ti}^{3+}$, $\text{Ti}^{4+}$, $\text{Ag}^+$, $\text{Rb}^{3+}$, $\text{Rb}^{3+}$, $\text{Ru}^{2+}$, and $\text{Ru}^{3+}$;
- $M^2_{\text{d}}$ is at least one metal ion selected from the group consisting of $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Co}^{2+}$, $\text{Co}^{3+}$, $\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{V}^{4+}$, $\text{V}^{5+}$, $\text{Cr}^{2+}$, $\text{Cr}^{3+}$, $\text{Rh}^{3+}$, $\text{Ru}^{2+}$, and $\text{Ir}^{3+}$;
- $A$ and $X$ are each, independently of one another, an anion selected from the group consisting of halide, hydroxide, sulfate, carbonate, cyanide, thiocyanate, isocyanate, cyanate, carboxylate, oxalate, nitrate, nitrosyl, hydrogensulfate, phosphate, dihydrogenphosphate, hydrogenphosphate and hydrgenocarbonate;
- $L$ is a water-miscible ligand selected from the group consisting of alcohols, aldehydes, ketones, ethers, polyethers, esters, polyesters, polycarbonate, ureas, amides, primary, secondary and tertiary amines, ligands having a pyridine nitrogen, nitriles, sulfides, phosphides, phosphites, phosphanes, phosphonates and phosphates;
- $k$ is a fraction or integer greater than or equal to zero;
- $P$ is an organic additive;
a, b, c, d, g and n are selected such that the compound of Formula 4 is electrically neutral, with c being able to be 0;
e is the number of ligand molecules and is a fraction or integer equal to or greater than 0; and

f and h are each, independently of one another, a fraction or integer equal to or greater than 0.

Examples of an organic additive P may include, without limitation, polyethers, polyesters, polycarbonates, polyalkylene glycol sorbitan esters, polyalkylene glycol glycidyl ethers, polyacrylamide, poly(acrylamide-co-acrylic acid), polyacrylic acid, poly(acrylamide-comaleic acid), polyacrylonitrile, polyalkyl acrylates, polyalkyl methacrylates, polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl acetate, polyvinyl alcohol, poly-N-vinylpyrrolidone, poly(N-vinylpyrrolidone-co-acrylic acid), polyvinyl methyl ketone, poly(4-vinylphenol), poly(acrylic acid-co-styrene), oxazoline polymers, polyalkyleneamines, malic acid and maleic anhydride copolymers, hydroxyethylcellulose, polyacetates, ionic surface-active and interface-active compounds, bile acids or their salts, esters or amides, carboxylic esters of polyhydric alcohols and glycosides. Examples of some DMC catalysts and their preparation may be found in U.S. Patents 3,427,334; 3,941,849; 4,477,589; 5,158,922; 5,470,813; 5,482,908; and 7,348,460.

Use of a DMC catalyst to prepare a secondary hydroxyl containing polyether polyl, polyester polyl, or polyether-ester polyl for use as a starting material in the present invention may be found in, for example, U.S. Patents 5,223,583; 5,145,883; 4,472,560; 3,941,849; 3,900,518; 3,538,043; 3,404,109; 3,278,458; 3,278,457; and in J.L. Schuchardt and S.D. Harper, *SPI Proceedings, 32nd Annual Polyurethane tech./Market. Conf.*, (1989) 360, which are incorporated herein by reference in their entireties. In general, polyether polyols are made by the reaction of epoxides (oxiranes) with active hydrogen-containing starter compounds, while polyester polyols are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. Use of propylene oxide to extend the polyols results in mainly (90 to 95 percent by weight) secondary capped materials, while use of combinations of propylene oxide and ethylene oxide results in species that include both primary and secondary hydroxyl groups, with the molar ratio of the two alkoxides
helping to determine the proportion of secondary versus primary end capping. The amount of the ethylene oxide in the mixed feed is, in certain preferred embodiments, not higher than 75 percent of the total number of moles, in order to avoid broad polydispersity and heterogeneity of the resulting product. In this case, primary hydroxyl level in the resulting polyol may, in some embodiments, be preferably not higher than 70 percent.

[0022] Following selection of a desired polyol which is predominantly secondary hydroxyl-capped, it is reacted, preferably at a temperature ranging from 90 degrees Celsius (°C) to 180°C, with a cyclic anhydride of a polycarboxylic acid. In certain particular embodiments the temperature ranges from 120°C to 150°C, and in other particular embodiments, it ranges from 130°C to 140°C. The cyclic anhydride of a polycarboxylic acid may be prepared, in general, by the dehydrogenation of the given polycarboxylic acid, though methods involving oxidation or carbonylation may be used, depending on the character of the polycarboxylic acid. For example, maleic anhydride may be produced by the oxidation of butane, but it is still a cyclic anhydride of a polycarboxylic acid (maleic acid). Similarly, phthalic anhydride can be produced by catalytic oxidation of o-xylene. Other useful acids that may be used as starting materials to prepare the anhydride may include, but are not limited to, succinic acid, maleic acid, phthalic acid, and combinations thereof.

[0023] This first-step reaction is desirably carried out in the presence of an amine catalyst and a DMC catalyst. The DMC catalyst may be selected from any described hereinabove. The amine catalyst may be selected from any effective amine, but such may typically include the N-alkylmorpholines, N-alkyl-alkanolamines, aminoalcohols, N,N-diarylalkylamines, alkylamines where the alkyl groups are methyl, ethyl, propyl, butyl and isomeric forms thereof, and heterocyclic amines. Typical but non-limiting specific examples thereof are 1-methyl-imidazole, triethylenediamine, tetramethylethylenediamine, bis(2-dimethyl-aminoethyl)ether, triethanolamine, triethylamine, tripropylamine, tributylamine, triamylamine, pyridine, quinoline, dimethylpiperazine, piperazine, N,N-diethyl-cyclohexylamine, N-ethyl-morpholine, 2-methylpropanedi amine, methyltriethylene-diamine, 2,4,6-tri-dimethyl-aminomethyl)phenol, N,N',N''-tris(dimethylaminopropyl)-sym-hexahydrotriazine, and combinations thereof. A preferred group of tertiary amines comprises 1-methyl-
imidazole, bis(2-dimethyl-aminoethyl)ether, dimethylcyclo-hexylamine, N,N-dimethyl-ethanolamine, triethylenediamine, triethylamine, triisopropylamine, 2,4,6-tri(dimethylaminomethyl)-phenol, N,N’,N-ethylmorpholine, and combinations thereof.

The result of the reaction of the starting polyol with the cyclic anhydride of a polycarboxylic acid is the half acid ester product. This reaction may be shown formulaically by the following first reaction sequence example, wherein a secondary hydroxyl-containing polyether polyol, prepared by the propoxylation of n-butanol, is reacted with one equivalent of succinic anhydride in the presence of 1000 parts per million (ppm) of 1-methylimidazole catalyst at 150°C for two hours, to form the corresponding half acid ester.

Step 1:

![Reaction Sequence](image)

(First reaction sequence)

It will be obvious, in view of the description herein, that the identification of starting reactants, product, catalyst, catalyst concentration, temperature and time are included only for illustrative, not limitative, purpose. In general, time for this first step may vary from 1 hour to 4 hours for commercial practicability; the amine catalyst amount may range from 100 parts per million (ppm) to 10,000 ppm, though it is preferred that an amount from 100 ppm to 1,000 ppm be employed; and the DMC catalyst amount may range from 10 ppm to 1,000 ppm, though it is preferred that an amount from 10 ppm to 50 ppm be employed. The half acid ester is determined, by proton nuclear magnetic resonance (^H-NMR) spectroscopy, to be approximately 85 percent to 95 percent acid-capped in the reaction sequence hereinabove.

Following this conversion to the half acid ester, a second step may be carried out. In this second step, the half acid ether-ester is reacted, preferably at a temperature from 50°C to 150°C, with ethylene oxide. In this case the reaction is again carried out in the presence of an amine catalyst and a DMC catalyst, which may be independently the same as, or different from, the catalysts used in the first step. For convenience, it is often preferable to employ the same catalysts, which may remain
from the first step and/or be replaced by or augmented with additional catalyst(s) added at the beginning of the second step.

[0026] Continuing the formulaic example reaction shown hereinabove, the second step may be represented by the second reaction sequence, shown hereinbelow. Again, it will be obvious, in view of the description herein, that the identification of reactants, product, catalyst, catalyst concentration, temperature and time are included only for illustrative, not limitative, purpose. In this portion of the process, the half acid ester is converted to the primary hydroxyl capped polyether polyl by reaction with ethylene oxide in the presence of 50 ppm of the DMC catalyst, at 140°C, as follows.

Step 2:

(Second reaction sequence)

[0027] Of particular advantage in the present invention is the fact that, if the starting polyol is prepared using a DMC catalyst, such may be allowed to remain in the polyol through the first step. In this case it is frequently not necessary to add more DMC catalyst for the second step. The presence of the amine catalyst serves to improve the DMC-catalyzed EO capping while carboxylic acid groups are present. However, once the acid is reacted away, the presence of the amine catalyst may facilitate an undesirable transesterification reaction. Thus, in preferred embodiments it is desirable to use as little of the amine catalyst as possible, while also minimizing the temperature and reaction time. Furthermore, because the amount of DMC needed is low (generally from 10 to 50 ppm), no additional polyol finishing step is required to remove residual catalyst.

[0028] In general, the reaction sequence may be carried out on a batch, semi-batch, or continuous basis. Time for the second step may range from 0.5 to 2 hours, and in certain embodiments may be, for commercial practicability, from 0.5 to 1 hour.

[0029] The final polyol may be characterized as a primary hydroxyl alkoxo ester compound, which may be alternatively characterized as a polyether-ester polyol, a polyester polyol or a polyether-polyester polyol having primary hydroxyl capping. The amount of primary hydroxyl capping may vary from 10 percent to 95 percent in certain
particular and non-limiting embodiments. Control of the percent primary hydroxyl capping achieved, that is, of the conversion rate from secondary to primary capping, will depend upon the relative amount of the cyclic anhydride in comparison with the amount of hydroxyl groups in the starting hydroxyl-capped polyol. Such may range from 0.1:1 to 1:1, cyclic anhydride:hydroxyl groups in the starting polyol. In general, the molar amount of ethylene oxide incorporated in the second step is generally closely comparable to the molar amount of the cyclic anhydride of a polycarboxylic acid used in the first step of the process, no matter how large an excess of ethylene oxide is used for the reaction. Desirably this ratio is from 1.05:1 to 1.5:1, ethylene oxide:cyclic anhydride of a polycarboxylic acid. Any unreacted polycarboxylic acid anhydride (generally, not more than 10 percent of the total amount of anhydride taken for the first step), that may have remained from the first step, will be incorporated together with the ethylene oxide into the polyol chain end-capping, forming primary hydroxyl-capped alternating polyester. If ethylene oxide is used in an amount such that its molar amount is less than that of the half acid ester, corresponding unreacted acidity will remain in the polyol. Thus, a small amount of ethylene oxide, in the amount of less than 5 percent by weight, may effectively convert a polyether polyl containing more than 50 percent of secondary hydroxyl functionality, based on total functionality, into a polyether-ester polyl containing more than 90 percent of primary hydroxyl functionality, based on total functionality. The remaining acidity of the product polyol is generally low (less than 1 mg/g as KOH). Additional polyol post-treatment may be introduced to neutralize this remaining acidity, for instance, addition of equimolar amounts of epoxy resins or amines/aminoalcohols.

[0030] Overall, the process of the invention represents a cost savings as well as a final product offering reduced hydrophilicity and miscibility problems, and also improved reactivity. These advantages may translate into better quality polyurethanes made therefrom, particularly as to properties such as cure rate, wet compression set, flame lamination properties, thermal insulation, demold expansion, thermal stability, and flame retardancy.

EXAMPLES
Catalyst Preparation
A DMC catalyst is synthesized by adding, in a three-necked, round-bottomed flask 11.1 grams (g) (0.033 moles (mol)) K₂Co(CN)₆, 453 g (25.17 mol) water (H₂O), and 58.5 g (0.789 mol) t-butanol and stirring at more than 200 revolutions per minute (rpm) for 30 minutes at 30°C. A mixture of 114 g (0.836 mol) ZnCl₂ and 114 g (6.33 mol) H₂O is then added at a rate of 5 milliliters per minute (mL/min). Temperature is maintained within a maximum range of ±4°C during mixing to avoid a drop in activity. Stirring is continued for 30 more minutes. The result, a milk-like dispersion, is centrifuged at 10,000 rpm for 30 minutes. The precipitate is washed for 30 minutes in a mix of 153 g (2.06 mol) t-butanol and 84 g (4.67 mol) H₂O, under vigorous stirring, prior to centrifugation at 10,000 rpm for 30 minutes. The second wash is a repeat of the first, but the amount of t-butanol and H₂O are altered to 214 g (2.89 mol) and 1.5 g (0.083 mol), respectively. Following centrifugation the precipitate is dried for 16 hours (hr) at 20-30 millibar (mbar) (2-3 kilopascals, kPa) at 50°C. The product is then milled in a mortar to break up any agglomerates, and the catalyst, approximately 15 g, is obtained as a fine white powder.

The catalyst is then analyzed for the metals cobalt, potassium, and zinc using X-Ray Fluorescence (XRF) and Inductively Coupled Plasma Emission Spectrometry (ICP-ES) in an aqua regia (nitro-hydrochloric acid) digest. The elemental composition is found to be as follows: Potassium, 0.31 weight percent; zinc, 25.2 weight percent; cobalt, 11.1028 weight percent; potassium/cobalt, 0.028 weight percent; and water, 7.0489 weight percent.

Preparation of Starting Polyether Polyol

About 0.0566 g (50 ppm based on the weight of the product) of the DMC catalyst is added to 280.9 g of n-butanol tripoxylate (DOWANOL™ TPnB, available from The Dow Chemical Company) in a 6-liter laboratory stainless steel alkoxylation reactor. The mixture is flushed with nitrogen (N₂) and stripped in vacuum of water and volatiles at 110°C for 1 hr with stirring. Temperature is raised to 130°C and 100 g of propylene oxide (PO) are added to the vacuumized reactor at a feed rate of 15 grams per minute (g/min) to establish a PO pressure of 3 bar (300 kilopascals, kPa). Activation of the catalyst is observed within 2 minutes following completion of the feed by an abrupt pressure drop in the reactor. The PO feed is resumed and 760 g PO
are fed to the reactor at a feed rate of 15 g/min. A 0.5 hr digestion time is allowed upon
the end of the second PO feed. The product is stripped of unreacted PO via vacuum for
0.5 hr at 100°C. A colorless liquid is obtained.

The product has the following properties: hydroxyl number 56.2 mg/g
KOH, water 205 ppm, unsaturation 0.003 meq/g, viscosity at 25°C 107 centistokes
(cSt).

Example 1

About 0.975 g (1000 ppm by weight) of N-methylimidazole is added to a
mixture of 885 g of an n-butanol-initiated monol, polypropylene oxide polyether
polyol, prepared similarly as described in the "Polyether Polyl Preparation" section
hereinabove (but having as properties: hydroxyl number 56.6 mg/g KOH, water 410
ppm, unsaturation 0.0071 meq/g, viscosity at 25°C 110 centistokes (cSt)), which also
contains the DMC catalyst used to prepare the polyol, and 89.4 g of crystalline succinic
anhydride (99 percent purity) in a 1 liter laboratory Pyrex glass esterification reactor.
The mixture is flushed with nitrogen (N₂) and heated in an N₂ atmosphere at 150°C for
1 hr and at 170°C for 1 hr with stirring. The reactor is cooled to room temperature. A
colorless liquid is obtained.

This liquid, the intermediate product, has the following properties:
hydroxyl value 11.1 mg KOH/g; acid value 54.7 mg KOH/g; total unsaturation 0.04
meq/g; water 640 ppm; viscosity at 25°C 331 cSt; ^1H-NMR: 86 percent of all chains are
acid-capped.

An additional amount, 0.04 g (50 ppm weight), of the DMC catalyst is
added to 748 g of the intermediate product in a 6-liter laboratory stainless steel
alkoxylation reactor. An amount of N-methylimidazole is also still present from the
first step. The reaction mixture is flushed several times with 3.5 bar (350 kPa) nitrogen
(N₂) pressure with stirring at 300 ppm, and vacuum is applied for 5 minutes to the
reactor at ambient temperature with 1 bar (100 kPa) of N₂ pressure added. The reactor
is thermostated at 140°C and pressurized with 2.6 bar (260 kPa) of N₂ pressure. An
amount, 50 g, of EO (1.14 mol, 1.5 eq/acid function) is fed to the reactor at once,
giving a maximum pressure of 5 bar (500 kPa). The immediate reaction is
accompanied by a visible exotherm. The mixture is allowed to digest for 1 hr following
completion of the feed. The product is stripped of unreacted EO in vacuum for 1 hr at 100°C. A colorless liquid is obtained.

[0038] The properties of the final product are as follows: hydroxyl value: 60.6 mg KOH/g; acid value: 0.55 mg KOH/g; total unsaturation: 0.0069 meq/g; water 650 ppm; viscosity at 25°C 265 cSt. ¹H+¹³C-NMR: 1 percent of all chains are half acid ester-capped; 85 percent of all chains are primary hydroxyl EO-capped; 14 percent are secondary hydroxyl PO-capped.

Comparative Example A

[0039] An amount, 104.0 g, of crystalline succinic anhydride (99 percent purity) is added to 1040 g of an n-butanol-initiated monol, polypropylene oxide polyether polyol, prepared as described in the "Polyether Polyol Preparation" section hereinabove, containing only DMC catalyst (no amine catalyst), in a 6-liter laboratory stainless steel alkoxylation reactor. The mixture is flushed with nitrogen (N₂) and heated in an N₂ atmosphere at 130°C for 1 hr and at 140°C for 2 hr with stirring. The reactor is cooled to room temperature. A colorless liquid is obtained.

[0040] This liquid, the intermediate product, has the following properties: hydroxyl value 13.0 mg KOH/g; acid value 52.9 mg KOH/g; total unsaturation 0.0028 meq/g; water 340 ppm; viscosity at 25°C 333 cSt; ¹H+¹³C-NMR: 75 percent of all chains are acid-capped.

[0041] An amount, 836 g, of the intermediate product is placed into a 6-liter laboratory stainless steel alkoxylation reactor. The reaction mixture is flushed several times with 3.5 bar (350 kPa) nitrogen (N₂) pressure with stirring at 300 ppm, and vacuum is applied for 5 minutes to the reactor at ambient temperature, followed by addition of 1.6 bar (160 kPa) of N₂ pressure. The reactor is thermostated at 140°C with stirring. An amount, 58 g, of ethylene oxide (EO) (1.32 mol, 1.5 eq/acid function) is fed to the reactor at once, giving a maximum pressure of 3.7 bar (370 kPa). The immediate reaction is accompanied by a visible exotherm. The mixture is allowed to digest for 17 hr following completion of the feed. The product is stripped of unreacted EO in vacuum for 1 hr at 100°C. A colorless liquid is obtained.

[0042] The properties of the final product are as follows: hydroxyl value: 41.6 mg KOH/g; acid value: 13.6 mg KOH/g; total unsaturation: 0.001 meq/g; water 430 ppm;
viscosity at 25°C 226 cSt. \textsuperscript{\textcircled{+}} C-NMR: 24.6 percent of all chains are half acid ester-capped; 39 percent of all chains are primary hydroxyl EO-capped; 30 percent are secondary hydroxyl PO-capped; and 6.4 percent of all chains are EO-capped and doubly-esterified.
CLAIMS

1. A process for the preparation of a polyol having primary hydroxyl functionality prepared by a process comprising the steps of
   (a) reacting a polyether polyol, a polyester polyol, polyether-ester polyol or a polyether-polyester polyol, having predominantly secondary hydroxyl functionality, with a cyclic anhydride of a polycarboxylic acid, under conditions such that a half acid ester is formed; and
   (b) reacting the half acid ester with ethylene oxide, under conditions such that a polyether-ester polyol, a polyester polyol or a polyether-polyester polyol, having primary hydroxyl functionality, is formed;
   provided that both steps are carried out in the presence of an amine catalyst and a double metal cyanide catalyst.

2. The process of Claim 1 wherein the primary hydroxyl functionality ranges from 10 to 95 percent of total functionality and the polycarboxylic acid is succinic acid, maleic acid, phthalic acid, or a combination thereof.

3. The process of Claim 1 wherein the cyclic anhydride of a polycarboxylic acid and the polyether polyol, polyester polyol, polyether-ester polyol or polyether-polyester polyol are employed in a molar ratio ranging from 0.1:1 to 1.1:1.

4. The process of Claim 1 wherein the ethylene oxide and the cyclic anhydride of a polycarboxylic acid are employed in a molar ratio ranging from 1.05:1 to 1.5:1.

5. The process of Claim 1 wherein the amount of the double metal cyanide catalyst ranges from 10 to 1,000 weight ppm and the amount of the amine catalyst ranges from 100 to 10,000 weight ppm.

6. The process of Claim 1 wherein the initiator of the polyether polyol, the polyester polyol, the polyether-ester polyol or the polyether-polyester polyol is a
polyhydric alcohol with 1 to 9 hydroxy groups, an organic amine or aminoalcohol with from 1 to 9 active hydrogen atoms; or a mono- or polycarboxylic acid, an alkoxo ester or a half acid ester prepared from a polyhydric alcohol having groups selected from (1) from 0 to 8 carboxy groups, (2) from 1 to 9 hydroxy groups, or (3) both (1) and (2).

7. The process of Claim 1 wherein step (a) is carried out at a temperature ranging from 90°C to 180°C.

8. The process of Claim 1 wherein the polyether polyl, polyester polyl, polyether-ester polyl or polyether-polyester polyl having predominantly secondary hydroxyl functionality has an equivalent weight ranging from 100 to 10,000 daltons.

9. The process of Claim 1 wherein step (b) is carried out at a temperature ranging from 50°C to 150°C.

10. A polyol having primary hydroxyl functionality prepared by a process comprising the steps of

(a) reacting a polyether polyl, a polyester polyl, polyether-ester polyl or a polyether-polyester polyl, having predominantly secondary hydroxyl functionality, with a cyclic anhydride of a polycarboxylic acid, under conditions such that a half acid ester is formed; and

(b) reacting the half acid ester with ethylene oxide, under conditions such that a polyether-ester polyl, a polyester polyl or a polyether-polyester polyl, having primary hydroxyl functionality, is formed;

provided that both steps are carried out in the presence of an amine catalyst and a double metal cyanide catalyst.

11. A polyurethane product prepared by a process comprising reacting an organic polyisocyanate and a polyol having primary hydroxyl functionality prepared by a process including the steps of

(a) reacting a polyether polyl, a polyester polyl, polyether-ester polyl or a polyether-polyester polyl, having predominantly secondary hydroxyl functionality,
with a cyclic anhydride of a polycarboxylic acid, under conditions such that a half acid ester is formed; and

(b) reacting the half acid ester with ethylene oxide, under conditions such that a polyether-ester polyol, a polyester polyol or a polyether-polyester polyol, having primary hydroxyl functionality, is formed;

provided that both steps are carried out in the presence of an amine catalyst and a double metal cyanide catalyst.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/48 C08G65/26 C08G65/332
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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