INSTRUCTIONS

(a) If Convention application insert "Convention"

AMENDED

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(a) convention

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(b) Delete one

APPLICATION FOR A (b) STANDARD/~~PETTY~~ PATENT

(c) Insert FULL name(s) of applicant(s)

I/We (c) THE DOW CHEMICAL COMPANY

(d) Insert FULL address(es) of applicant(s)

of (d) 2030 Dow Center, Abbott Road,
Midland, Michigan 48640,
United States of America

(e) Delete one

hereby apply for the grant of a (e) Standard/~~Petty~~ Patent for an invention entitled

(f) Insert TITLE of invention

(f) POLYURETHANE FOAM PREPARED USING HIGH FUNCTIONALITY CELL OPENERS AND PROCESS FOR PREPARING THE SAME

(g) Insert "complete" or "provisional" or "petty patent"

which is described in the accompanying (g) complete specification.

(Note: The following applies only to Convention applications)

Details of basic application(s)

(h) Insert number, country and filing date for the/or each basic application

Application No.	Country	Filing Date
(h) 186,418	United States of America	26 April, 1988
270,178	United States of America	14 November, 1988

Address for Service: PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

(i) Insert date of signing

M 009738 080689

Dated (i) 7 June, 1989

(j) Signature of applicant(s) (For body corporate see headnote*)

(k) Corporate seal if any

(k)

(j) PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
THE DOW CHEMICAL COMPANY

Note: No legalization or other witness required

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P17/2/83

CONVENTION

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619277

NOTICE OF ENTITLEMENT

We, THE DOW CHEMICAL COMPANY OF 2030 Dow Center, Abbott Road, Midland, Michigan 48640, United States of America state the following in connection with Australian Application No. 33177/89:

1. The nominated person is the assignee of the actual inventors.

2. The nominated person is the assignee of the applicants.

3. The basic applications are the applications first made in a Convention country in respect of the invention.

4. The inventors are as follows: Jerram B. Nichols, Douglas L. Hunter, Ronald M. Herrington and John F. Serratelli.

Dated: 30 October 1991

By PHILLIPS ORMONDE & FITZPATRICK
Patent Attorneys for the Applicant
By:

David B Fitzpatrick

.....

To: The Commissioner of Patents

Our Ref: 128914

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POLYURETHANE FOAM PREPARED USING HIGH FUNCTIONALITY CELL OPENERS AND PROCESS FOR PREPARING THE SAME

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(56) Prior Art Documents
US 3042631
GB 1450105

(57) Claim

1. A one shot process for making polyurethane foam, comprising reacting a reaction mixture comprising

(a) at least one relatively high equivalent weight polyester polyol or polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) an effective amount of a blowing agent;

(c) a high functionality polyether polyol based on an initiator or initiator mixture having at least 4.0 active hydrogens per molecule, which high functionality polyether polyol has a molecular weight of at least 5000 and contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction

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mixture, in an amount sufficient to measurably increase the proportion of open cells in the foam as compared with a similar foam prepared in the absence of said high functionality polyether polyol; and

(d) at least one polyisocyanate.

5. An active hydrogen-containing composition comprising

(a) at least one relatively high equivalent weight polyester polyol or polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) a high functionality polyether polyol based on an initiator or initiator mixture having at least 4.0 active hydrogens per molecule, which high functionality polyether polyol has a molecular weight of at least 5000 and contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture, in an amount sufficient to measurably increase the proportion of open cells in a foam made by reacting the active hydrogen-containing composition with a polyisocyanate as compared with a similar foam prepared in the absence of said high functionality polyether polyol; and optionally

(c) an effective amount of a blowing agent.

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Complete Specification for the invention entitled:

POLYURETHANE FOAM PREPARED USING HIGH FUNCTIONALITY CELL OPENERS AND PROCESS FOR PREPARING THE SAME

Our Ref : 128914
POF Code: 1037/1037

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

POLYURETHANE FOAM PREPARED USING HIGH FUNCTIONALITY CELL OPENERS AND PROCESS FOR PREPARING THE SAME

This invention relates to the preparation of flexible polyurethane foam, and more particularly to the preparation of such foam using cell opening or softening additives.

In preparing many types of polyurethane foam, particularly the flexible and semi-flexible types, it is necessary that the walls of the individual cells in the foam be ruptured at some point during the foam production. Unless the cells are opened in this manner, the gasses trapped within the cells contract as the foam cools, creating a vacuum in the foam and causing the foam to shrink or collapse.

In many instances, the cell walls will not spontaneously rupture as the foam is made. Accordingly, it is often necessary to promote cell wall rupture either through mechanical means such as crushing, or with the use of certain types of cell opening additives. Certain types of copolymer polyols, particularly those which are prepared by the <u>in situ</u> polymerization of ethylenically unsaturated monomers in a

continuous polyol phase, are effective cell openers. Other types of cell openers include certain polyolefins, particularly polybutene and polybutadiene rubbers, and polyethers of up to 3500 molecular weight which contain a high proportion (usually 50 percent or higher) of oxyethylene units or units derived from butylene oxide. The polyether types are most commonly used when the foam is based on a poly(propylene oxide) polyol.

These cell openers all have certain drawbacks which limit their use or effectiveness. The copolymer polyols must be used in relatively high amounts, so that the copolymer polyol itself becomes a substantial if not major component of the active hydrogen-containing composition which is used to make the foam. When other types of polyols are desired, the copolymer polyol cannot be used in effective amounts. Many of the polyolefins and polybutadienes are less effective than desired and have the additional drawback of bleeding out of the foam, giving it an oily feel and making it more difficult to paint or glue to other materials. They are also incompatible with the other materials used in making the foam, which prevents them from being formulated into the polyol or polyisocyanate blends used in making the foam. Thus, these cell openers must be metered separately into the foam formulation simultaneously with or immediately prior to the start of the foaming reaction. The polyethers are likewise less effective than desired and are often incompatible with the active hydrogen-containing materials used.

Certain types of starting materials provide foams in which the cells are particularly difficult to

open. Among these are the so-called "PIPA" polyols, which are dispersions of polyurea or polyurethane particles in a continuous polyol phase. Although foam made from these materials otherwise have many desirable properties, it is often very difficult to open their cells. Often, th use of particular surfactants and other raw materials compounds the problem.

Often, particularly when using an MDI-based polyisocyanate, the foam is stiffer and more boardy than desired. In those instances, it is often desirable to provide a means by which the foam is made softer.

Accordingly, it would be desirable to provide a cell opener which is effective at low levels and which is substantially compatible with the foam itself and with at least some of the components used in making the foam. It is further desirable to provide a cell opener which is effective in making certain foam in which the cells are particularly difficult to open, such as foam based on a PIPA polyol. In addition, it would be desirable to provide a means whereby a softer foam is prepared, particularly a foam prepared from an MDI--based polyisocyanate.

In one aspect, this invention is a method for making polyurethane foam, comprising reacting a reaction mixture comprising

(a) at least one relatively high equivalent weight polyester polyol, or a polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of

such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) an effective amount of a blowing agent;

(c) a high functionality polyether polyol based on an initiator or initiator mixture having an average of at least 4.0 active hydrogens per molecule, which polyether polyol has a molecular weight of at least 5000 and which contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture, in an amount sufficient to measurably increase the proportion of open cells in the foam as compared with a similar foam prepared in the absence of said high functionality polyether polyol; and

(d) at least one polyisocyanate.

In another aspect, this invention is a method for making polyurethane foam, comprising reacting a reaction mixture comprising

(a) at least one relatively high equivalent weight polyester polyol, or a polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) an effective amount of a blowing agent;

(c) from 1 to 10 parts, per 100 parts of component (a), of a polyether polyol based on an initiator or initiator mixture having an average

of at least 4.0 active hydrogens per molecule, which polyether polyol has a molecular weight of at least 5000 and which contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture; and

(d) at least one polyisocyanate which is based on MDI.

In another aspect, this invention is an active hydrogen-containing composition comprising

(a) at least one relatively high equivalent weight polyester polyol or polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixtures thereof; ~~(b) an effective amount of a blowing agent; and~~

(b) a high functionality polyether polyol based on an initiator or initiator mixture having an average of at least 4.0 active hydrogens per molecule, which polyether polyol has a molecular weight of at least 5000 and which contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture, in an amount sufficient to measurably increase the proportion of open cells in a foam made by reacting the active hydrogen-containing composition with a polyisocyanate as compared

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with a similar foam prepared in the absence of said high functionality polyether polyol; and optionally

(c) an effective amount of a blowing agent.

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~~with a similar foam prepared in the absence of said high functionality polyether polyol.~~

It has surprisingly been found that by using the high functionality polyether polyol described herein, polyurethane foams having significantly greater proportions of open cells are prepared. Accordingly, less shrinkage and distortion of the foam is experienced, and the need to mechanically open the cells is reduced or eliminated. It is further surprising that the high functionality polyether polyol is quite effective at very low levels, and thus has minimal effect on the other desirable properties of the foam. An additional advantage is that the high functionality polyether polyol is compatible with the polyol used in the foam formulation, and can be blended into an active hydrogen-containing composition prior to foaming. The high functionality polyether polyol also exhibits minimal tendency to leach out of the foam. It has been found that this high functionality polyether polyol is particularly effective in the preparation of foam from PIPA polyols.

In the preparation of foams using a polyisocyanate based on MDI, the use of the polyether polyol component (c) provides substantial softening of the foam, and often provides improved cell opening as well.

In this invention, a particular high functionality polyether polyol is used to promote the formation of an open-celled or softened polyurethane foam. The high functionality polyether polyol used herein is based on an initiator or initiator mixture having an average of at least 4.0 active hydrogens per molecule.

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The high functionality polyether polyol further has a molecular weight of at least 5000 and contains at least 50 weight percent oxyethylene units. It also contains sufficient oxypropylene units to render it compatible with the relatively high equivalent weight polyol used as component (a) herein, at the relative proportions thereof present in the reaction mixture.

The high functionality polyether polyol advantageously is based on an initiator or mixture thereof having an average of at least 4.0, preferably 4.5, and more preferably at least 5.0 active hydrogens per molecule. The initiator advantageously contains an average of up to 16, preferably up to 12, and more preferably up to 8 active hydrogens per molecule. Most preferably, the initiator contains an average of from 5.0 to 8.0 active hydrogens per molecule. Examples of such initiators are sucrose, methyl glucoside, ethylene diamine, diethylene triamine and low molecular weight alkylene oxide adducts thereof and sorbitol, or mixtures thereof with lower functionality initiators wherein the mixture has an average functionality of at least 4.0.

The high functionality polyether polyol also advantageously has a molecular weight of at least 5000, preferably at least 7500, more preferably at least 10,000. There is no specific maximum molecular weight as long as the high functionality polyether polyol is liquid and of a viscosity such that it can be processed in foaming equipment. Often, very high molecular weight high functionality polyether polyols can be diluted with an inert solvent, such as water or component (a), to reduce its viscosity to processable

levels. Preferably, the molecular weight of the high functionality polyether polyol is up to 100,000, more preferably up to 50,000.

The high functionality polyether polyol contains at least 50 weight percent oxyethylene units, and sufficient oxypropylene ($-CH_2-CH(CH_3)-O-$) units to render it compatible with the component (a) used in making the foam. It has been found that when the oxyethylene content is less than 50 weight percent, the high functionality polyether polyol is substantially less effective. Preferably, the high functionality polyether polyol contains from 50 to 90, more preferably from 60 to 85, most preferably from 65 to 80 weight percent oxyethylene units and the remainder oxypropylene units and the residue from the initiator material(s).

As mentioned before, the high functionality polyether polyol can be used neat or, if necessary, diluted with a solvent or diluent material which reduces its viscosity. The solvent or diluent material can be any material which reduces the viscosity of the high functionality polyether polyol, but does not have any undesired adverse effect on the reactivity of the foam formulation, or the properties of the resulting foam. Thus, preferred diluents include water, which will also act as a blowing agent, or a polyol, which forms all or part of component (a) in this invention.

When the high functionality polyether polyol is blended with component (a) prior to foaming, it is usually not necessary to use a diluent, even when very

high viscosity high functionality polyether polyols are used.

The high functionality polyether polyol is used in an amount sufficient to measurably increase the proportion of open cells in the foam as compared with a similar foam prepared in the absence of said high functionality polyether polyol, or to measurably soften the foam (e.g., reduce its 65 percent IFD). A reduction in the proportion of open cells can be indirectly determined by measuring the amount of shrinkage exhibited by a foam sample as it cools down from the exotherm released in its preparation. Shrinkage is advantageously decreased by 3 percentage points or more, preferably by 5 percentage points or more, more preferably 10 percentage points or more, and most preferably 20 percentage points or more, as compared to the shrinkage exhibited by foams made without the high functionality polyether polyol. In addition to the reduced shrinkage, the foam is usually easier to crush, that is, less force is required to open the remaining closed cells. Advantageously, from 0.1 to 10, preferably from 0.2 to 5, more preferably from 0.2 to 3 parts by weight of the high functionality polyether polyol are used per 100 parts by weight of component (a).

A softening effect is typically seen, particularly when the foam is made using an MDI-based polyisocyanate, when 1 to 20, preferably 2 to 10, more preferably 3 to 8, parts by weight of the high functionality polyether polyol are used per 100 parts of component (a).

In making a polyurethane foam according to this invention, a reaction mixture is used which comprises at least one relatively high equivalent weight polyester polyol, or a polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or a polymer polyol based on such polyester or polyether polyol (sometimes referred to herein as "component (a)"). Such polyols generally process well to provide a polyurethane foam having good properties. In addition, the high functionality polyether polyol of this invention is particularly effective when this type of polyol is used. Of these, the polyether polyols themselves, amine-terminated derivatives thereof and polymer polyols based on the polyether polyol are preferred, as the high functionality polyether polyol is especially effective when used in conjunction with such polyethers.

The component (a) material has an equivalent weight suitable for the preparation of flexible polyurethane foam. Advantageously, it has an equivalent weight of from 500 to 5000, preferably from 800 to 3000, more preferably from 1000 to 2500. In general, this material also advantageously has an average functionality of from 1.5 to 4, more preferably from 1.8 to 3.0. When the polyisocyanate is MDI or based on MDI, the component (a) material advantageously has an average functionality of from 1.5 to 2.2, more preferably from 1.8 to 2.1. With respect to component (a), and cross-linkers and chain extenders used in this invention, the term functionality refers to the average number of groups per molecule which contain one or more active hydrogen atoms.

Most preferred materials used as component (a) herein are polymers of propylene oxide having an average functionality of from 1.8 to 3.0 and an equivalent weight of 1000-2000 which are optionally end-capped with up to 30, preferably up to 20 weight percent ethylene oxide, as well as amine-terminated derivatives thereof and polymer polyols prepared therefrom, and mixtures thereof.

The amine-terminated derivatives of the polyether polyols can be prepared in the reductive amination of the polyether polyol using ammonia or a primary amine. Alternatively, the amine-terminated derivative can be prepared by reductively aminating the polyol with ammonia and then reacting the resulting primary amine with an ethylenically unsaturated compound such as acrylonitrile to form the corresponding secondary amine, as described in U.S. Patent 3,236,895. Aromatic, amine-terminated polyether can be prepared by reacting the polyol with a diisocyanate, followed by hydrolyzing the free isocyanate groups to amine groups, as described, for example, in U.S. Patent 4,578,500. Alternatively, the polyol can be reacted with a material such as o- or p-chloronitrobenzene to form an ether, followed by reduction of the nitro groups to corresponding amine group, as described in copending application serial no. 035,121, filed April 6, 1987.

Several types of polymer polyols based on polyether or polyester polyols are useful as component (a) in this invention. In this invention, a polymer polyol refers to a dispersion of a polymer in a continuous polyol phase. The dispersed polymer can be

polymer of one or more ethylenically unsaturated monomers, an epoxy resin, a polyurethane or a polyurea. Of these, dispersions of styrene and/or acrylonitrile polymer and copolymers, polyurea dispersions (the so-called ("PHD polyols") and polyurea-polyurethane dispersions (the so-called PIPA polyols) are preferred. Such dispersions are described, for example, in U.S. Patents 4,374,209, 4,092,275 and 4,042,537.

As mentioned before, this invention is particularly effective when component (a) comprises a PIPA polyol such as described in U.S. Patent 4,374,209. These polyols form notoriously closed-celled foams which are very difficult to open. This invention has been found to be very effective even when PIPA polyols are used as component (a).

When the component (a) material is a polyether polyol which is prepared in a base-catalyzed polymerization of one or more alkylene oxides, or a derivative of such a polyol, it is preferred that the base catalyst is neutralized and/or removed from the polyol prior to making a foam therewith. The high functionality polyether polyol used herein is much more effective when the catalyst is neutralized and/or removed.

The other critical component used in making foam according to this invention is a blowing agent. Any material which generates a gas under the conditions of the reaction of the active hydrogen-containing component and the polyisocyanate can be used has a blowing agent herein. Suitable blowing agents include, for example, low boiling organic compounds, water, the so-called "azo" blowing agents and finely divided solids.

Gases such as, for example, air, nitrogen and carbon dioxide may also be used. Preferred are water and low boiling halogenated alkanes such as, for example, refrigerant 11, refrigerant 12, refrigerant 22, refrigerant 123, refrigerant 112 and methylene chloride.

The blowing agent is used in an amount sufficient to provide the foam with a desired density. Typically, a density of from 0.5 (8) to 30 (480), preferably from 1 (16) to 6 (96), more preferably from 1 (16) to 3 (48) pounds per cubic foot (kg/m^3), is desired. When water is the sole blowing agent, such densities are obtained when from 0.1 to 8, preferably from 2 to 6 parts per 100 parts by weight of component (a) are used. However, when an aminated polyether is used as component (a), up to 10 parts water can be used. Such densities can also be obtained with the use of from 2 to 40, preferably from 5 to 20 parts by weight of halogenated alkane blowing agent per 100 parts by weight component (a).

Either aliphatic or aromatic polyisocyanates can be used in this invention to make foam. Suitable aliphatic polyisocyanates include, for example, ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1,5--diisocyanato-3,3,5-trimethylcyclohexane, 2,4- and/or 2,6-hexahydrotoluene diisocyanate, perhydro-2,4'- and/or -4,4'-diphenylmethane diisocyanate ($H_{12}MDI$) and isophorone diisocyanate.

Suitable aromatic polyisocyanates include, for example, 2,4- and/or 2,6-toluene diisocyanate (TDI), 2,4'-diphenylmethane diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 4,4'-diphenylmethane diisocyanate (including mixtures thereof with minor quantities of the 2,4'-isomer and/or 2,2'-isomer), 1,5-naphthylene diisocyanate, triphenylmethane-4,4',4''-triisocyanate and polyphenylpolymethylene polyisocyanates. When the polyisocyanate is MDI or a derivative of MDI (i.e, a polyisocyanate based on MDI), especially a mixture including a polymeric MDI, it is preferred that the amine-terminated compound be substantially difunctional, i.e., have an average functionality of from 1.5 to 2.2, preferably from 1.8 to 2.1, more preferably from 1.9 to 2.05. It has been found that the use of substantially difunctional polyols, as opposed to the higher functionality polyols conventionally used in making flexible foam, delays the gelling of the reaction mixture and thereby further promotes the formation of good quality foam. Mixtures of a relatively high equivalent weight compound having an actual functionality of from 1.5 to 1.95 and another relatively high equivalent weight compound having an actual functionality of 2.2 or higher wherein the average functionality of the mixture is from 1.5 to 2.2 can be used.

In addition, derivatives and prepolymers of the foregoing polyisocyanates such as those containing urethane, carbodiimide, allophanate, isocyanurate, acylated urea, biuret, ester and similar groups are useful herein. Of these, prepolymers of TDI and MDI, and the so-called "liquid MDI" products which contain carbodi-

imide groups and have an equivalent weight of 130-150, are of particular significance.

Of the foregoing polyisocyanates, TDI, MDI, isophorone diisocyanate, H_{12}MDI, hexamethylene diisocyanate, cyclohexane diisocyanate and derivatives thereof are preferred due to their cost, commercial availability and performance. TDI, MDI and derivatives of MDI are more preferred. TDI, particularly mixtures of the 2,4- and 2,6-isomers, is especially preferred.

The polyisocyanate is advantageously used in an amount sufficient to provide an isocyanate index of from 60 to 200, preferably from 90 to 125, more preferably 95 to 110, although higher indices may sometimes be used, such as in the production of dual hardness foam. At higher indices, trimerization of the polyisocyanate occurs, causing the foam to become less flexible. At lower indices, insufficient curing occurs, causing the foam to have poor properties. When MDI or a derivative thereof is used as the polyisocyanate, preferred isocyanate indices are from 60 to 110, with from 70 to 103 being more preferred, as MDI tends to provide a board-like foam at indices greater than 110, but provides a highly resilient foam at indices as low as 60. The "isocyanate index" is 100 times the ratio of isocyanate groups to active hydrogen-containing groups contained in the mixture which reacts to form the foam.

Flexible polyurethane foam is prepared according to this invention by contacting the various components under conditions such that the components react to form a cellular polymer. Generally, the reac-

tion mixture may contain additional components such as, for example, cross-linkers, catalysts, surfactants, colorants, high functionality polyether polyols, flame retardants, antioxidants and mold release agents, which may vary according to the desired attributes of the foam, and whether the foam is a molded or slabstock foam. The use of such additional components is well understood in the art.

A catalyst for the reaction of the active hydrogen-containing components and the polyisocyanate is also advantageously used in making foam according to this invention. Although a wide variety of materials are known to be useful for this purpose, the most widely used and preferred catalysts are the tertiary amine catalysts and the organometallic catalysts.

Exemplary tertiary amine catalysts, include, for example, triethylenediamine, N-methyl morpholine, N-ethyl morpholine, diethyl ethanolamine, N-coco morpholine, 1-methyl-4-N,N-dimethylaminoethyl piperazine, 3-methoxy-N-dimethylpropylamine, N,N-diethyl-3-diethylaminopropylamine, dimethylbenzylamine and bis(2--dimethylaminoethyl)ether. Tertiary amine catalysts are advantageously employed in an amount of from 0.01 to 5, preferably from 0.05 to 2 parts per 100 parts by weight of component (a).

Exemplary organometallic catalysts include organic salts of metals such as, for example, tin, bismuth, iron, mercury, zinc and lead, with the organotin compounds being preferred. Suitable organotin catalysts include, for example, dimethyltindilaurate, dibutyltindilaurate, stannous

octoate and mercaptoalkyltin compounds. Other suitable catalysts are taught, for example, in U.S. Patent 2,846,408. Advantageously, from 0.001 to 0.5 part by weight of an organometallic catalyst is used per 100 parts of component (a).

Cross-linkers may be used, particularly in making molded foam or high resiliency slabstock foam, in order to improve load-bearing and processing. Suitable such cross-linkers include alkanolamines and other compounds of 200 or lower equivalent weight having from 3 to 8, preferably from 3 to 4, active hydrogen-containing groups per molecule. Exemplary such compounds are glycerine and trimethylolpropane, as well as other alkylene triols. Preferred, however, are alkanolamines such as, for example, diethanolamine, triisopropanolamine, triethanolamine, diisopropanolamine, adducts of 4-8 moles of ethylene oxide and/or propylene oxide with ethylene diamine, and ammonia. Most preferred, on the basis of its optimum reactivity, is diethanolamine. When used, from 0.1 to 4 parts of the cross-linker are advantageously employed per 100 parts of component (a).

Chain extenders may also be used to further improve the load-bearing of the foam. "Chain extenders," for the purposes of this invention, include compounds having two active hydrogen-containing groups per molecule and an equivalent weight of from 31 to 300, preferably from 31 to 150. Hydroxyl-containing chain extenders include the alkylene glycols and glycol ethers such as, for example, ethylene glycol, 1,3--propylene glycol, 1,4-butylene glycol, 1,6-hexamethylene glycol, diethylene glycol, triethylene glycol,

dipropylene glycol, tripropylene glycol and 1,4-cyclohexanedimethanol. Amine chain extenders include, for example, diethyltoluene diamine, phenylene diamine, methylene bis(o-chloroaniline), NaCl-blocked methylene bis(aniline), toluene diamine and aromatic diamines which are substituted for at least one of the carbon atoms adjacent to the amine groups with a lower alkyl group. Such chain extenders, when used, are advantageously employed in a minor amount, i.e., from 2 to 30 parts per 100 parts component (a). It is usually preferable, however, to prepare the foam in the substantial absence of a chain extender.

In order to make a stable foam, i.e., one which does not collapse or contain significant quantities of large pores, it is preferred to employ a surfactant which stabilizes the foaming reaction mixture against collapse until the mixture is sufficiently cured to maintain its cellular configuration. Suitable surfactants include siloxane/poly(alkylene oxide) copolymers as described, for example, in U.S. Patents 3,887,500 and 3,957,842. The selection and use of such surfactants in preparing foams is well-known.

According to this invention, foam is prepared by mixing all reactive components, catalysts, and optional ingredients and permitting them to react. This reaction can be conducted via the formation of a prepolymer, in which most or all of component (a) is reacted with an excess of the polyisocyanate in a first step, followed by the reaction of the prepolymer in a second step with the remaining components. However, it is preferred to form the foam in a one-shot process wherein most or all of component (a) is reacted with

the polyisocyanate simultaneously with the other components. In preparing molded foam, all components except the polyisocyanate are preferably blended together and injected as a single stream into a mixing head. However, certain components such as catalysts or halogenated methane blowing agents are sometimes blended with the polyisocyanate. In addition, the water and surfactant, when used, can be introduced as a separate stream, if desired. The polyisocyanate is added to the mixing head as a separate stream where it is mixed with the other components and injected into the mold. In performing the mixing and mold filling steps, conventional, low pressure apparatus can be used, or high pressure impingement mixing processes, such as a reaction injection molding process, can be used. Generally, the components are mixed at approximately room temperature, although components such as pure MDI which are solid at room temperature may be heated above their melting points.

In one molding technique (hot molding process), the reactants are placed into a mold which is at ambient temperature. After filling, the mold is placed into an oven at a temperature of from 150°C to 275°C to effect curing. In a second technique (cold molding process), the reactants are placed into a mold which is preheated to 30°C to 75°C. After the mold is filled, it is placed in a 70°C-150°C oven to effect cure. In a third technique, the filled mold is maintained at ambient temperature during the curing process. In this third technique, the mold may or may not be preheated.

Sufficient of the reaction mixture is placed into the mold so that, after expansion, the mixture

completely fills the mold. Advantageously, a small excess of material is added over that minimally required to fill the mold. After filling the mold, the reaction mixture is permitted to cure in the mold at least to a state which permits the foam to be removed without undesired permanent distortion. In typical commercial procedures, an in-mold cure time of from 2 to 30 minutes is adequate for this purpose. If required, the foam can be postcured by heating to 50°C to 120°C for a period of from 10 minutes to 24 hours, preferably from 20 minutes to 2 hours.

In making slabstock foam, the reaction mixture also advantageously contains a surfactant and catalyst as described before. Cross-linkers, although they may be used, are often omitted from slabstock formulations. In the commercial production of slabstock foam, the components can be and typically are introduced individually to a mixing head where they are thoroughly blended and metered onto a bed where foaming takes place. However, the components, except for the polyisocyanate, can be preblended if desired. The components are advantageously at room temperature or a slightly elevated temperature when blended in the mixing head, although preheating may be necessary in some instances to melt components which are solid at room temperature.

It may be necessary or desirable to mechanically open the cells of the foam during or after cure. This can be done by crushing the foam, puncturing the foam, vacuum crushing the foam, or by releasing the pressure in the mold at a proper stage of cure as taught in U.S. Patent 4,579,700. However, due to the

presence of the high functionality polyether polyol used in this invention, the postcure shrinkage associated with inadequate cell opening is usually substantially reduced or eliminated, thereby reducing or eliminating the need to mechanically open the cells, as well as the force and energy required when mechanical cell opening is needed.

The foam of this invention is useful, for example, as bedding, furniture cushioning, padding, carpet underlayment, attached cushion carpet backing, automobile head rests, crash pads, door handles, head liners and seating.

The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Example 1

Molded polyurethane foams were prepared in this example using the formulation set out in Table I.

TABLE I

Component	Parts by Weight
Polyol A[1]	50
Copolymer Polyol A[2]	50
Diethanolamine	1.7
Water	3.8
triethylene diamine solution[3]	0.12
bis(N,N-dimethyl aminoethyl)ether[4]	0.075
Silicone Surfactant B[5]	1.65
dibutyltin-dialkylmercaptide	0.0042
bis(N,N-dimethylaminoethyl)amine	0.24
80/20 Toluene diisocyanate[3]	105 index
Cell opener	Variable

[1] A nominally trifunctional poly(propylene oxide) having an equivalent weight of 1650 and 14% by weight ethylene oxide end-capping.

[2] A copolymer polyol containing Polyol A as the base polyol and 25% dispersed 70/30 styrene/-acrylonitrile copolymer particles.

[3] A 33% solution in dipropylene glycol.

[4] As a 10% solution in Polyol A.

[5] Niax® Y-10184 surfactant, sold by Union Carbide Corporation.

[6] A mixture of 80% of the 2,4- isomer and 20% of the 2,6- isomer.

Polyurethane foam Comparative Sample A and Sample Nos. 1-12 were prepared by blending all components except the polyisocyanate. This "B-side" blend was then mixed with the polyisocyanate and shot into a 15" X 15" X 4.5" (381 x 381 x 114.3 mm) aluminum mold which was preheated to 140°F (60°C). The mixing was done using a nominal 150 lb/min (68 kg/min) low

pressure foam dispensing machine. The formulation was permitted to react in the mold for 120 seconds at ambient temperature and 240 seconds in a 250°F (121°C) oven, after which the part was immediately demolded.

Comparative Sample A was prepared without a high functionality polyether polyol. Sample Nos. 1-2 were made using Cell Opener A, a nominally 6.9 functional random copolymer of 75 percent ethylene oxide (EO) and 25 percent propylene oxide (PO) having an approximate molecular weight of 35,000. Cell Opener A was added as a 70/30 mixture with water. The other water in the formulation was reduced so that the total water content was as reported in Table I. The amount of Cell Opener A used was as reported in Table II.

Sample Nos. 3-8 and Comparative Sample B were made using Cell Openers B, C or D in amounts indicated in Table II. These are similar to Cell Opener A, except they were used neat, and their respective molecular weights are 10,000, 12,500 and 15,000.

To determine the amount of shrinkage, each foam was left uncrushed for 24 hours after demold. Each foam was then inspected for the area of greatest shrinkage. The thickness of the foam at the point of greatest shrinkage was measured. Percent shrinkage was then determined by the formula

$$100\% \times (T-P)/T$$

wherein T represents the thickness of the mold and P represents the thickness of the foam at the point of

maximum shrinkage. The results were as reported in Table II following.

Table II

Sample No.	Cell Opener	Parts by Weight	% Shrinkage
A*	None	0	39
1	A	0.25	27
2	A	0.5	28
B*	B	0.25	42
3	B	0.5	0
4	C	0.25	35
5	C	0.5	0
6	D	0.1	37
7	D	0.25	9
8	D	0.5	0

* - Not an example of this invention.

The data in Table II shows the effectiveness of the high functionality polyether polyols used in this invention. All were very effective at very low levels of use. Comparative Sample B is comparative only because Cell Opener B was not effective at the 0.25 part level. However, Cell Opener B was very effective at a slightly higher level of use. Similarly, although Cell Opener C was only slightly effective at the 0.25 part level, it was very effective at the 0.5 part level. Cell Opener D, showed slight effectiveness at a level as low as 0.1 part, and was very effective at 0.25 part or higher. When the high functionality polyether polyol had a lower molecular weight, a high use level was required to obtain good

results. For example, a high functionality polyether polyol similar to Cell Opener B, except its molecular weight is substantially below 5000, provides good cell opening only when used in amounts substantially in excess of one part. When the molecular weight of the high functionality polyether polyol dropped below 5000, much greater amounts were required. Similarly, when the functionality of the polyether polyol was less than 4.0, greater amounts were required to provide improvements in cell opening, and often, equivalent improvements in cell opening cannot be obtained at all.

Example 2

In a manner similar to that described in Example 1, polyurethane foams were prepared from a formulation including 100 parts by weight of a 10% solids PIPA polyol prepared in accordance with U.S. Patent No. 4,374,207, 4 parts water, diethanolamine, a mixture of amine catalysts, a silicone surfactant and varying amounts of a cell opener. The polyisocyanate was an 80/20 mixture of the 2,4- and 2,6- isomers of TDI, and the isocyanate index was 100. In Comparative Sample C, no high functionality polyether polyol was used. The amounts of high functionality polyether polyol in Examples 9-11 were as disclosed in Table III following.

Table III

Sample No.	Cell Opener	Parts by Weight	% Shrinkage
C*	None	0	57.3
9	C	0.5	56.1
10	C	1.0	49.4
11	C	2.25	17.3

* - Not an example of this invention.

This PIPA-based formulation is one which is known to be particularly difficult to produce open cells. However, the high functionality polyether polyol provided significant reduction in shrinkage compared to the control.

Example 3

In a manner similar to that described in Example 1, polyurethane foams were prepared from the formulation described in Table IV.

Table IV

Component	Parts by Weight
Polyol C[1]	100
water	4.5
triethylenediamine solution[2]	0.45
bis(N,N-dimethyl aminoethyl) ether	0.15
silicone surfactant[3]	0.5
silicone surfactant[4]	0.5
Polymeric MDI[5]	100 index
Cell Opener	variable

[1] A nominally trifunctional 5000 molecular weight poly(propylene oxide) containing 16% ethylene oxide end-capping.

[2] A 33% solution in dipropylene glycol.

[3] DC-5241, sold by Dow Corning Corporation.

[4] DC-5043, sold by Dow Corning Corporation.

[5] A 2.3 functional, 131 equivalent weight blend of MDI and polymeric MDI, in which 85% of the MDI is the 4,4'-isomer.

Foam Sample Nos. 12-13 and Comparative Sample D were prepared from the formulation described in Table V. Comparative Sample D contained no high functionality polyether polyol, whereas Sample Nos. 12 and 13 contained 3.0 and 5.0 parts of Cell Opener A, respectively. Shrinkage and physical properties of the foams were measured, and found to be as reported in Table V following.

Table V

Property	Sample No. D*	12	13
Parts Cell Opener	0	3	5
Density, pcf (kg/m^3)	2.2 (35.2)	2.3 (36.8)	2.3 (36.8)
Tensile Strength, psi[1] (kPa)	26.6 (183.4)	26.0 (179.3)	26.0 (179.3)
Elongation, %[1]	101	95	92
Tear Strength, pli[2] (N/m)	1.4 (245)	1.4 (245)	1.2 (210)
25% ILD, pounds[3] (kg)	71 (32)	68 (31)	68 (31)
65% ILD, pounds[3] (kg)	185 (84)	176 (80)	170 (77)

* - Not an example of this invention.

[1]ASTM D-3574-81 Test E.

[2]ASTM D-3574-81 Test F.

[3]ASTM D-3574-81 Test B. IFD is indentation load deflection.

Excellent improvement in cell opening was obtained, along with a desirable softening of the foam, as indicated by decreasing ILD values. Other properties remained substantially unchanged, as desired.

Example 4

In this example, two sets of experiments were run, using the formulations and conditions set out in Example 1 to prepare polyurethane foam Sample Nos. 14--23. In Sample Nos. 14, 16, 18, 20 and 22, the Polyol A component was not neutralized, and contained 1000 ppm potassium hydroxide. In Sample Nos. 15, 17, 19, 21 and

23, the Polyol A component was acid-treated and contained 300 ppm potassium hydroxide.

Cell opener A was used in Sample Nos. 14-18. In Sample Nos. 20-23, a high functionality polyether polyol similar to Cell Opener A was used, except its molecular weight was only 5000 (designated Cell Opener E). The amount of high functionality polyether polyol, and the results are indicated in Table VI following.

TABLE VI

Sample No.	Cell Opener Type	Cell Opener Amount①	Polyol A Neutralized?	Shrinkage
15	E	1.0	No	29%
16	E	1.0	Yes	39%
17	E	1.5	No	31%
18	E	1.5	Yes	7%
19	E	3.0	No	0%
20	E	3.0	Yes	0%
21	A	0.5	No	32%
22	A	0.5	Yes	0%
23	A	1.0	No	0%
24	A	1.0	Yes	0%

①Parts by weight per 100 parts by weight Polyol A and Copolymer Polyol A.

As can be seen from the data in Table VI, the neutralization of the polyol tended to reduce the level of high functionality polyether polyol needed to reduce shrinkage to negligible levels. In addition, the higher molecular weight high functionality polyether

polyol was shown to be more effective in reducing shrinkage than the 5000 molecular weight Cell Opener E, although Cell Opener E also worked very well.

The claims defining the invention are as follows:

1. A one shot process for making polyurethane foam, comprising reacting a reaction mixture comprising

(a) at least one relatively high equivalent weight polyester polyol or polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) an effective amount of a blowing agent;

(c) a high functionality polyether polyol based on an initiator or initiator mixture having at least 4.0 active hydrogens per molecule, which high functionality polyether polyol has a molecular weight of at least 5000 and contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture, in an amount sufficient to measurably increase the proportion of open cells in the foam as compared with a similar foam prepared in the

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absence of said high functionality polyether polyol; and

(d) at least one polyisocyanate.

2. A process as claimed in Claim 1 wherein the high functionality polyether polyol is based on a 4.0 to 8.0 functional initiator, and has a molecular weight of from 10,000 to 50,000; component (a) is a polyether polyol containing at least 50 weight percent of oxypropylene units, or an amine-terminated derivative thereof or a polymer polyol based thereon, which polyether polyol has an average functionality of from 1.8 to 4 and an equivalent weight of from 800 to 3000; and the polyisocyanate comprises toluene diisocyanate or prepolymer thereof, or diphenylmethane diisocyanate or derivative or prepolymer thereof.

3. A process as claimed in Claim 2 wherein the reaction mixture further comprises effective amounts of a surfactant and a catalyst; the high functionality polyether polyol is used in an amount of from 0.2 to 5 parts per 100 parts of component (a); and component (a) comprises a PIPA polyol or a dispersion of a polymer of an ethylenically unsaturated monomer in a polyol.

4. A process as claimed in Claim 3 wherein component (a) has an average functionality of from 1.8 to 2.1.

5. An active hydrogen-containing composition comprising

(a) at least one relatively high equivalent weight polyester polyol or polyether polyol con-

taining at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) a high functionality polyether polyol based on an initiator or initiator mixture having at least 4.0 active hydrogens per molecule, which high functionality polyether polyol has a molecular weight of at least 5000 and contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture, in an amount sufficient to measurably increase the proportion of open cells in a foam made by reacting the active hydrogen-containing composition with a polyisocyanate as compared with a similar foam prepared in the absence of said high functionality polyether polyol; and optionally

(c) an effective amount of a blowing agent.

6. A composition as claimed in Claim 5 wherein the high functionality polyether polyol is based on a 4.0 to 8.0 functional initiator, and has a molecular weight of from 10,000 to 50,000; and component (a) is a polyether polyol containing at least 50 weight percent of oxypropylene units, or an amine-terminated derivative thereof or a polymer polyol based thereon, which polyether polyol has an average functionality of from 1.8 to 4 and an equivalent weight of from 800 to 3000.

7. A composition as claimed in Claim 6 wherein the reaction mixture further comprises effective amounts of a surfactant and a catalyst; the high functionality polyether polyol is present in an amount of from 0.2 to 5 parts per 100 parts of component (a); and component (a) comprises a PIPA polyol or a dispersion of an ethylenically unsaturated monomer in a polyol.

8. A polyurethane foam produced by the process of claim 1 and containing the residue

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~~7. A composition as claimed in Claim 6 wherein~~ the reaction mixture further comprises effective amounts of a surfactant and a catalyst; the high functionality polyether polyol is present in an amount of from 0.2 to 5 parts per 100 parts of component (a); and component (a) comprises a PIPA polyol or a dispersion of an ethylenically unsaturated monomer in a polyol.

~~8. A polyurethane foam containing the residue~~ of a cell opening amount of a high functionality polyether polyol based on an initiator or initiator mixture having an average of at least 4.0 active hydrogens per molecule, which polyether polyol has a molecular weight of at least 5000 and which contains at least 50 weight percent oxyethylene units and a minor proportion of oxypropylene units.

9. A method for making polyurethane foam, comprising reacting a reaction mixture comprising

(a) at least one relatively high equivalent weight polyester polyol, or a polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) an effective amount of a blowing agent;

(c) from 1 to 10 parts, per 100 parts of component (a) of a polyether polyol based on an initiator or initiator mixture having an average of at least 4.0 active hydrogens per molecule, which polyether polyol has a molecular weight of

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at least 5000 and which contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture; and

(d) at least one polyisocyanate which is based on MDI,

under conditions such that a polyurethane foam is obtained.

10. An active hydrogen-containing composition comprising

(a) at least one relatively high equivalent weight polyester polyol or polyether polyol containing at least 50 weight percent of oxypropylene units, an amine-terminated derivative of such polyester or polyether polyol, or polymer polyol based on such polyester or polyether polyol or mixture thereof;

(b) an effective amount of a blowing agent; and

(c) from 1 to 10 parts, per 100 parts of component (a) of a high functionality polyether polyol based on an initiator or initiator mixture having at least 4.0 active hydrogens per molecule, which high functionality polyether polyol has a molecular weight of at least 5000 and contains at least 50 weight percent oxyethylene units and sufficient oxypropylene units to render it compatible with component (a) at the relative proportions thereof present in the reaction mixture.

11. A process as claimed in claim 1 or 9 substantially as hereinbefore described with reference to any one of the examples.

12. An active hydrogen-containing composition as claimed in claim 5 or 10 substantially as hereinbefore described with reference to any one of the examples.

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