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POLYURETHANE AND/OR POLYUREA DISPERSIONS IN ACTIVE HYDROGEN-CONTAINING COMPOSITIONS, A PROCESS FOR PREPARING SAME, AND REACTION PRODUCTS THEREOF WITH POLYISOCYANATES
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A process for preparing a product
polyurethane and/or polyurea dispersion comprising
reacting

(A) a polyisocyanate with

(B) a coreactant material having a equivalent
weight of up to 400 and a plurality of active
hydrogen atoms attached to oxygen or nitrogen
atoms, in the presence of

(C) a preformed solution or dispersion of a
material containing urethane and/or urea groups
in an isocyanate-reactive material which has an
equivalent weight greater than 400, wherein

(i) said product dispersion contains about
0.5 to about 40 weight percent solids, based on
the weight of the product dispersion, and

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(ii) the material containing urethane and/or urea groups dissolved and or dispersed in the preformed solution or dispersion constitutes from 0.5 to 50 percent of the weight of the solids of the product dispersion.

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Complete Specification for the invention entitled:

POLYURETHANE AND/OR POLYUREA DISPERSIONS IN ACTIVE HYDROGEN-CONTAINING COMPOSITIONS, A PROCESS FOR PREPARING SAME, AND REACTION PRODUCTS THEREOF WITH POLYISOCYANATES

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

POLYURETHANE AND/OR POLYUREA DISPERSIONS IN ACTIVE
HYDROGEN-CONTAINING COMPOSITIONS, A PROCESS FOR
PREPARING SAME, AND REACTION PRODUCTS THEREOF WITH
POLYISOCYANATES

5 This invention relates to dispersions of
polyurethane and/or polyurea particles in an isocyanate-
-reactive material.

10 It is known to prepare dispersions of
polyurethane particles in isocyanate-reactive materials.
This is conveniently accomplished by the in situ
reaction of a polyisocyanate with a low equivalent
weight hydroxyl-containing "coreactant" (as defined
herein) in the isocyanate-reactive material. The
15 isocyanate-reactive material, although having groups
which are reactive with the polyisocyanate, is generally
a higher equivalent weight material such that the
polyisocyanate predominantly reacts with the coreactant
to form discrete particles dispersed in the isocyanate-
20 -reactive material, which forms a continuous phase.
This process is described, for example, in U. S. Patent
No. 4,374,209. These polyurethane dispersions are
commonly known in the art as PIPA polyols, and will be
25 so referred to herein for convenience.

Dispersions of polyurea particles in an isocyanate-reactive material can be prepared in like manner by using certain nitrogen-containing compounds as coreactants, as described, for example, in U. S. Patent Nos. 4,324,716; 4,310,449; 4,310,448; 4,305,857; and 4,305,858. The nitrogen-containing compounds include primary amines, secondary amines, hydrazines, dihydrazides, urea and ammonia. These polyurea dispersions are commonly known in the art as PHD polyols.

The foregoing dispersions can be used to prepare polyurethanes. The dispersion is reacted with a polyisocyanate, usually but not necessarily in the presence of a blowing agent, to form a cured polyurethane polymer. The polyurethanes prepared using these dispersions generally have good properties, particularly in the areas of load-bearing and in certain circumstances flammability, where significant improvements in burn properties, based on tests conducted under laboratory conditions, are often seen compared to polyurethanes made using conventional isocyanate-reactive materials.

A significant problem associated with these dispersions is that their use tends to produce foams which exhibit great amounts of shrinkage. This is particularly seen with the PIPA polyols. Although this invention is not limited to any theory, this phenomenon is believed to be due to poor cell-opening during the foaming process, causing the foam to contain large numbers of closed cells. Since the foam is hot when cured, as the foam cools the gases trapped in the closed

cells contract. This in turn causes the pressure in the cells to drop, and the foam shrinks under the pressure of the surrounding atmosphere.

5 This problem can be partially overcome with the use of special cell-opening additives, or by mechanically crushing the foam after cure. However, these solutions require the use of additional components in the foam formulation, or additional process steps in
10 the manufacturing process, both of which increase manufacturing costs. In addition, with PIPA polyols especially, these methods have found only limited use. Although useful, cell opening additives most often do not eliminate the need for mechanical crushing.

15 Similarly, crushing does not always fully eliminate the shrinkage, and often the foam must be crushed repeatedly or under severe conditions to adequately open the cells. This sometimes results in splits which render the foam unusable or require that it be repaired.
20

Another problem with these dispersions is that they tend to have a viscosity which is higher than
25 desired. High viscosity makes these dispersions difficult to process, and limits the solids content of the dispersions.

Because of the other useful properties of PIPA polyols and PHD polyols, it would be desirable to
30 provide a polyurethane and/or polyurea dispersion in an isocyanate-reactive material which provides for improved cell opening when made into polyurethane foam.

The present invention provides a process for preparing a product polyurethane and/or polyurea dispersion comprising reacting

5 (A) a polyisocyanate with

(B) a coreactant material having a equivalent weight of up to 400 and a plurality of active hydrogen atoms attached to oxygen or nitrogen atoms, in the presence of

10 (C) a preformed solution or dispersion of a material containing urethane and/or urea groups in an isocyanate-reactive material which has an equivalent weight greater than 400, wherein

15 (i) said product dispersion contains about 0.5 to about 40 weight percent solids, based on the weight of the product dispersion, and

20 (ii) the material containing urethane and/or urea groups dissolved and or dispersed in the performed solution or dispersion constitutes from 0.5 to 50 percent of the weight of the solids of the product dispersion.

25 The present invention also provides a dispersion prepared according to the process described above.

30 The present invention further provides a product dispersion of polyurethane and/or polyurea particles wherein the particles are formed by the reaction of

(A) a polyisocyanate with

35 (B) a coreactant material having a equivalent weight of up to 400 and a plurality of active hydrogen atoms attached to oxygen or nitrogen atoms, in the presence of

(C) a preformed solution or dispersion of a

material containing urethane and/or urea groups in an isocyanate-reactive material which has an equivalent weight greater than 400, wherein

5 (i) said product dispersion contains about 0.5 to about 40 weight percent solids, based on the weight of the product dispersion, and

10 (ii) the material containing urethane and/or urea groups dissolved and or dispersed in the performed solution or dispersion constitutes from 0.5 to 50 percent of the weight of the solids of the product dispersion

15 wherein said particles have a bimodal particle size distribution wherein at least about 60 volume percent of the particles fall into two discrete size ranges, about 5 to about 75 volume percent of said particles in said discrete size ranges, being larger particles having an average particle size, as measured by hydrodynamic chromatography (HDC), of at least about 200 nm, and 25 to 95 volume percent of the particles in said discrete size ranges being smaller particles having an average particle size, as measured by HDC, of 10 to 700 nm.

~~(ii) the material containing urethane and/or urea groups dissolved and or dispersed in the preformed solution or dispersion constitutes from 0.5 to 50 percent of the weight of the solids of the product dispersion.~~

5

The term "solids" is used herein as a shorthand term to designate the combined weight of (1) the polyisocyanate, (2) the coreactant and (3) material containing urethane and/or urea groups dissolved and/or dispersed in the preformed solution or dispersion. The weight of the dispersed or dissolved material containing urethane and/or urea groups in the preformed solution or dispersion will in normal cases be considered to equal the weight of polyisocyanate and coreactant used in its formation. The term "solids" is not used herein to designate the physical state of any component material or reaction product.

20

~~In a third aspect, this invention is a dispersion prepared as described in the preceding paragraphs.~~

25

The dispersion of this invention, when used to prepare a polyurethane foam, provides improved cell opening characteristics to the foam, as compared to a similar foam made with a dispersion of like composition, but which is prepared in a conventional one-step process. This advantage is especially seen with the polyurethane dispersions (PIPA polyols) of this invention. In addition, the product dispersion usually has a lower viscosity than conventional dispersions of comparable solids content, and is therefore easier to

30

process. Further, foams prepared from this dispersion often exhibit improved physical properties, better curing and decreased compression sets. Yet another advantage is that with this invention, stable
5 dispersions can be prepared having equivalent weights and reactivities suitable for use in preparing general purpose slabstock foam.

As described before, one aspect of this
10 invention is a dispersion in an isocyanate-reactive material of a plurality of polyurethane and/or polyurea particles having a certain bimodal particle size distribution. By "bimodal particle size distribution", it is meant that at least about 60 volume percent of the
15 particles fall into two discreet and separate size ranges which are separated by a particle size range into which relatively few particles fall.

Of the particles falling into the discreet size
20 ranges, the larger particles advantageously have an average particle size from 2000 (200 nm) to in excess of 10,000 (1000 nm), preferably up to 10,000 (1000 nm), more preferably to 8000 Angstroms (800 nm). In
25 addition, the smaller of these particles have an average particle size from 100 (10 nm) to about 7000 (700 nm), preferably to 4000 (400 nm), more preferably to 2000 Angstroms (200 nm).

30 For the purposes of this invention, particle sizes are as determined using hydrodynamic chromatography (HDC), as described, for example in J. Colloid Interface Science, Vol. 89, page 94 (1982). All particles sizes refer to the average particle diameters as measured by HDC. In making such

measurements, it is suitable to calibrate the device for latex dispersions.

5 It is understood that the distribution of particle sizes in any dispersion may contain a minor amount of particles having sizes outside the two predominant size ranges. For example, a minor proportion of particles may have sizes larger than, smaller than and/or intermediate to the predominant size ranges. 10 The use of the term "bimodal" herein is not intended to exclude the presence of these minor amounts of off-size particles, provided that at least 60, preferably at least 80, volume percent of the particles fall into the two predominant size ranges.

15 The dispersion of this invention has a continuous phase comprising an isocyanate-reactive material having an equivalent weight of greater than 400. The isocyanate-reactive material is any liquid 20 material having a plurality of active hydrogen-containing groups per molecule in which a useful polyurethane and/or polyurea dispersion can be prepared. An active hydrogen-containing group is a group 25 containing at least one hydrogen atom which displays significant activity according to the well-known Zerewitnoff test. Examples of such groups include hydroxyl, thiol, carboxylic acid and primary and/or secondary amine groups. Because the dispersed polymers 30 are formed in situ in the isocyanate-reactive material, it is preferable that the active hydrogen-containing groups be less reactive with a polyisocyanate than the coreactant. For this reason, it is preferred that the isocyanate-reactive material contain substantially only hydroxyl, thiol or carboxylic acid groups, and more

preferred that its active hydrogen-containing groups are essentially all primary and/or secondary hydroxyl groups. Isocyanate-reactive materials containing mostly primary hydroxyl groups are most preferred, as such polyols have been found to provide stable dispersions, and also have excellent processing characteristics when used to prepare polyurethanes. However, an advantage of this invention is that stable product dispersions having equivalent weights and reactivities suitable for preparing slabstock polyurethane foam can be made.

The functionality and equivalent weight of the isocyanate-reactive material are advantageously selected in accordance with the desired characteristics of the polyurethane to be prepared therefrom. Generally, the isocyanate-reactive material advantageously has an average functionality (active hydrogen-containing groups/molecule) from 1.7 to 16, preferably 1.8 to 8. When the dispersion is intended for use in preparing cellular or noncellular elastomeric polyurethanes, an average functionality of 1.8 to 4 is more preferred and 2 to 3 is most preferred. The isocyanate-reactive material preferably has an equivalent weight from 400 to 5000, more preferably 700 to 3000, most preferably 800 to 2000.

Suitable isocyanate-reactive materials for use as the continuous phase in this invention include those described in Col. 3-5 of U. S. Patent No. 4,394,491. Of these, the polyethers, polyesters, hydroxyl-terminated alkanes and glycol ethers are preferred. Particularly preferred are the polyether, especially polymers of C_2-C_4 alkylene oxides and polymers of tetrahydrofuran. The most preferred polyethers are polymers of propylene

oxide, particularly polymers of propylene oxide which are end-capped with 5 to 25 weight percent, based on the weight of the polyether, of ethylene oxide.

5 Often, the continuous phase is a mixture of two or more isocyanate-reactive materials. This often occurs when the product dispersion is prepared using a preformed dispersion containing one isocyanate-reactive material, to which a second isocyanate-reactive material
10 is added during or after the preparation of the product dispersion. In this manner, it is possible to provide a stable dispersion in an isocyanate-reactive material which is suitable for preparing general purpose slabstock polyurethane foam. Isocyanate-reactive materials
15 most suitable for preparing slabstock polyurethane foam are generally polyethers having primarily (>50 percent, preferably >90 percent) secondary hydroxyl groups and an equivalent weight from 500 to 2500. Using
20 conventional processes, it has been very difficult to prepare a stable dispersion with these polyethers as the continuous phase. With this invention, the isocyanate-reactive material in the preformed solution or
dispersion can be a polyether having a higher (40
25 percent, preferably 70 percent or more) proportion of primary hydroxyl groups. Then, during the formation of the product dispersion, a substantial quantity of a slabstock polyether is added. The resulting product has
30 as the continuous phase a mixture of polyethers having an average equivalent weight and proportion of primary hydroxyl groups such that it is suitable for the production of general purpose slabstock polyurethane foam.

The dispersed particles are polymers containing a plurality of polyurethane and/or polyurea linkages. Their precise composition depends on the raw materials used in their preparation, as discussed more fully below. The particles are of such molecular weight and crosslinking that they are substantially insoluble in the isocyanate-reactive material. However, it is understood that the dispersion may additionally contain quantities of oligomeric polyurethane and/or polyurea which are soluble in the continuous phase. The more preferred particles are polyurethane or polyurethane/urea particles, especially polyurethane particles, as the conventional PIPA polyols which contain particles of this type present particular cell-opening problems when used to make flexible foam.

The solids content of the dispersion is advantageously 0.5 to 40, preferably 5 to 30, more preferably 10 to 25 percent of the weight of the dispersion.

As stated before, the term "solids", when applied to the product dispersion, refers to the combined weight of the coreactant, polyisocyanate and polyurethane or polyurea-containing material from the preformed solution or dispersion which are used in making the product dispersion. The weight of the polyurethane or polyurea containing material in the preformed solution or dispersion is likewise normally considered to be equal to the combined weight of the coreactant and polyisocyanate used in its manufacture. The exception to this is the case when the preformed solution or dispersion has been centrifuged or otherwise treated to remove part of the polyurethane or polyurea-

-containing material. In such case, the weight of the polyurethane or polyurea-containing material is determined analytically, or calculated from the initial solids and the amount of material removed.

5 Another aspect of this invention is a process for preparing polyurethane and/or polyurea dispersions in an isocyanate-reactive material. In this process, the coreactant is reacted with a polyisocyanate in the
10 presence of a preformed polyurethane and/or polyurea solution or dispersion. Further, the weight of the polyurethane and/or polyurea containing material in the preformed solution or dispersion constitutes from 0.5 to 50, preferably 1 to 35, more preferably 5 to 25, percent
15 of the weight of the solids of the product dispersion.

The preformed dispersion has as a continuous phase an isocyanate-reactive material, also as described before. The isocyanate-reactive material present in the
20 preformed dispersion may be the only such material used in preparing the final product. However, it is usually more convenient to prepare a high solids preformed dispersion, since such are more economical to manufacture. This preformed dispersion can then be diluted
25 by adding additional isocyanate-reactive material during the production of the product dispersion. When the preformed dispersion is made in this manner, the isocyanate-reactive material used for dilution may be
30 the same or different as that used in preparing the initial dispersion, but the two isocyanate-reactive materials are preferably compatible. As stated before, the preferred isocyanate-reactive material for both purposes is a poly(propylene oxide) which is end-capped with 5 to 25 weight percent ethylene oxide.

However, when making a product dispersion for use in making general purpose slabstock foam, it is most preferred to use a 2-4 functional poly(propylene oxide) which is end-capped with 5 to 25 weight percent ethylene oxide to make the preformed solution or dispersion, and a 500-2500 equivalent weight, 2-3 functionality homopolymer of propylene oxide or a random copolymer of propylene oxide and a minor amount of ethylene oxide to dilute same while preparing the product dispersion. The ratio of the two polyethers is advantageously such that of the mixture, less than half the hydroxyl groups are primary hydroxyls. More preferably, the weight ratio of the polyethers is 1:0.5 to 1:100, preferably 1:2 to 1:50.

The preformed solution or dispersion advantageously contains from 0.5 to 40, preferably 1 to 30, more preferably 5 to 25 weight percent solids. The solids are advantageously the reaction product of a polyisocyanate with a "coreactant", as described hereinafter. Of course, the use of higher solids preformed solution or dispersions will require the addition of more isocyanate-reactive material during the preparation of the product dispersion. The preformed solution or dispersion is advantageously prepared according to the same general procedure as described hereinafter, except of course it is not necessary to use a preformed solution or dispersion in its manufacture. Suitable methods for preparing the preformed dispersion are described, for example, in U. S. Patent Nos. 4,374,209; 4,324,716; 4,310,449; 4,310,448; 4,305,857; 4,293,470; 4,518,720; 4,518,778; 4,523,025; 4,525,488;

4,785,026; 4,497,913; 4,296,213; 4,506,040; and
4,305,858.

5 It is preferred that the particles of the
preformed solution or dispersion have an average
particle size of at least 100 to 10,000 (10 to 1000 nm),
more preferably up to 6000 (600 nm), most preferably to
4000 Angstroms (400 nm).

10 The preformed solution or dispersion may be
treated to remove some or all of the particulate matter,
if desired. It has been found that the advantages of
this invention are obtained even when the dispersed
polyurethane and/or polyurea particles are removed from
15 the preformed solution or dispersion. Although it is
not intended to limit this invention to any theory, it
is believed that after removal of particulate matter,
there remains in the preformed solution or dispersion a
quantity of dissolved polyurethane and/or polyurea
20 polymers or oligomers. The presence of these dissolved
materials during the manufacture of the product
dispersion provides it with the improved properties
discussed before.

25 The polyisocyanate used in making the
dispersion (and the preformed solution or dispersion as
well) is any organic compound having at least two,
preferably 2 to 4 isocyanate groups per molecule. The
30 polyisocyanate may be aliphatic, aromatic or
cycloaliphatic, although aromatic types are preferred
due to their desirable properties and reactivity.
Representative of these types are diisocyanates such as
m- or p-phenylene diisocyanate, toluene-2,4-
-diisocyanate, toluene-2,6-diisocyanate, hexamethylene-

-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate (and isomers), naphthylene-1,5-diisocyanate, 1-methylphenyl-2,4-phenyldiisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, 4,4'-biphenylenediisocyanate, 3,3'-dimethoxy-4,4'-biphenylenediisocyanate and 3,3'-dimethyldiphenylpropane-4,4'-diisocyanate; triisocyanates such as toluene-2,4,6-triisocyanate and polyisocyanates such as 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate and the diverse polymethylenepolyphenylpolyisocyanates.

A crude polyisocyanate may also be used in the practice of this invention, such as the crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamines or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude diphenylmethanediamine. The preferred undistilled or crude polyisocyanates are disclosed in U. S. Patent No. 3,215,652.

Toluene diisocyanate, diphenylmethane diisocyanate, polymethylene polyphenylene polyisocyanate (PMDI) and their respective derivatives are most preferred.

The coreactant is a material having a plurality of -OH, >NH and/or -NH₂ groups and an equivalent weight per active hydrogen atom of up to 400, preferably up to 300, more preferably up to 200. Since the coreactant reacts with the polyisocyanate in situ in the isocyanate-reactive material which forms the continuous phase, it is also preferred that the coreactant be more

reactive with the polyisocyanate than the isocyanate-
reactive material is. Suitable such materials are
described, for example, in U. S. Patent Nos. 4,374,209;
4,324,716; 4,310,449; 4,310,448; 4,305,857; 4,293,470;
4,518,778; 4,523,025; 4,525,488; 4,785,026; 4,497,913;
5 4,506,040; and 4,305,858; incorporated by reference.
Preferred among these are alkanolamines, low equivalent
weight amine-initiated polyether polyols, alkylene
oxide, acrylonitrile, or acrylic ester adducts of
10 amines, primary amines, secondary amines, hydrazines,
dihydrazides, urea, ammonia, Mannich condensates, low
equivalent weight hydroxyl-terminated compounds such as
ethylene glycol, glycerine, glycol ethers, pentaery-
thritol or the like, aminobenzenes, or mixtures thereof.
15 Of these, the alkanolamines and other hydroxyl-
-terminated compounds are generally preferred, as the
polyurethane dispersions prepared therewith have in the
past been found to form polyurethane foams whose cells
are especially difficult to open. Thus, the benefits of
20 this invention are particularly evidenced in the
preparation of polyurethane dispersions.

Suitable alkanolamines include mono-, di- and
25 trialkanolamines, particularly those wherein the alkanol
groups have from 2 to 6, preferably 2 to 3 carbon atoms.
The mono- and dialkanolamines may also have a single
N-alkyl substituent, preferably having from 1 to 6
carbon atoms. The alkanol and alkyl substituent, when
30 present, may also contain inert substituent groups such
as halogen atoms. Preferred among these are
monoethanolamine, diethanolamine, triethanolamine,
N-methylethanolamine, N-ethylethanolamine,
N-butylethanolamine, N-methyldiethanolamine,
N-ethyldiethanolamine, N-butyldiethanolamine,

monoisopropanolamine, diisopropanolamine, triisopropanolamine, N-methylisopropanolamine, N-ethylisopropanolamine, and N-propylisopropanolamine.

5 Suitable primary and/or secondary amines
include polyhydric aliphatic, arylaliphatic, cycloaliphatic and aromatic amines including, for example, ethylene diamine, 1,2- and 1,3-propylene diamine, tetramethylene diamine, hexamethylene diamine,
10 dodecamethylene diamine, trimethyldiaminohexane, N,N'-dimethylethylenediamine, higher homologues of ethylene diamine such as diethylene triamine, triethylene-tetramine and tetraethylenepentamine, homologues of propylene diamine, 4-aminobenzylamine, 4-
15 -aminophenylethylamine, piperazine, N,N'-bisaminoethyldipropylene triamine, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, and others as disclosed in U. S. Patent No. 4,324,716.

20 Suitable hydrazines include hydrazine itself and monosubstituted or N,N'-disubstituted hydrazines having substituent groups such as C₁-C₆ alkyl, cyclohexyl or phenyl groups. Hydrazine itself is
25 preferred among these.

30 Suitable hydrazides include the hydrazides of multifunctional carboxylic acids such as carbonic acid, oxalic acid, malonic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid and terephthalic acid; the esters of a hydrazine monocarboxylic acid with dihydric or polyhydric alcohols and phenols; and the amides of hydrazinemonocarboxylic acids. These

hydrazides preferably have a molecular weight from 90 to 1000.

The reaction of the coreactant with the polyisocyanate is preferably done by mixing the preformed dispersion and coreactant, and then adding the polyisocyanate to the resulting mixture. The reactants are advantageously mixed at any temperature at which the mixture is a liquid and at which the reactants do not degrade, but are preferably mixed at 0 to 170°C, more preferably 15 to 70°C and most preferably 15 to 45°C.

The isocyanate and coreactant are advantageously mixed with stirring, in order to promote the formation of a plurality of small particles. Usually, rapid agitation is desired to optimize particle size and minimize the viscosity of the resulting dispersion. The process can be conducted batch-wise or continuously, as described in U. S. Patent No. 4,374,209.

The ratio of polyisocyanate and coreactant is selected such that they react to form a plurality of particles dispersed in the isocyanate-reactive material. Advantageously, sufficient of the polyisocyanate is provided to react with in excess of one active hydrogen atom/molecule of the coreactant, and preferably from 1.5 to 3 active hydrogen atoms/molecule of the coreactant.

The reaction between the polyisocyanate and the coreactants is often exothermic, and proceeds rapidly, being essentially completed in most cases in 1 minute to 1 hour, preferably 1 to 30 minutes, although this depends somewhat on the choice of polyisocyanate and

coreactant, the batch size, initial temperature and other variables. Agitation is preferably effected throughout the reaction period.

5 If desired, a catalyst for the reaction between the polyisocyanate and the coreactant may be used to accelerate the reaction. Suitable catalysts include those described below with respect to the use of this dispersion to prepare polyurethanes, with the organotin catalysts being preferred. The amount of catalyst is 10 advantageously up to 1 weight percent based on polyol, preferably up to 0.1 weight percent and more preferably up to 0.05 weight percent. However, the catalyst may not be necessary, particularly with the more reactive 15 coreactants.

As discussed in U. S. Patent Nos. 4,374,209 and 4,324,716, it is possible, although not preferred, to provide increased control over the molecular weight of the dispersed particles through the use of a minor 20 quantity of monofunctional reactants, i.e., a monofunctional isocyanate and/or a monofunctional coreactant. Exemplary monoisocyanates include cyclohexyl isocyanate, phenyl isocyanate, toluene 25 monoisocyanate, 4-chlorophenyl isocyanate and diisopropylphenyl isocyanate. Exemplary monofunctional coreactants include dialkyl amines such as dimethyl-amine, diethylamine, dibutylamine; N- 30 -dialkylalkanolamines such as dimethylethanolamine and diethylethanolamine. When used, these monofunctional reactants constitute only a minor portion, based on equivalents, of the total amount of reactant used.

In preparing the dispersion, sufficient polyisocyanate and coreactant are used that, together with the solids from the preformed solution or dispersion, the product dispersion has the desired solids level. As stated before, the solids advantageously constitute 0.5 to 40, preferably 5 to 30, more preferably 10 to 25 percent of the weight of the product dispersion.

The product prepared according to the process of this invention is in most cases an opaque liquid containing a continuous phase in which are dispersed a plurality of polyurethane and/or polyurea particles. Usually, but not always, the product has particles having a bimodal size distribution as described before.

The dispersion of this invention is useful for preparing polyurethanes by reacting it with a polyisocyanate. The dispersion of this invention is particularly suited for preparing flexible polyurethane foams.

The preparation of polyurethanes from isocyanate-reactive materials is well-known, and described, for example, in U. S. Patent Nos. 4,269,945; 4,632,943; 4,596,665; and 4,774,040. In general, the dispersion of this invention can be reacted with polyisocyanates in the same way as other polymer-modified isocyanate-reactive materials to form polyurethanes.

The polyisocyanate used in preparing the polyurethane is as described before, although the particular polyisocyanate used in the polyurethane

production may be the same or different than that used in preparing the dispersion. For most applications, toluene diisocyanate (TDI), diphenylmethanediisocyanate (MDI), polymethylene polyphenylene polyisocyanates (PMDI), isophorone diisocyanate, hydrogenated MDI and
5 PMDI, cyclohexane diisocyanate and their respective derivatives are preferred on the basis of cost and desirable properties, with TDI, MDI and PMDI and their derivatives and prepolymers being especially preferred.

10 In addition to the dispersion of this invention and the polyisocyanate, other components can be used in the preparation of polyurethanes. The selection of these depends to a great extent on the type of poly-
15 urethanes desired, as is well understood in the art.

In making flexible polyurethane foams, it is often useful to employ an additional polyol, a blowing agent or mixture thereof, a cell opener, a catalyst as
20 described below, a surfactant to stabilize the foaming reaction mixture until it is sufficiently cured to maintain its shape, and/or a crosslinker or chain extender, as well as other additives which are useful in
25 preparing polyurethane. Suitable materials and processes for preparing flexible foam are disclosed, for example, in U. S. Patent No. 4,596,665. In making flexible foam, it is especially desired to employ a formulation comprising a dispersion wherein the
30 isocyanate-reactive material is a polyether polyol an average equivalent weight of 800 to 2000, from 1 to 6 parts water per 100 parts relatively high equivalent weight isocyanate-reactive material(s), toluene diisocyanate and/or diphenylmethanediisocyanate or derivatives thereof, organotin and/or tertiary amine

catalyst, and up to 5 parts of a crosslinker or chain extender per 100 parts relatively high equivalent weight isocyanate-reactive material. In this formulation, it is preferred to dilute the dispersion of this invention with additional relatively high equivalent weight polyether polyol, particularly if the dispersion contains more than about 10 weight percent dispersed particles.

Other types of polyurethanes can be made using the dispersion of this invention. In making noncellular or microcellular elastomers, additional relatively high equivalent weight active hydrogen-containing materials, chain extenders, crosslinkers, mold release agents, small quantities of blowing agents (in the case of microcellular elastomers), catalysts, fillers, reinforcing fibers and similar additives are advantageously used.

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-dimethylaminoethyl piperazine, 3-methoxy-N-dimethylpropylamine, N,N-diethyl-3-diethylaminopropylamine, dimethylbenzyl amine, and bis(2-dimethylaminoethyl)ether. Tertiary amine catalysts are advantageously employed in an amount from 0.01 to 5, preferably 0.05 to 2 parts per 100 parts by weight of the relatively high equivalent weight active hydrogen-containing materials.

Exemplary organometallic catalysts include organic salts of metals such as tin, bismuth, iron, mercury, zinc, lead and the like, with the organotin compounds being preferred. Suitable organotin catalysts include dimethyltindilaurate, dibutyltindilaurate, 5 stannous octoate and the like. Other suitable catalysts are taught, for example, in U. S. Patent No. 2,846,408. Advantageously, 0.001 to 0.5 part by weight of an organometallic catalyst is used per 100 parts of 10 relatively high equivalent weight active hydrogen-containing materials.

Suitable such crosslinkers include alkanolamines and other compounds of about 200 or lower 15 equivalent weight having 3 to 8, preferably 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 diethanolamine, 20 triisopropanolamine, triethanolamine, diisopropanolamine, adducts of 4 to 8 moles of ethylene oxide and/or propylene oxide with ethylene diamine and the like, and polyamines such as methylene bis(o-chloroaniline), 25 ethylenediamine and ammonia. Most preferred, on the basis of its optimum reactivity, is diethanolamine. The amount used depends to a large extent on the type of polyurethane being prepared. In preparing the preferred flexible polyurethane foam, advantageously up to 10, 30 preferably up to 5, more preferably 0.1 to 4 parts of the crosslinker are advantageously employed per 100 parts of relatively high equivalent weight isocyanate-reactive materials.

"Chain extenders", for the purposes of this invention, include compounds having two active hydrogen-containing groups per molecule and an equivalent weight from 31 to 300, preferably 31 to 150. Hydroxyl-containing chain extenders include the alkylene glycols and glycol ethers such as ethylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, 1,6-hexamethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, 1,4-cyclohexanedimethanol and the like. Amine chain extenders include diethyltoluenediamine, phenylene diamine, methylene bis(o-chloroaniline), NaCl-blocked methylene bis(aniline), toluene diamine, aromatic diamines which are substituted at least one of the carbon atoms adjacent to the amine groups with a lower alkyl group. Such chain extenders, when used in making the preferred flexible foam, are advantageously employed in amounts similar as described with respect to the crosslinkers, although significantly higher amounts are often used in making noncellular and microcellular elastomers.

In preparing foams, a surfactant may be used to stabilize the foaming reaction mixture against cell 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 in the art. The surfactant is advantageously used in an amount from 0.01 to 2, preferably 0.2 to 1.5, parts per 100 parts of relatively high equivalent weight isocyanate-reactive material.

Suitable blowing agents include materials which are capable of generating a gas under the conditions of the reaction of a polyisocyanate and a polyol. Such materials include air, carbon dioxide, nitrogen, water, formic acid, low-boiling halogenated alkanes, finely divided solids, the so-called "azo" blowing agents such as azobis(formamide). Preferred are water, the low-boiling halogenated alkanes, or mixtures thereof. In preparing low density foam, the blowing agents are advantageously employed in a quantity sufficient to provide the foam with a bulk density from 0.5 lb/ft³ (8 kg/m³), preferably 0.9 lb/ft³ (14.5 kg/m³), more preferably 1.1 lb/ft³ (18 kg/m³) to 25 lb/ft³ (400 kg/m³), preferably 6 lb/ft³ (96 kg/m³), more preferably 4 pounds per cubic foot (64 kg/m³). When water is used as the sole blowing agent, such densities are commonly obtained with the use of 1.0 to 8, preferably 1.5 to 5 parts of water per 100 parts relatively high equivalent weight compound. The halogenated alkanes, including methylene chloride, dichlorodifluoromethane, monochlorodifluoromethane, monochlorotrifluoromethane, generally provide the desired density when employed in amounts from 5 to 50 parts per 100 parts relatively high equivalent weight compound. Lesser amounts are useful when employed in conjunction with another blowing agent, such as water.

The resulting polyurethanes, depending on type, are useful as cushioning materials, furniture padding, bedding, packaging materials, automobile fascia and the like dynamic elastomers such as automobile engine belts.

The following examples are given to illustrate the invention and should not be interpreted as limiting

it in any way. Unless stated otherwise, all parts and percentages are given by weight.

Example 1

5 A. Preparation of Preformed Dispersion

In a suitable reactor was placed a mixture of 900 parts Polyol A, 0.1 part dibutyltindilaurate and 42.9 parts triethanolamine. Polyol A was a 5000
10 molecular weight, nominally trifunctional poly(propylene oxide) having about 16 percent by weight terminal poly(ethylene oxide) capping. This mixture was maintained at a temperature of 25°C. With stirring, 57.1 parts of TDI (80/20 mixture of 2,4- and
15 2,6-isomers) was added over about 15 seconds. Stirring was continued for about 15 minutes. During this time, an exotherm and viscosity increase were observed. About 15 minutes after the TDI was added, the product was
20 permitted to cool. The resulting dispersion was smooth and free of visible lumps. It contained about 10 percent dispersed polyurethane having an average particle size of about 2200 Angstroms (220 nm) and had a viscosity of about 3100 mPa.s at 25°C. For
25 convenience, this dispersion is referred to hereon as "Preformed Dispersion A".

B. Preparation of Dispersions Using the Preformed Dispersion

30

Five hundred parts of Preformed Dispersion A were diluted with 350 parts Polyol A, in which 0.15 part of dibutyltindilaurate was dissolved. This diluted dispersion was then mixed with 67 parts triethanolamine and heated to 48°C. With stirring, 83 parts of TDI were

added over 20 seconds, and the resulting mixture was stirred for about 15 minutes. An exotherm and viscosity rise were noted. A smooth, white dispersion was obtained, which contains 20 percent solids. The solids from the preformed dispersion constitute 25 percent of the solids of the final product. This product had a viscosity of 10,100 mPa.s at 25°C as measured on a Brookfield viscometer using a #5 spindle. It exhibited a bimodal particle size distribution, with most particles having sizes of about 500 Angstroms (50 nm) and about 4500 Angstroms (450 nm). This dispersion is referred to herein as Dispersion Sample No. 1.

In a similar manner, Dispersion Sample Nos. 2-6 were prepared, differing only in the amount of dilution of Preformed Dispersion A. All of these Samples had 20 percent solids. In preparing each Sample, Preformed Dispersion A was diluted sufficiently with Polyol A that the the proportion of the product solids content attributable to the polyurethane in Preformed Dispersion A was as indicated in Table 1 following. Similarly, the amounts of triethanolamine and TDI were chosen so that, in combination with the polyurethane in Preformed Dispersion A, the Samples each contained 20 percent solids.

For comparison, a similar dispersion prepared at 20 percent solids but without benefit of a preformed dispersion had an average particle size of about 8000 Angstroms (800 nm) and a viscosity of 11,200 mPa.s. This dispersion is referred to herein as Comparative Dispersion A.

TABLE 1

Sample No.	Total Solids ¹	% of Product Solids from PFD solids ²	Viscosity ³	Particle Size ⁴
2	20%	0.5%	7450	850
3	20%	2.5%	7200	850; 70
4	20%	5%	7650	700; 70
5	20%	10%	6700	600; 50
6	20%	37.5%	13,800	400; 50

¹By weight of product dispersion.

²The proportion of final product solids attributable to the solids from the preformed dispersion.

³mPa.s, measured on a Brookfield viscometer at 25°C using a #5 spindle.

⁴Reported in nm. Measured by hydrodynamic chromatography. Two values indicate bimodal distribution.

20

Of particular interest are the bimodal particle sizes of Sample Nos. 1 and 3-6, as well as the substantially reduced viscosity of all Samples except No. 6 as compared with Comparative Dispersion A.

25

C. Preparation of Flexible Molded Polyurethane Foam

30

Dispersion Sample Nos. 1-3 and 5 and Comparative Dispersion A were used to prepare flexible molded polyurethane foam using the formulation described in Table 2. All components except the TDI were mixed thoroughly. This blend was mixed with the TDI and poured into a 15" X 15" X 4½" 38 x 38 x 11.4 cm mold which was preheated to 60°C. The mold was closed and placed in a 100°C oven. After five minutes, the mold was removed from the oven and the foam sample was

demolded. The demolded foam was crushed to 2" (5 cm) and again to 1" (2.54 cm). Physical properties of the resulting foams are as reported in Table 3. Shrinkage was measured on uncrushed foam by bisecting the foam sample and measuring the height of the foam at the point of maximum shrinkage along the cut. The difference between the height at the point of maximum shrinkage and the nominal height of the foam is reported as a percentage of the nominal height.

TABLE 2

Component	Parts by Weight
Dispersion ¹	50
Polyol A	50
Water	4.0
Diethanolamine	1.5
Catalyst A ²	0.15
Amine Catalyst ³	0.45
Silicone Surfactant	1.0
TDI ⁴	100 index

¹As indicated in Table 3.

²Bis(N,N-dimethylaminoethyl)ether.

³A 33% solution of triethylene diamine in dipropylene glycol.

⁴An 80/20 mixture of 2,4- and 2,6-isomers.

TABLE 3

Foam Property		Dispersion or Comparative Dispersion				
		2	3	5	1	A*
5	% of Product Solids from PFD solids ¹	0.5	2.5	5	25	0
	Shrinkage, %	53	46	23	7	54
	65% IFD, N ²	411	392	390	420	412
10	Modulus ²	2.6	2.6	2.6	2.6	2.6
	Tensile, KPa ²	139	146	135	151	126
	Tear, N/m ²	285	290	263	215	255
	Elongation, % ²	122	132	122	119	115
15	Compression Set, % ²	22	19	16	15	23
	Core Density, kg/m ³	28.9	28.8	29.2	32.0	28.9

* - Not an example of this invention.

¹See note 2 of Table 1.

²ASTM D-3754

25

30

As can be seen from the data in Table 3, reduced shrinkage was obtained in all cases, as compared with the control. Particularly good improvements were seen with Samples 1, 3 and 5, especially 1 and 5, where very substantial reductions in shrinkage were obtained. In addition, significant improvements in tensile strength, elongation and compression set were obtained without loss in other properties.

Example 2

A preformed dispersion was prepared in the same general manner as that in Example 1-A, except the ratios of components were such that the preformed dispersion had a solids content of 20 percent by weight. This preformed dispersion is referred to herein as Preformed Dispersion B. It had particles with an average size of about 8000 Angstroms (800 nm) and a viscosity of 11,200 mPa·s at 25°C.

In the same general manner as described in Example 1-B, Preformed Dispersion B was used to make Dispersion Sample Nos. 7-12. Each was a 20 percent solids dispersion prepared using varying amounts of preformed dispersion as indicated in Table 4.

TABLE 4

Dispersion Sample No.	% of Product Solids from PFD solids ¹	Total Solids ²	Viscosity ³	Particle Size ⁴
7	0.5%	20%	8450	>1,000; 800
8	5%	20%	9350	>1,000; 550
9	10%	20%	12,000	>1,000; 500
10	25%	20%	13,200	>1,000; 350
11	35%	20%	18,200	>1,000; 250
12	50%	20%	39,200	>1,000; 150

¹See note 2 of Table 1.

²By weight of the product dispersion.

³mPa·s, measured on a Brookfield viscometer at 25°C using a #5 spindle.

⁴Reported in nm. Measured by hydrodynamic chromatography.

Two values indicate bimodal distribution.

20

A bimodal distribution was obtained in all Samples, and some Samples showed a decreased viscosity compared with Comparative Dispersion A.

25

Using the general procedure described in Example 1-C, flexible polyurethane foams were prepared using Dispersion Sample Nos. 8 and 10. The resulting foams had properties as reported in Table 5 following.

30

TABLE 5

	<u>Foam Property</u>	<u>Dispersion Sample No.</u>	
		8	10
5	% of Product Solids from PFD solids ¹	5.0	25.0
	Shrinkage, %	34	20
	65% IFD, N ²	393	399
10	Modulus ²	2.5	2.6
	Tensile, KPa	127	132
	Tear, N/m ²	263	243
	Elongation, % ²	115	114
	Compression Set, % ²	18	18
15	Core Density, kg/m ³	28.8	28.9

¹See note 2 of Table 1.

²ASTM D-3754

20 Again, substantial improvements in shrinkage and compression set were obtained, as compared with Comparative Dispersion A, with other physical properties not being significantly changed.

25 Example 3

30 A preformed dispersion was prepared in the same general manner as that in Example 1-A, except that the temperature of the components at the beginning of the reaction was 45°C, and 44.2 parts triethanolamine and 55.8 parts TDI were used. The resulting dispersion is referred to as Preformed Dispersion C. It had a solids content of 10 percent by weight with an average particle

size of 4200 Angstroms (420 nm) and a viscosity of 2340 mPa·s at 25°C.

In the same general manner as described in Example 1-B, Preformed Dispersion C was used to make Dispersion Samples 13-16. Each was a 20 percent solids dispersion prepared using varying amounts of Preformed Dispersion C as indicated in Table 6. Also, Dispersion Samples 13-16 were used to make polyurethane foams using the general procedure described in Example 1-C and foam shrinkage results were determined as described before. The viscosity and particle size of the dispersions and the shrinkage results of the foams were as reported in Table 6.

TABLE 6

<u>Property</u>	<u>Dispersion Sample No.</u>				
	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>Control*</u>
% of Product Solids from PFD Solids ¹	2.5%	5%	12.5%	25%	0
Total Solids ²	20%	20%	20%	20%	20%
Viscosity ³	5500	7850	7100	10,100	11,200
Particle Size ⁴	>1000; 480	>1000; 320	900; 160	710; 600	800
Foam Shrinkage	42%	24%	4%	4%	54%

* - Comparative Dispersion A - Not an example of this invention. ¹See Note 2 of Table 1. ²By weight of the product dispersion. ³mPa.s, measured on a Brookfield viscometer at 25°C using a #5 spindle. ⁴Reported in nm, as measured by hydrodynamic chromatography. Two values indicate bimodal distribution.

20 As can be seen from the data in Table 6, reduced shrinkage and viscosity were obtained in all cases, compared with the control.

25 Dispersion Sample No. 15 was used to make a polyurethane foam using the same formulation as described in Example 1. The foam was prepared on a low pressure foam machine. The physical properties of the foam are reported in Table 7. For comparison, a similar
30 foam was prepared in like manner, except Comparative Dispersion A was used instead of Dispersion Sample No. 15. The properties of the resulting foam are also reported in Table 7. Cure ratings were determined by impressing each of four replicate, foam samples with a jig containing four indenter feet to regionally deflect

the foam to 1" (2.54 cm), 3/4" (1.9 cm), 1/2" (1.27 cm) and 1/4" (0.63 cm) residual thickness. The samples were so impressed for periods of 15, 30, 45 and 60 seconds, respectively. The jig was then removed and the percentage loss of foam height was measured at each point of deflection. This data was fitted into the following form.

10	Deflection Time (sec)	Deflection to:			
		1"	3/4"	1/2"	1/4"
15	15	A	B	C	D
	30	E	F	G	H
	45	I	J	K	L
	60	M	N	O	P

The cure rating was calculated by adding the values of A through P. Since smaller losses in foam height are desired, small cure ratings indicate superior results.

TABLE 7

	<u>Property</u>	<u>Dispersion Sample No.</u>	
		A*	15
5	Density, lb/ft ³ (kg/m ³)	1.84 (29.5)	1.92 (30.8)
	Tensile Str., psi ¹ (kPa)	21.6 (149)	23.9 (165)
	Elongation, % ¹ (N/m)	155	169
	Tear Str., lb/in ¹	1.06 (186)	1.29 (226)
10	Resiliency, % ¹	56	50
	50% HACS, % ¹	80	66
	ILD, 25%, lb ¹ (N)	28 (124)	28 (124)
	ILD, 65%, lb ¹ (N)	80 (356)	80 (356)
15	ILD, return 25%, lb ¹ (N)	21 (93)	22 (98)
	Air flow, uncrushed ²	1.6 (.00075)	1.4 (.00052)
	Air flow, crushed ²	2.8 (.0013)	2.4 (0.0011)
	Cure rating ³	208	100

* -- Not an example of this invention.

¹ASTM D-3,54. HACS is humid aged compression set.

ILD is indentation load deflection. ²Air flow values reported in cubic foot of air per minute m³/S. ³Determined by method discussed in text.

Smaller values indicate superior cure.

As can be seen from the data in Table 7, the properties of the foam made using Dispersion Sample No. 15 were equivalent or superior to those obtained using the Comparative Dispersion. In particular, the cure obtained with Dispersion Sample No. 15 was markedly superior, and improvements in humid aged compression set, tensile, elongation and tear strength were also seen.

Example 4

Two duplicate preformed dispersions were made as described in Example 1-A, except that in each 44.2 parts of triethanolamine and 55.8 parts of TDI were used. These preformed dispersions were then blended to provide Preformed Dispersion D, which contained 10 percent solids and had a viscosity of 3240 cps at 25°C. The average particle size was 2200 Angstroms (LLD nm).

Fifty parts by weight of Preformed Dispersion D were diluted with 755 parts of Polyol B in which was dissolved 0.2 part dibutyltin dilaurate. Polyol B was a 1200 equivalent weight, nominally trifunctional random copolymer of 88 percent propylene oxide and 12 percent ethylene oxide) which contained mostly secondary hydroxyl groups. To the resulting mixture were added 86.2 parts triethanolamine. The mixture was then heated to 36°C, and with stirring 108.8 parts of TDI were added over 23 seconds. An exotherm was noted. Stirring was continued for about fifteen minutes, at which time a smooth dispersion containing 20 percent solids was obtained. The solids from the preformed dispersion constituted 2.5 percent of the solids of the product dispersion. The product dispersion had a viscosity of 3800 mPa·s and a bimodal particle size distribution, with smaller particles having an average diameter of about 5400 Angstroms (540 nm) and larger particles having an average diameter in excess of 10,000 Angstroms (1000 nm).

This product dispersion was suitable for preparing general purpose slabstock foam.

The claims defining the invention are as follows:

1. A process for preparing a product polyurethane and/or polyurea dispersion comprising reacting

(A) a polyisocyanate with

(B) a coreactant material having a equivalent weight of up to 400 and a plurality of active hydrogen atoms attached to oxygen or nitrogen atoms, in the presence of

(C) a preformed solution or dispersion of a material containing urethane and/or urea groups in an isocyanate-reactive material which has an equivalent weight greater than 400, wherein

(i) said product dispersion contains about 0.5 to about 40 weight percent solids, based on the weight of the product dispersion, and

(ii) the material containing urethane and/or urea groups dissolved and or dispersed in the preformed solution or dispersion constitutes from 0.5 to 50 percent of the weight of the solids of the product dispersion.

2. The process of Claim 1 wherein said product dispersion contains polyurethane particles.

3. The process of Claim 2 wherein said isocyanate-reactive material is a polyether polyol having an equivalent weight from 700 to 3000 and a functionality of 1.8 to 4.

4. The process of Claim 3 wherein said isocyanate-reactive material in the preformed solution or dispersion is an oxyethylene-capped poly(propylene oxide) having an equivalent weight from 700 to 3000 and a functionality of 1.8 to 4, and said reaction is further conducted in the presence of

(D) a 500 to 2500 equivalent weight, nominally 1.8-4 functional homopolymer of propylene oxide or random copolymer of propylene oxide and a minor amount of ethylene oxide having at least 90 percent secondary hydroxyl groups,

the weight ratio of the isocyanate-reactive material in the preformed solution or dispersion to component (D) being from 1:2 to 1:50.

5. The process of Claim 4 wherein the coreactant is an alkanolamine and said polyisocyanate is TDI, MDI, PMDI or a mixture thereof.

6. The process of Claim 5 wherein said material containing urethane and/or urea groups in the preformed dispersion is the reaction product of an alkanolamine and TDI, MDI, PMDI or a mixture thereof.

7. The process of any of the foregoing claims wherein said product dispersion has a bimodal particle size distribution wherein at least about 60 volume percent of the particles fall into two discrete size ranges, 5 to 75 volume percent of said particles in the two discrete size ranges being larger particles having an average particle size, as measured by (HDC), of at least about 200 Angstroms nm, and 25 to 95 volume percent in the two discrete size ranges of the particles being smaller particles having an average particle size, as measured by HDC, of 10 to 70 nm.

8. The process of any of the foregoing claims wherein said preformed solution or dispersion is previously treated to remove particulate matter.

9. A dispersion prepared according to the process of any of the foregoing claims.

~~10. A dispersion of polyurethane and/or polyurea particles in an isocyanate-reactive material having an equivalent weight greater than 400, wherein said particles have a bimodal particle size distribution wherein at least about 60 volume percent of the particles fall into two discrete size ranges, about 5 to about 75 volume percent of said particles in said discrete size ranges, being larger particles having an average particle size, as measured by hydrodynamic chromatography (HDC), of at least about 200 nm, and 25 to 95 volume percent of the particles in said discrete size ranges being smaller particles having an average particle size, as measured by HDC, of 10 to 700 nm.~~

10. A product dispersion of polyurethane and/or polyurea particles wherein the particles are formed by the reaction of

(A) a polyisocyanate with

(B) a coreactant material having a equivalent weight of up to 400 and a plurality of active hydrogen atoms attached to oxygen or nitrogen atoms, in the presence of

(C) a preformed solution or dispersion of a material containing urethane and/or urea groups in an isocyanate-reactive material which has an equivalent weight greater than 400, wherein

(i) said product dispersion contains about 0.5 to about 40 weight percent solids, based on the weight of the product dispersion, and

(ii) the material containing urethane and/or urea groups dissolved and or dispersed in the performed solution or dispersion constitutes from 0.5 to 50 percent of the weight of the solids of the product dispersion.

wherein said particles have a bimodal particle size distribution wherein at least about 60 volume percent of the particles fall into two discrete size ranges, about 5 to about 75 volume percent of said particles in said discrete size ranges, being larger particles having an average particle size, as measured by hydrodynamic chromatography (HDC), of at least about 200 nm, and 25 to 95 volume percent of the particles in said discrete size ranges being smaller particles having an average particle size, as measured by HDC, of 10 to 700 nm.

11. A reaction product of a polyisocyanate with an active hydrogen-containing composition comprising the dispersion of Claim 10.

12. A process of claim 1 substantially as hereinbefore described with reference to any one of the Examples.

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