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(21) International Application Number: PCT/US98/06367 (22) International Filing Date: 1 April 1998 (01.04.98) (30) Priority Data: 60/043,058 4 April 1997 (04.04.97) US (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Mid- land, MI 48674 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SCHROCK, Alan, K. [US/US]; 97 Rosewood, Lake Jackson, TX 77566 (US). WHITE, Douglas, P. [US/US]; 104 Sandlewood, Lake Jackson, TX 77566 (US). PARKS, Franklin, E. [US/US]; 7118 S.F. Austin Road, Jones Creek, TX 77541 (US). LIDY, Werner, A. [US/US]; 135 Arrow Wood, Lake Jackson, TX 77566 (US). HERRINGTON, Ronald, M. [US/US]; Route 5, Box 5509, Brazoria, TX 77422 (US). SANCHEZ, Thelma, C. [US/US]; Apartment 128, 400 Flag Lake Drive, Lake Jackson, TX 77566 (US). MOBLEY, Larry, W. [US/US]; 4404 Honeysuckle Lane, Cohutta, GA 30710 (US). (74) Agent: DOBSON, Kevin, S.; Patent Dept., B-1211, 2301 Brazosport Boulevard, Freeport, TX 77541 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LOW RESILIENCY POLYURETHANE FOAMS HAVING SOME GEL CHARACTERISTICS (GELFOAMS) (57) Abstract The present invention is a closed cell polyurethane foam having low modulus, low T_g, and low resiliency, wherein the foam is prepared by mechanically frothing a polyurethane-forming mixture in the absence of water and added amine functionality. Gelfoams of the present invention can be useful in applications such as cushioning, padding, and mechanical dampening.		

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LOW RESILIENCY POLYURETHANE FOAMS HAVING SOME GEL
CHARACTERISTICS (GELFOAMS)

5 The present invention relates to polyurethane foamed articles. The present invention particularly relates to polyurethane foamed articles having gel-like characteristics (gelfoams) and to a process for making same.

10 It is known to prepare polyurethane foams from polyols, polyisocyanates and other additives by mechanically frothing, or foaming, a polyurethane-forming mixture. Mechanical frothing is a known technique by which closed-cell foams can be prepared. A polyurethane-forming mixture can be frothed by mechanically agitating a polyurethane-forming formulation such that air from the surrounding atmosphere is mixed with the formulation thereby creating gas pockets, or cells, within the mixture.

15 Closed cell foams can be prepared in this manner because air trapped in the polyurethane foam as it cures is at atmospheric pressure, and the trapped gas does not have the force required to open the cell and escape. Mechanically frothed foams are described in, for example, U.S. Patent No. 3,706,681; U.S. Patent No. 3,755,212; and U.S. Patent No. 3,821,130. Conventional polyurethane foams do not have the

20 characteristics of a gel, however. Conventional polyurethane foams typically have high resiliency. High resiliency is not characteristic of gel-like materials. Gel-like materials typically have low resiliency, and can be slow to regain their original form if depressed by a load.

25 Gels are semi-solid materials that exhibit fluid-like behavior. For example, a gel can be molded into the shape of its container without breaking apart or shearing. Gels are typically soft to the touch, can be molded, and are capable of bearing a load. Gels can be used in cushioning and padding applications, and as such find use in articles such as bicycle seats, shoe inserts, and glove padding. Conventional polymeric

30 gels can be prepared from thermoplastic materials such as polyvinyl chloride,

polyethylene, thermoplastic polyurethane and the like. Conventional polymeric gels typically include a high concentration of plasticizers, which promote the formation of the gel by preventing the polymer from forming an ordered, rigid structure. Such gels are described, for example, in U.S. Patent Nos.: 5,121,962; 4,666,968; and 4,666,969.

5

The use of gels in certain applications can be a problem, however.

Conventional polymeric gels are typically sticky substances that can adhere to other objects such as clothing, skin, floors and other surfaces. This characteristic can be undesirable in an application wherein the gel can come in contact with other materials.

10 For this reason, conventional gels are typically contained within a shell having a harder outer coating. However, if the container ruptures the gel can escape from the shell and contaminate the surrounding environment.

It would be desirable in the art of preparing polyurethane foams to prepare a foamed article having the characteristics of a gel without the use of plasticizers. It would also be desirable in the art of preparing polyurethane foams to have an article having characteristics of a gel without the stickiness and tackiness associated with conventional gels. It would also be desirable to prepare a foamed article having some characteristics of a gel, without requiring a hard outer coating to isolate it from the environment.

20

In one aspect, the present invention is a closed cell polyurethane foam having low modulus, low Tg, and low resiliency.

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In another aspect, the present invention is a process for preparing a closed cell polyurethane foam having low modulus, low Tg, and low resiliency comprising the steps: (1) admixing a polyisocyanate A-side formulation and a polyol B-side formulation in the presence of a polyurethane catalyst to obtain a polyurethane-forming mixture, wherein the polyurethane forming mixture is substantially free of water; (2)

mechanically frothing the mixture; and, (3) curing the froth to a tack-free state to obtain the polyurethane foam.

The polyurethane gelfoams described herein can be prepared from a
5 polyisocyanate formulation (A-side formulation) and a polyol formulation (B-side formulation) in the presence of a polyurethane catalyst. Except that inclusion of water in a polyurethane-forming mixture is specifically excluded in the practice of the present invention, any known polyurethane-forming formulation can be used in the practice of the present invention to prepare a polyurethane gelfoam. In general, the A- and B-side
10 reactants are admixed in the presence of a suitable catalyst and other optional components, the mixture is mechanically frothed and then cured to a tack-free state.

A polyisocyanate suitable for use in the practice of the present invention can be any polyisocyanate known to be useful in the preparation of polyurethane foams. A
15 suitable polyisocyanate can be either aliphatic or aromatic. Aromatic polyisocyanates suitable for use herein include: phenyl diisocyanate; 2,4-toluene diisocyanate; 2,6-toluene diisocyanate; ditoluene diisocyanate; naphthalene 1,4-diisocyanate; 2,4'-diphenylmethane diisocyanate and 4,4'-diphenylmethane diisocyanate (MDI), individually or in mixture; polymethylene polyphenylenepolyisocyanates (polymeric
20 MDI); like compounds, and mixtures thereof. Suitable aliphatic polyisocyanates include: the hydrogenated derivatives of suitable aromatic polyisocyanates such as 1,6-hexamethylene diisocyanate; isophorone diisocyanate; 1,4-cyclohexyl diisocyanate; like compounds and mixtures thereof. Also suitable for use in the practice of the present invention are prepolymers prepared from polyisocyanates and polyols described
25 herein, as is known in the art.

Suitable prepolymers useful with the present invention are prepolymers having NCO contents of from 5 to 40 weight percent, more preferably from 15 to 30 weight percent. These prepolymers are prepared by reaction of the di- or poly-isocyanates, or
30 mixtures thereof, with materials including lower molecular weight diols, triols, but also

they can be prepared with multivalent active hydrogen compounds such as di- and tri- amines and di- and tri-thiols. Individual examples are aromatic polyisocyanates containing urethane groups, preferably having NCO contents of from 5 to 40 weight percent, more preferably 20 to 35 weight percent, obtained by reaction of diisocyanates or polyisocyanates, or mixtures thereof, with, for example, lower molecular weight diols, triols, oxyalkylene glycols, dioxyalkylene glycols or polyoxyalkylene glycols having molecular weights up to 800. These polyols can be employed individually or in mixtures as di- or polyoxyalkylene glycols, or mixtures thereof. For example, diethylene glycols, dipropylene glycols, polyoxyethylene glycols, polyoxypropylene glycols and polyoxypropylenepolyoxyethylene glycols can be used.

A B-side formulation of the present invention can include an active hydrogen containing compound, capable of reacting with isocyanate functionality, in addition to other optional components. Active hydrogen containing compounds, as the term is used herein, are compounds having functionality that is reactive with Zerewitinoff reagent. Generally, active hydrogen-containing compounds include alcohols, amines, and mercaptans, for example. Polyols are active hydrogen containing compounds suitable for use in the practice of the present invention. Representatives of polyols suitable for use with the process of the present invention are generally known and are described in such publications as High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology" by Saunders and Frisch, Interscience Publishers, New York, Vol. I, pp. 32-42, 44-54 (1962) and Vol. II, pp. 5-6, 198-199 (1964); Organic Polymer Chemistry by K. J. Saunders, Chapman and Hall, London, pp. 323-325 (1973); and Developments in Polyurethanes, Vol. I, J. M. Burst, ed., Applied Science Publishers, pp. 1-76 (1978). Examples of such materials include those selected from the following classes of compositions, alone or in admixture: (a) alkylene oxide adducts of polyhydroxyalkanes; (b) alkylene oxide adducts of non-reducing sugars and sugar derivatives; (c) alkylene oxide adducts of polyphenols; and (d) polyester polyols. Also

preferred are poly(oxypropylene) glycols, triols, tetrols and hexols and any of these that are capped with ethylene oxide. These polyols also include poly(oxypropyleneoxyethylene)polyols.

5 The A-side and the B-side formulations can be admixed in any ratio known in the art to be suitable for preparing polyurethane foams. For example, the components can be admixed at an isocyanate index of from 85 to 130. The isocyanate index can be calculated by multiplying the ratio of isocyanate equivalents to active hydrogen equivalents by 100.

10 Catalysts useful in the present invention are conventional and are known in the art of preparing polyurethane foams. Suitable catalysts include: tertiary amine catalysts such as triethylenediamine, N-methyl morpholine, N-ethyl morpholine, diethyl ethanolamine, N-coco morpholine, 1-methyl-4-dimethylaminoethyl piperazine, 3-
15 methoxy-N-dimethylpropylamine, N,N-diethyl-3-diethyl aminopropylamine, dimethylbenzyl amine; organotin catalysts such as dimethyltin dilaurate, dibutyltin dilaurate, dioctyltin dilaurate, stannous octoate; and isocyanurate catalysts such
aliphatic and aromatic tertiary amine compounds, organometallic compounds, alkali
metal salts of carboxylic acids, phenols, symmetrical triazine derivatives, and similar
20 compounds as these. Both an amine type catalyst and an organometallic catalyst can be employed in combination.

 An amount of catalyst is advantageously employed such that a relatively rapid cure to a tack-free state is obtained. If an organometallic catalyst is employed, such a
25 cure can be obtained using from 0.01 to 0.5 parts per 100 parts of the polyurethane-forming composition, by weight. If a tertiary amine catalyst is employed, the catalyst preferably provides a suitable cure using from 0.01 to 3 parts of tertiary amine catalyst per 100 parts of the polyurethane-forming composition, by weight.

The present invention optionally includes a chain extender. A chain extender is typically a low equivalent weight active hydrogen containing compound having 2 active hydrogen groups per molecule. Preferred chain extenders include glycols and glycol ethers such as: ethylene glycol; 1,4-butane diol; 1,6-hexamethylene glycol; 5 dipropylene glycol; tripropylene glycol; diethylene glycol; triethylene glycol; cyclohexanedimethanol; the diverse bisphenols; like compounds and mixtures thereof. Amine compounds are also useful chain extenders in the practice of the present invention. An amine chain extender can be blocked, encapsulated, or otherwise rendered less reactive. Amine compounds suitable for use as chain extenders in the 10 practice of the present invention include, for example: methylene bis(o-chloroaniline); NaCl-blocked methylene dianiline; diethyltoluenediamine; like compounds, and mixtures thereof.

The foams of the present invention can be prepared using a frothing agent. The 15 frothing agent is preferably air, however, other gasses, such as carbon dioxide, nitrogen, and similar materials can be used. Any method of mechanical frothing can be used to prepare a foam of the present invention. For example, a hand-held mixer can be used to agitate the polyurethane-forming mixture or, alternatively, a frother can be used to mix the formulation and introduce the frothing agent. A frother is a device which injects 20 gas into an admixture as it agitates the admixture. In the practice of the present invention, frothing can be carried out simultaneously with admixing the A- and B-side components, or after the polyurethane-forming mixture is obtained. The frothing agent is preferably introduced into the polymer by a frother.

25 The present invention can include other optional components. For example, the present invention optionally includes a filler material. Conventional fillers such as milled glass, calcium carbonate, ATH, talc, bentonite clays, antimony trioxide, kaolin, fly ash, or other known fillers can be used in the practice of the present invention. A polyurethane-forming composition of the present invention can optionally include:

surfactants; fire retardants; pigments; anti-static agents; reinforcing fibers; antioxidants; preservatives; water scavengers; and acid scavengers.

A polyurethane gelfoam of the present invention is a closed-cell foamed article
5 having the properties of a semi-solid with a hydraulic feel. To prepare a gelfoam of the present invention a polyisocyanate A-side formulation can be admixed with a polyol B-side formulation to obtain a polyurethane-forming mixture. The polyurethane-forming mixture is mechanically frothed. The gelfoam is prepared by frothing the polyurethane-forming mixture under conditions sufficient to prepare a stable polymer foam matrix,
10 wherein a polyurethane foam that contains a low amount of hard segments is obtained. By "a low amount of hard segments" it is meant that the hard segment content in the foam is preferably equal to or less than 8 weight percent, based on the total weight of polymer. The hard segment content is more preferably equal to or less than 7 weight percent. The hard segment content is most preferably equal to or less than 6 weight
15 percent. Hard segment content as described herein is calculated by adding the number of parts of chain extender to the number of parts of MDI reacting with the chain extender, then dividing the total by the total weight of the formulation.

The hydraulic feel of a gelfoam results from the fluidity exhibited by the
20 gelfoam as a result of force, or stress, applied to the article. The hydraulic feel is defined herein as the feel of fluidity, or movement, resulting from force applied to a gelfoam article. For example, pressing or squeezing a gelfoam results in movement of the of the polymer away from the applied pressure in a manner such that the stress is dissipated throughout the polymer.

25

A gelfoam of the present invention has low resiliency, as measured by a ball rebound test. A gelfoam of the present invention has resiliency of less than or equal to 50 percent in a ball rebound test. Preferably, a gelfoam of the present invention has resiliency of less than or equal to 45 percent, more preferably less or equal to than 40
30 percent, and most preferably less than or equal to 35 percent.

A gelfoam of the present invention has a low modulus, as determined by dynamic mechanical spectrometry and measured at 25 °C. A gelfoam of the present invention has a modulus of less than 1×10^7 dynes per cm^2 . Preferably, the modulus is within 1×10^5 and 1×10^7 dynes per cm^2 , more preferably within 5×10^5 and 5×10^6 , and most preferably within 7×10^5 and 1×10^6 .

A gelfoam of the present invention has a low glass transition temperature (T_g). A gelfoam of the present invention has a T_g of less than 25°C, preferably less than 0°C. More preferably, a gelfoam of the present invention has a T_g of less than -25°C, and most preferably less than -30°C.

A gelfoam of the present invention has a density in the range of from 0.1 grams per cm^3 to 0.8 g per cm^3 . Preferably, the density of the gelfoam is in the range of from 0.2 g per cm^3 to 0.7 g per cm^3 .

15

EXAMPLES

Example 1

100 grams of Voranol® 4703 (Voranol is a registered Trademark of the Dow Chemical Company), 1.9 grams of monoethyleneglycol, 4 grams of L-5614, 16 grams of MDI-50 op, and 0.1 gram of UL-6 were mixed together in a plastic beaker for 2 minutes, using a hand mixer to froth the mixture. The mixture was poured into a paper bowl and then placed into an oven at 120°C for 15 minutes.

Example 2
100 grams of Voranol® 3137, 4 grams of L-5614, 12.9 grams of MDI-50 op, and 0.15 gram of UL-6 were mixed together in a plastic beaker for 2 minutes, using a hand mixer to froth the mixture. The mixture was poured into a paper bowl and then placed into an oven at 120°C for 15 minutes.

Example 3

63 parts by weight of VORANOL® 9240, 35 parts of VORANOL® 9815, 2 parts VORANOL® 9800, 2 parts of Niax® silicone L-5614, 0.0125 parts of Polycat® DBU, 0.025 parts of XUS 14051.00 experimental catalyst, and 10.7 parts of MDI-50 op, were mixed together with air on a continuous basis through an Oakes frother to produce a frothed foam. The mixture was poured onto a release belt and cured by passing through a 120°C heated zone for approximately 10 minutes.

Example 4

63 parts by weight of VORANOL® 9240, 35 parts of VORANOL® 9815, 2 parts VORANOL® 9800, 2 parts of Niax® silicone L-5770, 0.0125 parts of Polycat® DBU, 0.025 parts of XUS 14051.00 experimental catalyst, and 10.7 parts of MDI-50 op, were mixed together with air on a continuous basis through an Oakes frother to produce a frothed foam. The mixture was poured onto a release belt and cured by passing through a 120°C heated zone for approximately 10 minutes.

Example 5

98 parts by weight of VORANOL® 9815, 2 parts of diethylene glycol, 2 parts of Niax® silicone L-5770, 0.0125 parts of Polycat® DBU, 0.025 parts of XUS 14051.00 experimental catalyst, and 11.9 parts of MDI-50 op, were mixed together with air on a continuous basis through an Oakes frother to produce a frothed foam. The mixture was poured onto a release belt and cured by passing through a 120°C heated zone for approximately 10 minutes.

Table 1

	Example 3	Example 4	Example 5
Density (lb/ft ³)		23.9	
Thickness (inches)		0.399	
50 percent Compression set (percent)		29.3	
25 percent Compress resistance (lb)		10.7	
65 percent Compression resistance (lb)		51.6	
25 percent Return (lb)		9.8	
Resiliency (percent)		40	
Observations	coalescence	normal	normal

Density was determined according to ASTM D 3676 Volume Density.

Compression Set was determined according to a method similar to ASTM D 3676 except the samples were returned to the oven for 30 minutes after un-clamping, then measured when cool.

Thickness was determined according to ASTM D 3676.

Compression Resistance was determined according to a method similar to ASTM D 3676 except the plied specimens were compressed with a circular presser foot having an area of 1 in². 65 percent compression and a 25 percent return were also measured.

Resiliency was determined according to ASTM D 3574 Test H.

CLAIMS

What is claimed is:

1. A closed cell polyurethane foam having low modulus, low Tg, and low
5 resiliency.
2. The polyurethane foam of Claim 1 wherein the foam has a resiliency of
less than 50 percent, a modulus of less than 1×10^7 dynes per cm^2 , and a Tg of less than
25°C.
- 10 3. The polyurethane foam of Claim 2 wherein the foam has a resiliency of
less than 45 percent.
4. The polyurethane foam of Claim 3 wherein the foam has a resiliency of
15 less than 40 percent.
5. The polyurethane foam of Claim 4 wherein the foam has a resiliency of
less than 35 percent.
6. The polyurethane foam of Claim 5 wherein the foam has a density in a
20 range of from 0.1 to 0.8 grams per cm^3 .
7. The polyurethane foam of Claim 6 wherein the foam has a density in a
range of from 0.2 to 0.7 grams per cm^3 .
- 25 8. The polyurethane foam of Claim 7 wherein the foam has a Tg of less
than 0°C.
9. The polyurethane foam of Claim 8 wherein the foam has a modulus
within 1×10^5 and 1×10^7 dynes per cm^2 .

10. A process for preparing a closed cell polyurethane foam having low modulus, low Tg, and low resiliency comprising the steps:

- (1) admixing a polyisocyanate A-side formulation and a polyol B-side formulation in the presence of a polyurethane catalyst to obtain a polyurethane-forming mixture, wherein the polyurethane forming mixture is substantially free of water;
- (2) mechanically frothing the mixture; and
- (3) curing the froth to a tack-free state to obtain the polyurethane foam.

11. The process of Claim 10 wherein the A-side formulation includes polyisocyanate prepolymers.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/06367

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J9/30 //C08L75:04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 333 088 A (DUNLOP HOLDINGS LTD) 10 October 1973 see claims 1-3, 7-14 see page 3, line 39 - line 54 ---	1, 2
A	US 4 158 087 A (WOOD LOUIS L) 12 June 1979 see column 1, line 1 - line 21 see column 5, line 66 - column 6, line 37 ---	1
A	US 5 541 614 A (LAM JUAN F ET AL) 30 July 1996 see claim 1 see column 13, line 48 - line 65 see column 15, line 50 - line 65 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 252 625 A (MCLAUGHLIN ANDY I ET AL) 12 October 1993 see claims 1,11 see column 4, line 15 - line 68 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/06367

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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