

Description

Background of the invention

1. Field of the invention

This invention relates to a process of preparing flame retardant flexible polyurethane foams.

2. Description of the prior art

Flame retardant flexible polyurethane foams having been made with flame retardant siloxane-polyoxyalkylene block copolymers. Non-flame retardant foams have been made utilizing low molecular weight polyols to improve physical properties such as tear and elongation or load-bearing characteristics.

From GB-PS 1 422 913 the production of flexible polyurethane foams from a homogeneous foam formulation is known containing in addition to the polyether and polyisocyanate for the urethane reaction the catalyst necessary therefor, a blowing agent, a flame retardant and a foam stabilizer, the flame retardant being a commonly used, optionally halogenated organophosphate or organophosphonate, and the foam stabilizer being a commonly used polyoxyalkylene polysiloxane block copolymer.

From GB-PS 1 507 194 a process for the production of flame and smoke resistant flexible polyurethane foams is known using in the foam formulation in addition to the foam stabilizer, the catalyst for the urethane reaction, and the blowing agent for the reaction with tolylene diisocyanate as polyol component a polyether polyol having an average molecular weight of 3000 to 6000, and a low molecular polyol. In this known process too the flame retardant is a halogenated phosphoric ester and the foam stabilizer is an unspecified polyoxyalkylene polysiloxane block copolymer.

Summary of the invention

It has now been found that dipropylene glycol can be utilized along with specific flame retardant siloxane-polyoxyalkylene block copolymers in a process to produce flame retardant flexible polyurethane foams having combustibility properties unexpectedly superior to those of similar foams made without said low molecular weight polyols.

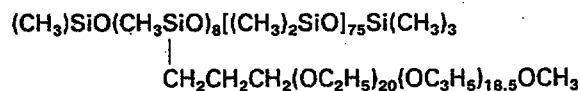
Description of the preferred embodiments

Processes for the production of flexible polyurethane foams are well known in industry. The most important components of the foam-forming reaction mixtures, in terms of weight, are aromatic polyisocyanates, such as tolylene diisocyanates, and polyether polyols, particularly those having hydroxyl numbers ranging from 45 to 60 and molecular weights ranging from 2500 to 4000.

However, the foam-forming reaction mixtures invariably contain other ingredients which, although they are present in relatively small proportions by weight, have controlling influence over the properties of the foam produced by the reaction between the aromatic diisocyanate and the polyether polyol. Among them are conventional compounds such as amine and tin catalysts, blowing agents such as water and trichlorofluoromethane, and surfactants. Less usually, perhaps, other conventional additives such as flame retardant agents (e.g., Thermolin-101®) may be present.

The present invention is based upon the unexpected discovery that the use together, in the preparation of flame retardant flexible polyurethane foams, of two classes of compounds, each in itself known for use in other contexts as a suitable ingredient for some types of polyurethane foam-forming reaction mixtures, can significantly increase combustibility properties of flame retardant polyurethane foams.

The first of said class of compounds are flame retardant polysiloxane-polyoxyalkylene block copolymer surfactants known per se of the formula



the surfactant is used at a rate of from 1 to 2 weight percent, based on the polyether polyol.

The second compound used at a rate of from 0.4 to 2.0 weight percent, based on the weight of the polyether polyol is dipropylene glycol.

The combinations of the dipropylene glycol and the surfactant are indefinitely stable and, as such, produce a homogeneous product which may be shipped and stored until needed.

The foams produced in accordance with this invention can be used in the same areas and for the same purposes as conventional flexible foams designed for use in applications when their response to flaming situations is of importance (e.g., in cushioning materials, mattresses, and automotive interior parts).

Experimental

The foams used in evaluating this invention involve the following components and formulating technique:

	Weight in grams
5 NIAX® Polyol 16—46 (A secondary hydroxyl polyol having a hydroxy number of 46 produced by reacting glycerol with ethylene oxide and propylene oxide)	325
10 Thermolin®-101 (A flame retardant additive of the nominal formula $(\text{ClCH}_2\text{CH}_2\text{O})_n\text{P}(=\text{O})[\text{OCH}_2\text{CH}_2\text{OP}(=\text{O})\text{OCH}_2\text{CH}_2\text{Cl}]_n$ wherein $n=0-2$)	Varied
Water	9.33
15 NIAX Amine catalyst A-10 (A blend of bis[2-(N,N-dimethylamino)ethyl]ether, 2-[2-(N,N-dimethylamino)ethoxy]ethanol, and dipropylene glycol)	0.70
Stannous Octoate	0.788
20 Fluorotrichloromethane	56.0
The flame retardant surfactant	Varied
25 Dipropylene glycol	Varied
TDI (A mixture of 80 wt% 2,4-tolylene diisocyanate and 20 wt% 2,6-tolylene diisocyanate)	Formulated to an index of 110
30 Foams were prepared by the following procedure:	
(a) A cardboard container was charged with 350 grams of the polyol.	
(b) Varied amounts of the "Thermolin-101" were added to the polyol and dispersed therein with a spatula.	
35 (c) A combination of a varied amount of the surfactant and a varied amount of the dipropylene glycol was added, via a 10 cm ³ syringe, to a mixture as produced in (b) and was dispersed therein with a spatula.	
(d) A baffle was set into the cardboard box containing the mixture produced in (c).	
(e) 9.33 grams of water and 0.70 grams of the amine catalyst were added to the mixture obtained in (d), without express dispersion.	
40 (f) 56.0 grams of fluorotrichloromethane were added to the mixture produced in (f), without dispersion.	
(g) The cardboard box containing the mixture obtained in (f) was placed under a drill press. The mixture was agitated for 15 seconds at 2700 revolutions per minute.	
(h) 0.788 grams of stannous octoate was added to the mixture obtained in (g), utilizing a 2 cm ³ syringe.	
45 (i) The mixture produced in (h) was agitated for 8 seconds at 2700 revolutions per minute, at which point the entire amount of TDI was rapidly added; the agitation was continued for an additional 7 seconds.	
(j) Immediately, thereafter, the mixture was poured into a 356×365×305 mm parchment-lined cake box supported by a metal frame.	
(k) The foam was allowed to remain in the box for at least 3 minutes (This is to avoid the dense ridge that will appear if the cake box is removed from the metal frame when the foam is green)	
50 (l) The foam was then cured for 15 minutes at 125°C.	
(m) The foam was then cut.	
Rise, breathability, and burning extent were measured. The terms "rise," "burning extent", and "breathability" used in the Examples below have the following meanings:	
Rise—denotes the foam height. Rise is directly proportional to surfactant potency.	
55 Burning extent—denotes the burned length of a test specimen of foam measured in accordance with ASTM D-1692-68 and California Bulletin 117. The flammability of an MVSS 302 foam is proportional to its burning extent as measured by this test.	
Breathability—denotes the porosity of a foam and is roughly proportional to the number of open cells in a foam. Breathability is measured as follows: A 50×50×25 mm piece of foam is cut from near the center of a bun. Using a Nopco Foam Breathability Tester, GP-2 Model 40GD10, air is drawn through the 25.4 mm portion at a pressure differential of 1.27 mbar less than atmospheric pressure. The air flow is parallel to direction of original foam rise. The degree of openness of the foam (or foam breathability) is measured by air flow and is designated as standard dm ³ /min (cubic feet per minute).	
60 The following Examples illustrate the present invention. Unless otherwise specified, parts and percentages are on a relative weight basis.	
65	

Example 1 and 2

In both of these Examples, the foam-forming reaction mixture contained 100 parts NIAX Polyol 16—46, 2.0 parts Thermolin-101, 16 parts fluorotrichloromethane, 2.95 parts water, 0.2 parts NIAX Amine Catalyst A-10, 0.225 parts stannous octoate, and 39.5 parts TDI. In Example 1, Flame Retardant Surfactant was present in 1.3 parts and in example 2 in 1.8 parts.

In both Examples, the dipropylene glycol content was graduated as indicated in the Tables. The ambient temperature in all cases was 26°C (79°F).

TABLE 1
Example 1 1.3 parts surfactant

Dipropylene glycol	0.2	0.4	0.6	0.8	1.0	1.5	2.0
Cream time (s)	11—12	11—12	11—12	12	12—13	12—13	13—14
Rise time (s)	138	187	187	138	140	141	142
Top collapse (mm)	10.16	12.7	11.43	10.16	10.16	7.62	10.16
Height of rise (mm)	269.24	266.7	274.32	274.32	274.32	266.7	266.7
Breathability (cb.ft/min) dm ³ /min	(4.75) 134.4	(4.24) 120	(4.50) 127.3	(4.25) 120.3	(4.5) 127.3	(3.0) 84.9	(4.0) 113.2
Density (lbs/cb.ft) kg/m ³	(1.22) 19.54	(1.22) 19.54	(1.22) 19.54	(1.22) 19.54	(1.23) 19.70	(1.23) 19.70	(1.24) 9.86
Flammability test MVSS 302 (avg. 3 samples)							
Burning extent (mm)	330	330	330	281.94	292.1	177.8	124.46
Extinguishing time (s)	127	129	123	113	111	67	40

The data indicate that, at a surfactant level of 1.3, dipropylene glycol concentrations of 0.8 parts to 2.0 parts significantly improved combustibility properties of the foams embodying them.

TABLE 2
Example 2 1.8 parts surfactant

Dipropylene glycol	0.2	0.4	0.6	0.8	1.0	1.5	2.0
Cream time (s)	12	12	12	12	12	12	12
Rise time (s)	133	134	132	133	134	131	133
Top collapse (mm)	3.556	5.08	5.08	5.08	5.08	5.08	5.08
Height of rise (mm)	266.7	269.24	271.78	266.7	266.7	264.16	269.24
Breathability (cb.ft/min) dm ³ /min	(4.25) 120.3	(4.25) 120.3	(3.74) 105.8	(3.50) 99.0	(4.0) 113.2	(3.50) 99.0	(3.75) 106.1
Density (lbs/cb.ft) kg/m ³	(1.21) 19.38	(1.22) 19.54	(1.23) 19.70	(1.23) 19.70	(1.23) 19.70	(1.24) 19.86	(1.24) 19.86
Flammability test MVSS 302 (avg. 3 samples)							
Burning extent (mm)	330	330	330	330	330	213.36	68.58
Extinguishing time (s)	132	141	133	141	141	77	15.3

The data indicate that, at a surfactant level of 1.8, dipropylene glycol concentrations of 1.5 parts to 2.0 parts significantly improved combustibility properties of the foams embodying them.

Example 3 and 4

In both of these Examples, the foam-forming reaction mixture contained 100 parts NIAX Polyol 16—46, 4.0 parts Thermolin-101, 16 parts fluorotrichloromethane, 2.95 parts water, 0.2 parts NIAX Amine Catalyst A-10, 0.225 parts stannous octoate, and 39.5 parts TDI. In Example 3, the surfactant was present in 1.3 parts and in Example 4 in 1.8 parts. The ambient temperature was (80°F) 26.5°C.

In both Examples, the dipropylene glycol content was graduated as indicated in the Tables.

TABLE 3
Example 3 1.3 parts surfactant

Dipropylene glycol	0.2	0.4	0.6	0.8	1.0	1.5	2.0
Cream time (s)	12	12	12	12	12	12	12
Rise time (s)	131	132	132	135	135	133	138
Top collapse (mm)	6.35	6.60	5.08	6.35	5.08	6.35	5.08
Height of rise (mm)	266.7	271.78	269.24	274.3	266.7	269.24	269.24
Breathability (cb.ft/min) dm ³ /min	(4.50) 127.3	(4.50) 127.3	(4.25) 120.3	(4.25) 120.3	(4.00) 113.2	(3.25) 92.0	(4.00) 113.2
Density (lbs/cb.ft) kg/m ³	(1.22) 19.54	(1.22) 19.54	(1.23) 19.70	(1.22) 19.54	(1.22) 19.54	(1.24) 19.86	(1.25) 20.02
Flammability test MVSS 302 (avg. 3 samples) Burning extent (mm)	208.3	137.2	116.8	66	68.6	50.8	40.6
Extinguishing time (s)	79	47	38	16	14	7	2.7

The data indicate that, at a surfactant level of 1.3, dipropylene glycol concentrations of 0.4 parts to 2.0 parts significantly improved combustibility properties of the foams embodying them.

TABLE 4
Example 4 1.8 parts surfactant

Dipropylene glycol	0.2	0.4	0.6	0.8	1.0	1.5	2.0
Cream time (s)	12	12	12	12	12	12	12
Rise time (s)	136	136	137	138	141	140	141
Top collapse (mm)	5.08	5.08	6.35	5.08	5.08	5.08	6.35
Height of rise (mm)	271.78	269.24	22.86	266.7	269.24	269.24	274.32
Breathability (cb.ft/min) dm ³ /min	(4.25) 120.3	(4.25) 120.3	(4.25) 120.3	(4.50) 127.3	(4.50) 127.3	(4.50) 127.3	(4.50) 127.3
Density (lbs/cb.ft) kg/m ³	(1.22) 19.54	(1.25) 20.02	(1.25) 20.02	(1.24) 19.86	(1.24) 19.86	(1.24) 19.86	(1.25) 20.02
Flammability test MVSS 302 (avg. 3 samples) Burning extent (mm)	210.8	144.8	111.8	76.2	76.2	55.9	61
Extinguishing time (s)	68	49.6	41.3	22	20	10.7	13.7

The data indicate that, at a surfactant level of 1.8, dipropylene glycol concentrations of from 0.4 to 2.0 parts significantly improved combustibility properties of the foams embodying them.

Examples 5 and 6

In both of these Examples, the ambient temperature was in all cases (78°F 25.5°C). The foam-forming

0 069 338

reaction mixtures contained 100 parts NIAx Polyol 16-46, 2.0 parts Thermolin-101, 16 parts fluorotrichloromethane, 2.95 parts water, 0.2 parts NIAx Amine Catalyst A-10, and 0.225 parts stannous octoate. In Example 5, the surfactant was present in 1.3 parts and in Example 6 in 1.8 parts.

Since dipropylene glycol contains active hydroxyl groups, it will react with TDI during the foaming process. Likewise since it is a small molecule (*i.e.*, low molecular weight) not much of it is needed in order to affect the actual TDI index, making it lower than it would be without recognizing the presence of dipropylene glycol. To investigate this index effect, a series of foams were made similar to those in Examples 1 and 2. However, this time the TDI index was corrected to account for the dipropylene glycol in the formulation. The major effect of correcting the index for dipropylene glycol on the physical properties of the foam was a decrease in foam breathability.

TABLE 5
Example 5 1.5 parts surfactant

Dipropylene glycol	0.2	0.4	0.6	0.8	1.0	1.5	2.0
Cream time (s)	12-13	12-13	12-13	12-13	12-13	12-13	12-13
Rise time (s)	137	131	133	130	131	131	134
Top collapse (mm)	7.62	8.89	7.62	6.35	6.35	5.08	3.81
Height of rise (mm)	256.6	271.8	271.8	274.3	276.9	284.5	287
Breathability (cb.ft/min) dm ³ /min	(3.8) 107.5	(4.0) 113.2	(3.9) 110.4	(2.8) 79.2	(2.2) 62.3	(0.8) 26.4	(0.18) 5.1
Density (lbs/cb.ft) kg/m ³	(1.24) 19.86	(1.21) 19.38	(1.21) 19.38	(1.22) 19.54	(1.23) 19.70	(1.24) 19.86	(1.23) 19.70
Flammability test MVSS 302 (avg. 3 samples) Burning extent (mm)	330	302.2	269.2	238.2	170.2	172.8	114.3
Extinguishing time (s)	122	100	99.7	90	66	69	38

The data indicate that, at a surfactant level of 1.3, dipropylene glycol concentrations of from 0.4 to 2.0 parts significantly improved combustibility properties of the foams embodying them.

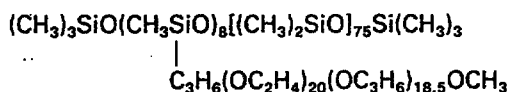
TABLE 6
Example 6 1.8 parts surfactant

Dipropylene glycol	0.2	0.4	0.6	0.8	1.0	1.5	2.0
Cream time (s)	12-13	12-13	12-13	12-13	12-13	12-13	12-13
Rise time (s)	133	129	133	129	130	136	136
Top collapse (mm)	6.35	7.62	6.35	5.08	3.81	2.54	2.54
Height of rise (mm)	274.3	274.3	274.3	271.8	274.3	284.5	289.6
Breathability (cb.ft/min) dm ³ /min	(4.2) 118.9	(3.7) 104.7	(3.4) 96.2	(1.35) 38.2	(2.0) 56.6	(0.3) 8.5	(0.21) 5.9
Density (lbs/cb.ft) kg/m ³	(1.22) 19.54	(1.23) 19.70	(1.23) 19.70	(1.23) 19.70	(1.25) 20.02	(1.24) 19.86	(1.23) 19.70
Flammability test MVSS 302 (avg. 3 samples) Burning extent (mm)	330	330	330	330	330	330	236.2
Extinguishing time (s)	126	127	119	122	119	123	88

The data indicate that at a surfactant level of 1.8, a dipropylene glycol concentration of 2.0 parts significantly improved combustibility properties of the foam embodying it.

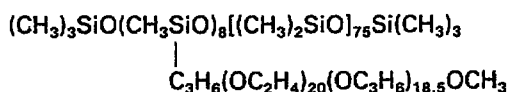
Claim

A process for producing flame retardant flexible polyurethane foams by foaming a mixture of flame retardant additives, aromatic polyisocyanates, and polyether polyols, from 1 to 2 percent of a polysiloxane-polyoxyalkylene-blockcopolymer as surfactant and from 0.4 to 2.0 percent of dipropylene glycol—based on the weight of the polyether polyol—characterized in that the surfactant has the formula:



Patentanspruch

Verfahren zur Herstellung von flammwidrigen Polyurethan-Weichschaumstoffen durch Aufschäumen eines Gemischs von flammhemmenden Zusätzen, aromatischen Polyisocyanaten und Polyetherpolyolen sowie 1 bis 2% eines oberflächenaktiven Mittels in Form eines Polysiloxan/Polyoxyalkylen-Blockcopolymeren und 0,4 bis 2% Dipropylenglykol—bezogen auf das Gewicht von Polyetherpolyol—dadurch gekennzeichnet, daß das oberflächenaktive Mittel der Formel



entspricht.

Revendication

Procédé de production de mousses flexibles de polyuréthane résistant à la flamme, par moussage d'un mélange d'additifs retardateurs de flamme, de polyisocyanates aromatiques et de polyéther-polyols, de 1 à 2% d'un copolymère séquencé polysiloxane-polyoxyalkylène comme surfactant et de 0,4 à 2,0% de dipropylèneglycol—sur la base du poids du polyéther-polyol—, caractérisé en ce que le surfactant répond à la formule:

