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(54) Title: MOLDED POLYURETHANE FOAMS		
(57) Abstract This invention relates to molded polyurethane foams prepared by reacting a specific polyisocyanate with a specific polyol in the presence of water as a blowing agent and a catalyst, wherein (a) the polyisocyanate comprises a mixture of (i) a specified amount of polymethylene polyphenyl polyisocyanate and (ii) an NCO-terminated prepolymer prepared from the reaction of an organic polyisocyanate with a specified amount of poly(oxytetramethylene)glycol, or a specific NCO-terminated prepolymer prepared from the reaction of (i) an organic polyisocyanate, (ii) a specified amount of polymethylene polyphenyl polyisocyanate and (iii) a specified amount of poly(oxytetramethylene)glycol, (b) the polyol contains a specified amount of polymer polyol prepared from the reaction of a polyetherpolyol with an ethylenic unsaturated monomer, and (c) the catalyst contains an organotin compound. The molded polyurethane foams can be prepared under good demoldability and have excellent abrasion resistance, and therefore, can be useful for automotive steering wheels, headrests, armrests and the like.		

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MOLDED POLYURETHANE FOAMS

BACKGROUND OF THE INVENTION

The present invention relates to molded polyurethane foams having excellent abrasion resistance useful for automotive material for steering wheels, headrests and armrests, material for furniture and the like.

Integral skin polyurethane foams having fine skin are well-known to the public and are widely utilized as automotive material for steering wheels, headrests and armrests, and material for furniture and the like in various fields. The formation of the skin layer in the integral skin foams is based on the function of a blowing agent such as chlorofluorocarbon ("CFC") in the exothermic reaction of a polyisocyanate with a polyol. The use of a physical blowing agent such as CFC provides to the foams excellent skin properties which are required to the stated products. On the contrary, the use of a chemical blowing agent such as water does not usually provide any excellent skin properties to the foams.

Some approaches to provide excellent skin properties to molded polyurethane foams have included, for example, those described in Japanese Kokai Patent No. H03-24108, in which a specific catalyst mixture comprising a urethane catalyst and a carbodiimide catalyst is employed to provide low core density in the presence of a non-reactive physical blowing agent, and Japanese Kokai Patent No. H03-33120, in which a specific catalyst mixture is employed in the presence of water as the primary blowing agent. Especially, the technology disclosed in the latter patent may be useful as an alternative technology of a CFC based blowing agent under the Freon Regulation.

Since several years ago, it has been pointing out that CFC destroys the ozone layer of the Earth, and consequently, the use of CFC is globally expected to be restricted or abolished in various industrial fields in present and future. In such situation, some approaches to employ water as the primary blowing agent have been trying. However, in such prior arts, there is a technical problem that demolding time of the process employing water as a sole blowing agent is longer than the one of the process employing CFC as a blowing agent, and also that the former foams are not better in skin properties and abrasion resistance than the latter foams prepared by employing CFC.

SUMMARY OF THE INVENTION

The inventors researched to overcome the stated prior technical problems. That is, the purpose of the present invention is to provide molded polyurethane foams having excellent abrasion resistance under shorter demolding time.

The inventors discovered that the stated purpose of the invention can effectively be achieved by employing a specific polyisocyanate, polyol and catalyst in the presence of water as a blowing agent. That is, the present invention provides molded polyurethane foams prepared by reacting a polyisocyanate with a polyol in the presence of water as a blowing agent and a catalyst wherein (a) the polyisocyanate comprises a mixture of (i) from 2 to 30 weight percent polymethylene polyphenyl polyisocyanate ("Polymeric MDI") and (ii) a NCO-terminated prepolymer prepared from the reaction of an organic polyisocyanate with 20 to 45 weight percent poly(oxytetramethylene)glycol ("PTMG"), said weight percents being based on the total weight of organic polyisocyanate, poly(oxytetramethylene)glycol and polymethylene polyphenyl polyisocyanate, and (b) the polyol contains at least 30 weight percent polymer polyol prepared from the reaction of a polyetherpolyol with an ethylenic unsaturated monomer, and (c) the catalyst contains an organotin compound. The present invention also provides molded polyurethane foams prepared by reacting a polyisocyanate with a polyol in the presence of water as a blowing agent and a catalyst wherein (a) the polyisocyanate comprises a NCO-terminated prepolymer prepared from the reaction of (i) an organic polyisocyanate, (ii) from 2 to 30 weight percent polymethylene polyphenyl polyisocyanate and (iii) from 20 to 45 weight percent poly(oxytetramethylene)glycol, said weight percents based on the total weight of the polyisocyanate, polymethylene polyphenyl polyisocyanate and poly(oxytetramethylene)glycol, and (b) the polyol contains at least 30 weight percent polymer polyol prepared from the reaction of a polyetherpolyol with an ethylenic unsaturated monomer, and the catalyst contains an organotin compound.

DETAILED DESCRIPTION OF THE INVENTION

Suitable polyisocyanates useful in the present invention include, for example, a mixture of a polymeric MDI and a NCO-terminated prepolymer prepared from the reaction of an organic polyisocyanate with PTMG, or a NCO-terminated prepolymer prepared from the reaction of an organic polyisocyanate containing a polymeric MDI with PTMG.

Suitable organic polyisocyanates useful in the present invention include, for example, aliphatic polyisocyanates, alicyclic polyisocyanates, aromatic polyisocyanates or heterocyclic polyisocyanates which are well-known to the public in polyurethane or polyurea industrial field. More specifically, suitable organic polyisocyanates include, for example, 1,6-hexamethylene diisocyanate, cyclohexane-1,4 diisocyanate, 1,4-xylilene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene

diisocyanate, 4,4'-diphenylmethane diisocyanate ("MDI"), 2,4-diphenylmethane diisocyanate, Polymeric MDI and modified polyisocyanates having a group such as urethane group, urea group, biuret group, carbodiimide group or isocyanurate group, and the mixture thereof. Among the polyisocyanates, preferable polyisocyanates are aromatic polyisocyanates such as MDI, a polymeric MDI, modified polyisocyanates thereof and the mixture thereof.

Suitable poly(oxytetramethylene)glycol ("PTMG") is a linear polyetherpolyol having a primary hydroxy group in its both terminals and has an weight average molecular weight of about 300 to about 3,000. The preferable molecular weight of PTMG to be employed in the preparation of the NCO-terminated prepolymer of the present invention is from about 500 to about 2,400.

The NCO-terminated prepolymer is prepared by reacting PTMG with an excess amount of an organic polyisocyanate in the range of temperature of about 40 to about 100°C. The NCO content of the prepolymer is from about 14 to about 28 weight percent ("wt%") and the PTMG content of the prepolymer is from about 10 to about 50 wt%, preferably, about 20 to about 45 wt%.

One of the polyisocyanates useful in the present invention is a mixture of a polymeric MDI and the stated PTMG-based prepolymer. The polymeric MDI content of the poly- isocyanate mixture is from about 1 to about 40 wt%, preferably, about 2 to about 30 wt%, more preferably, about 5 to about 20 wt%. The another polyisocyanate useful in the present invention is a prepolymer prepared from the reaction of an organic polyisocyanate containing a polymeric MDI with PTMG. The NCO content of the prepolymer is from about 14 to about 28 wt% and the PTMG content of the prepolymer is from about 10 to about 50 wt%, preferably, about 20 to about 45 wt%. The polymeric MDI content in the prepolymer is from about 1 to about 40 wt%, preferably, about 2 to about 30 wt%, more preferably, about 5 to about 20 wt%.

Suitable polyols useful in the present invention include, for example, polyetherpolyols prepared from the reaction of alkyleneoxides such as ethyleneoxide, propyleneoxide and butyleneoxide with low molecular weight polyols such as ethyleneglycol, propyleneglycol, glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose, or polyamines such as ethylenediamine, xylenediamine, piperazine and N-N-dimethylamino alkylamine, polymer polyols prepared from the reaction of the stated polyetherpolyols with ethylenic unsaturated monomers such as acrylonitrile, styrene, butadiene, methyl methacrylate, acrylic amide and vinyl acetate, or polyesters prepared from the reaction of the stated low molecular weight polyols with polycarboxylic acids such as succinic acid, maleic acid, sebacic acid, adipic acid, fumaric acid, phthalic acid and dimeric acid.

The inventors discovered that a polymer polyol is recommended to use as a polyol in order to improve abrasion resistance of molded polyurethane foams of the present invention. Suitable polymer polyols include, for example, polymer polyols prepared from the reaction of a polyetherpolyol with acrylonitrile only or a mixture of acrylonitrile and other ethylenic unsaturated monomer such as styrene. However, though the use of such polymer polyols is of good advantage to improvement of abrasion resistance of molded polyurethane foams, the amount employed of the polymer polyol should be determined under consideration of other properties such as processability since the polymer polyols have generally high viscosity. The amount employed of the polymer polyol in the total polyol is at least 30 wt%, preferably, about 30 to about 70 wt%, more preferably, about 35 to about 60 wt%.

Suitable blowing agents useful in the present invention include, for example, water, chlorofluorocarbon ("CFC") or a mixture thereof. The suitable blowing agent is water only or a blowing agent containing water as primary component. The amount employed of water is from about 0.05 to about 5 parts by weight ("pbw") based on the total polyol, preferably, about 0.1 to about 3 pbw, more preferably, about 0.3 to about 2 pbw. Solvents, having low boiling point, such as pentane, methylenechloride, dichloromethane and 4,4'-diaminodiphenylmethane, can optionally be employed as a blowing agent together with water.

In the present invention, it is essential to employ an organotin compound as a catalyst. Suitable organotin catalysts include, for example, organotin compounds such as dibutyltin dilaurate, dibutyltin diacetate, dihexyltin diacetate, dimethyltin dimercaptide, dibutyltin dimercaptide, dioctyltin dimercaptide, di-2-ethylhexyltin oxide, stannous octoate and stannous oleate. Among the stated organotin compounds, more preferable compound is a mercaptide type organotin compound such as dibutyltin dimercaptide, having good hydrolysis resistance. The amount employed of the organotin catalyst is less than 0.5 pbw, preferably about 0.01 to about 0.5 pbw, more preferably about 0.03 to about 0.1 pbw, based on the total polyol of 100 pbw.

Suitable other catalysts to be optionally employed in the present invention include, for example, tertiary amine compounds such as trialkylamines like trimethylamine and triethylamine, heterocyclic amines like N-alkylmorpholine, ethers like 2,2'-bis-(dimethylamino)diethylether, aliphatic polyamines like 1,4-dimethylpiperazine, triethylenediamine, N,N,N',N'-tetramethyl-1,3-butanediamine and N-methyldiethanolamine, or a mixture thereof. The amount employed of the amine type catalyst is usually within the range well-known to the public in the polyurethane chemistry.

Suitable cross-linking agents to be optionally employed in the present invention include, for example, amine-based low molecular weight polyols such as triethanolamine and diethanolamine, and low molecular weight polyols such as ethyleneglycol, diethyleneglycol, butanediol, trimethylolpropane and glycerol, or a mixture thereof. The amount employed of the cross-linking agent is usually from about 2 to about 20 pbw based on the total polyol, preferably, about 3 to about 10 pbw.

In addition to the stated components, other additives such as emulsifying agent, stabilizing agent, surfactant, filler, pigment and antioxidant can optionally be employed in the present invention. Incidentally, molded polyurethane foams of the present invention can be manufactured in accordance with prior making methods such as open-mold process or closed-mold process.

EXAMPLES

The present invention is described more specifically in the following Examples and Comparative Examples. It is to be understood, however, that the invention is not to be limited by the embodiments described in the following Examples. Reactive components employed in Examples and Comparative Examples are as follows. The term "pbw" or "%" is on the basis of weight unless there is specific description.

(1) Polyisocyanates:

Three polyisocyanates, diphenylmethane diisocyanate ("MDI") (I-125; NCO content:33.6 wt%), a modified MDI (I-143; NCO content:29.4 wt%) and Polymeric MDI (PAPI-135; NCO content:31.0 wt%) were selected as organic polyisocyanate component. Three PTMGs having different average molecular weight of 700, 1,000 and 1,500 (respectively "PTMG700", "PTMG1000" and "PTMG1500") were selected as polyol component. In addition, a polyetherpolyol having an average equivalent weight of 1,600 and capped ethyleneoxide (EO) content of 14 wt% ("Polyol P1"), prepared from the reaction of glycerol as an initiator with propyleneoxide (PO), was selected as another polyol component. Various NCO-terminated prepolymers were prepared employing the stated polyisocyanate components and polyols components. The composition of each prepolymer and polyisocyanate mixture is shown in Table 1, Table 2 and Table3.

(2) Polyols:

Polyol P2: A propyleneoxide ("PO")-added polyetherpolyol initiated with glycerol (Functionality:3, Average equivalent weight ("EW"):1,600, PO content:83 wt%, Capped EO content:17

wt%) This polyetherpolyol was prepared capping EO after the reaction of glycerol as an initiator with PO in the presence of potassium hydroxide as a catalyst.

Polyol CPP1: A polymer polyol (Functionality:3, OH value:28, solid content:20 wt%)

This polymer polyol was prepared polymerising the stated Polyol P2 with acrylonitrile.

Polyol CPP2: A polymer polyol (Functionality:3, OH value:28, solid content:20 wt%)

This polymer polyol was prepared polymerising the stated Polyol P2 with a monomer mixture of acrylonitrile/styrene (70/30 weight ratio).

(3)Additives:

Catalyst:

Organotin type catalyst: Dibutyltin dimercaptide (FOMREZ UL-1:Witco)

Amine type catalyst 1: Triethylenediamine (dipropyleneglycol 33 % solution)

(Dabco 33LV: Air Products)

Amine type catalyst 2: Bis(dimethylaminoethyl)ether

(NIAX A-1: Union Carbide)

Cross-linking agent: monoethyleneglycol (MEG)

Blowing agent: Water; Trichlorofluoromethane (CFC-11)

EXAMPLES 1 TO 35 AND COMPARATIVE EXAMPLES 1 TO 4

According to the formulations shown in Table 4, 5, 6, 7 8, 9 and 10, various molded polyurethane foams (steering wheels) were prepared based on the following manner.

A polyol and other additives except a polyisocyanate were mixed for 10 seconds at 3,000 r.p.m. Next, the polyisocyanate measured was mixed with the polyol mixture for 3 seconds at 3,000 r.p.m. and continually the mixture was injected into an iron-made mold being maintained under 50 °C. After curing for certain time (e.g. 180 seconds, 150 seconds, 120 seconds, 90 seconds and 60 seconds), a polyurethane foam was demolded from the mold. The surface properties such as blistering and skin delamination of the foam obtained were immediately observed as an evaluation of demoldability. The results are shown in each Table. The meaning of each mark is as follows. "A" means "good", "B" means "almost good" and "C" means "not good". Some samples for abrasion test were prepared from the normal foam obtained. The abrasion test was carried out in the following manner. The results of the abrasion test are shown in each Table.

Evaluation of Abrasion Resistance: Testing samples having outer peripheral length of about 80 mm were cut and prepared from a foam moldings (steering wheel) obtained as stated above. The foam

moldings was prepared covering an iron-made pipe (outside diameter: 14 mm) with polyurethane foam (shape of a cross section to the diameter-direction: ellipse having a 28 mm long diameter and a 23 mm short diameter). The abrasion resistance of the testing sample was evaluated using a testing machine for abrasion resistance, "SUGA FR-2-S Type" (produced by Suga Test Instruments in Japan). The testing sample was set in the machine as the outer surface of the sample contacted a white cloth (Canvas Cloth No.10) having a 100 g weighting in its one end. The surface of the sample was rubbed against the cloth for certain times (3×10^4 , 5×10^4 and 10×10^4 times) under the stated conditions. The abrasion test was evaluated by visual observation and the ranking of 1 to 5 was given to each result. The meaning of each rank shown as "5", "4" and "3" in each Table is as follows.

- 5: no abrasion (no change)
- 4: slight abrasion with polish
- 3: more abrasion

As evident from results shown in each Table, all Invention Examples show better demoldability even in the use of water as a sole blowing agent and also show excellent abrasion properties than Comparative Examples. Accordingly, the molded polyurethane foams of the present invention can be produced under very cycle times and can be useful for automotive material such as steering wheels, headrests and armrests, material for furniture and the like, in which abrasion resistance is required.

Table 1

Polyisocyanates (Examples)

	I	II	III	IV	V	VI	VII
(Prepolymer)							
Isocyanate							
I-125	48	48	48	53	38	28	48
I-143L	16	16	16	18	14	12	16
PAPI-135	-	-	-	-	-	-	5
Polyol							
PTMG700	26	-	-	-	-	-	-
PTMG1000	-	26	-	24	28	30	26
PTMG1500	-	-	26	-	-	-	-
(Polyisocyanate)							
PAPI-135	10	10	10	5	20	30	5
Total NCO% of the mixture	20.6	21.5	22.4	22.5	20.6	19.8	20.5

Table 2

Polyisocyanates (Examples)

	VIII	IX	X	XI	XII	XIII
(Prepolymer)						
Isocyanate						
I-125	53	48	48	48	38	28
I-143L	18	16	16	16	14	12
PAPI-135	5	10	10	10	20	30
Polyol						
PTMG700	-	26	-	-	-	-
PTMG1000	24	-	26	-	28	30
PTMG1500	-	-	-	26	-	-
Total NCO% of the Prepolymer	22.5	20.6	21.5	22.4	20.6	19.8

Table 3

Polyisocyanates (Comparative Examples)

	XIX	XV
(Prepolymer)		
Isocyanate		
I-125	-	50
I-143L	86	15
Polyol		
Polyol P1	14	35
Total NCO% of the Prepolymer	24.5	20.2

Table 4

Formulations and Properties (Examples 1 to 7)

No.	1	2	3	4	5	6	7
Polyisocyanate I	100	-	-	-	-	-	-
Polyisocyanate II	-	100	-	-	-	-	-
Polyisocyanate III	-	-	100	-	-	-	-
Polyisocyanate IV	-	-	-	100	-	-	-
Polyisocyanate V	-	-	-	-	100	-	-
Polyisocyanate VI	-	-	-	-	-	100	-
Polyisocyanate VII	-	-	-	-	-	-	100
Polyol P2	60	60	60	60	60	60	60
Polyol CPP1	40	40	40	40	40	40	40
MEG	7	7	7	7	7	7	7
Fomrez UL-1	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Dabco 33LV	1.5	1.5	1.5	1.5	1.5	1.5	1.5
NIAX A-1	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Water	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(Demoldability)							
180 seconds	A	A	A	A	A	A	A
150 seconds	A	A	A	A	A	A	A
120 seconds	A	A	A	A	A	A	A
90 seconds	A	A	A	B	A	A	B
60 seconds	B	B	B	C	B	A	C
(Abrasion Resistance)							
at 3×10^4 times	5	5	5	5	5	5	5
at 5×10^4 times	5	5	5	5	5	5	5
at 10×10^4 times	4.5	4.5	4.5	4.5	4.5	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

Table 5

Formulations and Properties (Examples 8 to 15)

No.	8	9	10	11	12	13	14	15
Polyisocyanate II	100	100	100	100	100	100	100	100
Polyol P2	30	50	70	100	60	60	60	60
Polyol CPP1	70	50	30	-	40	40	40	-
Polyol CPP2	-	-	-	-	-	-	-	40
MEG	7	7	7	7	7	7	7	7
Fomrez UL-1	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Dabco 33LV	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
NIAX A-1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Water	0.5	0.5	0.5	0.5	0.3	0.8	0.2	0.5
CFC-11	-	-	-	-	-	-	5	-
(Demoldability)								
180 seconds	A	A	A	A	A	A	A	A
150 seconds	A	A	A	A	A	A	A	A
120 seconds	A	A	A	B	A	A	A	A
90 seconds	A	A	B	C	A	A	B	A
60 seconds	B	B	C	C	B	B	C	B
(Abrasion Resistance)								
at 3×10^4 times	5	5	5	4.5	5	5	5	5
at 5×10^4 times	5	5	5	4	5	5	5	5
at 10×10^4 times	4.5	4.5	4.5	3.5	4.5	4.5	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

Table 6

Formulations and Properties (Examples 16 to 18)

No.	16	17	18
Polyisocyanate II	100	100	100
Polyol P2	60	60	60
Polyol CPP1	40	40	40
MEG	7	7	7
Fomrez UL-1	0.03	0.05	0.1
Dabco 33LV	1.5	1.5	1.5
NIAX A-1	0.4	0.4	0.4
Water	0.5	0.5	0.5
(Demoldability)			
180 seconds	A	A	A
150 seconds	A	A	A
120 seconds	A	A	A
90 seconds	B	A	A
60 seconds	C	B	A
(Abrasion Resistance)			
at 3×10^4 times	5	5	5
at 5×10^4 times	5	5	5
at 10×10^4 times	4.5	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

Table 7

Formulations and Properties (Examples 19 to 24)

No.	19	20	21	22	23	24
Polyisocyanate VIII	100	-	-	-	-	-
Polyisocyanate IX	-	100	-	-	-	-
Polyisocyanate X	-	-	100	-	-	-
Polyisocyanate XI	-	-	-	100	-	-
Polyisocyanate XII	-	-	-	-	100	-
Polyisocyanate XIII	-	-	-	-	-	100
Polyol P2	60	60	60	60	60	60
Polyol CPP1	40	40	40	40	40	40
MEG	7	7	7	7	7	7
Fomrez UL-1	0.07	0.07	0.07	0.07	0.07	0.07
Dabco 33LV	1.5	1.5	1.5	1.5	1.5	1.5
NIAX A-1	0.4	0.4	0.4	0.4	0.4	0.4
Water	0.5	0.5	0.5	0.5	0.5	0.5
(Demoldability)						
180 seconds	A	A	A	A	A	A
150 seconds	A	A	A	A	A	A
120 seconds	A	A	A	A	A	A
90 seconds	B	A	A	A	A	A
60 seconds	C	B	B	B	B	A
(Abrasion Resistance)						
at 3×10^4 times	5	5	5	5	5	5
at 5×10^4 times	5	5	5	5	5	5
at 10×10^4 times	4.5	4.5	4.5	4.5	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

Table 8

Formulations and Properties (Examples 25 to 32)

No.	25	26	27	28	29	30	31	32
Polyisocyanate X	100	100	100	100	100	100	100	100
Polyol P2	30	50	70	100	60	60	60	60
Polyol CPP1	70	50	30	-	40	40	40	-
Polyol CPP2	-	-	-	-	-	-	-	40
MEG	7	7	7	7	7	7	7	7
Fomrez UL-1	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Dabco 33LV	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
NIAX A-1	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Water	0.5	0.5	0.5	0.5	0.3	0.8	0.2	0.5
CFC-11	-	-	-	-	-	-	5	-
(Demoldability)								
180 seconds	A	A	A	A	A	A	A	A
150 seconds	A	A	A	A	A	A	A	A
120 seconds	A	A	A	B	A	A	A	A
90 seconds	A	A	B	C	A	A	B	A
60 seconds	B	B	C	C	B	B	C	B
(Abrasion Resistance)								
at 3×10^4 times	5	5	5	4.5	5	5	5	5
at 5×10^4 times	5	5	5	4	5	5	5	5
at 10×10^4 times	4.5	4.5	4.5	3.5	4.5	4.5	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

Table 9

Formulations and Properties (Examples 33 to 35)

No.	33	34	35
Polyisocyanate X	100	100	100
Polyol P2	60	60	60
Polyol CPP1	40	40	40
MEG	7	7	7
Fomrez UL-1	0.03	0.05	0.1
Dabco 33LV	1.5	1.5	1.5
NIAx A-1	0.4	0.4	0.4
Water	0.5	0.5	0.5
(Demoldability)			
180 seconds	A	A	A
150 seconds	A	A	A
120 seconds	A	A	A
90 seconds	B	A	A
60 seconds	C	B	A
(Abrasion Resistance)			
at 3×10^4 times	5	5	5
at 5×10^4 times	5	5	5
at 10×10^4 times	4.5	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

Table 10

Formulations and Properties (Comparative Examples 1 to 4)

No.	1	2	3	4
Polyisocyanate XIV	100	-	-	-
Polyisocyanate XV	-	100	-	-
Polyisocyanate II	-	-	100	-
Polyisocyanate X	-	-	-	100
Polyol P2	100	100	60	60
Polyol CPP1	-	-	40	40
MEG	7	7	7	7
Dabco 33LV	2.5	2.5	2.5	2.5
NIAX A-1	0.4	0.4	0.4	0.4
Water	-	0.5	0.5	0.5
CFC-11	15	-	-	-
(Demoldability)				
180 seconds	A	B	A	A
150 seconds	A	C	A	A
120 seconds	A	C	B	B
90 seconds	B	C	C	C
60 seconds	B	C	C	C
(Abrasion Resistance)				
at 3×10^4 times	5	3.5	5	5
at 5×10^4 times	5	3	5	5
at 10×10^4 times	4.5	-	4.5	4.5

(Note) Amount employed: pbw (Polyisocyanate: NCO Index)

WHAT IS CLAIMED IS:

1. Molded polyurethane foams prepared reacting a polyisocyanate with a polyol in the presence of water as a blowing agent and a catalyst, wherein (a) the polyisocyanate comprises a mixture of (i) from about 1 to about 40 weight percent polymethylene polyphenyl polyisocyanate and (ii) a NCO-terminated prepolymer prepared from the reaction of an organic polyisocyanate with from about 10 to about 50 weight percent poly(oxytetramethylene)glycol, said weight percents being based on the total weight of organic polyisocyanate, poly(oxytetramethylene)glycol and polymethylene polyphenyl polyisocyanate, (b) the polyol contains at least 30 weight percent polymer polyol prepared from the reaction of a polyetherpolyol with an ethylenic unsaturated monomer, and (c) the catalyst contains an organotin compound.
2. Molded polyurethane foams prepared by reacting a polyisocyanate with a polyol in the presence of water as a blowing agent and a catalyst, wherein (a) the polyisocyanate comprises a NCO-terminated prepolymer prepared from the reaction of (i) an organic polyisocyanate, (ii) from about 1 to about 40 weight percent polymethylene polyphenyl polyisocyanate and (iii) from about 10 to about 50 weight percent poly(oxytetramethylene)glycol, said weight percents based on the total weight of the polyisocyanate, polymethylene polyphenyl polyisocyanate and poly(oxytetramethylene)glycol, (b) the polyol contains at least 30 weight percent polymer polyol prepared from the reaction of a polyetherpolyol with an ethylenic unsaturated monomer, and (c) the catalyst contains an organotin compound.
3. The molded polyurethane foams of Claim 1 wherein the organic polyisocyanate is 4,4'-diphenylmethane diisocyanate or a modified 4,4'-diphenylmethane diisocyanate.
4. The molded polyurethane foams of Claim 1 wherein the weight average molecular weight of the poly(oxytetramethylene)glycol is from about 500 to about 2,400, the polymethylene polyphenyl polyisocyanate and poly(oxytetramethylene)glycol contents are from about 2 to 30 weight percent and from about 20 to 45 weight percent respectively, based on the total weight of polyisocyanate component (a), and the polyol contains from about 30 to about 70 weight percent polymer polyol based on the total weight of polyol component (b).
5. The molded polyurethane foams of Claim 1 wherein the ethylenic unsaturated monomer is acrylonitrile.
6. The molded polyurethane foams of Claim 1 wherein the water content is from about 0.3 to about 2 parts by weight based on the total weight of the polyol component.

7. The molded polyurethane foams of Claim 1 wherein the organotin compound is a mercaptide type organotin compound.

8. The molded polyurethane foams of Claim 7 wherein the mercaptide type organotin compound is dimethyltin dimercaptide, dibutyltin dimercaptide or dioctyltin dimercaptide.

9. The molded polyurethane foams of Claim 2 wherein the organic polyisocyanate is 4,4'-diphenylmethane diisocyanate or a modified 4,4'-diphenylmethane diisocyanate.

10. The molded polyurethane foams of Claim 2 wherein the weight average molecular weight of the poly(oxytetramethylene)glycol is from about 500 to 2,400, the polymethylene polyphenyl polyisocyanate and poly(oxytetramethylene)glycol contents are from about 2 to 30 weight percent and from about 20 to 45 weight percent respectively, based on the total weight of polyisocyanate component (a), and the polyol contains from about 30 to about 70 weight percent polymer polyol based on the total weight of the polyol component (b).

11. The molded polyurethane foams of Claim 2 wherein the ethylenic unsaturated monomer is acrylonitrile.

12. The molded polyurethane foams of Claim 2 wherein the water content is from about 0.3 to about 2 parts by weight based on the total polyol component (b).

13. The molded polyurethane foams of Claim 2 wherein the organotin compound is a mercaptide type organotin compound.

14. The molded polyurethane foams of Claim 2 wherein the mercaptide type organotin compound is dimethyltin dimercaptide, dibutyltin dimercaptide or dioctyltin dimercaptide.

INTERNATIONAL SEARCH REPORT

 Intern: Application No
 PCT/US 94/05173

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 C08G18/10 C08G18/48

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 5 C08G

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 451 559 (BASF) 16 October 1991 see page 2, line 41 - page 6, line 41; claims ---	1-6,9-12
Y	WO,A,91 17197 (DOW ITALIA) 14 November 1991 see page 4, line 34 - page 14, line 35; claims 1-10 ---	1-6,9-12
P,X	EP,A,0 567 824 (DOW CHEMICAL/DOW MITSUBISHI) 3 November 1993 see page 2, line 28 - page 3, line 36; claims 1-12; examples ---	1-6,9-12
E	EP,A,0 601 383 (BASF) 15 June 1994 see claims ---	1-6,9-12
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Internat. Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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