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INTEGRAL-SKIN POLYURETHANE FOAM, PREPARATION PROCESS AND USE OF SAME

Background of the Invention

1. Field of the Invention

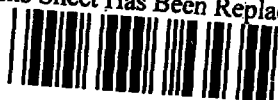
The present invention relates to an integral-skin polyurethane foam and a preparation process and use of the foam. The integral-skin polyurethane foam is used for automotive parts such as steering wheels and air spoilers and furnitures such as arm rests and chair legs.

2. Related Art of the invention

The integral-skin polyurethane foam is characterized in constructing a skin layer and foam layer at the same time by pouring reactive components into a mold, foaming, curing and successively demolding. The integral-skin polyurethane foam has excellent elasticity and wear resistance and is thus widely used for cushioning materials in the field of automobiles and furnitures. In order to form the skin layer, a low boiling point organic compound is required as a blowing agent and trichloromonofluoromethane (Code No. CFC-11) has been commonly used in particular.

However, so-called trifluoromethane base compounds (hereinafter referred to simply as CFC compounds) which are represented by trichloromonofluoromethane have been in recent years understood to destruct the ozone layer in the atmosphere. Thus, laws for regulating the CFC compounds are realizing in the world.

As an alternative to the CFC compounds, hydrochlorofluorocarbons (hereinafter referred to simply as HCFC) having a low ozone destruction parameter (hereinafter referred to as ODP) have been proposed as the second generation.



HCFC which can be used includes, for example, monochlorodifluoromethane (Code No. HCFC-22), 2,2-dichloro-1,1,1-trifluoroethane (Code No. HCFC-123), 1,1-dichloro-1-fluoroethane (Code No. HCFC-141 b), and 1-monochloro-1,1-difluoroethane (Code No. HCFC-142 b).

Further, as the third generation, hydrofluorocarbons (hereinafter referred to simply as HFC) which ODP is 0 have been proposed. Exemplary HFC includes 1,1,1,2-tetrafluoroethane (Code No. HFC-134 a).

It has, however, been worried that these HCFC and HFC blowing agents also cannot be used with complete safety in view of protecting the global atmosphere.

That is, although HCFC has a low ODP, it is still a group of compounds which destruct the ozone layer. Although HFC is zero in ODP and has no worry about the ozone layer destruction, it has a high greenhouse effect ; global warming parameter (hereinafter referred to simply as GWP) and henceforth cannot be used with a feeling of security.

As mentioned above, the so-called alternative chlorofluorocarbons are merely a short term countermeasure for the regulation of chlorofluorocarbons. Consequently, it has been desired to develop a permanent and completely non-chlorofluorocarbon blowing technique, that is, a so-called carbon dioxide gas blowing technique.

In the field of usual polyurethane foams, the carbon dioxide gas blowing technique using water as a blowing agent has been individually developed in the field of a flexible foam, semirigid foam and rigid foam. In the current state of the art, the so-called water blown foam already been manufactured to a considerable extent.

On the other hand, in the field of the integral-skin polyurethane foam, a low boiling-point blowing agent is advantageously used in view



of the mechanism for forming the skin layer. Application of water to an blowing agent leads to various problems and thus is not yet in the actual use.

That is, the term "water blown technique" refers to a technique for blowing the foam with carbon dioxide gas generated by reaction of water with an isocyanate group in the raw material. Consequently, when the common preparation process of the integral-skin polyurethane foam which uses a CFC-11 (boiling point 27.5 °C) blowing agent is carried out by water blown technique without CFC, the carbon dioxide gas generated on the mold surface, that is, in the vicinity of the polyurethane foam surface forms a foam layer and does not form a skin layer. As a result, the integral-skin structure cannot be constituted. As to the countermeasure for such phenomenon, Japanese Laid-Open Patent HEI 3-32811 has proposed to maintain the mold temperature at 15 ~ 40°C, to use a temperature sensitive catalyst having a high dependence on temperature for the reaction of water with isocyanate. On the other hand, a catalyst having a low dependence on temperature has been proposed to use for the reaction of isocyanate with a OH-containing compound. Japanese Laid-Open Patent HEI 3-33120 has disclosed practical examples of the temperature sensitive catalyst. However, the process for using the temperature sensitive catalyst leads to delayed curing of the polyurethane surface due to decreased temperature of the mold surface, even though a high density skin layer is formed, and impairs appearance and quality of the resulting foam.

Further, a high content of closed cells and the resultant low damping factor of blowing are liable to cause blisters and cracks on the polyurethane foam in the stage of mold release. As a result, the



temperature sensitive catalyst has a disadvantage of requiring an extended demolding time.

Further, the water blown technique leads to another problem. That is, the urea bond formed by the reaction of water with isocyanate constitutes a very strong hard segment, results in an increased hardness of the polyurethane foam obtained, and impairs tactile feeling of the resultant foam.

On the other hand, it has been considered a reaction mechanism to similarly generate carbon dioxide gas by the reaction of isocyanate without forming the urea bond. For example, Japanese Laid-Open Patent HEI 3-24108 has disclosed a process for reacting the isocyanate groups each other to form a carbodiimide group and using carbon dioxide evolved by the reaction for the blowing agent. Japanese Laid-Open Patent HEI 3-152111 has proposed a process for reacting a cyclic carbonate with isocyanate to form an oxazolidone group and using carbon dioxide generated by the reaction for the blowing agent.

However, these processes have problems such as difficulty for regulating the reaction velocity, use of an expensive catalyst and requirement for combined use of chlorofluorocarbons in order to provide a sufficient extent of foaming. Consequently, problems on the carbon dioxide blown technique can not be substantially solved by these techniques.

As mentioned above, the preparation process of the integral skin polyurethane foam by using the carbon dioxide gas blowing technique in place of chlorofluorocarbons or alternative HCFC and HFC has not yet been realized, although the subject is an urgent desire of those who are skilled in the art. The reason is that the technique has following



disadvantages as compared with the use of chlorofluorocarbons or alternative HCFC and HFC.

- (1) Extended demolding time is required and impairs productivity.
- (2) Thick-walled molded articles are liable to generate blisters and punctures in the demolding stage.
- (3) The polyurethane foam expands in the demolding stage and marks of the mold surface are liable to remain on the product surface.
- (4) The foam is rigid and tactile feeling is poor.
- (5) The skin layer is thin.

The countermeasure for individually overcoming each disadvantage of (1) ~ (5) has already been found. However, a carbon dioxide gas blown technique which can solve the whole items (1)~(5) at the same time and can be employed for an actual production line has not yet been developed.

Japanese Laid-Open Patent HEI 2-199136 has proposed to use organic carboxylic acid as a blowing agent. In the process, however, the organic carboxylic acid which is used as the blowing agent leads to a problem on time dependent stability in the isocyanate reactive ingredient. As a countermeasure for solving the problem, Japanese Laid-Open Patent HEI 3-153721 has proposed to use for the blowing agent an organic carboxylic acid salt of nitrogen base having at least one N-H bond. However, the process is difficult to control the reaction velocity of the total system because the nitrogen base having the N-H bond reacts too rapidly with isocyanate.

Summary of the Invention

The object of the invention is to provide a process for preparing an integral-skin polyurethane foam by using carbon dioxide as a blowing



agent.

As a result of an intensive investigation on the use of carbon dioxide gas as a blowing agent of the integral-skin polyurethane foam, the present inventors have found that the integral-skin polyurethane foam obtained by using boric acid or an ester thereof as a blowing agent can eliminate all of the above disadvantages and provide a molded article which is excellent in productivity and moldability and has good touch. Thus, the present invention has been completed.

That is, the aspect of the invention is:

(1) An integral-skin polyurethane foam having a molding density of 0.3 ~ 0.8 g/cm³ and obtained by pouring into a mold a reaction mixture of an aromatic polyisocyanate, isocyanate reactive high molecular weight compound, blowing agent and other additives, comprising using boric acid and/or an ester thereof as the blowing agent.

(2) An integral skin polyurethane foam of the above (1) wherein the blowing agent is a mixture of boric acid and/or an ester thereof with an organic carboxylic acid and/or an ester thereof.

(3) A preparation process of an integral-skin polyurethane foam having a molding density of 0.3~0.8 g/cm³ by pouring into a mold a reaction mixture of an aromatic polyisocyanate, isocyanate reactive high molecular weight compound, blowing agent, and other additives, comprising using boric acid and/or an ester thereof as the blowing agent.

(4) A preparation process of an integral-skin polyurethane foam of the above (3) wherein the blowing agent is a mixture of boric acid and/or an ester thereof with an organic carboxylic acid and/or an ester thereof.



(5) A preparation process of an integral-skin polyurethane foam of the above (1) or (2) wherein the preparation process is a reaction injection molding process.

(6) An automotive steering wheel, interior or furniture prepared by the preparation process of the above (3), (4) or (5).

The present invention uses:

(1) Boric acid and/or an ester thereof, or

(2) A mixture of boric acid and/or an ester thereof with an organic carboxylic acid and/or an ester thereof, as a blowing agent.

Conventionally, in the process used water as a blowing agent, mold filling ability of a reaction composition comprising an aromatic polyisocyanate, isocyanate reactive high molecular weight compound, blowing agent, and other additives was poor. As a consequence, an amount of the water used as blowing agent must be increased in order to improve the mold filling ability, however, using an increased amount of water give rise to the disadvantages which excess expansion of the polyurethane foam is liable to remain marks of the mold surface on the product surface and to generate blisters and punctures in the demolding stage.

Extending demolding time is effective in order to improve the disadvantages, but it decrease productivity of the foam, further the foam is rigid and tactile feeling is poor because of urea linkage formed by reacting water and isocyanate.

The reaction composition comprising the blowing agent of the present invention and aromatic isocyanate, isocyanate reactive high molecular weight compound and other additives has excellent mold filling ability and demolding ability compared from the composition using water as a



blowing agent. Accordingly, the integral-skin polyurethane foam of the present invention can be obtained in high productivity without remaining marks of the mold surface on the product surface and generating blisters and punctures in the molding stage. The foam having excellent tactile feeling can also be obtained because carbon dioxide generated by reacting isocyanate with the blowing agent forms the foams and formation of a urea linkage is little.

As mentioned above, in the present invention, water as the blowing agent does not use at all or slightly use as a coexisting blowing agent, therefore, the disadvantage of the process used water as a blowing agent can be solved by the present invention.

Additionally, the blowing agent used in the present invention does not corrode a metal, on the contrary, use of formic acid represented an organic carboxylic acid as the blowing agent corrode a metal.

The integral-skin polyurethane foam of the invention can be prepared by pouring a mixture of urethane raw materials into a mold with a reaction injection molding process. In the course of molding, foam expansion is pressed down in the portion which comes into contact with the interior surface of the mold and an elastomer like skin layer is constituted. Thus, the skin layer and foam layer are formed at the same time to build up an integral structure. The integral-skin polyurethane foam obtained in the invention has excellent elasticity and tactile feeling and can be favorably used for automotive interiors such as a steering wheel, horn pad, crush pad, instrument panel. lid of a console box and glove box, head rest, arm rest and air spoiler ; and furnitures such as a seat, leg and arm of a chair.

Detailed Description of the Invention



The invention will be illustrated hereinafter.

Known aromatic polyisocyanates can be used for the invention. Preferred isocyanates are diphenylmethane diisocyanate, polymethylenepolyphenyl isocyanate, an isocyanate terminated prepolymer which is a reaction product of these polyisocyanates with active hydrogen containing compounds and urethonimine modified polyisocyanate.

Particularly preferred aromatic polyisocyanate is polymethylenepolyphenyl isocyanate having a high content of poly benzene ring compounds of more than three benzene ring compounds, more specifically 60 % by weight or more content of three or more benzene ring compounds. Further, a mixture with a urethane modified prepolymer of diphenylmethane diisocyanate or urethonimine modified liquid diphenylmethane diisocyanate can also be preferably used.

The isocyanate reactive high molecular weight compound which can be used in the invention is a polyol which is obtained by addition polymerization of propylene oxide alone or propylene oxide and ethylene oxide on an active hydrogen containing compound such as water, propylene glycol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, sucrose, triethanolamine, ethylenediamine tolylenediamine, diaminodiphenylmethane or a mixture of these compounds so as to obtain an average functionality of 2 ~ 4. The polyol has a hydroxyl value of 24 ~ 55 mg KOH/g, ethylene oxide content of 10 ~ 25 % by weight for the polyol, and terminal primary hydroxyl content of 70~95 % by mole.

Polymer polyol (Trade Mark) which is obtained by grafting an ethylenically unsaturated monomer such as styrene, acrylonitrile or methyl methacrylate on the above polyol can also be favorably used.

When the ethylene oxide content is less the 10 % by weight, terminal



primary hydroxyl content also decreases to less than 70 % by mole and productivity becomes poor due to reduced reactivity.

On the other hand, when the ethylene oxide content exceeds 25 % by weight or the terminal primary hydroxyl content exceeds 95 % by mole, the reaction becomes too rapid and unfavorably leads to blisters in thick walled portions of the foam obtained or sink marks in thickness changing portions of the foam.

The blowing agent which can be used in the invention is boric acid and/or an ester thereof, or a mixture of these compounds with an organic carboxylic acid and/or an ester thereof.

Boric acid and an ester thereof include, for example, boric acid, methyl borate, ethyl borate, dimethyl borate, diethyl borate, trimethyl borate, triethyl borate and other borate esters. These compounds can be used singly or as a mixture.

The organic carboxylic acid and an ester thereof include, for example, formic acid, acetic acid, propionic acid, lauric acid, stearic acid, oleic acid, 2-ethyl hexoic acid, oxalic acid, itaconic acid, adipic acid, maleic acid, acetyl dicarboxylic acid, acetone dicarboxylic acid, malonic acid, succinic acid, tartaric acid, diglycolic acid, cyclopropane diglycolic acid, gultaconic acid, tartronic acid, gultaconic acid, aconitic acid, citric acid, benzenetricarboxylic acid, nitrilo triacetic acid, benzene tetracarboxylic acid and mellitic acid, and methyl malonate, ethyl malonate, butyl malonate, methyl maleate, ethyl maleate, butyl maleate, methyl malate, ethyl malate, butyl malate, methyl succinate, ethyl succinate, butyl succinate, methyl adipate, ethyl adipate, butyl adipate, methyl tartrate, ethyl tartrate and butyl tartrate, methyl



benzoate, ethyl benzoate, methyl phthalate, ethyl phthalate. These organic carboxylic acids and esters thereof can be used singly or as a mixture.

The amount of the blowing agent is 10 parts by weight or less, preferably 0.5 ~ 2.5 parts by weight for 100 parts by weight of the isocyanate reactive high molecular weight compound.

The blowing agent can also be used in combination with a blowing agent. Exemplary blowing agents which can be used include water and a hydrocarbon, for example, pentane. The hydrocarbon has a lower boiling point and must be free chlorine and fluorine in view of the object of the invention as a countermeasure for the chlorofluorocarbon problem.

Various kinds of known catalyst for preparing urethane may be used in the present invention. Exemplary catalysts include organometallic catalysts such as dibutyltin dilaurate and dimethyltin dilaurate, or a tertiary amine such as triethylendiamine, N,N,N',N'-tetramethylhexane-1,6-diamine, N,N,N',N'',N'''-pentamethyldiethylenetriamine, N,N'-bis (N'',N''-dimethyl-3-aminopropyl)-N',N'-dimethylethylenediamine, N-methyl-N'-(2-dimethylamino)ethylpiperazine, N-ethylmorpholine, 1-methylimidazole, 1,2-dimethylimidazole, 3-(dimethylamino)propylimidazole, dimethylaminoethanol, bis(2-dimethylaminoethyl)ether and 1-isobutyl-2-methylimidazole. A particularly preferred tertiary amine is 1-isobutyl-2-methylimidazole. These catalysts can be used singly or as a mixture.

The tertiary amine can also be added to the reaction system as a salt previously formed with boric acid or an ester thereof or the organic carboxylic acid or an ester thereof. Additionally, the salt may be added to the reaction system as the solution dissolved in a crosslinking agent such as diethyleneglycol when the salt is solid.



The below described crosslinking agent, surfactant and other additives are used in the invention, when needed.

Known crosslinking agents which are commonly used for preparing integral-skin polyurethane foams can also be used in the invention. Exemplary crosslinking agents include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol and other polyalkylene glycols; diethylene glycol, dipropylene glycol, triethylene glycol and other polyoxyalkylene glycols; diethanolamine, triethanol amine and other alkanolamines; and low molecular weight polyols obtained by addition of alkylene oxide in an amount of 1~2 mols for an active hydrogen radical to polyhydric alcohols such as trimethylolpropane and glycerol, and amines such as ethylene and a mixture of 2,4-/2,6-tolylenediamine isomers. These crosslinking agents can be used singly or as a mixture. A particularly preferred crosslinking agent is diethylene glycol.

Surfactants which can be used include, for example, Nippon Unicar's L-5430 and L-3601; Toray Silicone's SRX-274C, SF-2961 and SF-2962; and other organic silicone surfactants.

Other additives which can be used are colorants, antioxidants, flame retardants, viscosity reducers, and internal mold release agents. Known additives can be used.

An open mold process and reaction injection molding process can be used for molding the integral-skin polyurethane foams. The reaction injection molding process is particularly preferred.

The present invention will hereinafter be illustrated further in detail by way of examples and comparative examples.

In these examples and comparative examples, the following aromatic polyisocyanates, polyols, crosslinking agents, catalyst and blowing



agents were used.

Aromatic polyisocyanates (A) : Polyisocyanate having an NCO content of 27.5 % which was obtained by subjecting a 70 : 30 mixture of diphenylmethane diisocyanate and polymethylenepolyphenyl isocyanate to urethane modification by dipropylene glycol. Polymethylenepolyphenyl isocyanate had an NCO content of 31.5 % and contained 70 % by weight of three or more benzene ring compounds.

Aromatic polyisocyanate (B) : Polyisocyanate having an NCO content of 29.2 % which was a 70 : 30 mixture of carbodiimide modified diphenylmethane diisocyanate and polymethylenepolyphenyl isocyanate. Polymethylenepolyphenyl isocyanate had an NCO content of 31.5 % and contained 70% by weigh of three or more benzene ring compounds.

Polyol (A) ; Polyol which had an average functionality of 3, average molecular weight of 6000 and ethylene oxide content of 15 % by weight.

Crosslinking agent (A) ; Diethylene glycol

Catalyst (A) ; A 33 % dipropylene glycol solution of triethyenediamine.

Catalyst (B) ; 1-Isobutyl-2-methylimidazole.

Catalyst (C) ; Bis(2-dimethylaminoethyl) ether.

Catalyst (D) ; Dibutyltin dilaurate.

Blowing agent (A); Boric acid.

Blowing agent (B); 2-ethylhexanoic acid.

Blowing agent (C); Methyl borate.

Blowing agent (D); Trichlorofluoromethane (CFC-11).

Blowing agent (E); Water.



Example 1

A polyol component was prepared by mixing 100 parts of polyol (A), 10 parts of crosslinking agent (A), 0.7 part of catalyst (B), 0.72 part of catalyst (C), 0.01 part of catalyst (D) and 0.58 part of blowing agent (A). Aromatic polyisocyanate (B) and the above polyol component were mixed at an NCO/OH ratio of 1.05. Free blow foaming and mold foaming were carried out.

In the free blow foaming the time from the mixing of polyisocyanate and polyol components to the initiation of foam expansion (cream time) and the end of foam expansion (rise time) were measured. The density of resultant foam (free blow density) was also measured.

In the mold foaming, a mold having dimensions of $400 \times 100 \times 10$ mm was previously warmed to 40°C .

A urethane raw material mixture was poured into the mold, the mold lid was closed, and the mold was allowed to stand for 3 minutes at room temperature. Thereafter the molded item was taken out of the mold and surface hardness at the demolding time was measured with an Asker-Type-C hardness meter. Final hardness was measured after allowing the item to stand for 24 hours after demolding. No blister occurred and mold filling ability (Comformability to the configuration of the interior surface of the mold) was good as illustrated in Table 1.

Example 2

The same procedures as described in Example 1 were carried out except that 0.2 part of blowing agent (E) was added. No blister occurred and mold filling ability was good as illustrated in Table 1.

Example 3

The same procedures as described in Example 1 were carried out



except that blowing agent (A) was replaced by 1.0 part of the blowing agent and catalyst (B) and (C) were replaced by 1.0 part of these catalysts respectively. No blister was found and mold filling ability was good as illustrated in Table 1.

Example 4

The same procedures as described in Example 1 were carried out except that blowing agent (A) was replaced by 0.58 part of blowing agent (C). No blister was found and mold filling ability was good as illustrated in Table 1.

Example 5

The same procedures as described in Example 1 were carried out except that blowing agent (A) was replaced by 0.3 part of blowing agent (A) and 0.47 part of blowing agent (B) and catalyst (C) was replaced by 0.53 part of the catalyst, respectively. No blister was found and mold filling ability was good as illustrated in Table 1.

Example 6

The same procedures as described in Example 1 were carried out except that blowing agent (A) was replaced by 0.47 part of blowing agent (B) and 0.3 part of blowing agent (C) and catalyst (C) was replaced by 0.53 part of the catalyst, respectively. No blister was found and mold filling ability was good as illustrated in Table 1.

Comparative Example 1

The same procedures as described in Example 1 were carried out except that blowing agent (A) and catalysts (B), (C) and (D) were replaced by 16 parts of blowing agent (D) and 1.5 parts of catalyst (A) and 0.01 part of catalyst (D) and aromatic polyisocyanate (B) was replaced by aromatic polyisocyanate (A). Free blow density was



lowered. No blister was found and mold filling ability was good as illustrated in Table 1.

Comparative Example 2

The same procedures as described in Example 1 were carried out except that blowing agent (A) and catalysts (B), (C) and (D) were replaced by 0.3 part of blowing agent (E) and 1.0 part of catalyst (B), 1.0 part of catalyst (C) and 0.01 part of catalyst (D). Free blow density was lowered. No blister was found and mold filling ability was poor as illustrated in Table 1.

Comparative Example 3

The same procedures as described in Comparative Example 2 were carried out except that blowing agent (E) was replaced 0.6 part of the blowing agent. Free blow density was lowered and blister occurred on the foam. Results were poor as illustrated in Table 1.



Table

	Compara. Example			Example					
	1	2	3	1	2	3	4	5	6
Polyol (A)	100	100	100	100	100	100	100	100	100
Crosslinking agent(A)	10	10	10	10	10	10	10	10	10
Catalyst (A)	1.5								
(B)		1.0	1.0	0.7	0.7	1.0	0.7	0.7	0.7
(C)		1.0	1.0	0.72	0.72	1.0	0.72	0.53	0.53
(D)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Blowing agent (A)				0.58	0.58	1.0		0.3	
(B)								0.47	0.47
(C)							0.58		0.3
(D)	16								
(E)		0.3	0.6		0.2				
Aromatic polyiso- cyanate NCO/OH ratio	(A) 1.05	(B) 1.05	(B) 1.05	(B) 1.05	(B) 1.05	(B) 1.05	(B) 1.05	(B) 1.05	(B) 1.05
Free blow									
Cream time (sec)	14	13	13	16	16	16	15	16	16
Rise time (sec)	30	26	30	32	34	33	30	29	33
Density (g/cm ³)	0.10	0.29	0.20	0.24	0.20	0.23	0.22	0.23	0.22
Molding (10 mm sheet)									
Density (g/cm ³)	0.60	0.59	0.60	0.63	0.62	0.62	0.62	0.60	0.61
Hardness									
Demolding stage	45	68	70	73	70	73	67	67	69
Final	75	77	81	83	78	80	78	76	77
Demolding time (min)	3	3	3	3	3	3	3	3	3
Blister	○	○	×	○	○	○	○	○	○
Mold filling ability	○	×	○	○	○	○	○	○	○

Note) Blister: ○ No blister, × Blister
 Mold filling ability: ○ Good, × Poor

This Sheet Has Been Replaced



(6) An automotive steering wheel, interior or furniture prepared by the preparation process of claim (3), (4) or (5).