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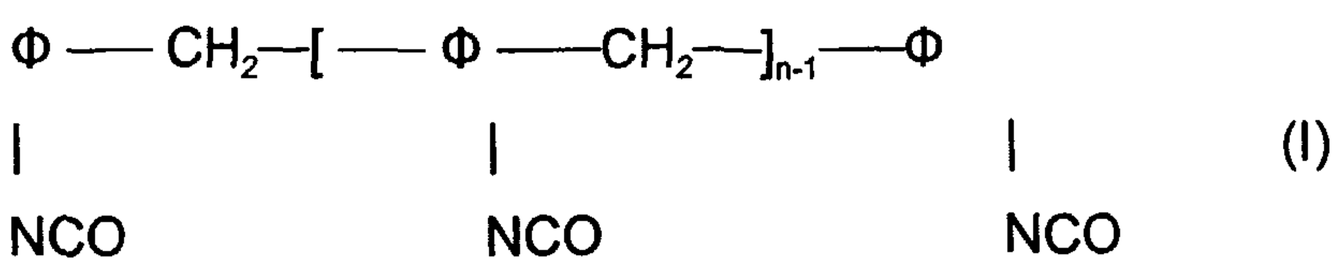

(57) Abrégé/Abstract:
A process for the preparation of a visco-elastic foam having a density from 50 to 100 kg/m^{3} involving reacting an isocyanate component having a functionality from 2.1 to 2.7 of general formula (I): wherein Φ represents a phenyl group and n is an integer greater than or equal to 1 with a polyol component comprising 80 to 100 % by weight of a bifunctional polyol polyether having an average molecular weight from 1000 to 4000, 0 to 5 % by weight of a monofunctional alcohol, 0 to 20 % by weight of a polyol having a functionality equal to or greater than three and an average molecular weight from 92 to 4000.

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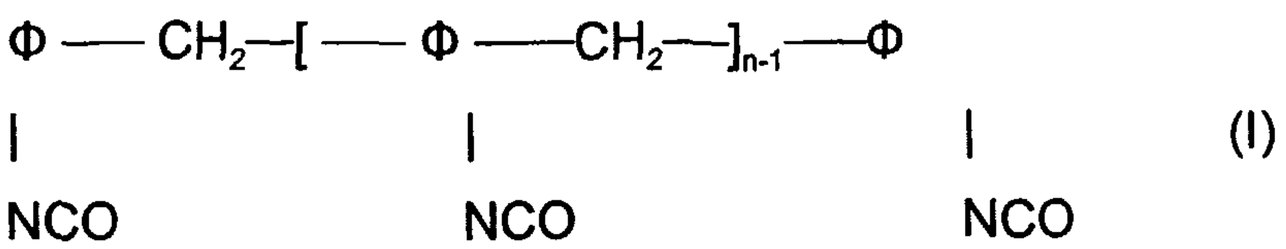
(54) Title: PROCESS FOR THE PREPARATION FO POLYURETHANE FOAMS



(I)

(57) Abstract: A process for the preparation of a visco-elastic foam having a density from 50 to 100 kg/m^3 involving reacting an isocyanate component having a functionality from 2.1 to 2.7 of general formula (I): wherein Φ represents a phenyl group and n is an integer greater than or equal to 1 with a polyol component comprising 80 to 100 % by weight of a bifunctional polyol polyether having an average molecular weight from 1000 to 4000, 0 to 5 % by weight of a monofunctional alcohol, 0 to 20 % by weight of a polyol having a functionality equal to or greater than three and an average molecular weight from 92 to 4000.

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PROCESS FOR THE PREPARATION OF POLYURETHANE FOAMS.

This invention relates to a process for the preparation of a polyurethane foam. In particular, this invention relates to a process for the preparation of a visco-elastic polyurethane foam using an isocyanate component based on MDI (diphenylmethane diisocyanate).

The term "visco-elastic polyurethane foam", as used herein refers particularly to block and moulding (hot and cold) polyurethane expanded materials or foams with a density substantially from 50 to 100 kg/m^3 and suitably having a resilience value, measured according to the test method UNI 6357-68 (Flexible Urethane Cellular Material – Determination of resilience (ball rebound)), lower than 30% and a 50 % compression set value at 23°C, measured according to the test method ISO 1856-80, of less than 4%, preferably less than 3%. These foams have the characteristic of slowly returning to their original form after being compressed.

Materials having this characteristic are used in the preparation of impact absorption articles, in the furnishing industry for the preparation of mattresses and cushions and, more generally, in applications where an object capable of moving without bouncing or rebounding needs to be supported and in healthcare furniture market for example in the production of anti-sore seats and beds.

Visco-elastic polyurethane foams may be prepared by reacting toluene diisocyanate (TDI) with a polyol compound which comprises a polyol polyether or polyester, as well as conventional additives for this type of reaction. The use of TDI however may cause problems of a hygienic-environmental nature both in the preparation phase of the foam and during use, due to the possible presence of non-reacted monomer which may be released from the end-product after its preparation.

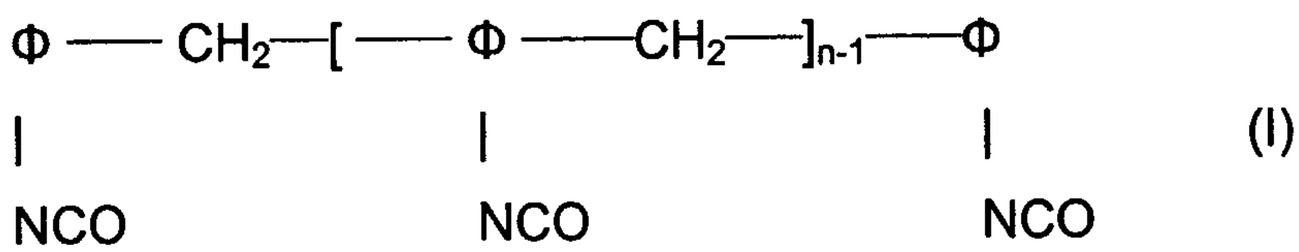
The use of alternative isocyanates, such as MDI, typically requires the use of certain materials, polyethers, polyesters or additives to secure the desired visco-elastic properties. The use of MDI with conventional raw materials typically produces traditional flexible foams (resilience higher than

30 %) or non-expanded materials (collapsed products) since MDI is difficult to process.

It has now surprisingly been found that visco-elastic polyurethane foams may be prepared from an isocyanate component based on MDI and certain types of conventional polyether polyols and drawbacks for example, high resilience and collapsing foam typical in the art may be reduced or avoided.

In a first aspect, the invention provides a process for the preparation of a visco-elastic foam having a density from 50 to 100 kg/m^3 which comprises reacting:

a) an isocyanate component with a functionality from 2.1 to 2.7 having general formula (I):



(I)

wherein Φ represents a phenyl group and n is an integer greater than or equal to 1;

b) a polyol component comprising:

i) 80 to100% and preferably 85 to 95% by weight based on the total polyol component, of a bifunctional polyol polyether having an average molecular weight from 1000 to 4000, preferably from 1500 to 3000;

ii) 0 to 5% and preferably 1 to 5% by weight based on the total polyol component, of a monofunctional alcohol R-OH wherein R is selected from a C_1 to C_{20},and preferably a C_1 to C_{12}, alkyl and/or isoalkyl radical (referred to herein as an (iso)alkyl radical) and a group obtained by the condensation of a C_2 to C_6 olefinic oxide on a C_1 to C_{20} alkyl and/or isoalkyl radical;

iii) 0 to 20% and preferably 5 to15% by weight, based on the total polyol component, of a polyol having a

functionality equal to or greater than three and an average molecular weight from 92 to 4000; and

c) water.

The amount of water present is selected so as to ensure that the desired density of the polyurethane foam is secured.

The isocyanate component having general formula (I) is suitably obtained from the phosgenation of formaldehyde-aniline condensates and generally called raw MDI or polymeric MDI. To obtain the desired isocyanate functionality of 2.1 to 2.7, the isocyanate component having formula (I), if necessary, may be diluted with 4,4'-diphenylmethane diisocyanate, optionally mixed with 2,4'-diphenylmethane diisocyanate.

The bifunctional polyol polyether (i) used in the preparation of visco-elastic expanded materials according to the process, is suitably selected from polyol polyethers obtained by the condensation of a C_2 to C_6 olefinic oxide on a compounds having two active hydrogen atoms (referred to herein as a "starter"), for example diethyleneglycol and dipropyleneglycol or water. Ethylene oxide, propylene oxide or mixtures of them are preferred olefinic oxides.

The monofunctional alcohol ii) suitably has a molecular weight of 200 to 1500 and especially 250 to 1200. Where the alcohol ii) is a group obtained by the condensation of an olefin oxide on a C_1 to C_{20} alkyl and/or isoalkyl radical, the olefin oxide preferably comprises ethylene oxide and/or propylene oxide. In a preferred embodiment R is a group obtained by the condensation of ethylene oxide, and optionally propylene oxide, on a C_1 to C_{12} and especially a C_2 to C_8 alkyl and/or isoalkyl radical.

Examples of suitable polyols with a functionality of three or higher include polyol polyethers based on ethylene oxide and/or propylene oxide and in which the starter is a triol such as glycerin or trimethylolpropane; a tetrol such as pentaerythritol; an alkanolamine such triethanolamine, or a polyfunctional hydroxy alkane such as xylitol, arabitol, sorbitol, mannitol, and the like.

These polyols can be used as such or they may contain, in dispersion or partially grafted to the polyol chains, solid particles, preferably polymeric,

which suitably have dimensions lower than 20 micrometers. Polymers suitable for this purpose include polyacrylonitrile, polystyrene, polyvinylchloride polyurea, mixtures of them, copolymers of them and . These solid particles may be prepared by means of polymerization in situ in the polyol or, as desired they may be prepared separately and subsequently added to the polyol.

The polyol composition may also comprise further additives commonly used in the preparation of polyurethane expanded products such as amine catalysts, for example triethylenediamine, and/or metal catalysts such as stannous octoate, crosslinkers, cell regulators, thermo-oxidation stabilizers, pigments, antiflame agents, etc. Details on the polymerization of polyurethanes are provided in the test "Saunders & Frisch - Polyurethanes, Chemistry and Technology" Interscience, New York, 1964, and in "Polyurethane Handbook, edited by G. Oertel, Hanser Publishers, Munich, New York, 1993.

In the production of the visco-elastic polyurethane foams according to the invention, the expanding agent suitably comprises water and an auxiliary blowing agent for example CO_2 in liquid or gaseous form, and preferably consists of water. Water has a critical function as it causes the formation of urea bonds associated with the development of carbon dioxide which causes the expansion process of the polyurethane polymer , obtaining visco-elasticity. Quantities of water from 1 to 3 parts by weight with respect of 100 parts of polyol component are suitably employed.

In a preferred embodiment the resiliency of the foam is lower than 30% and desirably lower than 10 %. Suitably, the polyol component comprises at least some mono alcohol of formula R-OH as herein defined as this assists in providing a lower resiliency..

Suitably the process of the invention uses an isocyanate index of at least 70 and preferably of at least 90

Some illustrative but non-limiting examples are provided below.

EXAMPLE 1

42.7 parts by weight of an isocyanate component having general formula (I) and an isocyanate functionality of 2.2 (TEDIMON 4420 of Enichem S.p.A.) are reacted, according to the "free rising" technique, with a polyol formulation consisting of 95 parts by weight of a bifunctional polyether polyol having an average molecular weight equal to 2000 (TERCAROL VD 2000 of Enichem S.p.A.); 5 parts by weight of trifunctional polyether having an average molecular weight of 300 (TERCAROL G 310, Enichem S.p.A.); 1.5 parts by weight of water; 0.7 parts of a silicone based surface-active agent (TEGOSTAB B 8002 of Goldschmidt); 0.05 parts by weight of tertiary aliphatic amine (NIAX A-1, Crompton Corporation); 0.23 parts by weight of a solution of tin dibutyldilaurate and 0.5 parts by weight of diethanolamine. The reaction index is equal to 100.

At the end of the reaction, a visco-elastic foam is obtained, having a density of 65 kg/m^3, a compression set of 2.35% and resilience of 24%.

EXAMPLE 2 (Comparative)

The same procedure is adopted as described in example 1 except for the use of 39.2 parts of 4,4'-diphenylmethane diisocyanate which has a functionality of 2, instead of TEDIMON 4420 and 0.25 parts by weight of an aminic catalyst (NIAX A 107 of Witco Corporation). At the end of the reaction, a collapsed product is obtained.

EXAMPLE 3

43.3 parts by weight of TEDIMON 4420 are reacted, according to the "free rising" technique, with a polyol formulation consisting of 93 parts by weight of a bifunctional polyol polyether having an average molecular weight equal to 2000 (TERCAROL VD 2000); 7 parts by weight of trifunctional polyether having an average molecular weight of 300 (TERCAROL G 310); 1.5 parts by weight of water; 0.7 parts of a silicone based surface-active agent (TEGOSTAB B 8002); 0.3 parts by weight of a solution of tin dibutyldilaurate, 0.05 parts by weight of NIAX A 107 and 0.01 parts by weight

of dimethylethanolamine (DABCO DMEA of Air Products). The reaction index is equal to 98.

At the end of the reaction, a visco-elastic foam is obtained, having a density of 55 kg/m^3, a compression set of 3.5% and resilience of 29%.

EXAMPLE 4

43.75 parts by weight of TEDIMON 4420 are reacted, according to the "free rising" technique, with a polyol formulation consisting of 95 parts by weight of a bifunctional polyol polyether having an average molecular weight equal to 2000 (TERCAROL VD 2000); 5 parts by weight of trifunctional polyether having an average molecular weight of 300 (TERCAROL G 310); 1 part by weight of trifunctional polyol polyether having an average molecular weight of 4000 and containing a high level of ethylene oxide (TERCAROL 241 of Enichem S.p.A.) acting as cell opener; 1.6 parts by weight of water; 0.8 parts of a siliconic surface-active agent (TEGOSTAB B 8002); 0.23 parts by weight of a solution of tin dibutyldilaurate and 0.5 parts by weight of dimethylethanolamine. The reaction index is equal to 100.

At the end of the reaction, a visco-elastic foam is obtained, having a density of 77 kg/m^3, a compression set of 2.70% and resilience of 28%.

EXAMPLE 5 (Comparative)

60.5 parts by weight of TEDIMON 4420 are reacted, according to the "free rising" technique, with a polyol formulation consisting of 90 parts by weight of a trifunctional polyol polyether having an average molecular weight equal to 6000 (TERCAROL 427 of Enichem S.p.A.); 10 parts by weight of trifunctional polyol polyether having an average molecular weight of 4000 (TERCAROL 241); 3.1 parts by weight of water; 3.5 parts by weight of diethanolamine; 0.15 parts by weight of tertiary aliphatic amine (DABCO 33 LV); 0.6 parts of a siliconic surface-active agent (TEGOSTAB B 8636); 0.15 parts of a solution of tin dibutyldilaurate (DABCO T-12 of Air Products). The reaction index is equal to 100.

At the end of the reaction, a high resilience foam is obtained, having a density of 36 kg/m^3, a compression set of 11.5% and resilience of 51%.

EXAMPLE 6

37.6 parts of TEDIMON 4420 and a polyol formulation consisting of 90 parts by weight of a bifunctional polyol polyether having an average molecular weight equal to 2000 (TERCAROL VD 2000); 10 parts by weight of a hexafunctional polyether having an average molecular weight of 2700 (GLEDION PS 1504 of Enichem S.p.A.); 1.6 parts by weight of water; 0.3 parts of a silicone based surface-active agent (TEGOSTAB B 8002); 0.3 parts by weight of amine catalyst (NIAX A-1) and 0.6 parts by weight of diethanolamine, are fed, after premixing, into a cubic-shaped mould. The reaction index is equal to 95.

At the end of the reaction, a visco-elastic foam is obtained, having a density of 100 kg/m^3, a compression set of 2.1% and resilience of 18%.

CLAIMS

1. A process for the preparation of a visco-elastic foam having a density from 50 to 100 kg/m^3 which comprises reacting:

a) an isocyanate component having a functionality from 2.1 to 2.7 of general formula (I):

(I)

wherein Φ represents a phenyl group and n is an integer greater than or equal to 1;

b) a polyol component comprising:

i) 80 to100% by weight based on the total polyol component, of a bifunctional polyol polyether having an average molecular weight from 1000 to 4000;

ii) 0 to 5% by weight based on the total polyol component, of a monofunctional alcohol R-OH wherein R is selected from a C_1 to C_{20} alkyl and/or isoalkyl radical and a group obtained by the condensation of a C_2 to C_6 olefinic oxide on a C_1 to C_{20} alkyl and/or isoalkyl radical;

iii) 0 to 20% by weight, based on the total polyol component of a polyol having a functionality equal to or greater than three and an average molecular weight from 92 to 4000; and

c) water.

2. A process according to claim 1, wherein the isocyanate component having general formula (I) is obtained by the phosgenation of a formaldehyde-aniline condensate and optionally 4,4'-diphenylmethane diisocyanate, the 4,4' isomer optionally being mixed with its 2,4' isomer.

3. A process according to any one of claims 1 or 2, wherein the bifunctional polyol polyether comprises a polyol polyether obtained from the condensation of a C_2 to C_6 olefinic oxide on a compound (starters) having two active hydrogen atoms.

4. A process according to any one of the preceding claims, wherein the polyol having a functionality equal to or greater than three and an average molecular weight from 92 to 4000 is present at a level of 5 to 15% by weight.

5. A process according to any one of the preceding claims, wherein the polyol having a functionality equal to or greater than three comprises a polyol polyether based on ethylene oxide and/or propylene oxide condensed on a triol, a tetrol, an alkanolamine or a polyfunctional hydroxy alkane.

6. A process according to any one of the preceding claims, wherein water is present at a level from 1 to 3 parts by weight with respect to 100 parts of polyol component.

7. A visco-elastic polyurethane foam having a density from 50 to 100 kg/m^3, a 50% compression set value at 23°C, measured according to the regulation ISO 1856-80 of lower than 4% and a resilience lower than 30% measured according to regulation UNI 6357-68 obtainable by a process as defined in any one of claims 1 to 6.