(CONVENTION. By one or more persons and/or a Company.) 641959 Form 4.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address(es).

~~I~~/We (1) HOECHST AKTIENGESELLSCHAFT of 50 Bruningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2) PROCESS FOR PRODUCING FOAMS

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3) P39 40 447.1 and P40 08 041.2

(3) Here insert number(s) of basic application(s).

(4) Here insert Name of basic Country or Countries, and basic date or dates.

for a patent or similar protection made in (4) Federal Republic of Germany on 7th December 1989 and 14th March 1990

~~My~~/Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS 290 Burwood Road, Hawthorn, Victoria, Australia.

DATED this 5th day of December 19 90

(5) Signature(s) of Applicant(s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) HOECHST AKTIENGESELLSCHAFT

by

D. B. Mischlewski

Registered Patent Attorney

To: THE COMMISSIONER OF PATENTS.

89 1F 3264

COMMONWEALTH OF AUSTRALIA - Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION UNDER PART XVI., FOR A PATENT

In support of the Convention application made under Part XVI. of the Patents Act 1952 by HOECHST AKTIENGESELLSCHAFT D-6230 Frankfurt am Main 80, Federal Republic of Germany

for a patent for an invention entitled:

Process for producing foams

I/We, Kurt Euler, Riedmühlstraße 39, D-6367 Karben
Adalbert Otto, Bienerstraße 26, D-6238 Hofheim am Taunus / Fed.Rep.of Germany

do solemnly and sincerely declare as follows:

1. We are authorized by HOECHST AKTIENGESELLSCHAFT the applicant/s for the patent to make this declaration on its/their behalf.

2. The basic application/s as defined by Section 141 of the Act was/were made by HOECHST AKTIENGESELLSCHAFT

Federal Republic of Germany P 39 40 447.1 of December 7, 1989
Federal Republic of Germany P 40 08 041.2 of March 14, 1990

3.

1) Klaus-Jürgen BEHME, Kurmainzerstraße 25, D-6239 Eppstein/Taunus
2) Hans-Matthias DEGER, Am Rheingauer Weg 8, D-6238 Hofheim am Taunus
1)-2) Fed.Rep.of Germany

is/are the actual inventor/s of the invention and the facts upon which HOECHST AKTIENGESELLSCHAFT is/are entitled to make the application are as follows:
The said HOECHST AKTIENGESELLSCHAFT is/are the assignee/s of the said inventor/s

4. The basic application/s referred to in paragraph 2 of this Declaration was/were the the first application/s made in a Convention country in respect of the invention the subject of the application.

Dated Frankfurt am Main, Fed.Rep.of Germany, November 7, 1990

HOECHST AKTIENGESELLSCHAFT

ppa. Euler i.V. Otto

To the Commissioner of Patents

AU9067816

(12) PATENT ABRIDGMENT (11) Document No. AU-B-67816/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 641959

(54) Title
PROCESS FOR PRODUCING FOAMS

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(56) Prior Art Documents
AU 61958/90 C08J 9/14 C08L 75/04
US 1193122

(57) Claim

1. A process for producing foams based on polyisocyanates by reacting polyisocyanates, compounds having at least two hydrogen atoms reactive towards isocyanate groups, blowing agents and, if appropriate, further additives, which comprises using a blowing agent which is composed to the extent of at least 10 mol % of one or more fluorinated ethers of the formula I

$$C_aH_bF_c - O - C_dH_eF_f$$ where

a = 1-5 d = 1-2
B = 1-6 e = 1-3
c = 5-10 f = 2-4

or

a = 1-3 d = 1-2
b = 1-4 e = 1-3
c = 1-6 f = 2-4

.../2

except for $C_aH_bF_c = C_2HF_4$ or

$C_dH_eF_f = CHF_2$

6. A process for producing foams based on polyisocyanates by reacting polyisocyanates, compounds having at least two hydrogen atoms reactive towards isocyanate groups, blowing agents and, if appropriate, further additives, which comprises using a blowing agent which is composed to the extent of 10-80 mol % of one or more fluorinated ethers of the formula I

$$C_aH_bF_c - O - C_dH_eF_f$$ where

a = 1-6 d = 1-2
b = 1-12 e = 0-5
c = 1-12 f = 0-5,

and

wherein the remainder of the blowing agent is composed at least partially of CO_2 which is formed by addition of water during the reaction fo the polyisocyanates.

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Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

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Lodged:

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Related Art :

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Complete Specification for the invention entitled:

PROCESS FOR PRODUCING FOAMS

The following statement is a full description of this invention, including the best method of performing it known to :- us

Description

Process for producing foams

The invention relates to a process for producing foams based on polyisocyanates, in particular polyurethane foams and polyisocyanurate foams. The production of such foams is known and has been described, for example, in Kunststoff-Handbuch [Plastics Handbook], Volume VII, Polyurethane [Polyurethanes], Carl Hanser Verlag, Munich, Vienna (1983), pages 246 to 331, and also in EP-A1-0,077,964, EP-A1-0,334,059 and German Auslegeschrift 1,694,138 (= British Patent 1,209,243).

In Ullmanns Enzyklopädie der technischen Chemie [Ullmann's Encyclopedia of Industrial Chemistry] (1980), Volume 19, pages 301 to 341, the raw materials which can be used and the possible processes for producing rigid polyurethane foams are described in summary.

Further relevant references can be found in Kirk-Othmer, Encycl. of Chem. Technology, 3rd edition, Volume 11 (1980), pages 87-89, and Volume 23 (1983), pages 576-607.

The usual blowing agents for polyurethanes are carbon dioxide - which is generated by addition of water during the production of the polyurethanes from polyisocyanates and compounds having reactive hydrogen - and/or so-called "physical blowing agents", namely readily volatile organic substances such as acetone, ethyl acetate, halogen-substituted alkanes such as methylene chloride, chloroform, ethylidene chloride, vinylidene chloride and dichlorodifluoromethane, and also butane, hexane, heptane or diethyl ether. The applicability of fluorinated hydrocarbons for producing heat-insulating polyurethane foams is known, for example, from German Patent 1,111,381. Inorganic blowing agents, for example air, CO_2 or N_2O, can also be used. Further details on the use

of blowing agents are described in Kunststoff-Handbuch, [Plastics Handbook], Volume VII, Carl-Hanser-Verlag, Munich (1966), for example on pages 108 and 109, 453 to 455 and 507 to 510.

Physical blowing agents for polyurethane foams must meet certain demands. Good miscibility of the blowing agents with the usual raw materials is necessary, but they should be insoluble in the polyurethane being formed, in order to ensure good material quality of the foams. Furthermore, because of the heat of reaction which arises during foaming and can lead to a temperature rise up to about 200°C when large-volume parts are foamed up, high thermal stability of the blowing agent is expected. In addition, the blowing agents will preferably be non-flammable. In the course of the development of polyurethane foam technology, all these demands led to the use of fluorinated chlorocarbons (CFC), especially trichlorofluoromethane (CFC 11), as physical blowing agents.

However, the CFCs are now suspected of damaging the ozone layer around the Earth. It is therefore necessary to dispense with the use of these compounds as soon as possible and, instead, to use other substances, which have no potential for ozone damage, as physical blowing agents.

The abandonment of CFCs as blowing agents in favor of CO_2 which - as mentioned above - is formed by addition of water during the production of polyurethanes from polyisocyanates, is under discussion. Although this method is acceptable for some foams, it causes great disadvantages, especially in the case of rigid foams, because the foams produced in this way have an increased thermal conductivity and hence a lower heat insulation capacity than the foams produced with the aid of CFCs.

Surprisingly, it has now been found that fluorinated

ethers are suitable in the same way as CFCs for producing foams based on polyisocyanates and that the thermal conductivity of the rigid foams produced with them is substantially lower than that of those formed with CO_2. In particular, it has been found that these fluorinated ethers and CO_2 can be used simultaneously as blowing agents, a considerable improvement in the heat insulation effect being achieved even with a relatively small proportion of fluorinated ethers (and a correspondingly high CO_2 proportion and therefore a high water content in the rigid foam formulation).

The invention relates to a process for producing foams based on polyisocyanates by reacting polyisocyanates, compounds having at least two hydrogen atoms reactive towards isocyanate groups, blowing agents and, if appropriate, further additives, which comprises using a blowing agent which is composed to the extent of at least 10 mol % of one or more fluorinated ethers of the formula I

$$C_aH_bF_c - O - C_dH_eF_f \qquad \text{where}$$

a = 1-6 d = 1-2
b = 1-12 e = 0-5
c = 1-12 f = 0-5.

Preferably, at least 20 mol %, especially 50-80 mol %, of the blowing agent is composed of one or more of the said fluorinated ethers. However, the blowing agent can in principle also be composed of these ethers to the extent of 100 mol %. However, if - which in general will be the case - not all the blowing agent is composed of these ethers, then the remainder is composed of one of the abovementioned conventional blowing gases. Preferably, the remainder then is composed at least partially of CO_2, which is formed by addition of a suitable quantity of water during the reaction of the polyisocyanates to give the foams. A "suitable" quantity of water is here a

quantity which forms the desired proportion of CO_2. Particularly preferred is a blowing gas which is composed only of one or more of the said ethers and CO_2 (formed by addition of water), i.e. that the "remainder", mentioned above, of the blowing gas is composed only of CO_2.

Amongst the fluorinated ethers of the formula I, those are preferred for which

a = 1-5 d = 1-2
b = 1-6 e = 1-3
c = 5-10 f = 2-4. Those are particularly preferred for which
a = 1-3 d = 1-2
b = 1-4 e = 1-3
c = 1-6 f = 2-4.

The preparation of the fluorinated ethers is described in Ullmann's Encyclopedia of Industrial Chemistry, Volume A 11 (1988), pages 349-389, in particular page 367; A. M. Lovelace et al., Aliphatic Fluorine Compounds (1958); H. Liebig and K. Ulm, Herstellung und Anwendung aliphatischer Fluorverbindungen [Preparation and use of aliphatic fluorine compounds] II, Chemiker-Zeitung (1976), pages 3-13.

The invention also relates to foams which are based on polyisocyanates and which are obtainable by the above process.

When the said fluorinated ethers are used, the hitherto usual foam raw materials can be used and, as stated above, the proportions of water or conventional physical blowing agent can be greatly reduced or even eliminated altogether.

Polyisocyanates suitable for the process according to the invention are the aliphatic, cycloaliphatic and aromatic diisocyanates or polyisocyanates usual for this purpose.

2,4- and 2,6-toluyl diisocyanate, diphenylmethane diisocyanate, polymethylenepolyphenyl isocyanate and mixtures thereof are preferred. Polyisocyanates which contain carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups and which are termed "modified polyisocyanates" and "isocyanate prepolymers", can also be used.

The polyisocyanates are reacted with compounds which contain at least two hydrogen atoms reactive towards isocyanate groups, for example compounds containing hydroxyl groups and based on polyethers, polyesters and amines, and also compounds having amino groups and/or carboxyl groups and/or thiol groups. As a rule, these compounds have 2-8 hydrogen atoms reactive towards isocyanates.

The catalysts used in this reaction are, as usual, tertiary amines which, if desired, can also contain hydrogen atoms active towards isocyanate groups, and/or organic metal compounds, preferably tin salts of carboxylic acids.

In addition, surface-active additives such as emulsifiers and foam stabilizers are in general also used. The emulsifiers are, for example, salts of fatty acids. Polyethersiloxanes are frequently used as foam stabilizers.

Examples 1-7 which follow explain the invention. They relate to typical rigid foam formulations with different proportions of various fluorinated ethers. In the comparison example, however, exclusively CO_2 formed from water is used as the blowing agent. When the fluorinated ethers according to the invention are also used in addition to CO_2, a marked reduction in the thermal conductivity of the foams is found even at relatively small ether proportions of, for example, 25 mol %, relative to the total quantity of blowing agent. This effect even

increases on prolonged storage.

The fluorinated ethers are also suitable for foaming up flexible foams having an open-cell structure and for producing foam moldings having a porous core and a compact skin, according to German Auslegeschrift 1,694,138 (corresponding to British Patent 1,209,243).

The properties of the foams produced in the examples which follow are indicated in the table after the examples.

Comparison example
(use of CO_2 as the sole blowing agent)

85 g of sucrose/propylene oxide polyether of OH number 380, 15 g of ethylenediamine/propylene oxide polyether of OH number 480, 1 g of foam stabilizer (type DC 193 from Dow Corning Corp.), 1.5 g of dimethylcyclohexylamine and 3.8 g of water were intimately mixed for 15 seconds by means of a stirrer at 2500 revolutions, then intimately mixed for 10 seconds with 192 g of crude diphenylmethane diisocyanate (MDI of usual commercial quality) and subsequently cast into a paper mold. Foaming of the mixture started after about 15 seconds and was complete after about 75 seconds. This gave a rigid foam having the properties indicated in the table.

Example 1

The procedure of the comparison example was followed, but with the difference that 2.0 g of dimethylcyclohexylamine, 2.0 g of water, 15 g of 1-hydro-tetrafluoroethyl methyl ether (CHF_2-CF_2-O-CH_3) and 165 g of MDI were used.

Example 2

The procedure of Example 1 was followed, but the proportion of water was increased to 3.0 g and the proportion

of MDI was increased to 180 g, and the 15 g of 1-hydrotetrafluoroethyl methyl ether were replaced by 10 g of 2-hydrohexafluoropropyl methyl ether (CF_3-CHF-CF_2-O-CH_3).

Example 3

The procedure of Example 2 was followed, but the proportion of water was increased to 3.4 g and the proportion of MDI was increased to 186 g. Instead of 2-hydrohexafluoropropyl methyl ether, 4.5 g of 1-hydrotetrafluoroethyl ethyl ether (CHF_2-CF_2-O-CH_2-CH_3) were used.

Example 4

15 g of glycerol/ethylene oxide polyether of OH number 750, 50 g of sucrose/propylene oxide polyether of OH number 490, 15 g of ethylene diamine/propylene oxide polyether of OH number 480, 20 g of tetrabromophthalate diol of OH number 220 (PHT-4-diol from Great Lakes Chemical), 20 g of trichloroethyl phosphate, 1 g of foam stabilizer, 1.5 g of dimethylcyclohexylamine, 1 g of water, 28 g of 1-hydro-tetrafluoroethyl methyl ether (CHF_2-CF_2-O-CH_3) and 147 g of MDI were foamed up as in the comparison example.

Example 5

The procedure of Example 4 was followed, but instead of 15 g only 10 g of glycerol/ethylene oxide polyether of OH number 750 and 55 g of sorbitol/glycerol/propylene oxide polyether of OH number 560 were used instead of 50 g of sucrose/propylene oxide polyether of OH number 490, and the 1-hydrotetrafluoroethyl methyl ether blowing agent was replaced by 40 g of 1,1-difluoro-2,2-difluoroethyl 1,1,1-trifluoroethyl ether (CHF_2-CF_2-O-CH_2-CF_3).

Example 6

15 g of a polyether obtained from ethylenediamine and

equal proportions of ethylene oxide and propylene oxide and having an OH number of 630 were, as in Example 1, mixed and foamed up with 45 g of sorbitol/glycerol/propylene oxide polyether of OH number 560, 20 g of glycerol/propylene oxide polyether of OH number 160, 20 g of tetrabromophthalate diol of OH number 220 and 20 g of trichloroethyl phosphate as well as 1.0 g of foam stabilizer, 1.0 g of dimethylcyclohexylamine, 2.2 g of water, 13 g of 1,1-difluoro-2,2-difluoroethyl ethyl ether ($CHF_2-CF_2-O-CH_2-CH_3$) and 137 g of MDI.

Example 7

The procedure of Example 4 was followed, but the 28 g of 1-hydrotetrafluoroethyl methyl ether were replaced by 35 g of 1,1,1-trifluoro-2-fluoro-3,3-difluoropropyl methyl ether ($CF_3-CHF-CF_2-O-CH_3$).

Table:

	Water/fluorinated ether molar ratio	Properties of the foam: Bulk density (kg/m^3)	Thermal conductivity (23°C, mW/(m x K)) after 1 day	after 6 weeks
Comparison example	100/0	37	25.8	34.7
Example 1	49/51	36	23.0	26.4
Example 2	75/25	37	22.8	26.4
Example 3	86/14	34	23.9	29.0
Example 4	21/79	32	22.1	23.8
Example 5	22/78	26	21.0	21.9
Example 6	58/42	32	23.1	26.3
Example 7	22/78	35	21.3	22.1

Example 8

85 g of sucrose/propylene oxide of OH number 380, 15 g of ethylenediamine/propylene oxide polyether of OH number 480, 1 g of foam stabilizer (type DC 193 from Dow Corning Corp.), 2 g of dimethylcyclohexylamine, 3,5 g of water and 5 g of 1.1.1-trifluoro-2-fluoro-3.3-difluoropropyl-1.1.1-trifluoroethylether (CF_3-CHF-CF_2-O-CH_2-CF_3) were intimately mixed for 15 seconds by means of a stirrer at 2500 revolutions, then intimately mixed for 10 seconds with 170 g of crude diphenylmethane diisocyanate (MDI of usual commercial quality) and subsequently cast into a paper mold. Foaming of the mixture started after about 15 seconds and was complete after about 80 seconds. This gave a rigid foam having the properties indicated in the table.

Example 9

15 g of glycerol/ethylene oxide polyether of OH number 750, 50 g of sucrose/propylene oxide polyether of OH number 490, 15 g of ethylene diamine/propylene oxide polyether of OH number 480, 20 g of tetrabromophthalate diol of OH number 220 (PHT-4-diol from Great Lakes Chemical), 20 g of trichloropropyl phosphate, 2 g of foam stabilizer, 2.5 g of dimethylcyclohexylamine, 1 g of water, 35 g of 2.2-difluoroethyl-1.1.1-trifluoroethylether (CH_3-CF_2-O-CH_2-CF_3) and 147 g of MDI were foamed up as in the example 8.

Example 10

The procedure of Example 9 was followed, but the proportion of water was increased to 3 g, the proportion of MDI was increased to 165 g and the proportion of 2.2-difluoroethyl-1.1.1-trifluoroethylether was decreased to 15 g.

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Table

	Water/fluorinated ether molar ratio	Properties of the foam		
		Bulk density (kg/m^3)	Thermal conductivity (23°C, mW/(m·K))	
			after 1 day	after 6 weeks
Example 8	90/10	36	23.8	28.2
Example 9	20/80	33	20.6	23.5
Example 10	65/35	27	22.5	26.0

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for producing foams based on polyisocyanates by reacting polyisocyanates, compounds having at least two hydrogen atoms reactive towards isocyanate groups, blowing agents and, if appropriate, further additives, which comprises using a blowing agent which is composed to the extent of at least 10 mol % of one or more fluorinated ethers of the formula I

$C_aH_bF_c - O - C_dH_eF_f$ where

a = 1-5	d = 1-2
b = 1-6	e = 1-3
c = 5-10	f = 2-4

or

a = 1-3	d = 1-2
b = 1-4	e = 1-3
c = 1-6	f = 2-4

except for $C_aH_bF_c = C_2HF_4$ or
$C_dH_eF_f = CHF_2$

2. The process as claimed in claim 1, wherein a blowing agent is used which is composed to the extent of at least 20 mol % of one or more of the said fluorinated ethers.

3. The process as claimed in claim 1, wherein a blowing agent is used which is composed to the extent of 50-80 mol % of one or more of the said fluorinated ethers.

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4. The process as claimed in any of claims 1 to 3, wherein the remainer of the blowing agent is composed at least partially of CO_2 which is formed by addition of water during the reaction of the polyisocyanates.

5. The process as claimed in any of claims 1 to 3, wherein the remainder of the blowing agent is composed of CO_2 which is formed by addition of water during the reaction of the polyisocyanates.

6. A process for producing foams based on polyisocyanates by reacting polyisocyanates, compounds having at least two hydrogen atoms reactive towards isocyanate groups, blowing agents and, if appropriate, further additives, which comprises using a blowing agent which is composed to the extent of 10-80 mol % of one or more fluorinated ethers of the formula I

$$C_aH_bF_c - O - C_dH_eF_f$$ where

a = 1-6 d = 1-2
b = 1-12 e = 0-5
c = 1-12 f = 0-5,

and
wherein the remainder of the blowing agent is composed at least partially of CO_2 which is formed by addition of water during the reaction fo the polyisocyanates.

7. The process as claimed in claim 6, wherein a blowing agent is used which is composed to the extent of 50-80 mol % of one or more of the said fluorinated ethers.

8. The process as claimed in any of claims 6 to 7, wherein one or more fluorinated ethers of the formula I where

a = 1-5 d = 1-2
b = 1-6 e = 1-3
c = 5-10 f = 2-4 are used.

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9 The process as claimed in any of claims 6 to 7, wherein one or more fluorinated ethers of the formula I where

a = 1-3 d = 1-2
b = 1-4 e = 1-3
c = 1-6 f = 2-4 are used.

10. The process as claimed in any one of claims 6 to 7 wherein the fluorinated ether is selected from the group comprising C_2HF_4-O-CH3, C_3HF_6-O-CH_3, C_2HF_4-O-C_2H_5 and C_2HF_4-O-$C_2H_2F_3$.

DATED this 27th day of July, 1993

HOECHST AKTIENGESELLSCHAFT

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