

Description

This invention relates to a method for the production of flexible, flame-retardant polyurethane foams and to novel foams obtained thereby.

5 The term "flexible" as used herein includes, but is not restricted to, the categories of foams known to those skilled in the art as "low-resilience", "conventional" and "high-resilience" foams. Flexible cellular materials have been interpreted by the International Standards Organisation (I.S.O.) TC.45 (Cellular Plastics Committee) as "Cellular polymeric materials capable of significant deflection and recovery or used in applications requiring significant deflection and recovery."

10 The physical and mechanical properties of polyurethane foams make them useful for a wide variety of applications, including upholstery and bedding. However, polyurethane foams are inherently flammable and this leads to melting and spread of burning debris and (in the case of "conventional" foams) may also lead to the sustaining of combustion by progressive smouldering even after the actual flames have extinguished.

15 It is considered that cellular materials manufactured from flammable polymers are more flammable than the solid materials because the insulating effect of their cellular nature allows a rapid build-up of heat at the heating surface with a consequent high rate of pyrolysis. In solid materials this heat build-up is at a lower rate because of the higher conductivity of the solid material. Although rigid foams have similar thermal conductivity behaviour to flexible foams the high crosslinked nature of their chemical structure makes them less flammable as polymers and also inherently more inclined to form a protective char rather than to form the flaming molten polymer droplets which occur with flexible foams. Thus both solid and rigid cellular materials burn less easily than flexible foams and are easier to extinguish.

Improvement of flame retardance of rigid foams is disclosed in U.S. patent specification no. 3574644, U.K. patent specification no. 1404822 and Chemical Abstract Vol 85 no. 16 page 36 no. 109453f. The improvement of flame retardance of flexible foams is disclosed in European patent application no. 25 0051347A.

An object of this invention is to make flexible polyetherurethane foams behave more like rigid foams when subjected to flame and thus produce a protective char with little or no burning melt or drips. This is achieved by including a particular type of graphite in the foam-forming reaction mixture.

30 According to one aspect of the present invention there is provided a method for the production of a flexible flame-retardant polyurethane foam from a foam-forming reaction mixture including a polymeric polyol and an organic polyisocyanate characterized in that the polymeric polyol is a polyether polyol and the foam-forming reaction mixture also contains, as flame retardance conferring additive, expandable graphite as hereinafter defined.

40 According to a further aspect of the present invention a flexible flame-retardant polyetherurethane foam comprises the reaction product of a polyether polyol and an organic polyisocyanate characterized in that the foam contains, as flame-retardant ingredient, expandable graphite as hereinafter defined.

The conditions needed to produce a flexible foam will vary according to the reactants selected. A person of ordinary skill in the art will know whether to include additives, e.g. a catalyst or a blowing agent, and what reaction conditions are required. The molecular weights of the polymeric polyols used in flexible foam manufacture are usually from 1000 to 10,000, preferably from 3000 to 7000, with a functionality of up to 4, preferably 2 to 3. The functionality of the polyisocyanate is usually at least 2.

By "expandable graphite" is meant graphite containing one or more exfoliating agents such that considerable expansion will occur at high temperatures.

45 The foam-forming reaction mixture usually contains graphite in an amount such that there will be at least 10% by weight, preferably at least 15% by weight or at least 25% by weight of graphite in the final foam. The amount of graphite required will depend upon the degree of flame retardance required of the foam but usually the amount of graphite will not exceed 30% by weight in the final foam.

The graphite may constitute the sole flame-retardant additive in the foam-forming reaction mixture.

50 Alternatively, other flame-retardant ingredients, known per se, may be used in addition to the graphite. Examples of such ingredients include the hydrated aluminas (e.g. BACO FRF 40), halogen- and/or phosphorus-containing compounds, antimony oxides, and boron-containing compounds. "BACO" is a Registered Trade Mark.

If desired, intumescent-generating ingredients, e.g. ammonium polyphosphates, may be included in the foam-forming reaction mixture.

55 Usually the foams produced according to the present invention will pass the burning test described in the British Standards Specification No. 4735 September 1974. Usually the foams of the present invention are sufficiently flame-retardant that if used with selected textile cover materials the resulting combinations would pass the No. 4 crib test of the British Standards Specification No. 5852: Part 2: 1982, preferably the

No 5 crib test, more preferably the No. 6 crib test and advantageously the No. 7 crib test. In view of the varying degree of flammability of different textile materials it is impossible to give absolute directions as to which textile materials are to be selected. However, a person of ordinary skill in the art would know which materials are likely to be suitable and simple trial and error would then establish whether they were indeed suitable. In order to prepare a foam capable of passing the No. 7 crib test it would generally be necessary for the amount of expandable graphite in the foam to be at least 25% by weight.

The present invention will be illustrated by way of the following Examples using the 3 main types of flexible polyurethane foams.

10 I: LOW RESILIENCE FOAMS

EXAMPLES 1 to 3

Free-rise, low-resilience polyurethane foams were made from the formulations shown in TABLE A.
15 (Quantities are parts by weight)

TABLE A

20	Ingredient (see notes below)	CONTROL X	CONTROL Y	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
25	Polymeric polyol (a)	100	100	100	100	100
	Water	0.8	0.8	0.8	0.8	0.8
30	Glycerol	2.5	2.5	2.5	2.5	2.5
	Amine catalyst (b)	2.3	2.3	2.3	2.3	2.3
	Surfactant (c)	0.67	0.67	0.67	0.67	0.67
35	Polybutene (d)	17	17	17	8.5	8.5
	Dimethyl Ethanolamine catalyst (e)	0.3	0.3	0.3	0.3	0.3
40	Alumina hydrate (f)	-	40	-	-	-
	Expandable Fine grade graphite	-	-	40	20	-
45	Expandable Coarse grade graphite	-	-	-	-	20
50	Blowing agent (g)	-	-	5	5	5
55	Polyiso- cyanate (h)	50	50	50	50	50

Notes to TABLE A

- (a) A polyether polyol, available from Lankro Chemicals Limited as G 1000.
- (b) Triethylene diamine, available from Air Products Limited as DABCO 33 LV (DABCO is a Registered Trade Mark).
- (c) A polyalkylene oxide polysiloxane silicone copolymer, available from B P Chemicals Limited as SC 246.
- (d) Available from B P Chemicals Limited as HYVIS 5 (HYVIS is a Registered Trade Mark).
- (e) Dimethylethanolamine, available from Diamond Shamrock Limited as PROPAMINE A. (PROPAMINE is a Registered Trade Mark).
- (f) Available from British Aluminium Co Limited as BACO FRF 40 (BACO is a Registered Trade Mark).
- (g) A fluorocarbon blowing agent, available from I.C.I. Limited as ARCTON 11.
- (h) A 20 : 80 mixture of methylene-bis-2,4-phenyldiisocyanate (M.D.I.) and tolylene diisocyanate (T.D.I.) available from B P Chemicals Limited as I 13-17.

Samples of each of the above foams were subjected to the burning tests described in British Standards Specification No 4735 and the results were as follows:

CONTROL X	Average burn length 125 mm in 121 seconds, i.e. the whole sample was burnt.
CONTROL Y	The addition of alumina hydrate gave only a slight improvement, the average burn length of this sample being 125 mm in 159 seconds.
EXAMPLE 1	Average burn length using 40 php fine-grade graphite was 38 mm in 113 seconds. The foam charred (as opposed to the foam of the two CONTROL examples which melted and dripped).
EXAMPLE 2	Reduction of the polybutene level and of the graphite level to 8.5 php and 20 php respectively led to an average burn length of 40 mm in 133 seconds.
EXAMPLE 3	Substitution of coarse-grade graphite (20 php) in the formulation of EXAMPLE 2 produced an average burn length of 42 mm in 120 seconds, i.e. not significantly different from that of EXAMPLE 2.

The formulations of CONTROL EXAMPLE X and of EXAMPLES 1 and 2 (above) were also moulded and the resultant mouldings tested according to British Standards Specification No 2782, Method 141 (Oxygen Index Test).

The following results were obtained:

Example	Oxygen Index
CONTROL X	23.8
EXAMPLE 1	33
EXAMPLE 2	30.5

II : CONVENTIONAL FOAMS

EXAMPLES 4 to 6

Conventional polyurethane foams were made by moulding the formulations shown in TABLE B (below) followed by curing for 14 minutes at 150°C.
(Quantities are parts by weight).

TABLE B

Ingredient (see notes below)	EXAMPLE 4	EXAMPLE 5	EXAMPLE 6
Polymeric polyol (a)	600	600	600
Water	7.5	7.5	7.5
Amine catalyst (b)	5	5	5
N-ethylmorpholine	3.5	3.5	3.5
Surfactant (c)	0.6	0.6	0.6
Graphite (d)	120	120	240
F.R. additive (e)	-	60	-
Polyisocyanate (f)	115	115	115

Notes to TABLE B

(a) A polyoxyethylene/polyoxypropylene triol, of

approximate molecular weight 3500, having a high proportion of terminal primary hydroxyl groups.

(b) DABCO 33 LV (see TABLE A)

(c) SC246 (see TABLE A)

(d) Fine grade expandable graphite.

(e) A material containing chlorine and phosphorus, available from Tenneco Organics Limited as TOLGARD V6 (TOLGARD is a Registered Trade Mark).

(f) An 80 : 20 mixture of the 2,4 - and 2,6 - isomers of tolylene diisocyanate (T.D.I.).

Samples of each of the above foams were tested according to the various crib tests described in British Standards Specification No. 5852, Part 2, the weights of the wooden cribs being as follows:

No. 4 crib	8.5 g
No. 5 crib	17 g
No. 6 crib	60 g

EXAMPLE 4 A No. 4 crib was placed directly on the top surface of the moulding and ignited.

Burning time of crib	3½ minutes
Flaming of foam ceased	6 minutes
Progressive smouldering	None

EXAMPLE 5 As EXAMPLE 4, but with No. 5 crib.

Burning time of crib	4 minutes
Flaming of foam ceased	6 minutes
Progressive smouldering	None

EXAMPLE 6 As EXAMPLE 4, but with No. 6 crib.

Burning time of crib	8 minutes
Flaming of foam ceased	11 minutes
Progressive smouldering	None

III : HIGH-RESILIENCE FOAMS

EXAMPLES 7 and 8

High-resilience foams were made by moulding the formulations shown in TABLES C and D (below) in a mould at 50 °C, followed by curing for 10 minutes at room temperature. (Quantities are parts by weight).

TABLE C

Ingredient (see notes below)	EXAMPLE 7
Polymeric polyol (a)	100
Water	2.5
Surfactant (b)	0.9
Amine catalyst (c)	1.2
Tertiary amine catalyst (d)	0.2
Blowing agent (e)	10
Dibutyltin dilaurate	0.03
Graphite (f)	20
Chlorinated paraffin (g)	10
Polyisocyanate (h)	60

Notes to TABLE C

(a) A polyoxypropylene/polyoxyethylene triol of approximate molecular weight 6000, having a high proportion of terminal primary hydroxyl groups and available from Bayer AG under the reference 7963.

(b) A silicone surfactant, available from Goldschmidt AG under the reference B8629.

(c) DABCO 33 LV (see TABLE A)

(d) Available from Union Carbide under the reference A1

(e) ARCTON 11 (see TABLE A)

(f) Fine grade expandable graphite

(g) Available from I.C.I. Limited as CERECOLOR S52 (CERECOLOR is a Registered Trade Mark)

(h) A modified MDI, available from I.C.I. Limited under the reference VM 25.

A sample of this foam was tested using a No. 5 crib.

Burning time of crib	3½ minutes
Flaming of foam ceased	6 minutes
Emission of smoke ceased	20 minutes
Progressive smouldering	None

TABLE D

Ingredient (see notes below)	EXAMPLE 8
Polymeric polyol (a)	100
Cross-linking agent (b)	6
Water	8
Amine catalyst (c)	1.2
Tertiary amine catalyst (d)	0.2
Surfactant (e)	0.9
Graphite (f)	20
Chlorine/phosphorus compound (g)	10
Dibutyl tin dilaurate	0.03
Polyisocyanate (h)	41.5

Notes to TABLE D

(a) Polyol 7963 (See TABLE C)

(b) Available from Lankro Chemicals Limited under the reference A260

(c) DABCO 33 LV (see TABLE A)

(d) A1 (see TABLE C)

(e) B8629 (see TABLE C)

(f) Fine grade expandible graphite

(g) TOLGARD V6 (see TABLE B)

(h) I 13-17 (see TABLE A)

A sample of this foam was also tested using a No. 5 crib.

Burning time of crib	5 minutes
Emission of smoke ceased	13 minutes
Progressive smouldering	None

EXAMPLES 9 and 10

High-resilience foams were made by including formulations as shown in Table E in a mould at 45°C followed by curing for 10 minutes at room temperature.
(Quantities are parts by weight).

TABLE E

Ingredient	Examples 9 and 10
Polymeric polyol (a)	50
Polymeric polyol (b)	50
Water	3.2
Amine catalyst (c)	3
Tertiary Amine Catalyst (d)	0.2
Surfactant (e)	0.6
Expandable graphite	43.7
Sodium tetra borate decahydrate	5
Polyisocyanate (f)	75

Notes to Table E

- (a) A polyoxypropylene/polyoxyethylene triol of approximate molecular weight 6000, having a high proportion of terminal primary hydroxyl groups and available from Bayer AG under the reference 7963.
- (b) Available from B P Chemical Limited under the reference U1315
- (c) Triethylene diamine, available from Air Products Limited as DABCO 33LV
- (d) Available from Union-Carbide under the reference NiAX A1
- (e) Polyalkylene oxide polydimethyl siloxane silicone available under the reference B4113
- (f) Modified diphenyl methane diisocyanate available from ICI under reference VM25.

For Example 9, foam was tested in combination with a woollen fabric of weight approximately 400g/ m² using a No. 6 wooden crib (weight 60g) according to BS 5852 Part 2, 1982. Flaming of the foam/fabric combination ceased 11.5 minutes from the ignition of the wooden crib and there was no progressive smouldering revealed by examination one hour after ignition. The weight loss shown by the foam component was about 3%.

For Example 10, foam was tested in combination with a wool moquette fabric of weight approximately 800g/m² using a No. 7 Wooden crib (weight 120g) according to BS 5852 Part 2 1982. Flaming of the foam/fabric combination ceased 15 minutes from ignition of the crib. There was no progressive smouldering.

Claims

1. A method for the production of a flexible flame-retardant polyurethane foam, from a foam-forming reaction mixture including a polymeric polyol and an organic polyisocyanate, characterised in that the polymeric polyol is a polyether polyol and the foam-forming reaction mixture also contains, as flame-retardance conferring additive, "expandable graphite" which is graphite containing one or more exfoliating agents such that considerable expansion will occur at high temperatures.
2. A method according to Claim 1 characterized in that the amount of expandable graphite in the foam-forming reaction mixture is such that there will be at least 10% by weight of expandable graphite in the foam.
3. A method according to Claim 1 or 2 characterized in that the foam-forming reaction mixture contains one or more further flame-retardant ingredients.
4. A method according to any of Claims 1 to 3 characterized in that the foam-forming reaction mixture also contains an intumescent-generating ingredient.
5. A flexible flame-retardant polyetherurethane foam which comprises the reaction product of a polyether polyol and an organic polyisocyanate characterized in that the foam contains, as flame-retardant ingredient, "expandable graphite" which is graphite containing one or more exfoliating agents such that considerable expansion will occur at high temperatures.

TABLE E

Ingredient	Examples 9 and 10
Polymeric polyol (a)	50
Polymeric polyol (b)	50
Water	3.2
Amine catalyst (c)	3
Tertiary Amine Catalyst (d)	0.2
Surfactant (e)	0.6
Expandable graphite	43.7
Sodium tetra borate decahydrate	5
Polyisocyanate (f)	75

Notes to Table E

(a) A polyoxypropylene/polyoxyethylene triol of approximate molecular weight 6000, having a high proportion of terminal primary hydroxyl groups and available from Bayer AG under the reference 7963.

(b) Available from B P Chemical Limited under the reference U1315

(c) Triethylene diamine, available from Air Products Limited as DABCO 33LV

(d) Available from Union-Carbide under the reference NiAX A1

(e) Polyalkylene oxide polydimethyl siloxane silicone available under the reference B4113

(f) Modified diphenyl methane diisocyanate available from ICI under reference VM25.

For Example 9, foam was tested in combination with a woollen fabric of weight approximately 400g/ m² using a No. 6 wooden crib (weight 60g) according to BS 5852 Part 2, 1982. Flaming of the foam/fabric combination ceased 11.5 minutes from the ignition of the wooden crib and there was no progressive smouldering revealed by examination one hour after ignition. The weight loss shown by the foam component was about 3%.

For Example 10, foam was tested in combination with a wool moquette fabric of weight approximately 800g/m² using a No. 7 Wooden crib (weight 120g) according to BS 5852 Part 2 1982. Flaming of the foam/fabric combination ceased 15 minutes from ignition of the crib. There was no progressive smouldering.

Claims

1. A method for the production of a flexible flame-retardant polyurethane foam, from a foam-forming reaction mixture including a polymeric polyol and an organic polyisocyanate, characterised in that the polymeric polyol is a polyether polyol and the foam-forming reaction mixture also contains, as flame-retardance conferring additive, "expandable graphite" which is graphite containing one or more exfoliating agents such that considerable expansion will occur at high temperatures.
2. A method according to Claim 1 characterized in that the amount of expandable graphite in the foam-forming reaction mixture is such that there will be at least 10% by weight of expandable graphite in the foam.
3. A method according to Claim 1 or 2 characterized in that the foam-forming reaction mixture contains one or more further flame-retardant ingredients.
4. A method according to any of Claims 1 to 3 characterized in that the foam-forming reaction mixture also contains an intumescent-generating ingredient.
5. A flexible flame-retardant polyetherurethane foam which comprises the reaction product of a polyether polyol and an organic polyisocyanate characterized in that the foam contains, as flame-retardant ingredient, "expandable graphite" which is graphite containing one or more exfoliating agents such that considerable expansion will occur at high temperatures.



6. A foam according to Claim 5 characterized in that the foam contains at least 10% by weight expandable graphite.
7. A foam according to Claim 5 or 6 characterized in that it passes the burning test of BS 4735 September 1974.
8. A foam according to Claim 5 or 6 characterized in that, when used with a textile cover, it passes the No. 7 crib test of BS 5852 Part 2 1982.
9. A foam according to any of Claims 5 to 8 characterized in that the foam-forming reaction mixture contains one or more further flame-retardant ingredients.
10. A foam according to any of Claims 5 to 9 characterized in that the foam-forming reaction mixture also contains an intumescent-generating ingredient.

Patentansprüche

1. Verfahren zur Herstellung eines flexiblen flammhemmenden Polyurethanschaums aus einer schaumbildenden Reaktionsmischung, die ein polymeres Polyol und ein organisches Polyisocyanat umfaßt, dadurch gekennzeichnet, daß das polymere Polyol ein Polyetherpolyol ist, und die schaumbildende Reaktionsmischung auch als Flammhemmung verleihendes Additiv "expandierbaren Graphit" enthält, bei dem es sich um Graphit handelt, welcher eines oder mehrere Exfoliations-Mittel enthält, derart, daß bei hohen Temperaturen eine erhebliche Expansion stattfindet.
2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die Menge des expandierbaren Graphits in der schaumbildenden Reaktionsmischung derart ist, daß zumindest 10 Gew.-% an expandierbarem Graphit in dem Schaum vorliegen.
3. Verfahren gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß die schaumbildende Reaktionsmischung einen oder mehrere weitere flammhemmende Bestandteile enthält.
4. Verfahren gemäß einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die schaumbildende Reaktionsmischung auch einen Intumeszenz-erzeugenden Bestandteil enthält.
5. Flexibler flammhemmender Polyetherurethanschaum, welcher das Reaktionsprodukt eines Polyetherpolyols und eines organischen Polyisocyanats umfaßt, dadurch gekennzeichnet, daß der Schaum als flammhemmenden Bestandteil "expandierbaren Graphit" enthält, bei dem es sich um Graphit handelt, der eines oder mehrere Exfoliations-Mittel enthält, derart, daß bei hohen Temperaturen eine erhebliche Expansion stattfindet.
6. Schaum gemäß Anspruch 5, dadurch gekennzeichnet, daß der Schaum zumindest 10 Gew.-% expandierbaren Graphit enthält.
7. Schaum gemäß Anspruch 5 oder 6, dadurch gekennzeichnet, daß er den Brenntest gemäß BS 4735 September 1974 besteht.
8. Schaum gemäß Anspruch 5 oder 6, dadurch gekennzeichnet, daß er, wenn er bei einer textilen Beschichtung verwendet wird, den Nr. 7 Behälter-Test gemäß BS 5852 Teil 2 1982 besteht.
9. Schaum gemäß einem der Ansprüche 5 bis 8, dadurch gekennzeichnet, daß die schaumbildende Reaktionsmischung einen oder mehrere weitere flammhemmende Bestandteile enthält.
10. Schaum gemäß einem der Ansprüche 5 bis 9, dadurch gekennzeichnet, daß die schaumbildende Reaktionsmischung auch einen Intumeszenz-erzeugenden Bestandteil enthält.



Revendications

1. Procédé de fabrication d'une mousse de polyuréthane, flexible, retardatrice de flamme, à partir d'un mélange réactionnel capable de former une mousse, comprenant un polyol polymère et un polyisocyanate organique, caractérisé par le fait que le polyol polymère est un polyéther polyol et le mélange réactionnel capable de former une mousse contient également, en tant qu'additif conférant un effet retardeur de flamme, du "graphite expansible" qui est un graphite contenant au moins un agent de gonflement de telle sorte qu'une forte expansion se produira aux températures élevées.
2. Procédé selon la revendication 1, caractérisé par le fait que la quantité de graphite expansible dans le mélange réactionnel capable de former une mousse est telle qu'il y aura au moins 10% en poids de graphite expansible dans la mousse.
3. Procédé selon la revendication 1 ou 2, caractérisé par le fait que le mélange réactionnel capable de former une mousse contient au moins un ingrédient retardateur de flamme supplémentaire.
4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé par le fait que le mélange réactionnel capable de former une mousse contient également un ingrédient générateur d'intumescence.
5. Mousse de polyéther uréthane, flexible, retardatrice de flamme, qui comprend le produit de réaction d'un polyéther polyol et d'un polyisocyanate organique, caractérisée par le fait que la mousse contient, en tant qu'ingrédient retardateur de flamme, du "graphite expansible" qui est un graphite contenant au moins un agent de gonflement de telle sorte qu'une forte expansion se produira aux températures élevées.
6. Mousse selon la revendication 5, caractérisée par le fait que la mousse contient au moins 10% en poids de graphite expansible.
7. Mousse selon la revendication 5 ou 6, caractérisée par le fait qu'elle passe avec succès le test de combustion de BS 4735, Septembre 1974.
8. Mousse selon la revendication 5 ou 6, caractérisée par le fait que, lorsqu'elle est utilisée avec un revêtement textile, elle passe avec succès le test au support ajouré (crib) N° 7 de la norme BS 5852, Partie 2, 1982.
9. Mousse selon l'une des revendications 5 à 8, caractérisée par le fait que le mélange réactionnel capable de former une mousse contient au moins un ingrédient retardateur de flamme supplémentaire.
10. Mousse selon l'une des revendications 5 à 9, caractérisée par le fait que le mélange réactionnel capable de former une mousse contient également un ingrédient générateur d'intumescence.

