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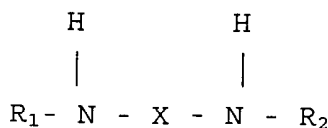
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(54) Title: ISOCYANATE COMPOSITIONS AND THEIR USE IN THE PREPARATION OF EXPANDED POLYURETHANE MATERIALS WITH ENDOWED FLAME-RESISTANCE



(I)

(57) Abstract: An isocyanate component with an isocyanate functionality from t15 to 40 % obtained from the reaction of at least one organic isocyanate which is at least bifunctional, with a secondary amine having general formula (I): wherein R₁ and R₂ are independently the same or different and represent a C₁-C₈ (iso) alkyl radical and X represents a 4,4' methylenediphenylene radical and wherein the molar ratio between the NCO groups of the said isocyanate and functional amine groups in the

amine of formula (I) is from 2 to 10, and use of the component in the preparation of a flexible expanded polyurethane material with endowed flame-resistance.

ISOCYANATE COMPOSITIONS AND THEIR USE IN
THE PREPARATION OF EXPANDED POLYURETHANE
MATERIALS WITH ENDOWED FLAME-RESISTANCE

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The present invention relates to an isocyanic composition and its use in the preparation of flexible expanded polyurethane material with endowed flame-resistance.

The term "flexible expanded polyurethane materials with endowed flame-resistance", as used herein refers to block and moulded (hot and cold) polyurethane expanded products and foams capable of providing flame-resistance performance which passes, for example, the CSE RF4 test, even up to the 1.IM classification, without the use of any flame retardant of the halogenated or phospho-halogenated type, and without the use of auxiliary additives such as melamine and its derivatives.

Both block and moulded flexible polyurethane foams are used in furniture and in the car industry. It is recognised that flame-resistance performance is especially important in these fields.

Flame retardancy may be obtained by using flame retardant additives which are pre-dispersed in the polyurethane reagents. For example GB-A-2,163,762 describes a process for the preparation of flexible polyurethane foams according to which an isocyanic component is reacted with a polyol component in the presence of an expanding agent and a flame-retardant additive. The flame-resistant polyurethane foams may be obtained using melamine as a flame-retardant additive and a modified polyol.

Russian patent SU 729,207 describes a process for preparing flame-resistant polyurethane foams which comprises the use of a flame retardant additive, selected from bis (chloromethyl)-phosphonates, pre-dispersed in one of the two polyurethane reagents.

5 U.S.-A-4,425,447 describes the use of tribromocumene as a flame-retardant agent for polyurethane foams.

The presence of a flame retardant agent or additive in a polyurethane foam, whilst providing satisfactory flame-resistance properties may introduce disadvantages, for example, poorer physico-mechanical properties of the foam
10 itself or the discharge of toxic fumes in the case of combustion.

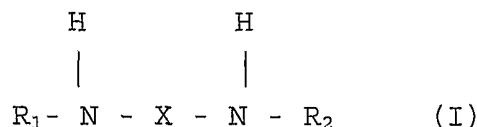
In EP-A-884,340 the problem of the presence of flame retardant additives or agents is said to be overcome by using an isocyanic component selected so as to give the end polyurethane foam flame-resistance characteristics without having to resort to the use of particular additives. Said isocyanic component
15 consists of a mixture which comprises:

- 20-30% by weight of toluene diisocyanate (TDI);
- 30-50% by weight of TDI oligomers with an isocyanic functionality ranging from 3 to 4;
- 30-40% by weight of diphenylmethane diisocyanate (MDI) with a content
20 of 2,4' isomers higher than 40% by weight.

To reduce or avoid drawbacks associated with the use of flame retardant agents in the art and to provide an alternative to the solution proposed in EP-A-884,340, the Applicant has found that polyurethane expanded products or foams with a high flame-resistance may be secured without necessarily having
25 to resort to particular flame retardant agents or additives, by using a new iso-

cyanic composition suitably modified to be able to be used in a combination with a polyol component to produce the polyurethane.

The invention provides, in a first aspect, an isocyanic component which is obtainable from the reaction of at least one organic isocyanate which is at least
 5 bifunctional with a secondary amine having general formula (I):



wherein R_1 and R_2 are independently, the same or different and represent a C_1 - C_8 (iso) alkyl radical and X represents a 4,4'-methylenediphenylene radical and
 10 wherein the molar ratio between the NCO groups of the said isocyanate and functional amine groups in the amine of formula (I) is from 2 to 10.

Preferably, the isocyanic component has isocyanic functionality from 15 to 40%.

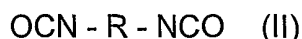
The invention further provides the use of an isocyanic component according to the first aspect of the invention in the preparation of a flexible expanded polyurethane material endowed with flame resistance.
 15

A preferred isocyanic component for use according to the present invention suitably has a viscosity at 25°C from 40 to 10,000 mPa.sec.

Secondary amines according to formula (I) are known per se and examples are described in for example US-A-5,166,185. Secondary amines of formula (I) may be prepared with conventional methods such as those described, for example, in J. March, "Advanced Organic Chemistry", second Edition, McGraw-Hill Kogakusha, 1977. A product having a linking group joining two secondary amine groups is also available on the market under the trade name
 20 of UNILINK 4200 of UOP.
 25

The invention further provides an article comprising an expanded flexible polyurethane material of the present invention.

According to the present invention, any organic isocyanate which is at least bifunctional, may be used in the preparation of the isocyanic component of the present invention. Preferably, diisocyanates having a low or medium molecular weight having general formula (II), are used:

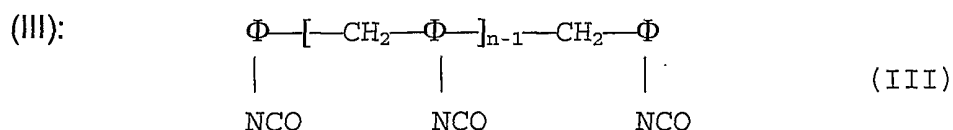


wherein R represents a C₁-C₁₂ (iso) alkyl, a C₅-C₁₅ cycloalkyl or a C₆-C₁₈ aromatic radical which is optionally substituted with a C₁-C₄ alkyl radical. Exam-

10 ples of these products are hexamethylene diisocyanate, meta phenylene diisocyanate, para-phenylene diisocyanate, 2,4-toluenediisocyanate (TDI), 2,6-toluenediisocyanate, 4,4'-diphenylmethane-diisocyanate (MDI), 2,4' diphenylmethane-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, and 1-isocyanate-3-isocyanatemethyl-3,3,5-trimethylcyclohexane. Mixtures of these
15 products may be employed if desired, for example 2,4-toluenediisocyanate and 2,6-toluenediisocyanate, 4,4'- diphenylmethane-diisocyanate and 2,4'-diphenylmethane-diisocyanate.

Polyisocyanates with a high molecular weight may also be employed, for example those compounds obtained by the phosgenation of aniline-

20 formaldehyde condensates. The number of condensation units in such compounds which are suitable for use in the present invention may vary. These products are polymethylenepolyphenyl polyisocyanates having general formula



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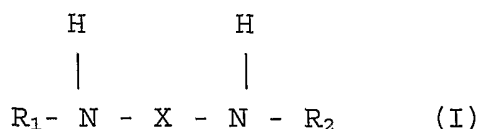
wherein Φ represents a phenyl group and n an integer greater than or equal to 1.

Preferred polyisocyanates with a medium or high molecular weight according to the present invention include polymethylenepolyphenyl polyisocyanates with an average functionality ranging from 2.6 to 2.8. These products are available on the market under various trade names such as "TEDIMON 31" (Enichem S.p.A.), "SUPRASEC DNR" (ICI) or DESMODUR 44 V20 (Bayer).

Further examples of suitable polyisocyanates include isocyanic prepolymers obtained by reacting an excess in equivalents of one or more isocyanates having general formula (II) or (III) with at least one polyol polyether and/or polyester, optionally containing mixed ether or ester groups and/or groups of an aminic nature, having a functionality ranging from 2 to 8 and a molecular weight ranging from about 50 to 2000, of which a more detailed description follows.

A further object of the present invention relates to a process for the preparation of a flexible expanded polyurethane material endowed with flame resistance, which comprises reacting:

- a) an isocyanic component obtainable, and preferably obtained from the reaction of at least one organic isocyanate which is at least bifunctional, as previously described herein, with a secondary amine having the general formula (I):



wherein R₁ and R₂, independently are the same or different and, represent a C₁-C₈ (iso)alkyl radical and X represents a 4,4'-

methylenediphenylene radical and wherein the molar ratio between the NCO groups and functional amine groups of formula (I) is from 2 to 10; with

- b) a polyol component which comprises at least one polyol with a hydroxyl functionality from 2 to 8 and a molecular weight from 50 to 2,000.

The polyol used in the preparation of the flexible expanded products according to the process object of the present invention, is suitably selected from polyol polyethers, polyol polyethers containing an ester group, polyol polyethers containing an amine group, polyol polyesters, polyol polyesters containing an ester group, and polyol polyesters containing an amine group. Preferred polyols include polyol polyethers obtained by the condensation of C₂-C₆ olefinic oxides on compounds having at least two active hydrogen atoms referred to herein as "starters". Preferred olefinic oxides are ethylene oxide, propylene oxide and mixtures thereof.

Suitably the condensation takes place on starters such as glycols, triols, tetrols, amines, alkanolamines, polyamines and mixtures thereof.

Representative examples of polyol polyethers which can be used according to the present invention include those based on ethylene oxide and/or propylene oxide and in which the starter is a glycol such as dipropylene glycol; a triol such as glycerin or trimethylolpropane; a tetrol such as pentaerythritol; a diamine such as ethylenediamine, an aromatic amine such as ortho-toluenediamine, an alkanolamine such as triethanolamine, or a polyfunctional hydroxy alkane such as xylitol, arabitol, sorbitol, mannitol.

These polyols may be used as such in the process of the invention or they may contain in dispersion or partially grafted to the polyol chains, solid par-

ticles, preferably polymeric, with dimensions of less than 20 micrometers.

Polymers suitable for this purpose include polyacrylonitrile, polystyrene and polyvinylchloride and mixtures thereof or copolymers, or urea-based polymers.

These solid particles may be prepared by polymerization in situ in the polyol or
5 they may be prepared separately and subsequently added to the polyol.

The polyol composition suitably also comprises further additives commonly used in the preparation of expanded polyurethanes such as amine catalysts, for example, triethylenediamine, and/or metallic catalysts such as stannous octoate, cell-regulators, thermo-oxidation stabilizers, pigments, and the
10 like. Details on the polymerization of polyurethanes are provided in the text "Saunders & Frisch - Polyurethanes, Chemistry and Technology", Interscience, New York, 1964.

An expanding agent is suitably employed in the production of an expanded polyurethane material according to the process of the present invention.
15 Suitably, the expanding agent comprises water, which may be used alone or in combination with a secondary expanding agent. In the preparation of expanded polyurethanes, water causes the formation of ureic bonds associated with the development of carbon dioxide which produces the expansion/swelling process of the polyurethane resin, obtaining flexible expanded products. Quantities of
20 water from 1 to 10, preferably from 2 to 7 and even from 3 to 6 parts by weight with respect to 100 parts of polyol component are suitable.

Where water is employed as the expanding agent, carbon dioxide developed in situ by the chemical reaction between water and the NCO groups of the polyisocyanate is preferably used as primary agent for the expansion of the
25 polyurethane resin. Other methods for introducing the primary expanding agent

into the polymerization mass may be employed. Thus gases other than carbon dioxide and other techniques may be used, for example, the bubbling of air, liquid CO₂, nitrogen, fluorocarbon or another inert gas, into the reaction mass by external injection.

5 In the preparation of expanded polyurethane materials with a reduced density, for example having a density equal to or lower than 25 kg/m³, the expanding function of water alone may not be sufficient to reach such a density value without certain problems for example scorching, due to the exothermic reaction between water and the isocyanic groups. For this reason, the expanding
10 ing action of water can be supported by expanding agents of a physical nature, selected from hydrofluoro alkanes, for example, 1,1,1,2-tetrafluoroethane (HFC-134a) liquid CO₂, hydrocarbons such as n-pentane, i-pentane, cyclopentane, dimethylcarbonate and mixtures thereof.

The flexible expanded polyurethane materials obtained according to the
15 process of the present invention, suitably have a density from 20 to 200 kg/m³, preferably from 30 to 120 kg/m³, and an aerodynamic lift (according to the regulation ISO 2439) higher than 40 N, preferably from 80 to 400 N. Furthermore the materials suitably have no thermo-oxidative degradation phenomena of the scorching type and have excellent mechanical properties such as, ultimate
20 mate elongation, elastic failure, compression strength and air permeability. Foams of the present invention may advantageously be used in the furniture, household furnishing and transport and car industries which typically require materials having these properties. Additionally, when subjected to flame-resistance tests, foams of the present invention desirably pass the CSE RF4
25 test up to the classification 1.IM.

The invention is illustrated by the following non-limiting examples.

In the examples, the quantities of the various components of the formulations are expressed as parts by weight, unless otherwise specified.

EXAMPLE 1

5 43.8 kg of Tedimon 307 (mixture of 4,4' and 2,4' MDI in a ratio of 50/50) were charged into a reactor filled with nitrogen, equipped with stirring and a cooling system, and subsequently heated to 40°C. 6.2 kg of UNILINK 4200 of UOP was slowly added under vigorous stirring to this product. The reaction was exothermic and the temperature of the reaction mass was maintained at 70°C,
10 the amine being fed at a rate of 0.28 kg/min.

The reaction mass was maintained at this temperature for 1.5 hours. The product (A) was subsequently discharged and analyzed, providing the following characteristics:

NCO % = 26.1;

15 Viscosity 25°C = 240 mPa.sec;

Aspect: yellow liquid;

Crystallization point = 0°C.

EXAMPLE 2

The same procedure was adopted as described in Example 1 except for
20 the use of 43.8 kg of Tedimon 306 (mixture of 4,4' and 2,4' MDI in a ratio of 80/20) which was preheated to 50°C.

The product (B) was discharged and analyzed, providing the following characteristics:

NCO % = 25.9;

25 Viscosity 25°C = 210 mPa.sec;

Aspect: yellow/green liquid;

Crystallization point = 20°C.

EXAMPLE 3

42 kg of Tedimon 80 (mixture of 2,4 and 2,6 MDI in a ratio of 80/20) was
5 charged into a reactor filled with nitrogen, equipped with stirring and a cooling
system, and was subsequently heated to 40°C. 8 kg of UNILINK 4200 was
slowly added to this product under vigorous stirring. The reaction was exother-
mic and the temperature of the reaction mass was maintained at 70°C, the
feeding rate of the amine being controlled.

10 The reaction mass was maintained at this temperature for 1.5 hours. The
product (C) was subsequently discharged and analyzed, providing the following
characteristics:

NCO % = 36;

Viscosity 25°C = 60 mPa.sec;

15 Aspect: yellow/green liquid;

Crystallization point = 15°C.

EXAMPLE 4

20.8 kg of Tedimon 306 and 20.8 kg of Tedimon 307 preheated to 50°C
was charged into a reactor filled with nitrogen, equipped with stirring and a
20 cooling system. The products were reacted with 2.5 kg of TERCAROL 241
(oxyethylene/oxypropylene triol with a molecular weight of 4,000) for at least 30
minutes at 70°C.

5.9 kg of UNILINK 4200 was slowly added to this product under vigorous
stirring. The reaction was exothermic and the temperature of the reaction mass
25 was maintained at 70°C, the feeding rate of the amine being controlled.

The reaction mass was maintained at this temperature for 1.5 hours. The product (D) was subsequently discharged and analyzed, providing the following characteristics:

NCO % = 24.1;

5 Viscosity 25°C = 360 mPa.sec;

Aspect: yellow liquid;

Crystallization point = 10°C.

EXAMPLE 5

17.52 kg of Tedimon 306, 17.52 kg of Tedimon 307 and 10 kg of Tedi-
10 mon 31 preheated to 50°C, was charged into a reactor filled with nitrogen, equipped with stirring and a cooling system.

5.9 kg of UNILINK 4200 was slowly added to this product under vigorous stirring. The reaction was exothermic and the temperature of the reaction mass was maintained at 70°C, the feeding rate of the amine being controlled.

15 The reaction mass was maintained at this temperature for 1.5 hours. The product (E) was subsequently discharged and analyzed, providing the following characteristics:

NCO % = 26.7;

Viscosity 25°C = 250 mPa.sec;

20 Aspect: brown liquid;

Crystallization point = 5°C.

The compositions of Examples 1-5 were used for the preparation of flexible expanded polyurethane materials combined with the polyol component indicated in the following table. The same table also specifies the physico-
25

mechanical characteristics of the foams and the results of the flame-reaction tests.

TABLE

	Composition	a	b	c	d	e
	POLYOL PM 6000	100	100	100	100	100
	Chain extender	2	2	1	1	1
	Amine catalyst	0.23	0.23	0.25	0.25	0.25
5	Stabilizer	0.4	0.4	0.4	0.4	0.4
	Total water	2.3	2.3	2.3	2.3	2.3
	Organometallic cat.	0.1	0.1	0.12	0.12	0.12
	TDI 80/20	33.1				
	Product C		42.3			
	POLYMERIC MDI			36.2		
	Prod.A/Prod.B (50/50)				40.0	
10	Product D					38.9
	Density kg/m ³	43.1	46.5	60.9	55.4	54.7
	Comp.strength 40%,kPa	2.4	2.6	5.4	4.1	2.1
	Elastic failure 50%	3.8	5.1	7.5	12.9	10.8
	Elastic yield, %	61	58	43	49	53
	Tensile strength, kPa	89	90	43	74	80
	Ultimate elongation, %	165	123	61	100	115
15	MVSS 0302 Test	fail	pass	pass	pass	pass
	California 117	fail	pass	pass	pass	pass
	CSE RF4/83, class.	fail	3.1M	fail	1.IM	1.IM

The following definitions are indicated in the table:

PM 6000 POLYOL: TERCAROL 427 of ENICHEM S.p.A.

20 POLYMERIC MDI: TEDIMON 31 of ENICHEM S.p.A.

TDI 80/20: TEDIMON 80 of ENICHEM S.p.A.

Chain extender: Diethanolamine

Amine catalyst: DABC 33LV of AIR PRODUCTS

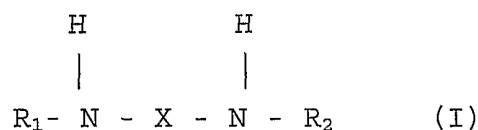
Organometallic catalyst: DABCO T12 of AIR PRODUCTS

25 Stabilizer: TEGOSTAB B 8681 of GOLDSCHMIDT

CLAIMS

1. A process for the preparation of a flexible expanded polyurethane material endowed with flame resistance, which comprises reacting:

a) an isocyanic component obtainable from the reaction of at least one organic isocyanate which is at least bifunctional, with a secondary amine having the general formula (I):



wherein R₁ and R₂ independently are the same or different and represent a C₁-C₈ (iso)alkyl radical and X represents a 4,4'-methylenediphenylene radical, and wherein the molar ratio between the NCO groups of the said isocyanate and functional amine groups in the amine of formula (I) is from 2 to 10;

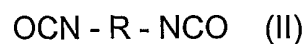
with

b) a polyol component which comprises at least one polyol with a hydroxyl functionality from 2 to 8 and a molecular weight from 50 to 2,000.

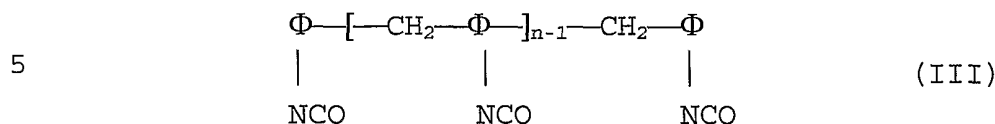
2. A process according to claim 1, wherein in the secondary amine having general formula (I) at least one of R₁ and R₂ is an isobutyl radical.

3. A process according to claim 2 in which both R₁ and R₂ are isobutyl radicals.

4. The process according to any one of the preceding claims wherein the isocyanic component is selected from those with a low or medium molecular weight having general formula (II):



wherein R represents a C₁-C₁₂ (iso) alkyl, a C₅-C₁₅ cycloalkyl or a C₆-C₁₈ aromatic radical which is optionally substituted with a C₁-C₄ alkyl radical or from polyisocyanates with a high molecular weight having general formula (III):



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

5. A process according to claim 4 wherein the polyisocyanate is a high molecular weight polyisocyanate obtained from the phosgenation of aniline-formaldehyde condensates.

6. A process according to claim 4 wherein the polyisocyanate is a low or medium molecular weight polyisocyanate selected from hexamethylene diisocyanate, meta phenylene diisocyanate, para-phenylene diisocyanate, 2,4-toluenediisocyanate (TDI), 2,6-toluenediisocyanate, 4,4'-diphenylmethane-diisocyanate (MDI), 2,4' diphenylmethane-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, and 1-isocyanate-3-isocyanatemethyl-3,3,5-trimethylcyclohexane.

7. A process according to any one of claims 1 to 6, wherein the polyol is selected from polyol polyethers, polyol polyethers containing ester groups, polyol polyethers containing amine groups and polyol polyesters.

8. A process according to any one of the preceding claims wherein the polyol is selected from polyol polyethers obtained by the condensation of a C₂-C₆ olefinic oxide with a compound having at least two active hydrogen atoms.

9. A process according to claim 8 wherein the olefinic oxide is selected from

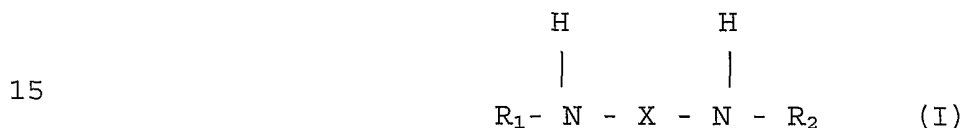
ethylene oxide and propylene oxide.

10. A process according to any one of claims 8 and 9 wherein the compound having at least two active hydrogen atoms is selected from a glycol, a triol, a tetrol, a diamine, an aromatic amine, an alkanol amine and a polyfunctional hydroxy alkane.

11. A process according to any one of the preceding claims wherein the polyurethane material is expanded by means of an expanding agent.

12. A process according to claim 11 wherein the expanding agent comprises water and optionally a hydrofluoroalkane, carbon dioxide a hydrocarbon and mixtures thereof.

13. An isocyanic component obtainable from the reaction of at least one organic isocyanate which is at least bifunctional, with a secondary amine having the general formula (I):



wherein R₁ and R₂ independently are the same or different and represent a C₁-C₈ (iso)alkyl radical and X represents a 4,4'-methylenediphenylene radical, and wherein the molar ratio between the NCO groups of the said isocyanate and functional amine groups in the amine of formula (I) is from 2 to 10.

14. An isocyanic component according to claim 13 having an isocyanic functionality from 15 to 40%.

15. An isocyanic component according to any one of claims 13 and 14 having a viscosity at 25C from 40 to 10000 mPa.sec.

16. Use of an isocyanic component according to any one of claims 13 to 15

in the preparation of a flexible expanded polyurethane material endowed with flame-resistance.

17. An expanded flexible polyurethane material having endowed flame resistance which is obtainable by a process according to any one of claims 1 to 12.

18. An expanded flexible polyurethane material according to claim 17 which passes the CSE RF4 test up to the classification 1.IM and which are substantially free of flame retardant of the halogenated or phospho-halogenated type

19. An article comprising an expanded flexible polyurethane material according to any one of claims 17 and 18.

INTERNATIONAL SEARCH REPORT

 Interna I Application No
 PCT/EP 01/07477

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08G18/32

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 7 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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 943 158 A (DIETRICH WERNER ET AL) 9 March 1976 (1976-03-09) column 1, line 12 -column 3, line 31	13-15
A	example 4	1,4,6-9, 11
X	US 5 288 768 A (GATTUSO MARK J ET AL) 22 February 1994 (1994-02-22) column 2, line 67 -column 4, line 34 column 6, line 18 -column 6, line 57	13-15
A	example I; table 1	1-4,6
A	US 4 340 712 A (REICHMANN WOLFGANG ET AL) 20 July 1982 (1982-07-20) example 4	13
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *P* document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

Internat Application No
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