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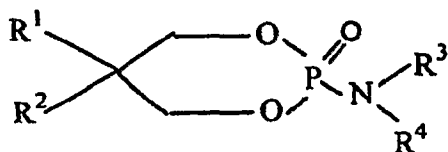
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(54) Title: PHOSPHORAMIDE ESTER FLAME RETARDANT AND RESINS CONTAINING SAME



(I)

(57) Abstract: Certain cyclic phosphoramidate ester compounds useful, inter alia, as halogen-free flame-retardant compounds, are disclosed. The compounds are particularly useful for providing flame retarded polyurethane foams. (I)

WO 2008/085926 A1

1321-179 (SUPD129)

## PHOSPHORAMIDE ESTER FLAME RETARDANT AND RESINS CONTAINING SAME

### FIELD OF THE INVENTION

[0001] This invention relates to cyclic phosphoramidate esters and their use as flame retardants in synthetic resins such as polyurethane foams.

### BACKGROUND OF THE INVENTION

[0002] Many kinds of synthetic organic resins are combustible to one extent or another, some more than others. Where their potential for combustion possesses heightened safety and/or health risks, it is a general practice to add one or a mixture of flame retardants to such resins.

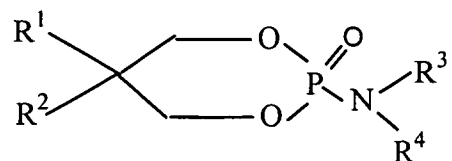
[0003] Flexible polyurethane foams are widely used as cushioning or padding materials, for example, in furniture and in automobiles, and it is known to incorporate fire-retardant additives in such foams. However, there are often considerable technical problems and toxicological concerns restricting the use of these flame retardants as is the case with conventional halogenated fire retardants.

[0004] Flame-retardant additives commonly used to make flame retarded polyurethane foams typically contain halogen compounds. However, for reasons of product sustainability there is a movement within the industry towards the use of non halogen-containing flame retardants.

[0005] Phosphates are known for incorporation in synthetic resins such as polyurethane foams where they function as flame retardants. It has now been discovered that certain novel cyclic phosphoramidate esters alone, or in combination with one or more other flame retardants, incorporated into polyurethane and polyisocyanurate foam results in flame retardant foam capable of meeting a variety of flame retardancy standards without the presence of halogen atoms.

## SUMMARY OF THE INVENTION

[0006] The present invention provides a cyclic phosphoramidate compound of the formula:



wherein, R<sup>1</sup> and R<sup>2</sup> are straight-chain or branched alkyl groups having from 1 to 6 carbon atoms, which optionally contains one or more non-terminal heteroatom substituents, R<sup>3</sup> and R<sup>4</sup> are independently either a hydrogen atom, aryl or substituted aryl group, or a straight-chain or branched alkyl groups having from 1 to 6 carbon atoms, which optionally contains one or more non-terminal heteroatom substituents.

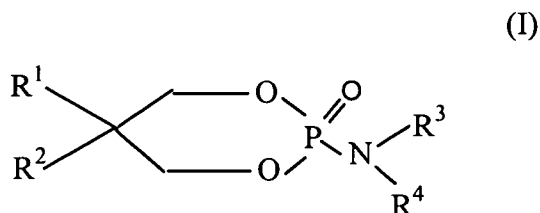
## DETAILED DESCRIPTION OF THE INVENTION

[0007] This invention is directed to certain cyclic phosphoramidate ester compounds which are particularly useful as halogen-free flame-retardant materials in flame retardant-effective amounts to any of a wide variety of resins to impart flame retardant properties thereto.

[0008] The novel cyclic phosphoramidate esters of this invention are satisfactorily employed by themselves and, if desired, in combination with one or more other flame retardants, e.g., one or more organohalogen, organophosphorous and/or melamine-based flame retardants as described, e.g., in U.S. Patent No. 6,967,252. Melamine-based flame retardants as used herein includes melamine compounds, melamine *per se*, i.e., the compound 2,4,6-triamino *s*-triazine, and its flame retardant-effective derivatives.

[0009] In accordance with the present invention, it has unexpectedly been found that a mixture of an effective flame-retardant amount of a novel non-halogen neopentyl phosphoramidate ester and a melamine compound incorporated into a polyurethane foam composition results in flame retarded foam capable of meeting a variety of flame retardancy standards, e.g., the California Technical Bulletin 117 test criteria, the Motor Vehicle Safety Standard 302 (MVSS 302) test criteria, and the stringent British Standard 5852 (BS 5852) test criteria.

[0010] The cyclic phosphoramidate ester of the present invention is represented by the general formula:



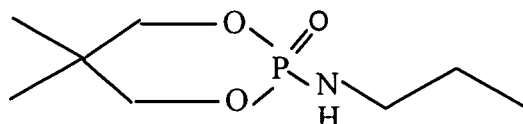
[0011] In the formula (I), R<sup>1</sup> and R<sup>2</sup> have 1 to 6 carbon atoms, which optionally contain heteroatom substituents, e.g., O, N, S, and the like, and can be straight-chain or branched alkyl groups, examples of which include straight-chain alkyl groups such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, etc., and branched alkyl groups such as iso-propyl, iso-butyl, sec-butyl, tert-butyl, iso-pentyl, tert-pentyl, neo-pentyl, iso-hexyl, and the like. Among these groups, straight-chain or branched alkyl groups having a carbon number of 1 to 4 are preferable, and methyl is the most preferable.

[0012] R<sup>3</sup> and R<sup>4</sup> are independently either a hydrogen atom, aryl or substituted aryl group, or a straight-chain or branched alkyl groups having from 1 to 6 carbon atoms, which may or may not contain additional heteroatom substituents, e.g., methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, iso-propyl, iso-butyl, sec-butyl, tert-butyl, iso-pentyl, tert-pentyl, neo-pentyl, and iso-hexyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, 2-aminoethyl, N,N-diethyl-2-aminoethyl, ethylene thiol and the like.

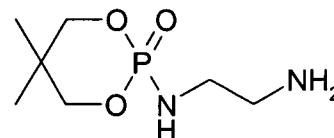
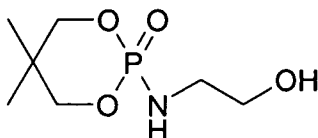
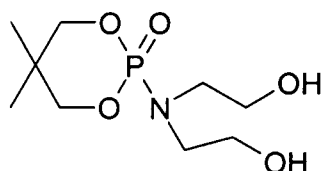
[0013] Specific examples of phosphoramidate esters in accordance with the invention include the following: cyclic neopentyl N-propyl phosphoramidate, cyclic neopentyl N-isopropyl phosphoramidate, cyclic neopentyl N-ethyl phosphoramidate, cyclic neopentyl N-methyl phosphoramidate, cyclic neopentyl N, N-dipropyl phosphoramidate, cyclic neopentyl N, N-diisopropyl phosphoramidate, cyclic neopentyl N, N-diethyl phosphoramidate, cyclic neopentyl N, N-dimethyl phosphoramidate, and cyclic neopentyl N-phenyl phosphoramidate.

[0014] According to one specific embodiment of the invention, the cyclic phosphoramidate of the invention has the following formula:

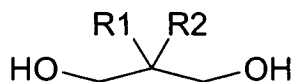
[0015]



[0016] Other cyclic phosphoramidates of the invention include:



[0017] The novel phosphoramidate esters of the present invention can be prepared by reacting, at least one trichlorophosphate with at least one disubstituted propylene glycol of the general formula:

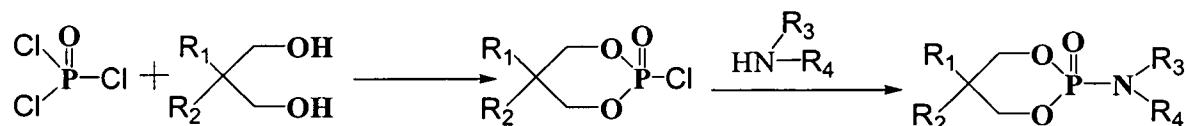


wherein R1 and R2 are as defined above, in at least the stoichiometrically required amounts (e.g., at least 1 mole of trichlorophosphate per mole of neopentyl glycol), to provide chlorophosphate, then adding at least one alkyl or aryl amine in at least the

stoichiometrically required amounts, e.g., at least 1 mole of the amine per mole of the chlorophosphate, to the reactor to finish the reaction.

[0018] A general reaction sequence of the synthesis of the novel phosphoramidate esters of the present invention is illustrated as follows:

[0019]



[0020] The phosphoramidate esters of the invention can be added in flame retardant-effective amounts to any of a wide variety of resins to impart flame retardant properties thereto. Resins to which the phosphoramidate esters can be added include, e.g., polyolefins such as polyethylene, polypropylene and polyethylene-co-propylene copolymer, polyvinyl chloride, polystyrene, polyacrylates, polymethacrylates, polycarbonates, polyesters, polyurethanes, and the like, blends of resins, as well as many other kinds of resins as described, e.g., in U.S. Patent No. 6,967,252, the entire contents of which are incorporated by reference herein.

[0021] The phosphoramidate esters of this invention are satisfactorily employed by themselves and, if desired, in combination with one or more other flame retardants, e.g., any of the organohalogen, organophosphorus, inorganic compounds and/or melamine-based flame retardants as described in, e.g., the aforementioned U.S. Patent No. 6,967,252 and in U.S. Patent Application 2006/0208238, the contents of which are also incorporated by reference herein.

[0022] Suitable organophosphorus-based flame retardants that can be used with the phosphoramidate esters of this invention include, but are not limited to, triethyl phosphate, ethyl diphenyl phosphate, dibutyl phenyl phosphate, butyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate,

alkylated triaryl phosphates, such as butylated or isopropylated triphenyl phosphate, dimethyl methylphosphonate, dimethyl propylphosphonate and the like and mixtures thereof. Examples of organohalogen-based flame retardants suitable for use with the phosphoramidate esters of the present invention include, e.g., tris(chloropropyl) phosphate and tris(dichloroisopropyl) phosphate, N-trifluoromethylmelamine, N-(2-chloroethyl)melamine, N-(3-bromophenyl)melamine and the like and mixtures thereof.

[0023] Examples of melamine-based flame retardants that can be used with the phosphoramidate esters of this invention include, but are not limited to, melamine, N-methylmelamine, N-cyclohexylmelamine, N-phenylmelamine, N,N-dimethylmelamine, N,N-diethylmelamine, N,N-dipropylmelamine, N,N'-dimethylmelamine, N,N',N''-trimethylmelamine, and the like. Also alcohol derivatives of melamine such as trimethylolmelamine or triethylolmelamine may be used. Melamine sulfate and melamine phosphates such as melamine orthophosphate, melamine polyphosphate, and dimelamine orthophosphate may also be used.

[0024] The phosphoramidate ester flame retardants of the invention can be added to the host resin(s) employing any suitable procedure, e.g., utilizing an extruder or roll-type blender in the case of a thermoplastic resin and adding the flame retardant(s) to a thermoset resin-forming reaction mixture or component thereof in the case of a thermoset resin.

[0025] The flame retardant performance of polyurethane foams and polyisocyanurate foams can be significantly improved by the addition of one or more phosphoramidate esters of this invention, with or without other flame retardant(s) such as those aforementioned. The flame retardant(s) can be introduced into these foams via the reaction mixtures from which the foams are produced. Typically, a polyurethane foam or polyisocyanurate foam-forming reaction mixture contains one or more polyols, e.g., polyether polyol or polyester polyol, polyisocyanates, chain extenders, silicone surfactants, blowing agents, catalysts and, if desired, other similarly known and conventional components.

[0026] The phosphoramidate ester flame retardants of the invention can be reactive phosphate flame retardant(s), i.e., those in which  $R^1$ ,  $R^2$ ,  $R^3$  or  $R^4$  can contain chemically reactive groups, e.g., hydroxyl, thiol or primary/secondary amine groups, the flame retardants will be chemically incorporated within the structure of the resulting foam. This chemical incorporation can be achieved by simply adding the reactive phosphoramidate ester(s) to the resin-forming components mentioned above or to its polyol component.

[0027] The flame retardant(s) of the present invention can be non-reactive and any other non-reactive flame retardant(s) that may be utilized herein will be substantially uniformly incorporated into, and mechanically entrained within, the resulting foam.

[0028] In contrast to the non-reactive phosphoramidate ester flame retardants, reactive phosphoramidate flame retardant(s) will be chemically incorporated within the structure of the resulting foam. This chemical incorporation can be achieved by first reacting polyol, polyisocyanate and reactive phosphoramidate ester(s) to provide a hydroxyl-terminated or isocyanate-terminated polyurethane prepolymer from which the polyurethane foam (or non-cellular polyurethane resin) is ultimately derived and/or to simply add the reactive phosphoramidate ester(s) to the resin-forming components mentioned above or to its polyol component.

[0029] It is, of course, contemplated that both non-reactive and reactive phosphoramidate ester flame retardant can be incorporated in a polyurethane foam or polyisocyanurate foam with the non-reactive flame retardant being mechanically entrained therein and the reactive flame retardant being chemically integrated in the foam structure.

[0030] The amounts of flame retardant(s) introduced into a resin or resin blend can vary widely provided that at least a flame retardant-effective amount is utilized. For many resins including those mentioned, the total amount of flame retardant (i.e.,

phosphoramidate ester flame retardant(s) of this invention alone or in combination with one or more other flame retardants) can vary from about 0.5 to about 45 weight percent of the resin(s), preferably from about 3 to about 40 weight percent of the resin(s) and more preferably from about 5 to about 35 weight percent of the resin(s). Optimum amounts of specific flame retardant(s) for a specific resinous composition can be readily determined employing known and conventional procedures.

[0031] The advantages of this invention are illustrated by the following examples. The reactants, proportions and other specific conditions are presented as being typical and should not be construed to limit the invention unduly.

#### EXAMPLES

[0032] Flame-retarded polyurethane foam Example 1 and Comparative Examples 1 and 2 were hand mixed laboratory pours made in a box (free rise). The components of the formulation used to prepare Example 1 and Comparative Examples 1 and 2 are identified in Table 1 below, shown as parts by weight in relation to 100 parts by weight of the polyol. Comparative Example 2 was prepared as a non-flame retardant foam.

[0033]

TABLE 1

ADDITIVE	ADDITION LEVEL
Vorinol 3136 (polyether polyol with an OH number of 54 available from Dow Chemical)	100
FR (Phosphoramidate and Phosphate prepared by Supresta, LLC)	13
Melamine (Melamine 003 Grade available from DSM)	18
H <sub>2</sub> O	3.55
D33LV/A-1: 3/1 ratio (Dabco BLV catalyst available from Air Products)	0.23
Silicone L-620 (Niax Silicone L-620 from General Electric Advanced Materials)	0.80
Stannous Octoate T-10 (Dabco T-10 available from Air Products)	0.55
TDI (Mondur TD-80 Grade A available from Bayer Material Science)	47.33
TDI Index	110

[0034] The novel cyclic neopentyl N-propyl phosphoramidate (NPPA) flame retardant of Example 1 was prepared as follows: 612 g (4 mol) of POCl<sub>3</sub> was placed in a reactor with an agitator, a thermometer, a nitrogen inlet, and a condenser connected to a scrubber as a nitrogen outlet. The scrubber was also connected to a vacuum system (water-pump). The reactor was cooled to 5°C, and 416 g (4 mol) of neopentyl glycol was added to the reactor in four equal 1 mol additions within a 4 hour period. The temperature of the reactor was allowed to rise to about 50°C after each addition. The reactor temperature was never allowed to exceed 50°C. After the 4 hour period, reactor cooling was stopped, and the reactor temperature was allowed to increase on its own to 50°C within 1 hour, at which time the reaction solidified. The reactor was heated to 100°C to melt the solid, after which vacuum was applied to the reactor to help remove any dissolved HCl in the reaction liquid. After removing the residual HCl, 500 ml of

toluene was added to the reactor. After cooling the reactor to 10°C, 472.9 g (8.0 mol) of propylamine was added dropwise within 1 hour. The reaction temperature was controlled below 35°C. After finishing the propylamine addition, the reactor was heated to 80°C and held for 1 hour. After cooling the reactor to room temperature and removing the propylamine-HCl salt, the product was washed with 100 ml of aqueous NaOH (5%) and 100 ml of water to further remove any remaining salt. Toluene and any remaining water were removed with a rotary evaporator at 50°C under vacuum.

[0031] Example 1 and Comparative Examples 1 and 2 were tested using a non-certified reduced-scale version of the British Standard 5852 (BS 5852) Supresta LLC developed for the specific purpose of screening new product candidates using less foam than required by the normal BS 5852. The reduced-scale test is run using foam samples that measured 11"x 11" x 3" for back and 11"x 8"x 3" for bottom. The ignition source used was a Crib # 4 (8.5 grams) and the reagent was isopropyl alcohol (1.4ml).

[0032] As presented in Table 2, the cured polyurethane foam of Example 1 and Comparative Examples 1 and 2 (Comparative Example 2 contained no flame-retardant compounds) included the following flame-retardant materials: cyclic neopentyl N-propyl phosphoramidate (NPPA); tris (chloropropyl) phosphate (TCPP); and melamine (obtained from the DSM Co. 99% having a particle size of 40 microns), respectively.

[0035]

TABLE 2

	Example 1: NPPA/melamine	Comparative Example 1: TCPP/melamine	Comparative Example 2:
FR	13	13	0
Melamine	18	18	0
Small Scale BS 5852 Weight Loss in grams	16	9	
% Weight Loss	5 %	3 %	EM*

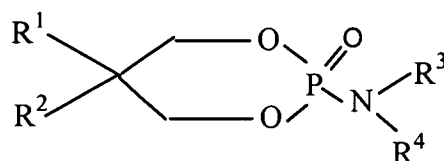
\* Extinguished manually

[0036] The foam containing the 13/18 blend of non-halogen flame-retardant mixture of cyclic neopentyl N-propyl phosphoramidate and melamine showed a significant improvement in weight lost over the non-flame retardant foam Comparative Example 2 (which had to be manually extinguished after >50% weight loss), with an overall weight loss comparable to that observed for the TCPP/melamine foam.

[0037] While the process of the invention has been described with reference to certain embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out the process of the invention but that the invention will include all embodiments falling within the scope of the appended claims.

CLAIMS:

1. A phosphoramidate compound of the general formula:



wherein,  $R^1$  and  $R^2$  are straight-chain or branched alkyl groups having from 1 to 6 carbon atoms, which optionally contains one or more non-terminal heteroatom substituents,  $R^3$  and  $R^4$  are independently either a hydrogen atom, aryl or substituted aryl group, or a straight-chain or branched alkyl groups having from 1 to 6 carbon atoms, which optionally contains one or more non-terminal heteroatom substituents.

2. The phosphoramidate of Claim 1 wherein any heteroatoms in  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are selected from the group consisting of O, S and N.
3. The phosphoramidate of Claim 1 wherein  $R^1$  and  $R^2$  are straight-chain or branched alkyl groups having from 1 to 4 carbon atoms, which optionally contains one or more non-terminal heteroatom substituents.
4. The phosphoramidate of Claim 1 wherein  $R^1$  and  $R^2$  are independently selected from the group consisting of methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, iso-propyl, iso-butyl, sec-butyl, tert-butyl, iso-pentyl, tert-pentyl, neo-pentyl, and iso-hexyl, which optionally contains one or more non-terminal heteroatom substituents.
5. The phosphoramidate of Claim 1 wherein  $R^3$  and  $R^4$  are independently selected from the group consisting of methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, iso-propyl, iso-butyl, sec-butyl, tert-butyl, iso-pentyl, tert-pentyl, neo-pentyl, iso-hexyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, 2-aminoethyl, N,N-diethyl-2-aminoethyl,

and ethylene thiol, which optionally contains one or more non-terminal heteroatom substituents.

6. The phosphoramidate of Claim 1 wherein  $R^1$  and  $R^2$  are methyl.
7. A phosphoramidate of Claim 1 selected from the group consisting of the cyclic neopentyl N-propyl phosphoramidate, cyclic neopentyl N-isopropyl phosphoramidate, cyclic neopentyl N-ethyl phosphoramidate, cyclic neopentyl N-methyl phosphoramidate, cyclic neopentyl N, N-dipropyl phosphoramidate, cyclic neopentyl N, N-diisopropyl phosphoramidate, cyclic neopentyl N, N-diethyl phosphoramidate, cyclic neopentyl N, N-dimethyl phosphoramidate, cyclic neopentyl N-phenyl phosphoramidate.
8. A flame retardant composition comprising at least one phosphoramidate of Claim 1.
9. The flame retardant composition of Claim 8 further comprising at least one flame retardant other than a phosphoramidate of Claim 1.
10. The flame retardant composition of Claim 9 wherein the flame retardant other than the phosphoramidate of Claim 1 is at least one member selected from the group consisting of organohalogen compound, organophosphorus compound and melamine compound.
11. The flame retardant composition of Claim 9 wherein the phosphoramidate of Claim 1 is cyclic neopentyl N-propyl phosphoramidate and the flame retardant other than the phosphoramidate of Claim 1 is melamine.
12. A resin containing a flame retardant-effective amount of at least one phosphoramidate of Claim 1.

13. A resin containing a flame retardant-effective amount of the flame retardant composition of Claim 8.
14. A resin containing a flame retardant-effective amount of the flame retardant composition of Claim 9.
15. A resin containing a flame retardant-effective amount of the flame retardant composition of Claim 10.
16. A resin containing a flame retardant-effective amount of the flame retardant composition of Claim 11.
17. The resin of Claim 12 which is a polyurethane foam.
18. The resin of Claim 13 which is a polyurethane foam.
19. The resin of Claim 14 which is a polyurethane foam.
20. The resin of Claim 15 which is a polyurethane foam.
21. The resin of Claim 16 which is a polyurethane foam.
22. A polyurethane foam-forming reaction mixture which comprises:
  - a) polyol;
  - b) phosphoramidate of Claim 1;
  - c) polyisocyanate; and, optionally,
  - d) at least one flame retardant other than a phosphoramidate of Claim 1,the total amount of (b) and (d) in the reaction mixture constituting a fire retardant effective amount in the foam obtained therefrom.

23. The reaction mixture of Claim 22 wherein polyol (a) is a polyether polyol or polyester polyol.
24. The reaction mixture of Claim 22 wherein polyol (a) is a polyether diol or polyester diol and polyisocyanate (c) is a diisocyanate.
25. The reaction mixture of Claim 22 wherein the flame retardant other than the phosphoramidate of Claim 1 is at least one member selected from the group consisting of organohalogen compound, organophosphorus compound and melamine compound.
26. The reaction mixture of Claim 22 wherein the phosphoramidate of Claim 1 is cyclic neopentyl N-propyl phosphoramidate and the flame retardant other than the phosphoramidate of Claim 1 is melamine.
27. The foam obtained from the polyurethane foam-forming reaction mixture of Claim 22.
28. The foam obtained from the polyurethane foam-forming reaction mixture of Claim 23.
29. The foam obtained from the polyurethane foam-forming reaction mixture of Claim 24.
30. The foam obtained from the polyurethane foam-forming reaction mixture of Claim 25.
31. The foam obtained from the polyurethane foam-forming reaction mixture of Claim 26.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2008/000174

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C07F9/6571 C08K5/527 C09K21/12

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)  
C07F C09K C08K

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, CHEM ABS Data, BEILSTEIN Data, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 26 20 643 A1 (CIBA GEIGY AG) 25 November 1976 (1976-11-25) compounds (2.4),(102) page 20, paragraph 3 claims 1-21  ----- -/--	1-31

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/000174

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International application No

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