

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 October 2002 (10.10.2002)

PCT

(10) International Publication Number
WO 02/079315 A1

(51) International Patent Classification⁷: **C08K 5/521**,
5/1539, C08L 75/04

(21) International Application Number: PCT/US01/51604

(22) International Filing Date:
13 November 2001 (13.11.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/247,541 13 November 2000 (13.11.2000) US

(71) Applicant (*for all designated States except US*): **AKZO NOBEL N.V.** [NL/NL]; Velperweg 76, NL-6800 SB Arnhem (NL).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **WILLIAMS, Barbara, A.** [US/US]; 790 Riverside Drive, New York, NY 10032 (US). **DE KLEINE, Lambertus, A.** [NL/NL]; Harzstraat 10, NL-7559 LM Hengelo (NL).

(74) Agent: **FENNELLY, Richard, P.**; Akzo Nobel Inc., Intellectual Property Dept., 7 Livinstone Avenue, Dobbs Ferry, NY 10522-3408 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BLEND OF ORGANOPHOSPHORUS FLAME RETARDANT, LACTONE STABILIZER, AND PHOSPHATE COMPATIBILIZER

(57) Abstract: A flame retardant blend, suitable for incorporation into a polyurethane foam, comprises: an oligomeric organophosphorus flame retardant, preferably an organophosphate, having a phosphorus content of no less than about 10%; a benzofuran-2-one stabilizer; and a monomeric phosphate ester containing alkyl and/or haloalkyl groups to act as a solubilizing additive for the oligomeric organophosphorus flame retardant and benzofuran-2-one stabilizer.



WO 02/079315 A1

BLEND OF ORGANOPHOSPHORUS FLAME RETARDANT, LACTONE
STABILIZER, AND PHOSPHATE COMPATIBILIZER

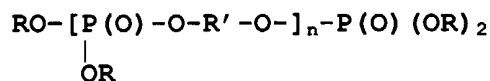
5 The present invention relates to the combination of three components in a flame retardant additive formulation that, when incorporated in a polyurethane foam, results in a considerable reduction in the discoloration (also referred to as "scorch") of that polyurethane foam as to compared to when only the two
10 organophosphorus components of the combination are employed. In addition, the present invention relates to the use of a solubilizing monomeric phosphate ester component with a combination of an organophosphorus flame retardant, which in certain embodiments can be an oligomeric phosphate ester, and a
15 benzofuran-2-one (or "lactone") stabilizer. The presence of this solubilizing component retards the normal solution instability that would be observed, over time, if just the organophosphorus flame retardant and benzofuran-2-one stabilizer were used together. Other advantages of the solubilizing component (for
20 example, PHOSFLEX® TBEP brand from Akzo Nobel Functional Chemicals) are that the viscosity is reduced when an oligomeric organophosphorus flame retardant is used and, unlike other flammable compatibilizers, the flame retardant performance is not influenced to an appreciable degree. The more solution-stable
25 composition of the present invention allows for a reduction of scorch, which normally occurs, for example, when a phosphate ester flame retardant is used, in low-density polyurethane flexible foams.

30 An essential component in the flame retardant blend of the present invention is an organophosphorus flame retardant which is present in a predominant amount compared to the other two components of the three part flame retardant blend of this invention. The amount of the organophosphorus additive in the blend will range from about 60% to about 98%, by weight of the
35 blend, more preferably from about 80% to about 96%.

The organophosphorus flame retardant can be a monomeric phosphate ester of the type conventionally used which has the formula $O=P(OR)_3$, where R is selected from alkyl and haloalkyl groups having from 1 to about 6 carbon atoms in such groups.

5 Representative examples of such flame retardants include tris(dichloroisopropyl)phosphate, tris(2-chloroisopropyl) phosphate, and tris(2-chloroethyl) phosphate.

Alternatively, the organophosphorus flame retardant component can be an oligomeric organophosphorus flame
 10 retardant, preferably having a phosphorus content of no less than about 5%, by weight and, in preferred embodiments when an organophosphate is desired, at least three phosphate ester units therein (i.e., at least two phosphate ester repeat units and a phosphate capping unit). The term "oligomeric" as used
 15 herein is meant to exclude either monomeric or dimeric species. A representative organophosphorus additive of this type is generally described in U.S. Patent No. 4,382,042 to T.A. Hardy with the non-halogenated versions being preferred (e.g., especially the ethyl group-containing composition). These
 20 preferred organophosphate oligomers can be formed by reacting phosphorus pentoxide with the selected trialkyl phosphate (e.g., triethyl phosphate) to form a polyphosphate ester containing P-O-P bonds that is then reacted with epoxide (e.g., ethylene oxide) to form the desired product. This preferred
 25 oligomeric organophosphate flame retardant is of the formula:

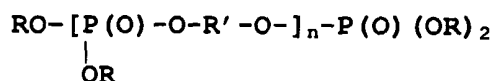


30 where n (which designates the "repeat" phosphate ester units) can range, on a number average basis, from 2 to about 20, preferably from 2 to about 10, and R is selected from the group consisting of alkyl and hydroxyalkyl and R' is alkylene. The
 35 alkyl and alkylene groups will generally contain from about two to about ten carbon atoms.

Especially preferred oligomeric phosphates for use herein will comprise ethyl and ethylene groups as the alkyl and alkylene moieties, will have a hydroxy functionality of no more than about 30 mg KOH/g, will have an acid number of no more than about 2.5 mg KOH/g, and will have a phosphorus content that ranges from about 15% to about 25%, by weight. It is referred to herein after as "PEEOP" (or "poly(ethyl ethyleneoxy)phosphate").

It is within the contemplation of the present invention to utilize oligomeric phosphonate-containing materials as component (b). Both substantially pure phosphonate and phosphonate/phosphate compositions are intended to be included. These have the same structure as depicted above for the oligomeric phosphate species with the exception that the internal (bracketed) RO- on the left side of the structure may be R- and one of the terminal -OR structures on the right side of the formula may be -R. A representative and commercially available example of an additive of this type is FYROL 51 from Akzo Nobel Chemicals Inc. which is made by a multistep process from dimethyl methylphosphonate, phosphorus pentoxide, ethylene glycol, and ethylene oxide.

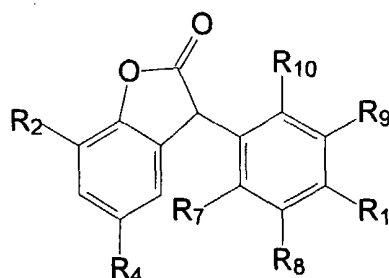
The product "FYROL® PNX" is a preferred product of this type for use herein. It is an oligomeric phosphate ester (CAS # 184538-58-7) of the formula:



where n (which designates the "repeat" phosphate ester units) is, on a number average basis, of from about 2 to about 20, R is ethyl, and R' is ethylene. This preferred has a phosphorus content of about 19 wt% and a viscosity at 25°C of about 2000 mPa.s.

The second essential component of the flame retardant blend of the present invention is of the type of benzofuran-2-one

stabilizer that is described in U.S. Patent No. 5,869,565, which is incorporated herein by reference for its illustration of such an additive. The structure of this class of stabilizer is provided in the following formulae:



5

wherein either two of R_1 , R_7 , R_8 , R_9 and R_{10} are each independently of the other C_1 - C_4 alkyl or C_1 - C_4 alkoxy, the others being hydrogen, or R_7 to R_{10} are hydrogen, or at most two of these radicals are each independently of the other methyl or methoxy, and R_1 is $-O-CHR_3-CHR_5-O-CO--R_6$, R_2 and R_4 are each independently of the other hydrogen or C_1 - C_6 alkyl, R_3 is hydrogen or C_1 - C_4 alkyl, R_5 is hydrogen, phenyl or C_1 - C_6 alkyl, and R_6 is C_1 - C_4 alkyl. The HP-136 brand product from Ciba Specialty Chemicals is a preferred species for use herein and is (5,7-di-t-butyl-3(3,4 dimethylphenyl)-3H-benzofuran-2-one, wherein R_2 and R_4 are each t-butyl and two of R_1 , R_7 , R_8 , R_9 and R_{10} are each methyl. This stabilizer component is present in the flame retardant blend of the present invention at from about 0.05% to about 1.0%, by weight of the blend, more preferably from about 0.2% to about 0.5%.

The third essential component of the blend is a monomeric phosphate ester of the formula $O=P-(OR)_3$, where R is independently selected from alkyl, alkoxyalkyl, or haloalkyl containing up to about 8 carbon atoms in the alkyl, alkoxyalkyl and/or haloalkyl groups. It is present at from about 1% to about 40%, by weight of the blend, more preferably from about 1% to about 20%. Preferred are substituents that are halogenated (e.g., chlorinated) or alkoxyalkyl with the carbon atom content

in the substituent being between one and four carbon atoms. Representative compounds of this type that can be selected include tributoxyethyl phosphate, tri(1,3 dichloroisopropyl) phosphate, tributyl phosphate, tri(2-chloroethyl)phosphate, 5 triethylphosphate, tri(2-chloroisopropyl)phosphate, isopropylated triarylphosphate, and a tert-butylated triphenyl phosphate mixture. While it is possible to select a monomeric phosphate compatibilizers from the same general type of organophosphorus compound that could be selected for the predominant component of 10 this invention (which will normally be a compound that does not form a compatible blend with the benzo-2-furanone stabilizer, the present invention contemplates that a differing compound from within that class will be selected so that there are three components in the flame retardant blend.

15 The previously described flame retardant blend can be incorporated in conventional polyurethane foams at use levels of up to about 24 parts by weight per one hundred parts of polyol (which will normally contain antioxidants for scorch inhibition) to confer the desired degree of flame retardancy and antiscorch 20 behavior on those foams.

The present invention is further described by the Examples that follow.

EXAMPLES

System 1, which is described below, uses FYROL® 38 as a solubilizer for the lactone additive HP-136 with FYROL® PNX.

- 5 System 2 uses a phosphate ester, PHOSFLEX® TBEP as a solubilizer for HP-136 with the FYROL® PNX material.

A microwave oven test method was used as a means to determine the degree of discoloration in the tested foams with a numerical scale of 1 to 5 being used to assign the degree of scorch present in the foam. A value of 1 was assigned to a white foam control showing no discoloration, whereas the value of 5 was assigned to a very dark brown scorch pattern. The values increased from 1 to 5 with increasing discoloration. Foams prepared with either system (flame retardant, solubilizer, and lactone additive) produced foams with a 1.5 to 2.0 rating, whereas without the use of the HP-136 lactone stabilizer the level of scorch was rated at 2.5 to 3.0. The nominal density was 1.20 pcf (pounds per cubic foot). This microwave test method is described in the Journal of Cellular Plastics (Dec.1979) in an article entitled " A Rapid Predictive Test for Urethane Foam Scorch" by Reale and Jacobs.

The following Examples illustrate the formulations used to produce flexible foams.

TABLE A - System 1

Polyether Polyol (3000 mw) from Arco	100.0	100.0
System 1*	9.0	
FYROL® PNX	(2.23)	5.00
FYROL® 38 (solubilizer)	(6.68)	----
Ciba's HP-136 Lactone	(0.09)	----
H ₂ O	5.0	5.0
Dabco 33LV/A-1 (3:1) ratio from OSi	0.22	0.22
Silicone surfactant L-620 from OSi	1.0	1.0
Stannous Octoate T-10 from Air Products	0.30	0.30
Toluene Diisocyanate TDI from Bayer	60.0	60.0
TDI Index	110	110

* the three components of System 1, which included FYROL PNX,
5 solubilizer and HP-136, were heated at 70°C for four hours

TABLE A-1

Polyether Polyol (3000 mw) from Arco	100.0	100.0
FYROL® PNX	4.95	5.00
Ciba's HP-136 Lactone	0.05	----
H ₂ O	5.0	5.0
Dabco 33LV/A-1 (3:1) ratio from OSi	0.22	0.22
Silicone surfactant L-620 from OSi	1.0	1.0
Stannous Octoate T-10 from Air Products	0.30	0.30
Toluene Diisocyanate TDI from Bayer	60.0	60.0
TDI Index	110	110

Fyrol® PNX mixed with only HP-136 was difficult to dissolve
10 and did not form a clear, stable solution; therefore, a
compatibilizer or solubilizer, in accordance with the present
invention, was necessary to maintain a stable solution.

The formulation components mentioned in Table A, above, were combined and poured into a (8.0" x 8.0" x 5.0") box and allowed to rise freely. The foam was then placed in a GE PROFILE SENSOR microwave oven and heated for one hundred and twenty
 5 seconds. The foam was removed from the oven. It was cooled to room temperature for two hours. The foam bun was cut into a 1 inch slice in a perpendicular to rise direction and was examined for its discoloration rating.

The performance of system 1 using the FYROL PNX
 10 oligomeric organophosphate, lactone stabilizer (HP-136, whose active ingredient is 5,7-di-t-butyl-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one) and the phosphate ester FYROL[®] 38 is tri[1,3 dichloroisopropyl] phosphate with an antioxidant package (as described in U.S. Patent No. 4,477,600) is provided in Table B:

15 TABLE B - System 1

SAMPLE	1	1A (Duplicate)	2 (Control)		3	4 (Control)
System 1	FYROL [®] PNX FYROL [®] 38 HP-136	FYROL [®] PNX FYROL [®] 38 HP-136	FYROL [®] PNX FYROL [®] 38 (No HP-136)		FYROL [®] PNX HP-136	FYROL [®] PNX (No HP-136)
Color Rating	2.0	1.5	3		2	3

In the runs reported for Table B the weight ratio of FYROL PNX to phosphate ester was 25:75 and the 9.0 parts refers to the parts per weight of this combination per 100 parts by weight of
 20 polyol used to make the foam. The weight percentage of antioxidant, when present, was 1.0%, based on the weight of the flame retardant and the solubilizer. In Run 3 in Table B where Fyrol[®] PNX was mixed only with the HP-136 lactone, it was difficult to dissolve and a clear, stable solution was not
 25 formed.

The following Example illustrates the formulation used to produce the present flexible foams.

A second set of foams was produced using system 2 but the scorch characteristics of the foams were measured using a
 5 colorimeter (namely, the DR LANGE Micro Color apparatus).

TABLE C - System 2

Polyether Polyol (3000 mw) from Shell	100.0
System 2 *	8.0
FYROL [®] PNX	7.60
FYROL [®] TBEP (solubilizer)	0.38
Ciba's HP-136 Lactone	0.02
H ₂ O	4.80
Dabco 33LV/A-1 3:1 from OSi	0.24
Silicone surfactant Dabco 5125 from OSi	1.0
Stannous Octoate T-10 from Air Products	0.36
Toluene Diisocyanate TDI from Bayer	58.9
TDI Index	110

The performance of system 2 using FYROL[®] PNX (the
 10 oligomeric organophosphate), the lactone stabilizer (HP-136),
 whose active ingredient is 5,7-di-t-butyl-3-(3,4-
 dimethylphenyl)-3H-benzofuran-2-one) and the phosphate ester
 solubilizer, PHOSFLEX[®] T-BEP (tributoxyethyl phosphate), is
 provided in Table D:

15

Table D-System 2

SAMPLE	1	2
System 2	FYROL [®] PNx PHOSFLEX [®] TBEP	FYROL [®] PNx PHOSFLEX [®] TBEP
Antioxidant	HP-136 at 0.25%	None
Colorimeter reading (b*)	*6.7	*23.7

b* = yellowness, with a lower number being indicative of a less colored foam.

5 In the runs reported for Table D the weight ratio of FYROL
PNx to phosphate ester was 95:5 and the 8.0 parts refers to the
parts per weight of this combination per 100 parts by weight of
polyol used to make the foam. The weight percentage of HP-136
brand antioxidant, when used in system 2, was 0.25 %, based on
10 the weight of the flame retardant and the solubilizer.

The foregoing Examples, since they are presented to merely
exemplify the present invention, should not be construed in a
limiting sense. The scope of protection that is desired is set
15 forth in the Claims that follow.

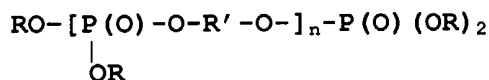
Claims:

1. A flame retardant composition which comprises: a predominant amount of an organophosphorus flame retardant; a
 5 benzofuran-2-one stabilizer; and a monomeric phosphate ester compatibilizer.

2. A composition as claimed in Claim 1 wherein the organophosphorus flame retardant is an oligomeric
 10 organophosphorus flame retardant which is a phosphate ester containing at least three phosphate ester units therein.

3. A composition as claimed in Claim 2 wherein the phosphate ester is of the formula

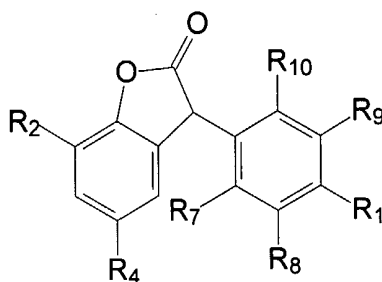
15



20

where n is, on a number average basis, of from about 2 to about 20, R is ethyl, and R' is ethylene.

4. A composition as claimed in Claim 1 wherein the
 25 benzofuran-2-one stabilizer has the formula



wherein either two of R₁, R₇, R₈, R₉ and R₁₀ are each independently of the other C₁-C₄ alkyl or C₁-C₄ alkoxy, the
 30 others being hydrogen, or R₇ to R₁₀ are hydrogen, or at most two of these radicals are each independently of the other methyl or

methoxy, and R_1 is $-O-CHR_3-CHR_5-O-CO--R_6$, R_2 and R_4 are each independently of the other hydrogen or C_1-C_6 alkyl, R_3 is hydrogen or C_1-C_4 alkyl, R_5 is hydrogen, phenyl or C_1-C_6 alkyl, and R_6 is C_1-C_4 alkyl.

5

5. A composition as claimed in Claim 4 wherein the benzofuran-2-one stabilizer is (5,7-di-t-butyl-3(3,4 dimethylphenyl)-3H-benzofuran-2-one.

10

6. A composition as claimed in Claim 1 wherein the monomeric phosphate ester compatibilizer is of the formula $O=P-(OR)_3$, where R is independently selected from alkyl, alkoxyalkyl, or haloalkyl containing up to about 8 carbon atoms in the alkyl, alkoxyalkyl and/or haloalkyl groups.

15

7. A composition as claimed in Claim 1 wherein the organophosphorus flame retardant is a monomeric phosphate ester having the formula $O=P(OR)_3$, where R is selected from alkyl and haloalkyl groups having from 1 to about 8 carbon atoms in such groups.

20

8. A flame retardant composition which comprises: from about 80% to about 98%, by weight of an organophosphorus flame retardant; from about 0.05% to about 1.0%, by weight of a benzofuran-2-one stabilizer; and from about 1% to about 40%, by weight of a monomeric phosphate ester compatibilizer.

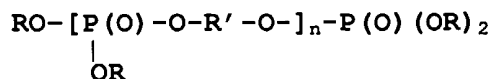
25

9. A composition as claimed in Claim 8 wherein the organophosphorus flame retardant is an oligomeric organophosphorus flame retardant which is a phosphate ester containing at least three phosphate ester units therein.

30

10. A composition as claimed in Claim 9 wherein the phosphate ester is of the formula

35

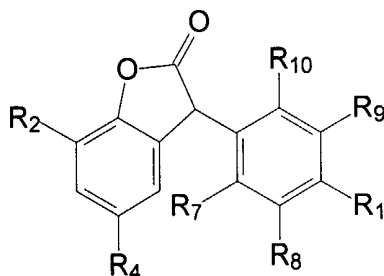


5

where n is, on a number average basis, of from about 2 to about 20, R is ethyl, and R' is ethylene.

10

11. A composition as claimed in Claim 8 wherein the benzofuran-2-one stabilizer has the formula



wherein either two of R₁, R₇, R₈, R₉ and R₁₀ are each independently of the other C₁-C₄ alkyl or C₁-C₄ alkoxy, the others being hydrogen, or R₇ to R₁₀ are hydrogen, or at most two of these radicals are each independently of the other methyl or methoxy, and R₁ is -O-CHR₃-CHR₅-O-CO--R₆, R₂ and R₄ are each independently of the other hydrogen or C₁-C₆ alkyl, R₃ is hydrogen or C₁-C₄ alkyl, R₅ is hydrogen, phenyl or C₁-C₆ alkyl, and R₆ is C₁-C₄ alkyl.

12. A composition as claimed in Claim 11 wherein the benzofuran-2-one stabilizer is (5,7-di-t-butyl-3(3,4 dimethylphenyl)-3H-benzofuran-2-one.

13. A composition as claimed in Claim 8 wherein the monomeric phosphate ester compatibilizer is of the formula

$\text{O}=\text{P}-(\text{OR})_3$, where R is independently selected from alkyl, alkoxyalkyl, or haloalkyl containing up to about 8 carbon atoms in the alkyl, alkoxyalkyl and/or haloalkyl groups.

- 5 14. A composition as claimed in Claim 8 wherein the organophosphous flame retardant is a monomeric phosphate ester having the formula $\text{O}=\text{P}(\text{OR})_3$, where R is selected from alkyl and haloalkyl groups having from 1 to about 8 carbon atoms in such groups.

10

15. A flame retarded polyurethane foam that comprises the composition of any of claims 1 to 14.

INTERNATIONAL SEARCH REPORT

 Int ☐ onal Application No
 PCT/US 01/51604

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/521 C08K5/1539 C08L75/04

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 C08K C08L

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 367 008 A (NESVADBA PETER) 22 November 1994 (1994-11-22) claims 1,12,14 examples 1,8 column 8, line 35 column 11, line 20-22 column 12, line 52 column 16, line 8,9 column 17, line 55-57 ---	1,4,6,7, 11,13,15
X	US 5 369 159 A (NESVADBA PETER) 29 November 1994 (1994-11-29) claims 1,9,11 ---	1,6,7, 13,15
Y	US 5 308 899 A (MICHAELIS PETER) 3 May 1994 (1994-05-03) claims 1,12 ---	1,2,4-7, 9,11-15
	--- -/--	



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
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

3 September 2002

Date of mailing of the international search report

12/09/2002

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Rose, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/51604

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 09, 13 October 2000 (2000-10-13) & JP 2000 154289 A (ASAHI CHEM IND CO LTD), 6 June 2000 (2000-06-06) abstract ---	1,2,4-7, 9,11-15
A	WO 99 03915 A (DOVER CHEMICAL CORP ;STEIN DARYL L (US); STEVENSON DONALD R (US)) 28 January 1999 (1999-01-28) claims 1,8,10 ---	1-15
A	EP 0 867 467 A (GEN ELECTRIC) 30 September 1998 (1998-09-30) claims 1,6,10 ---	1-15
A	WO 99 67223 A (CYTEC TECH CORP) 29 December 1999 (1999-12-29) claims 1,20 ---	1-15
A	US 5 844 026 A (SRINIVASAN RANGARAJAN ET AL) 1 December 1998 (1998-12-01) claims 1,32 -----	1-15

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 01/51604

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5367008	A	22-11-1994	BE 1006730 A4	29-11-1994
			CA 2096486 A1	23-11-1993
			CZ 9300919 A3	15-12-1993
			DE 4316876 A1	25-11-1993
			FR 2691470 A1	26-11-1993
			GB 2267088 A ,B	24-11-1993
			IT 1264453 B1	23-09-1996
			JP 6287185 A	11-10-1994
			NL 9300784 A	16-12-1993
			SK 49593 A3	11-05-1994
US 5369159	A	29-11-1994	BE 1007037 A3	28-02-1995
			CA 2096326 A1	23-11-1993
			CZ 9300917 A3	19-01-1994
			DE 4316611 A1	25-11-1993
			FR 2691468 A1	26-11-1993
			GB 2267491 A ,B	08-12-1993
			IT 1264452 B1	23-09-1996
			JP 3250055 B2	28-01-2002
			JP 6041109 A	15-02-1994
			NL 9300801 A	16-12-1993
			SK 49393 A3	06-04-1994
			US 5488117 A	30-01-1996
US 5308899	A	03-05-1994	BR 9204469 A	01-06-1993
			CA 2083111 A1	20-05-1993
			EP 0543778 A1	26-05-1993
			JP 3278730 B2	30-04-2002
			JP 6200143 A	19-07-1994
			KR 248536 B1	15-03-2000
			US 5422415 A	06-06-1995
JP 2000154289	A	06-06-2000	NONE	
WO 9903915	A	28-01-1999	AU 8399398 A	10-02-1999
			WO 9903915 A1	28-01-1999
			US 6224791 B1	01-05-2001
EP 0867467	A	30-09-1998	US 5922794 A	13-07-1999
			CN 1195671 A	14-10-1998
			EP 0867467 A1	30-09-1998
			JP 10338815 A	22-12-1998
			ZA 9802113 A	14-09-1998
WO 9967223	A	29-12-1999	AU 4425599 A	10-01-2000
			BR 9911448 A	20-03-2001
			EP 1087947 A2	04-04-2001
			JP 2002518485 T	25-06-2002
			TW 424104 B	01-03-2001
			WO 9967223 A2	29-12-1999
			US 6239275 B1	29-05-2001
US 5844026	A	01-12-1998	BR 9803109 A	14-03-2000
			CA 2241495 A1	30-12-1998
			CN 1211588 A	24-03-1999
			DE 69806696 D1	29-08-2002
			EP 0889085 A2	07-01-1999
			JP 11080569 A	26-03-1999