(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
10 May 2012 (10.05.2012)

PCT

(10) **International Publication Number**
WO 2012/060895 A1

(51) **International Patent Classification**:
C09J 7/02 (2006.01) ***C08K 5/5357*** (2006.01)
C08K 3/32 (2006.01)

(21) **International Application Number**:
PCT/US2011/028137

(22) **International Filing Date**:
11 March 2011 (11.03.2011)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/408,692 1 November 2010 (01.11.2010) US

(71) **Applicant** *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **BUETTNER, Joern** [DE/DE]; Carl-Schurz-Strasse 1, D-41453 Neuss (DE). **PYUN, Eumi** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **PLEPYS, Anthony R.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **LIM, Lisa S.** [SG/US]; 7908 S. Twelve Pines Drive, Sandy, Utah 84094 (US). **D'HAESE, Francois C.** [BE/BE]; Hermeslaan 7, B-1831 Deigem (BE). **PICK, Tobias** [DE/DE]; Carl-Schurz-Strasse 1, D-41453 Neuss (DE).

(74) **Agents**: **EHRICH, Dena M.** et al.; 3M Center, Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: PRESSURE SENSITIVE ADHESIVES CONTAINING A CYCLIC PHOSPHONATE ESTER FLAME RETARDANT

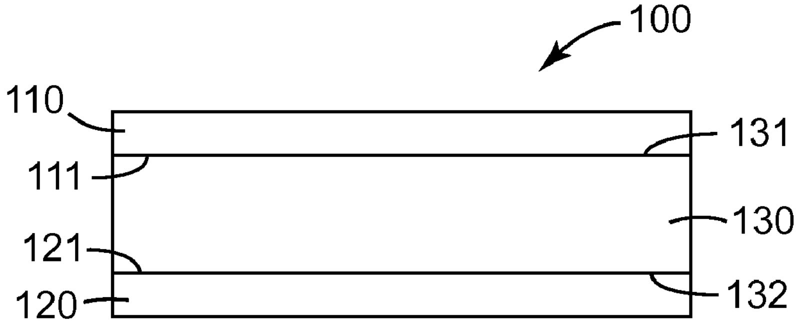


FIG. 1

(57) **Abstract**: Pressure sensitive adhesives containing a cyclic phosphonate ester are described. Methods of preparing such adhesives and articles comprising such adhesives are also described.

PRESSURE SENSITIVE ADHESIVES CONTAINING A CYCLIC PHOSPHONATE ESTER FLAME RETARDANT

FIELD

[0001] The present disclosure relates to flame retardant pressure sensitive adhesives. In particular, pressure sensitive adhesives containing a relatively low amount of a cyclic phosphonate ester flame retardant.

BACKGROUND

[0002] Generally, pressure sensitive adhesives are well-known and used in a wide variety of applications. Acrylic adhesives are a common class of pressure sensitive adhesive. However, acrylic adhesives may be flammable and can contribute to the formation of combustion gasses during a fire. As adhesive tapes are used widely in household, industrial, and electronic applications, there is a need to reduce or eliminate any contributions of adhesive tapes to the fire load.

[0003] Flame retardants have been added to adhesives including acrylic adhesives. For example, halogenated flame retardants such as polybrominated biphenylethers have been very effective. However, halogenated materials are being restricted or even banned due to environmental and health concerns associated with some such materials and there is a desire to find alternative flame retardants.

[0004] Other flame retardants such as metal hydroxides and red phosphorous have been used; however, typically these materials must be used at high concentrations in order to achieve the desired level of flame retardancy. In many cases, the required loadings of such flame retardants results in an unacceptable decrease in the mechanical and adhesive properties of the pressure sensitive adhesive.

[0005] Phosphites, phosphates, and phosphonates have also been used as flame retardants. For example, flame retardant radiation curable compositions containing both a cyclic phosphonate and at least one other flame retardant selected from phosphorous derivates different from cyclic phosphonates are described in EP 2 154 191 A1. EP 2 154 191 A1 exemplifies films that achieve UL 94 classification of V1 or V0, but only at relatively high loadings of the cyclic phosphonate flame retardant (at least 17 weight percent) in combination with relatively high loadings of anther phosphorous-derivative flame retardant (at least 15 weight %).

[0006] There remains a need to identify non-halogenated flame retardants for pressure sensitive adhesive compositions. In addition, there is a need to provide acceptable flame retardant properties at sufficiently low loading levels of the flame retardant so as to avoid unacceptable reductions in pressure sensitive adhesive performance.

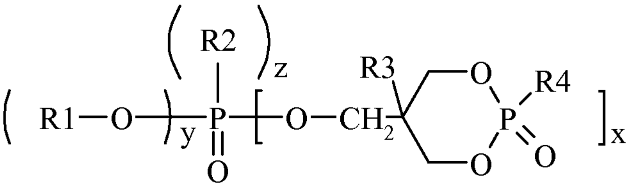
SUMMARY

[0007] Briefly, in one aspect, the present disclosure provides a flame retardant pressure sensitive adhesive comprising a polymeric component comprising an acrylic pressure sensitive adhesive and a flame retardant comprising at least one cyclic phosphonate ester, wherein the flame retardant comprises less than 2 parts by weight of a phosphorous containing flame retardant other than the cyclic phosphonate ester.

[0008] In some embodiments, the total amount of flame retardant is no greater than 20 parts by weight per 100 parts by weight of the polymeric component, e.g., between 3 and 15 parts by weight, inclusive, per 100 parts by weight of the polymeric component, or even between 3 and 6 parts by weight, inclusive, per 100 parts by weight of the polymeric component.

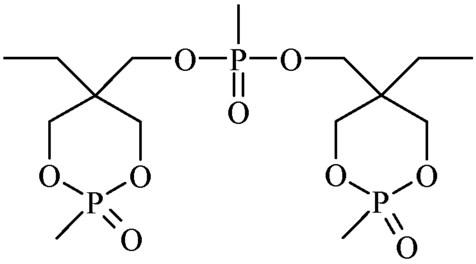
[0009] In another aspect, the present disclosure provides a flame retardant pressure sensitive adhesive comprising a polymeric component comprising an acrylic pressure sensitive adhesive and a flame retardant comprising at least one cyclic phosphonate ester, wherein the total amount of cyclic phosphonate ester is no greater than 6 parts by weight per 100 parts by weight of the polymeric component. In some embodiments, the total amount of cyclic phosphonate ester is no greater than 6 parts by weight per 100 parts by weight of the polymeric component, e.g., between 3 and 6 parts by weight, inclusive, per 100 parts by weight of the polymeric component.

[0010] In some embodiments of any of these aspects of the present disclosure, the flame retardant comprises at least one cyclic phosphonate ester having the formula:

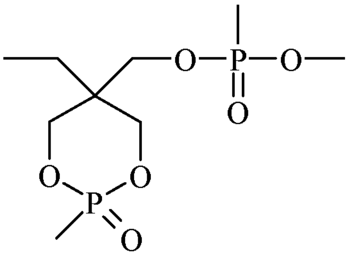


wherein R1 and R2 are independently selected from the group consisting of a C1 to C8 alkyl and a phenyl, wherein the alkyl and/or phenyl group may be substituted with at least one hydroxyl, hydroxyalkyl, or phenoxyalkyl, group; R3 and R4 are independently selected from the group consisting of C1 to C4 alkyl; x is 1, 2, or 3; y is 0, 1, or 2; and z is 0 or 1; wherein the sum of x, y, and z is equal to 3.

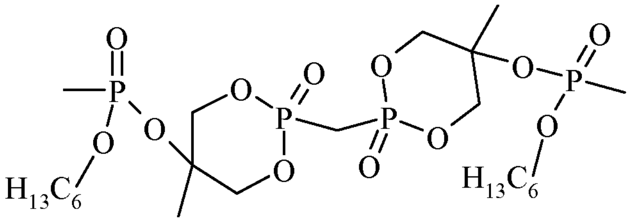
[0011] In some embodiments, the cyclic phosphonate ester comprises at least one of



,



, and



.

[0012] In another aspect, the present disclosure provides adhesive articles comprising a first substrate and a first adhesive adhered to a first major surface of the first substrate, wherein the first adhesive comprises the flame retardant pressure sensitive adhesives of the present disclosure. In some embodiments, the adhesive article further comprises a second adhesive wherein the first adhesive and the second adhesive are independently selected. In some embodiments, the adhesive article further comprising a second substrate adhered to the first adhesive such that the first adhesive is located between the first substrate and the second substrate. In some embodiments, at least one substrate comprises a polymeric film, e.g., polyester film. In some embodiments, at least one substrate comprises a foam, e.g., an adhesive foam.

[0013] The above summary of the present disclosure is not intended to describe each embodiment of the present invention. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **FIG. 1** illustrates an exemplary adhesive article according to some embodiments of the present invention, the article having a “Spacer” configuration.

[0015] **FIG. 2** illustrates an exemplary adhesive article according to some embodiments of the present invention, the article having a “Sandwich” configuration.

DETAILED DESCRIPTION

[0016] Acrylic pressure sensitive adhesives are well-known. Typically, acrylic pressure sensitive adhesive comprise the polymerization product of a monomer mixture comprising one or more (meth)acrylate ester and optionally, one or more vinyl carboxylic acids. Depending on the desired properties, other copolymerizable monomers may also be included in the monomer mixture.

[0017] As used herein, “(meth)acrylate” refers to one and/or both the acrylate ester and the methacrylate ester. Thus, for example, butyl (meth)acrylate refers to butyl acrylate and/or butyl methacrylate.

[0018] In some embodiments, at least one (meth)acrylate ester is an alkyl(meth)acrylate. In some embodiments, the alkyl group of at least one alkyl(meth)acrylate contains 5 to 18 carbon atoms, e.g., 5 to 12 carbon atoms. In some embodiments, the alkyl group of at least one alkyl(meth)acrylate contains 8 carbon atoms, e.g., isooctyl (meth)acrylate and 2-ethylhexyl (meth)acrylate. In some embodiments, the alkyl group of at least one alkyl(meth)acrylate contains 1 to 4 carbon atoms, e.g., butyl (meth)acrylate. In some embodiments, the alkyl group of at least one alkyl(meth)acrylate contains 1 to 3 carbon atoms, e.g., 2 carbon atoms.

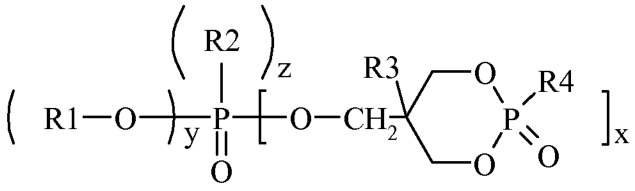
[0019] In some embodiments, the monomer mixture includes one or more vinyl carboxylic acids. Generally, any known vinyl carboxylic acid or mixture of vinyl carboxylic acids may be used. Exemplary vinyl carboxylic acids include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and β-carboxyethylacrylate. In some embodiments, the vinyl carboxylic acid may be selected from the group consisting of acrylic acid, methacrylic acid, and combinations thereof.

[0020] In some embodiments, it may be desirable to include one or more non-polar monomers. As used herein, a "non-polar" monomer is a monomer whose homopolymer has a solubility parameter as measured by the Fedors' method of no greater than 10.5. Examples of suitable non-polar monomers and their Fedors' solubility parameter ($(\mathrm{cal/cm}^3)^{1/2}$) include 3,3,5 trimethylcyclohexyl acrylate (9.35), isobornyl acrylate (9.71), butyl acrylate (9.77), cyclohexyl acrylate (10.16), and N-octyl acrylamide (10.33).

[0021] In some embodiments, the monomer mixture comprises at least 80 weight percent (wt.%) e.g., at least 90 wt.%, at least 95 wt.% or even at least 98 wt. % of the one or more alkyl (meth)acrylate monomers. In some embodiments, the monomer mixture comprises no greater than 10 wt. %, e.g., no greater than 8 wt.%, no greater than 5 wt. %, no greater than 2 wt.% or even no greater than 1 wt.% of the vinyl carboxylic acid monomers. In some embodiments, the monomer mixture comprises 0 to 4 wt.%, for example 0.1 to 4 wt.%, 0.1 to 2 wt.%, 0.1 to 1 wt.%, or even 0.1 to 0.5 wt.% of the vinyl carboxylic acid monomers. In other embodiments, the monomer mixture comprises at least 3 wt. %, e.g., at least 5 wt.% of the vinyl carboxylic acid monomers, e.g., 3 to 10 wt.%, or 5 to 10 wt.%, of the vinyl carboxylic acid monomers.

[0022] The pressure sensitive adhesives of the present disclosure also include at least one cyclic phosphonate flame retardant. Exemplary cyclic phosphonate esters suitable for use as flame retardants in the adhesive compositions of the present disclosure include those described in, e.g., U.S. Patent Numbers 3,789,091 and 3,849,368, as well as those available from Rhodia under the tradename AMGARD (e.g., AMGARD CU, and

AMGARD 1045). Suitable cyclic phosphonates include those having the general structure of Formula 1:



(1)

wherein R1 and R2 are independently selected from the group consisting of a C1 to C8 alkyl and a phenyl, wherein the alkyl and/or phenyl group may be substituted with at least one hydroxyl, hydroxyalkyl, or phenoxyalkyl, group;

R3 and R4 are independently selected from the group consisting of C1 to C4 alkyl;

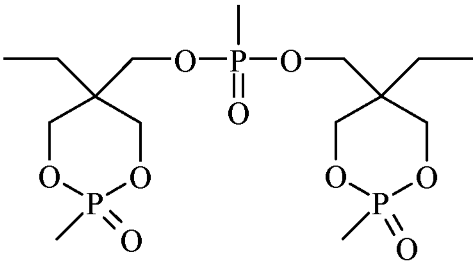
x is 1, 2, or 3;

y is 0, 1, or 2; and

z is 0 or 1;

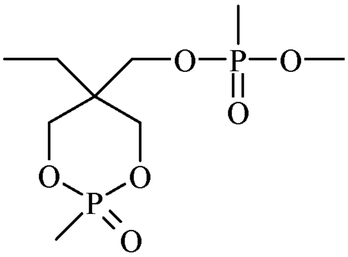
wherein the sum of x, y, and z is equal to 3.

[0023] Specific, exemplary cyclic phosphonates of Formula 1 include



(2)

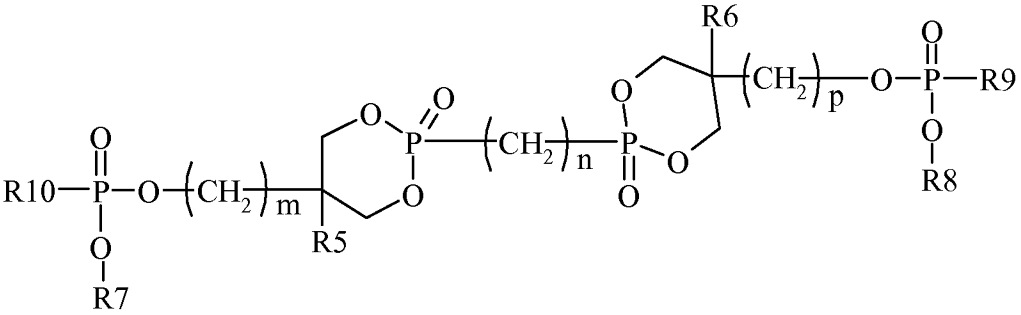
and



(3),

as well as dimmers and trimers of such materials, including those with longer aliphatic chains instead of methyl groups. Mixtures of such materials may also be used.

[0024] Other suitable cyclic phosphonate esters include those having the general Formula 4:



;

wherein R5 and R6 are independently selected from the group consisting of C1 to C4 alkyl groups;

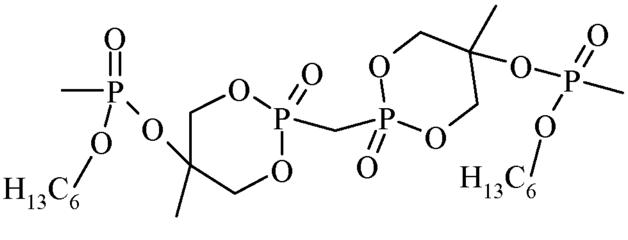
R7, R8, R9, and R10 are independently selected from the group consisting of a C1 to C8 alkyl and a phenyl, wherein the alkyl and/or phenyl group may be substituted with at least one hydroxyl, hydroxyalkyl, or phenoxyalkyl, group;

n is 0 to 6;

m is 0 to 8; and

p is 0 or 8.

[0025] Specific, exemplary cyclic phosphonates of Formula 4 include



(5),

as well as dimmers and trimers of such materials, including those with longer aliphatic chains instead of methyl groups. Mixtures of such materials, alone or in combinations with cyclic phosphonates of Formula 1 may also be used.

[0026] In addition to the acrylic adhesive and the flame retardant, the pressure sensitive adhesive compositions of the present disclosure may include any of a wide variety of know additives including, e.g., crosslinkers, initiators, fillers, tackifiers, dyes, pigments, and the like. The selection and relative amounts of such materials will depend on the desired end-use characteristics, as is well-understood by one of ordinary skill in the art.

[0027] Examples

Table 1: Materials used in the examples.

I.D.	Description	Source
SB-ADH-1	90:10 (IOA:AA)(a) acrylic adhesive (41 wt.% in a acetone, naptha, and hydrotreated naptha)	3M Company St. Paul, MN
SB-ADH-2	90:10 (IOA:AA) acrylic adhesive (15 wt.% in ethylacetate and toluene)	3M Company
UV-ADH-1	90:10 (IOA:AA) prepolymerized syrup	3M Company
UV-ADH-2	90:10 (IOA:AA) prepoylmerized syrup	3M Company
HM-ADH-1	90:10 (IOA:AA) acrylic adhesive	3M Company
HM-ADH-2	90:10 (2-EHA:AA) acrylic adhesive	3M Company
HM-ADH-3	90:10 (2-EHA:AA) acrylic adhesive with an ionic crosslinker	3M Company
CP-FR-1	Cyclic phosphonate flame retardant (AMGARD CU)(b)	Rhodia
CP-FR-2	Cyclic phosphonate flame retardant (AMGARD 1045)(b)	Rhodia
CP-FR-3	Cyclic phosphonate flame retardant (AMGARD SPDH)(c)	Rhodia
FR-4	Arylphosphate flame retardant (FYROL A710)	ICL
FR-5	Phosphororganic salt (EXOLIT OP935)	Clariant
FR-6	Aluminumtrihydrate ("ATH") (APYRAL 24)	Nabaltec
FR-7	Vinylphosphonatedimethylester (CAS 4685-32-3)	BASF
FR-8	3,4:5,6-Dibenzo-1,2-oxaphosphane-2-oxide	TCI Europe
HDDA	1,6-Hexanediol diacrylate crosslinker	
IR-651	2,2-Dimethoxy-1,2-diphenylethan-1-one (IRGACURE 651 photoinitiator)	Ciba Specialty Chemicals, Inc.

(a) IOA = isooctyl acrylate; 2-EHA = 2-ethylhexyl acrylate; AA = acrylic acid

(b) AMGARD CU and 1045 flame retardants are a blend of the cyclic phosphonates illustrated by Formulas (2) and (3).

(c) AMGARD SPDH is a cyclic phosphonate ester illustrated by Formula (4).

[0028] Test Methods

[0029] Horizontal Burn Procedure. Samples were evaluated according to the Federal Motor Vehicle Safety Standard No. 302 ("Flammability of Interior Materials"), (FMVSS302) test procedure. The results were rated as follows:

Rating	Description
DNI	Sample does not ignite
SE	Sample extinguishes before the start mark
SENBR	Sample extinguishes within 8.9 cm of the start mark
SEB	Sample extinguishes after 8.9 cm from the start mark, but before the end of the sample (burn rate (mm/min))
B	Sample burns to the end (burn rate (mm/min))

[0030] Vertical Burn Procedure. Samples were tested according Underwriters Laboratory Standard UL94. Generally, a 12.7 cm long by 1.27 cm wide sample was suspended vertically 10 mm above the burner and 30.5 cm above the cotton. A 20 mm high flame was applied to the free end of the sample at 45° angle for ten seconds and then removed until the flaming stops. The flame was reapplied for another ten seconds and again removed until the flaming stops. The results were rated as follows:

Rating	Description
V0	Burning stops within 10 seconds after each application of flame; drips of particles allowed as long as they do not ignite the cotton
V1	Burning stops within 30 seconds after each application of flame; drips of particles allowed as long as they do not ignite the cotton
V2	Burning stops within 30 seconds after each application of flame; drips of flaming particles that ignite the cotton are allowed

[0031] 180 Degree Peel tests were conducting according to FINAT Test Method No. 1 (FTM 1, "Peel adhesion (180 °) at 300 mm per minute," FINAT Technical Handbook 7th edition, 2005).

[0032] Static Shear tests were conducting according to FINAT Test Method No. 8 (FTM 8, "Resistance to shear from a standard surface," FINAT Technical Handbook 7th edition, 2005).

[0033] Dynamic Shear tests were conducting according to FINAT Test Method No. 18 (FTM 18, "Dynamic Shear," FINAT Technical Handbook 7th edition, 2005).

[0034] Solvent Based Adhesives. The desired solvent based adhesive (SB-ADH-1 or SB-ADH-2) was combined with 0.2 to 0.5 wt.% of a bisaziridine crosslinker and a flame retardant. The resulting composition was coated onto a release liner and sent through an oven. Here, the solvent was removed and the adhesive was thermally crosslinked to produce a 44 micrometer thick adhesive film.

[0035] Spacer. Two such adhesive films were laminated to opposite sides of a 12 micrometer thick polyester (PET) carrier film (MYLAR LBT2, from DuPont Teijin) to produce a “spacer” tape. Spacer tape **100** is illustrated in **FIG. 1**. First adhesive layer **110** comprises first surface **111** adhered to first surface **131** of carrier **130**. Similarly, first surface **121** of second adhesive layer **120** is adhered to second surface **132** of carrier **130**.

[0036] Sandwich. Samples were also prepared by laminating a 175 micrometer thick cover layer of PET to each of the first and second adhesive layers. As illustrated in **FIG. 2**, “sandwich” construction **200**, comprises spacer tape **100**. First cover layer **210** is adhered to second surface **112** of first adhesive layer **110**. Similarly, second cover layer **220** is adhered to second surface **122** of second adhesive layer **120**.

[0037] Neither the PET carrier film nor the PET cover films contained any flame retardant. Thus, all flame retardant characteristics are provided by flame retardant in the two adhesive layers.

[0038] These samples were subjected to the Horizontal Burn Procedure. The results are reported in Table 2. A commercially available sample (3M™ Double Linered Adhesive Transfer Tape 9553, from 3M Company) was also tested, and is identified as “REF-1.”

Table 2: Horizontal burn tests (FMVSS302) results for solvent based adhesives.

Example	Base Adhesive	Sample type	Flame Retardant	wt.% FR	Rating	Burn Speed (mm/min)
CE-1	SB-ADH-2	Spacer	none	0	B	268
EX-1	SB-ADH-2	Spacer	CP-FR-1	5	SE	N/A
EX-2	SB-ADH-2	Spacer	CP-FR-1	10	SE	N/A
EX-3	SB-ADH-2	Sandwich	CP-FR-1	10	SE	N/A
CE-2	SB-ADH-1	Spacer	none	0	B	265
EX-4	SB-ADH-1	Spacer	CP-FR-1	5	SE	N/A
EX-5	SB-ADH-1	Spacer	CP-FR-1	10	SE	N/A
EX-6	SB-ADH-1	Sandwich	CP-FR-1	10	SE	N/A
EX-7	SB-ADH-1	Spacer	CP-FR-2	5	SE	N/A
EX-8	SB-ADH-1	Spacer	CP-FR-2	10	SE	N/A
EX-9	SB-ADH-1	Spacer	CP-FR-3	5	SE	N/A
EX-10	SB-ADH-1	Spacer	CP-FR-3	10	SE	N/A

Example	Base Adhesive	Sample type	Flame Retardant	wt.% FR	Rating	Burn Speed (mm/min)
EX-11	SB-ADH-2	Sandwich	CP-FR-3	10	SE	N/A
EX-12	SB-ADH-1	Sandwich	CP-FR-3	10	SE	N/A
CE-3	SB-ADH-1	Spacer	FR-5	10	B	518
CE-4	SB-ADH-1	Spacer	FR-5	20	B	318
CE-5	SB-ADH-1	Spacer	FR-5	30	SE	N/A
CE-6	SB-ADH-1	Spacer	FR-4	5	B	202
CE-7	SB-ADH-1	Spacer	FR-4	10	SE	N/A
CE-8	SB-ADH2	Spacer	FR-8	5	B	365
CE-9	SB-ADH2	Spacer	FR-8	10	B	346
REF-1	acrylic	Spacer	none	0	B	492

[0039] The solvent based adhesive constructions were also evaluated to determine the effect of flame retardant loading on pressure sensitive adhesive properties. The samples were evaluated according to the 180 Degree Peel test ("180° Peel"), the Static Shear test at 20-22 °C, and the Dynamic Shear test at 85 °C. The results are summarized in Table 3.

Table 3: Pressure sensitive adhesive performance for solvent based adhesives.

Ex.	Base Adhesive	Sample type	Flame Retardant	wt.% FR	180° Peel (N/cm)	Static Shear (min.)	Dynamic Shear (min.)
CE-1	SB-ADH-2	Spacer	none	0	4.4	5000+	32.4
EX-1	SB-ADH-2	Spacer	CP-FR-1	5	N.T.	5000+	29.5
EX-2	SB-ADH-2	Spacer	CP-FR-1	10	5.1	5000+	18.4
CE-2	SB-ADH-1	Spacer	none	0	3.9	10000+	22.1
EX-4	SB-ADH-1	Spacer	CP-FR-1	5	N.T.	N.T	21.1
EX-5	SB-ADH-1	Spacer	CP-FR-1	10	5.1	10000+	13.7
EX-8	SB-ADH-1	Spacer	CP-FR-2	10	5.1	10000+	N.T.

N.T. = Not tested

[0040] Solventless UV-Cured Adhesive Samples. The desired solventless acrylic adhesive prepolymer (UV-ADH-1 or UV-ADH-2) was blended with 0.12 wt.% HDDA crosslinker, 0.2 wt.% IR-651 photoinitiator, and a flame retardant. The UV-ADH-1 adhesive was coated onto a release liner and passed through an ultraviolet curing station to form a 44 micrometer thick cured acrylic adhesive film. Two such films of UV-ADH-1 adhesive were laminated to opposite sides of the 12 micrometer PET carrier film to form a "spacer" construction. (See **FIG. 1**.) The UV-ADH-2 adhesive was coated onto a release liner and passed through an ultraviolet curing station to form a 1000 micrometer thick cured acrylic adhesive film, which was tested as is ("Thick" construction).

[0041] Samples prepared from the solventless, UV-cured, acrylic adhesives were tested for flammability according to the Horizontal Burn Procedure. The results are reported in Table 4. Samples were also tested for adhesive performance according to the 90 Degree Peel ("90° Peel") Procedure and the Static Shear Procedure at both 20-22 °C and 75 °C. The results are reported in Table 5.

Table 4: Horizontal burn tests (FMVSS302) results for solventless, UV-cured adhesives.

Example	Base Adhesive	Sample type	Flame Retardant	Wt.% FR	Rating	Burn Speed (mm/min)
EX-13	UV-ADH-1	Spacer	CP-FR-1	5	SE	N/A
EX-14	UV-ADH-1	Spacer	CP-FR-1	10	SE	N/A
CE-10	UV-ADH-2	Thick	none	0	B	75
EX-15	UV-ADH-2	Thick	CP-FR-1	5	SE	N/A
EX-16	UV-ADH-2	Thick	CP-FR-1	10	SE	N/A
EX-17	UV-ADH-2	Thick	CP-FR-1	20	SE	N/A
CE-11	UV-ADH-2	Thick	FR-7	10	B	102
CE-12	UV-ADH-2	Thick	FR-7	15	SE	N/A
REF-2	UV-ADH-2	Thick	none	0	SE	N/A

Table 5: Pressure sensitive adhesive performance for solventless, UV-cured adhesives.

						Static Shear	
Ex.	Base Adhesive	Sample type	Flame Retardant	wt.% FR	90° Peel (N/cm)	20-22 °C (min.)	75 °C (min.)
CE-10	UV-ADH-2	Thick	none	0	28.0	10000+	10000+
EX-15	UV-ADH-2	Thick	CP-FR-1	5	23.2	1835	109
EX-16	UV-ADH-2	Thick	CP-FR-1	10	22.2	388	33
EX-17	UV-ADH-2	Thick	CP-FR-1	20	18.5	53	7
CE-11	UV-ADH-2	VHB	FR-7	10	20.0	612	57
CE-12	UV-ADH-2	VHB	FR-7	15	24.4	7563	60
REF-2	UV-ADH-2	VHB	none	0	24.4	7563	318

[0042] Various amounts of the CP-FR-1 cyclic phosphonate flame retardant were combined with the UV-ADH-2 solventless, UV-cured adhesive. Thick (1000 microns) samples were prepared and tested according to the Vertical Burn Procedure. The results are summarized in Table 6.

Table 6: Vertical burn tests (UL94) results for VHB samples prepared using the UV-ADH-2 solventless, UV-cured adhesives with the CP-FR-1 cyclic phosphonate flame retardant.

Ex.	wt.% FR	Dripping UL94-V	UL94 (VTM)	UL94 (V)
EX-18	10	FDIC	VTM-0	Fail
EX-19	15	DNF	VTM-0	V-0
EX-20	20	DNF	VTM-0	V-0
EX-21	30	DNF	N/T	V-1

[0043] Hot Melt Coated Adhesives. Adhesive films were prepared by hot melt coating a blend of the desired adhesive (HM-ADH-1, HM-ADH-2, or HM-ADH-3) and a flame retardant to produce a 44 micrometer thick layer of acrylic adhesive. These adhesive films were combined with the 12 micrometer PET carrier to form a spacer construction. (See **FIG. 1**.) Additional 175 micrometer PET cover films were added to provide sandwich constructions. (See **FIG. 2**.)

[0044] The resulting hot melt adhesive samples were evaluated according to the Horizontal Burn Procedure, and the results are reported in Table 7. Reference sample REF-1, was also tested. Adhesive properties were also tested at both 20-22 °C and 85 °C. The results of the 180 Degree Peel test, the Static Shear test, and the Dynamic Shear test are summarized in Table 8.

Table 7: Horizontal burn tests (FMVSS302) results for hot melt adhesives.

Ex.	Base Adhesive	Sample type	Flame Retardant	wt.% FR	Rating	Burn Speed (mm/min)
EX-22	HM-ADH-1	Spacer	CP-FR-1	10	DNI	N/A
EX-23	HM-ADH-1	Sandwich	CP-FR-1	10	SE	N/A
EX-24	HM-ADH-2	Spacer	CP-FR-1	10	DNI	N/A
EX-25	HM-ADH-2	Sandwich	CP-FR-1	10	SE	N/A
EX-26	HM-ADH-3	Spacer	CP-FR-1	10	DNI	N/A
EX-27	HM-ADH-3	Sandwich	CP-FR-1	10	SE	N/A
EX-28	HM-ADH-3	Spacer	CP-FR-1	7.5	DNI	N/A
EX-29	HM-ADH-3	Sandwich	CP-FR-1	7.5	SE	N/A
EX-30	HM-ADH-3	Spacer	CP-FR-1	5	SE	N/A
EX-31	HM-ADH-3	Sandwich	CP-FR-1	5	SE	N/A
REF-1	acrylic	Spacer	none	0	B	492

Table 8: Pressure sensitive adhesive performance for hot melt adhesives.
(all samples contained 10 wt.% CP-FR-1 flame retardant)

			180 Degree Peel (N/cm)		Static Shear (min)		Dynamic Shear (min)	
Ex.	Adhesive	Sample	RT	HT	RT	HT	RT	HT
EX-22	HM-ADH-1	Spacer	5.8	3.7	10000+	53	374	30
EX-24	HM-ADH-2	Spacer	5.9	3.8	10000+	106	365	38
REF-1	acrylic	Spacer	4.8	3.0	10000+	1218	307	67

RT = 20-22 °C; HT = 85 °C.

[0045] The flame retardant pressure sensitive adhesives of the present disclosure may be used in a wide variety of applications, e.g., as free films, supported films, and single and double-sided tapes. Free films of adhesive may be disposed on a substrate such as a release liner, or may be located between two release liners. Supported films include adhesive layers incorporating any of a wide variety of well known supports such as scrims, woven and non-woven webs comprising organic and/or inorganic fibers, paper, and the like.

[0046] Tapes typical comprise a substrate with a layer of adhesive on one side (i.e., a single-coated tape) or on opposite sides (i.e., a double coated tape). Any of a wide variety of known substrates, including, e.g., those comprising papers, films (e.g., polymeric films), and foils, may be used. In some embodiments, the substrate may comprise a foam, e.g., an adhesive foam. Generally, the adhesive on the opposite sides a double-sided tape are independently selected. In some embodiments, both adhesives may comprise a flame retardant adhesive according to the present disclosure. In some embodiments, only one of the adhesive may comprise a flame retardant adhesive according to the present disclosure. In such embodiments, the second adhesive may be any known adhesive including known flame retardant, and non-flame retardant adhesives.

[0047] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

What is Claimed is:

1. A flame retardant pressure sensitive adhesive comprising a polymeric component comprising an acrylic pressure sensitive adhesive and a flame retardant comprising at least one cyclic phosphonate ester, wherein the flame retardant comprises less than 2 parts by weight of a phosphorous containing flame retardant other than the cyclic phosphonate ester.

2. The flame retardant pressure sensitive adhesive of claim 1, wherein the total amount of flame retardant is no greater than 20 parts by weight per 100 parts by weight of the polymeric component.

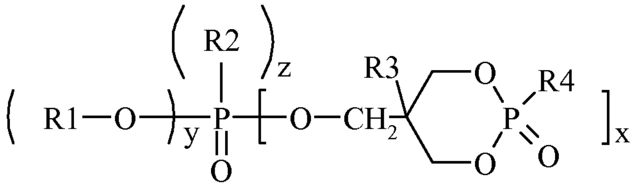
3. The flame retardant pressure sensitive adhesive of claim 2, wherein the total amount of flame retardant is between 3 and 15 parts by weight, inclusive, per 100 parts by weight of the polymeric component.

4. The flame retardant pressure sensitive adhesive of claim 3, wherein the total amount of flame retardant is between 3 and 6 parts by weight, inclusive, per 100 parts by weight of the polymeric component.

5. A flame retardant pressure sensitive adhesive comprising a polymeric component comprising an acrylic pressure sensitive adhesive and a flame retardant comprising at least one cyclic phosphonate ester, wherein the total amount of cyclic phosphonate ester is no greater than 6 parts by weight per 100 parts by weight of the polymeric component.

6. The flame retardant pressure sensitive adhesive of claim 5, wherein the total amount of cyclic phosphonate ester is between 3 and 6 parts by weight, inclusive, per 100 parts by weight of the polymeric component.

7. The flame retardant pressure sensitive adhesive according to any one of the preceding claims, wherein the flame retardant comprises at least one first cyclic phosphonate ester having the formula:


;

wherein R1 and R2 are independently selected from the group consisting of a C1 to C8 alkyl and a phenyl, wherein the alkyl and/or phenyl group may be substituted with at least one hydroxyl, hydroxyalkyl, or phenoxyalkyl, group;

R3 and R4 are independently selected from the group consisting of C1 to C4 alkyl;

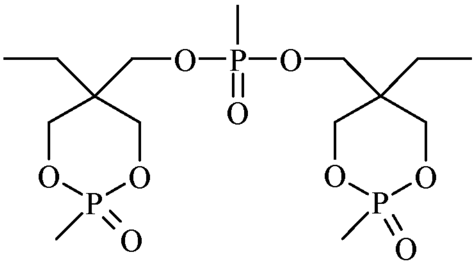
x is 1, 2, or 3;

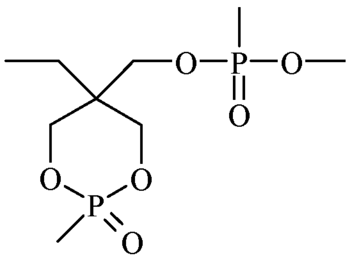
y is 0, 1, or 2; and

z is 0 or 1;

wherein the sum of x, y, and z is equal to 3.

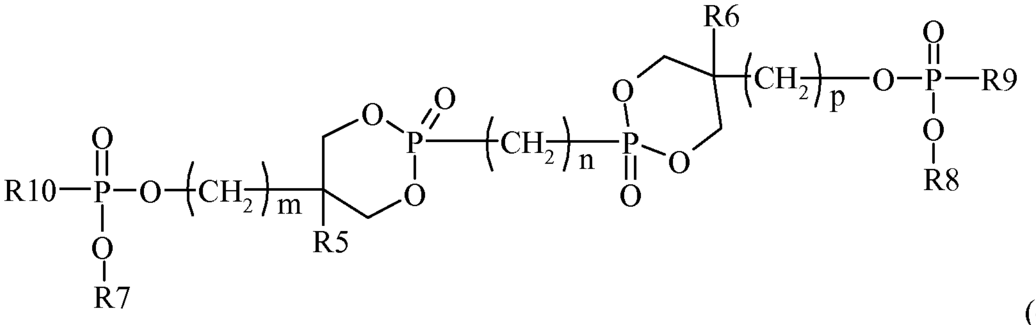
8. The flame retardant pressure sensitive adhesive according to claim 7, wherein the first cyclic phosphonate ester is selected from the group consisting of:


,


,

and combinations thereof.

9. The flame retardant pressure sensitive adhesive according to any one of the preceding claims, wherein the flame retardant comprises at least one second cyclic phosphonate ester having the formula:



(4),

wherein R5 and R6 are independently selected from the group consisting of C1 to C4 alkyl groups;

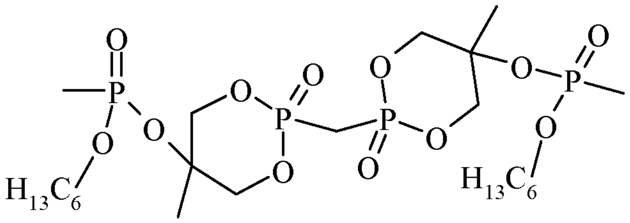
R7, R8, R9, and R10 are independently selected from the group consisting of a C1 to C8 alkyl and a phenyl, wherein the alkyl and/or phenyl group may be substituted with at least one hydroxyl, hydroxyalkyl, or phenoxyalkyl, group;

n is 0 to 6;

m is 0 to 8; and

p is 0 or 8.

10. The flame retardant pressure sensitive adhesive according to claim 9, wherein the second cyclic phosphonate ester is:



.

11. An adhesive article comprising a first substrate and a first adhesive adhered to a first major surface of the first substrate, wherein the first adhesive comprises the flame retardant pressure sensitive adhesive according to any one of claims 1 to 10.

12. The adhesive article of claim 11, further comprising a second adhesive adhered to a second major surface of the first substrate opposite the first major surface of the first

substrate, wherein the second adhesive comprises the flame retardant pressure sensitive adhesive according to any one of claims 1 to 10, and wherein the first adhesive and the second adhesive are independently selected.

13. The adhesive article of claim 11 or 12, further comprising a second substrate adhered to the first adhesive such that the first adhesive is located between the first substrate and the second substrate.

14. The adhesive article according to any one of claims 10 to 13, wherein the first substrate comprises a foam.

15. The adhesive article of claim 14, wherein the foam comprises an adhesive.

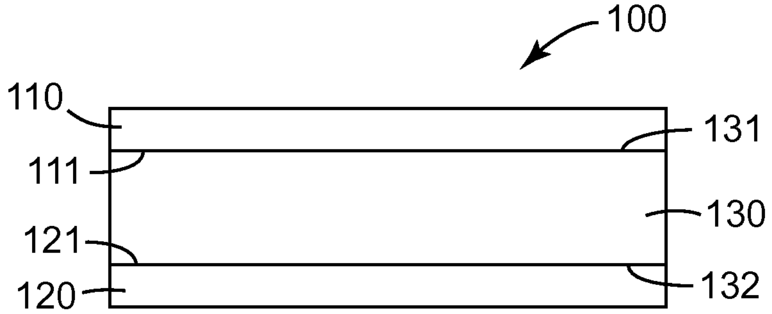

100
110
111
121
120
131
130
132

FIG. 1

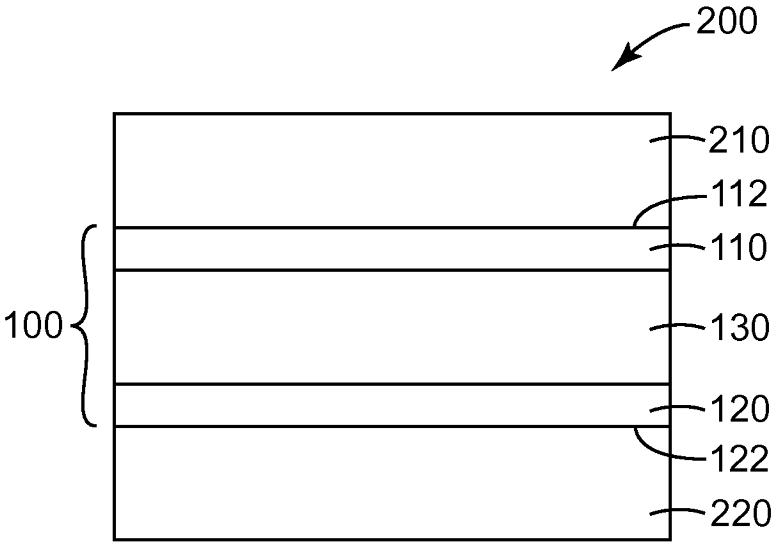

200
210
112
110
100
130
120
122
220

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/028137

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J7/02
ADD. C08K3/32 C08K5/5357

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)
C09J 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, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/50480 A1 (MINNESOTA MINING & MFG [US]; WAID ROBERT D [US]) 12 November 1998 (1998-11-12) page 3, line 15 - line 16 page 3, line 23 - line 26 page 4, line 1 - line 5 page 25, line 14 - page 26, line 3 page 36; example 7 and 8; table 3 page 36, line 15 - page 39, line 13; examples 11-16 claims 1,9,32,36 ----- -/--	1-15

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

☒ See patent family 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
25 November 2011

Date of mailing of the international search report
02/12/2011

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer
Siemsen, Beatrice

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/028137

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/077673 A1 (ALBEMARLE CORP [US]; CHEW HOOVER B [US]; LAYMAN WILLIAM J [US]; MACK A) 8 July 2010 (2010-07-08) page 1, line 30 - page 2, line 3 page 7, line 31 - page 8, line 5 page 13, line 27 - page 14, line 17 page 14, line 32 - page 15, line 23 claim 1 -----	1-15
X	EP 2 154 191 A1 (CYTEC SURFACE SPECIALTIES SA [BE]) 17 February 2010 (2010-02-17) cited in the application paragraph [0025] paragraph [0032] examples 1-12R; table 1 claims 1-3,7-9 -----	1-15
A	EDWARD D WEIL: "Flame Retardants, Phosphorus", KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, PAGE(S) 484 - 510 , 18 October 2001 (2001-10-18), XP002499618, Retrieved from the Internet: URL:http://mrw.interscience.wiley.com/emrw/9780471238966/kirk/article/phosweil.a01/c [retrieved on 2008-10-14] page 492, line 18 - line 26 -----	1-15
A	HOANG D ET AL: "Synthesis and performance of cyclic phosphorus-containing flame retardants", POLYMER DEGRADATION AND STABILITY, BARKING, GB, vol. 93, no. 11, 1 November 2008 (2008-11-01), pages 2042-2047, XP025589380, ISSN: 0141-3910, DOI: 10.1016/J.POLYMDEGRADSTAB.2008.02.017 [retrieved on 2008-07-23] page 2042, column 1, paragraph 1 page 2044; figure 1 page 2044, column 1, paragraph 2 -----	1-13
A	WO 2009/052335 A1 (3M INNOVATIVE PROPERTIES CO [US]) 23 April 2009 (2009-04-23) claims 1, 7, 8, 10, 22, 23 -----	1-13

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/028137

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9850480 A1	12-11-1998	AU 3058497 A	27-11-1998
		EP 0980409 A1	23-02-2000
		JP 2001523295 A	20-11-2001
		WO 9850480 A1	12-11-1998
WO 2010077673 A1	08-07-2010	CA 2744722 A1	08-07-2010
		CN 102239207 A	09-11-2011
		EP 2367873 A1	28-09-2011
		KR 20110094006 A	19-08-2011
		TW 201026763 A	16-07-2010
		US 2011237144 A1	29-09-2011
		WO 2010077673 A1	08-07-2010
EP 2154191 A1	17-02-2010	CA 2728101 A1	11-02-2010
		CN 102099411 A	15-06-2011
		EP 2154191 A1	17-02-2010
		EP 2313460 A1	27-04-2011
		US 2011129680 A1	02-06-2011
		WO 2010015603 A1	11-02-2010
WO 2009052335 A1	23-04-2009	CA 2702891 A1	23-04-2009
		CN 101827909 A	08-09-2010
		EP 2207861 A1	21-07-2010
		JP 2011500924 A	06-01-2011
		KR 20100072081 A	29-06-2010
		TW 200936721 A	01-09-2009
		US 2009104444 A1	23-04-2009
		WO 2009052335 A1	23-04-2009