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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 September 2012 (20.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/125915 A1

(51) International Patent Classification:
C09K 11/07 (2006.01) *F21K 2/06* (2006.01)

(21) International Application Number:
PCT/US2012/029412

(22) International Filing Date:
16 March 2012 (16.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/453,956 17 March 2011 (17.03.2011) US

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(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, QA, RO, RS, RU, RW, 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, RW, 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).

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

(54) **Title**: DEGRADABLE CHEMILUMINESCENT DEVICE

(57) **Abstract**: The instant disclosure provides chemiluminescent light producing devices comprising a biodegradable polyhydroxyalkanoate composition, said biodegradable polyhydroxyalkanoate composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial each containing one of at least one oxalate component and at least one peroxide component of said chemical light system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said polyhydroxyalkanoate outer containment device.

WO 2012/125915 A1

DEGRADABLE CHEMILUMINESCENT DEVICE

[001] The present application claims priority to U.S. Provisional Patent Application No. 61/453,956, filed March 17, 2011, which is incorporated herein by reference.

[002] This disclosure relates to chemiluminescent processes and products; particularly to a chemiluminescent article of manufacture and chemical system which are biodegradable subsequent to their use; and most particularly to a product capable of losing its physical form and re-entering the environment.

[003] Chemiluminescense relates to the production of visible light attributable to a chemical reaction. The important aqueous chemiluminescence substances luminal and lucigenin were discovered in 1928 and 1935, respectively. A series of organic soluble chemiluminescent materials were developed in the early 1960's based on a study of the luminescent reactions of a number of organic compounds. A typical organic system useful for chemiluminescence was disclosed by Bollyky et al., U.S. Pat. No. 3,597,362 and claimed to exhibit a quantum efficiency of about 23% compared with about 3% for the best known aqueous systems.

[004] In its most basic form a two-component, liquid phase oxalate ester chemical light system comprises an "oxalate component" comprising an oxalic acid ester and a solvent, and a "peroxide component" comprising hydrogen peroxide and a solvent or mixture of solvents. In addition, an efficient fluorescer can also be contained in one of these components. An efficient catalyst, which can maximize intensity and lifetime control, may also be contained in one of the components.

[005] The lifetime and intensity of the chemiluminescent light emitted can be regulated by the addition of a catalyst which changes the rate of reaction of hydroperoxide. Catalysts which accomplish that objective include those described in M. L. Bender, "Chem. Revs.," Vol. 60, p.53 (1960). Also, catalysts which alter the rate of reaction or the rate of chemiluminescence include, but are not limited to those accelerators of U.S. Pat. No. 3,775,366, and decelerators of U.S. Pat. Nos. 3,691,085 and 3,704,231.

[006] The lifetime and intensity of the chemiluminescent light emitted can also be regulated by the variation of hydroperoxide; wherein both the type and concentration of hydroperoxide are critical for the purposes of regulation.

[007] Certain chemical light device of the prior art comprise a polyethylene or polypropylene container with the two liquids inside, separated until light is needed, for example, by packaging one of the liquids in a sealed glass vial and floating the vial in the second liquid. Light is generated when the end user flexes the plastic outer container, fracturing the glass vial or alternatively by destroying the integrity of a separating member, e.g. a diaphragm or membrane, in any suitable manner thereby allowing the two liquids to mix.

[008] Certain of these polyolefin-containing chemical light devices are practically non-biodegradable due to the plastic utilized in their construction. Polyolefins can exist for hundreds of years in the normal environment without losing a significant portion of their physical properties. This fact has created problems and concerns in all chemical light devices markets, but especially in the military and commercial fishing markets. Additionally, the liquids inside these devices may not be designed for general release into the environment. Certain commercially practiced solvent systems can be considered marine pollutants in many parts of the world.

[009] Worldwide, over fifty million devices per year are consumed between the military and commercial fishing markets. This volume of consumption and the manner of the consumption can create a waste and waste disposal problem. The permanence of the plastic container making up the chemical light devices can contribute to this waste and waste disposal problem.

[010] Military use of chemical light devices includes providing basic light (illumination), safety marking, covert marking, and as training aids. The uses often involve wide dispersion of multiple chemical light devices over large surface areas of land (many acres). After use, evidence of the military's activities are left behind (the chemical light devices) and can persist for decades or longer. Depending on where the military exercise occurs, this may not be allowed (example: USA or Europe). Military personnel are required in these areas to attempt to collect all consumed chemical light devices.

[011] Commercial fishermen utilizing long lines to catch swordfish and some species of tuna use chemical light devices as lures or attractants. The long lines are

significant in length (often miles long) and deploy thousands of hooks pendent from the long line. A chemical light device is typically attached over each hook. Therefore, thousands of chemical light devices are deployed with each long line. This style of fishing typically occurs at night, with the line deployed in late afternoon or early evening and retrieved the next morning. The commercial fishermen are encouraged to disconnect the chemical light devices and to return them to shore for proper disposal. Unfortunately, many of the chemical light devices may not be returned to shore for disposal. This can create a significant problem on beaches in many parts of the world, with the possibility that numerous of plastic chemical light devices washing up onto a beach with the tides and currents.

[012] It is therefore desireable to provide a chemiluminescent product and chemical system which was inherently biodegradable in its environment of use, such that said device, inclusive of the chemiluminescent components, could re-enter the environment within a reasonable interval after its usefulness was at an end.

[013] As outlined above, chemical light is produced by mixing an oxalate ester and hydrogen peroxide together in the presence of a catalyst and a fluorescer. In certain embodiments, the oxalate ester and fluorescer are dissolved in one solvent, and the hydrogen peroxide and catalyst are dissolved in another.

[014] Chemiluminescent articles and methods for their production and use have now been developed which yield chemical light devices that do not create a waste or waste disposal problem. These new devices can be exemplified in two major forms with certain variations:

1. Devices that disintegrate but do not biodegrade; and
2. Devices that disintegrate and substantially biodegrade.

[015] Unlike "normal" plastics, which degrade very slowly, degradable plastics are manufactured so as to exhibit an accelerated rate of decomposition. This acceleration can be accomplished by either adding an additional component which degrades easily, or by reducing the inherent non-degradable characteristics of the particular plastic material. Plastics that disintegrate into small parts have been developed and marketed for years and are called biodegradable. Starch/polyolefin yard waste bags are an example of this technology. These bags disintegrate (lose coherent form) when they become wet (the starch dissolves in water and frees the bound polyolefin that gave the bag its physical strength and other characteristics).

This technology eliminates the disposal problem of the bag (which could present a hazard to small children and/or animals) by allowing the bag to lose its form. However, a significant part of the bag (the polyolefin) does not actually re-enter the food-chain. Therefore, by the above definition, these bags are not truly biodegradable. Photodegradable (UV degradable) polymers are another example of plastic materials that disintegrate into smaller parts but may not completely re-enter the food chain. Examples of this technology are polymers formed by inserting into the polymer chain irregularities that are subject to degradation by UV light. Illustrative of these irregularities are carbonyl groups (ketone carbonyl copolymers or carbon monoxide copolymers) or metal salts. Significant questions remain regarding the extent of degradation of most photodegradable plastics, i.e. do these degrade into non-plastic products or do they simply disintegrate into smaller pieces of plastic.

[016] True biodegradable plastics do exist. These materials are consumed by microorganisms such as bacteria, fungi, or algae. The microorganisms break down the polymer chain and consume the material through several methods. The polymers can be either hydrolysable or water soluble.

[017] Chemical light devices have now been produced which, dependent upon the materials of construction, either disintegrate (like the yard waste bag example above) or truly disintegrate and biodegrade.

[018] In certain embodiments of the instant disclosure, a device is provided which has the ability to both disintegrate and completely biodegrade. Such a device can include a biodegradable chemical light system comprising:

(a) a liquid carrier capable of solubilizing the oxalate ester and the fluorescer;

(b) a liquid carrier capable of solubilizing the hydrogen peroxide and catalyst; and

(c) a plastic that is formable, flexible and biodegradable,

wherein both liquids are biodegradable, and

wherein said plastic is compatible with both the liquids and the chemical light active ingredients.

[019] Accordingly, it is an objective of the instant disclosure to provide an article of manufacture, in the form of a chemiluminescent light producing device, which substantially or completely biodegrades.

[020] It is another objective of the instant disclosure to provide a container for retaining a chemiluminescent chemical light system which substantially or completely biodegrades.

[021] It is a further objective of the instant disclosure to provide a container for retaining a chemiluminescent chemical light system which disintegrates but does not biodegrade.

[022] It is yet another objective of the instant disclosure to provide a container for retaining a chemiluminescent chemical light system which disintegrates and substantially biodegrades.

[023] It is a still further objective of the instant disclosure to provide a methodology for selecting/formulating the constituents of a chemiluminescent chemical light system which is biodegradable, and any chemiluminescent chemical light system produced thereby.

[024] For example, one aspect of the present disclosure is directed to a chemiluminescent light producing device is provided comprising a biodegradable composition, said biodegradable composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial each containing one of at least one oxalate component and at least one peroxide component of said chemical light system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said outer containment device. In some embodiments, the biodegradable composition comprises a polyhydroxyalkanoate composition.

[025] Another embodiment of the present disclosure provides a chemiluminescent light producing device comprising a composition that disintegrates so as to lose its physical form, said composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial each containing one of at least one oxalate component and at least one peroxide component of said chemical light system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said outer containment device. In certain embodiments, the composition comprises a polyhydroxyalkanoate composition.

[026] A further embodiment of the instant disclosure provides a chemiluminescent light producing device comprising a composition that is photodegradable so as to lose its physical form, said composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial each containing one of at least one oxalate component and at least one peroxide component of said chemical system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said outer containment device, In some said composition comprises ultraviolet-sensitive components, whereby said ultraviolet-sensitive components photodegrade when subjected to ultraviolet light. In certain embodiments, the composition comprises a polyhydroxyalkanoate composition.

[027] Additional objects and advantages of the disclosure will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the disclosure. The objects and advantages of the present disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[028] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DESCRIPTION OF THE EMBODIMENTS

[029] The present disclosure includes chemiluminescent light producing devices, e.g. light sticks, wherein their materials of construction enable them to be characterized as being particularly susceptible to environmental degradation, and which may be categorized as follows:

CONTAINER PROPERTIES	CHEMICAL SYSTEM PROPERTIES
Disintegrates/does not Biodegrade	Standard Chemical System/ Biodegradable Chemical System
Disintegrates/Partially Biodegrades	Standard Chemical System/ Biodegradable Chemical System

Disintegrates and Biodegrades	Standard Chemical System/ Biodegradable Chemical System

[030] With reference to materials useful as containment devices in the present disclosure, the following definitions are relied upon:

[031] "Disintegrates" is defined as a material which self disintegrates so as to lose its physical form;

[032] "Biodegradable" is defined as a material whose component parts reenter the food chain within a reasonable period of time;

[033] "Reentering the food chain" means that the component can be utilized as a raw material (food) by either plants or bacteria.

[034] Examples of biodegradable plastics useful with the present disclosure include polyesters, polyhydroxybutyrates, and vinyl polymers. Examples of biodegradable polymers include those listed in Table 1.

TABLE 1

Plastic Type	**Name**	**Abbreviation**	**Description**
Polyesters	Polyglycolic Acid	PGA	Hydrolyzable polyhydroxy acid
	Polyhydroxyalkanoate	PHA	Semi-crystalline, linear polyesters produced in nature by bacterial fermentation of sugar or lipids
	Polyactic Acid	PLA	Hydrolyzable polyhydroxy acid;polymers derived from fermenting crops and dairy products; compostable
	Polycaprolactone	PCL	Hydrolyzable; low softening and melting points; compostable; long time to degrade
Polyhydroxy	Polyhydroxybutyrate	PHB	Hydrolyzable; produced as

Plastic Type	Name	Abbreviation	Description
butyrates			storage material by microorganisms; possibly degrades in aerobic and anaerobic conditions; stiff; brittle; poor solvent resistance
	Polyhydroxyvalerate	PHBV	Hydrolyzable copolymer; processed similar to PHB; contains a substance to increase degradability, melting point, and toughness
Vinyl	Polyvinyl Alcohol	PVOH	Water soluble; dissolves during composting
	Polyvinyl Acetate	PVAC	Water soluble; predecessor to PVOH
	Polyetherketone	PEK	Water soluble; derived from PVOH; possibly degrades in aerobic and anaerobic conditions

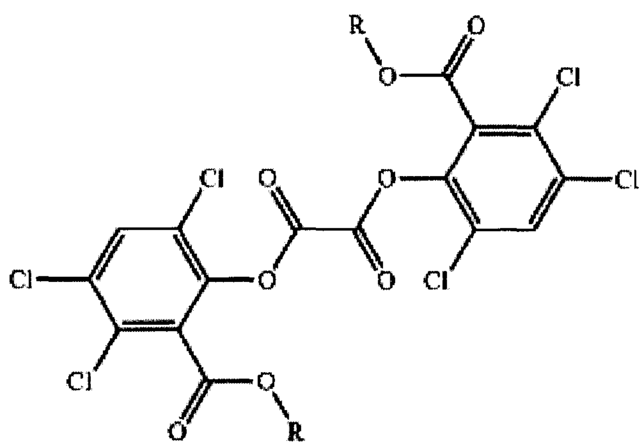
[035] As indicated above, suitable biodegradable polymers include polyhydroxyalkanoates (PHA). These PHA polymers are thermoplastic and typically can be processed on conventional processing equipment. These PHA polymers can exhibits properties similar to polyolefins such as polyethylene and polypropylene, but have the benefit of being fully compostable at the end of use due in part to the fact that they are bio-based. Other desirable properties for suitable PHA polymers include at least one of the following: high heat resistance; good gas, oil, and moisture barrier properties; high tensile strength and durability; good heat sealing

properties; good printability; compostability; degradability in marine environments; and good shelf-stability.

[036] The oxalate component of the instant disclosure can provide an oxalate ester-solvent combination which permits suitable ester solubility and storage stability. The peroxide component can provide a hydrogen peroxide-solvent combination that permits suitable hydrogen peroxide solubility and storage stability.

[037] The solvents of the two components may be different but must be miscible. At least one solvent solubilizes the efficient fluorescer and at least one of the solvents solubilizes the efficient catalyst.

[038] Suitable oxalate esters that may be used with the instant disclosure can be chosen from bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate; bis(2,4,5-trichlorophenyl)oxalate; bis(2,4,5-tribromo-6-carbohexoxyphenyl)oxalate; bis(2,4,5-trichloro-6-carboisopentoxyphenyl) oxalate; bis(2,4,5-trichloro-6-carbobenzoxyphenyl) oxalate; bis(2-nitrophenyl)oxalate; bis(2,4-dinitrophenyl)oxalate; bis(2,6-dichloro-4-nitrophenyl) oxalate; bis(2,4,6-trichlorophenyl)oxalate; bis(3-trifluoromethyl-4-nitrophenyl)oxalate; bis(2-methyl-4,6-dinitrophenyl)oxalate; bis(1,2-dimethyl-4,6-dinitrophenyl)oxalate; bis(2,4-dichlorophenyl)oxalate; bis(2,4-dinitrophenyl)oxalate; bis(2,5-dinitrophenyl)oxalate; bis(2-formyl-4-nitrophenyl)oxalate; bis(pentachlorophenyl)oxalate; bis(1,2-dihydro-2-oxo-1-pyridyl)glyoxal; bis(2,4-dinitro-6-methylphenyl)oxalate; bis-N-phthalimidyl oxalate, oxalates represented by the general formula (I)



(I)

wherein R = CH_2A and A is chosen from alkyl chains, alkyl rings, and aromatic rings or combinations thereof, such that R is nonlinear and such that R comprises from 4-15 carbons, and mixtures of any of the foregoing oxalates.

[039] Examples of oxalates represented by formula (I) include:
bis{3,4,6-trichloro-2-[(2-methylpropoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(cyclopropylmethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2-methylbutoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(3-methylbutoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2,2-dimethylpropoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2-methylpentyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(3-methylpentyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-tri chloro-2-[(4-methylpentyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(3,3-dimethylbutoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2-ethylbutoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(cyclopentylmethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2-methylhexyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(3-methylhexyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(4-methylhexyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(5-methylhexyloxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(cyclohexylmethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(phenylmethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2-phenylethoxy)carbonyl]phenyl} oxalate;
bis(3,4,6-trichloro-2-{[(2-methylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(3-methylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(4-methylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(2,3-dimethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(2,4-dimethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[3,4-dimethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(3,5-dimethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(2,6-dimethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(2-ethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(3-ethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[(4-ethylphenyl)methoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[2-(2-methylphenyl)ethoxy]carbonyl}phenyl) oxalate;
bis(3,4,6-trichloro-2-{[2-(3-methylphenyl)ethoxy]carbonyl}phenyl) oxalate;

bis(3,4,6-trichloro-2-{[2-(4-methylphenyl)ethoxy]carbonyl}phenyl) oxalate;
bis{3,4,6-trichloro-2-[(2-phenylpropoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(3-phenylpropoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[1-naphthalenylmethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[2-naphthalenylmethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(2,2-diphenylethoxy)carbonyl]phenyl} oxalate;
bis{3,4,6-trichloro-2-[(9-fluorenylmethoxy)carbonyl]phenyl} oxalate; and
bis{3,4,6-trichloro-2-[(9-anthracenylmethoxy)carbonyl]phenyl} oxalate.

[040] Additional examples of oxalates represented by general formula (1) are disclosed in U.S. Published Application No. 2011-0084243, the disclosure of such oxalates being incorporated herein by reference.

[041] The term "peroxide component," as used herein, means a solution of a hydrogen peroxide compound, a hydroperoxide compound, or a peroxide compound in a suitable diluent.

[042] The term "hydrogen peroxide compound" includes (1) hydrogen peroxide and (2) hydrogen peroxide producing compounds.

[043] Hydrogen peroxide is used as the hydroperoxide in certain embodiments, and may be employed as a solution of hydrogen peroxide in a solvent or as an anhydrous hydrogen peroxide compound such as sodium perborate, sodium peroxide, and the like. Whenever hydrogen peroxide is contemplated to be employed, any suitable compound may be substituted which will produce hydrogen peroxide. The hydrogen peroxide concentration in the peroxide component may range from about 0.2M to about 15M, such as from about 1M to about 2M.

[044] In addition to hydrogen peroxide as peroxide component, other suitable peroxide components include sodium peroxide, sodium perborate, sodium pyrophosphate peroxide, urea peroxide, histidine peroxide, t-butyl hydroperoxide, peroxybenzoic acid, sodium percarbonate, and mixtures thereof.

[045] In certain embodiments, the ratio of the amount of oxalate composition to peroxide component can range from 1:6 to 6:1. For example, suitable weight ratios of the amount of oxalate composition to peroxide component range from 1:6, from 1:4, from 1:2, from 1:1, from 2:1, from 3:1, from 4:1, from 5:1, and from 6:1. In further embodiments, the ratio of the amount of oxalate to peroxide component can range from 1:6 to 6:1. For example, suitable weight ratios of the amount of oxalate

to peroxide component range from 1:6, from 1:4, from 1:2, from 1:1, from 2:1, from 3:1, from 4:1, from 5:1, and from 6:1. In other embodiments, the ratio of the amount of oxalate composition to peroxide component can range from 1:6 to 6:1. For example, suitable weight ratios of the amount of oxalate composition to peroxide component range from 1:6, from 1:4, from 1:2, from 1:1, from 2:1, from 3:1, from 4:1, from 5:1, and from 6:1.

[046] In certain embodiments, the amount of oxalate composition can range of from 3 percent to 60 percent by weight, based on the total weight of the chemiluminescent composition. For example, the at least one oxalate can be present in an amount ranging from 3 percent to 50 percent by weight, based on the total weight of the chemiluminescent composition, such as from 3 percent to 40 percent by weight, from 3 percent to 30 percent by weight, from 5 percent to 25 percent by weight, and from 7 percent to 25 percent by weight. It is also intended that the amount of the at least one oxalate can range between any of the numerical values listed above.

[047] In certain embodiments, the at least one peroxide component is present in the liquid phase in an amount ranging from 0.25 percent to 25 percent by weight, based on the total weight of the chemiluminescent composition disclosed herein. For example, the at least one peroxide component can be present in an amount ranging from 0.25 percent to 20 percent by weight, based on the total weight of the chemiluminescent composition, such as from 0.5 percent to 20 percent by weight, from 0.5 percent to 15 percent by weight, from 0.5 percent to 10 percent by weight, and from 0.5 percent to 6 percent by weight. It is also intended that the amount of at least one peroxide component can range between any of the numerical values listed above.

[048] In certain embodiments, the chemiluminescent composition of the present disclosure can further comprise at least one fluorescer. Typical suitable fluorescent compounds for use in the present disclosure include those which have spectral emission falling between about 300 and 1200 nanometers and which are at least partially soluble in the diluent employed. Representative example include, for example, conjugated polycyclic aromatic compounds having at least 3 fused rings, such as: anthracene, substituted anthracene, benzanthracene, substituted benzanthracene, phenanthrene, substituted phenanthrene, naphthacene, substituted

naphthacene, naphthalene, substituted naphthalene, pentacene, substituted pentacene, perylene, substituted perylene, violanthrone, substituted violanthrone, and the like. Typical substituents for all of these are phenyl, alkyl (C_1-C_{16}), chloro, bromo, cyano, alkoxy (C_1-C_{16}), and other like substituents which do not interfere with the light generating reaction contemplated herein.

[049] Examples of the at least one fluorescer useful in the present disclosure include 1-methoxy-9,10-bis(phenylethynyl) anthracene; perylene; 16,17-didecycloxyviolanthrone; 2-ethyl-9,10-bis(phenylethynyl)anthracene; 2-chloro-9,10-bis(4-ethoxyphenyl)anthracene; 2-chloro-9,10-bis(4methoxyphenyl)anthracene; 9,10-bis(phenylethynyl) anthracene; 1-chloro-9,10-bis(phenylethynyl)anthracene; 1,8-dichloro-9,10-bis(phenylethynyl)anthracene; 1,5-dichloro-9,10-bis(phenylethynyl)anthracene; 2,3-dichloro-9,10-bis(phenylethynyl)anthracene; 5,12-bis(phenylethynyl)tetracene; 9,10-diphenylanthracene; 1,6,7,12-tetraphenoxy-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetraphenoxy-N,N'-bis(2,5-di-t-butylphenyl)-3,4,9,10-perylene dicarboximide; 1,7-di-chloro-6,12-diphenoxy-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetra(p-bromophenoxy)-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetraphenoxy-N,N'-di-neopentyl-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetra(p-t-butylphenoxy)N,N'-dineopentyl-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetra(o-chlorophenoxy)-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetra(p-chlorophenoxy)-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetra(o-fluorophenoxy)-N,N'-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetra(p-fluorophenoxy)-N,N'bis(2,6-diisopropylphenyl)-3,4,9,10-perylene dicarboximide; 1,6,7,12-tetraphenoxy-N,N'-diethyl-3,4,9,10-perylene dicarboximide; 1,7-dibromo-6,12-diphenoxy-N,N'-bis(2-isopropylphenyl)-3,4,9,10-perylene dicarboximide; 16,17-dihexyloxyviolanthrone; rubrene; 1,4-dimethyl-9,10-bis(phenylethynyl)anthracene; and mixtures thereof.

[050] In certain embodiments, the at least one fluorescer is present in an amount ranging from 0.05 percent to 0.9 percent by weight based on the total weight of the chemiluminescent composition. For example, the at least one fluorescer can be present in an amount ranging from greater than 0.05 percent by weight to 0.9 percent by weight, based on the total weight of the chemiluminescent composition,

such as from 0.1 percent or greater by weight, from 0.2 percent or greater by weight, from 0.3 percent or greater by weight, from 0.4 percent or greater by weight, from 0.5 percent or greater by weight, from 0.6 percent or greater by weight, from 0.7 percent or greater by weight, and from 0.8 percent or greater by weight. In addition, the at least one fluorescer can be present in an amount ranging from 0.05 percent by weight to less than 0.9 percent by weight, based on the total weight of the chemiluminescent composition, such as from 0.8 percent or less by weight, from 0.7 percent or less by weight, from 0.6 percent or less by weight, from 0.5 percent or less by weight, from 0.4 percent or less by weight, from 0.3 percent or less by weight, from 0.2 percent or less by weight, and from 0.1 percent or less by weight. It is also intended that amount of the at least one fluorescer can range between any of the numerical values listed above.

[051] In additional embodiments, the chemiluminescent composition of the present disclosure can further comprise at least one catalyst. Examples of the at least one catalyst useful in the present disclosure include sodium salicylate, various tetraalkylammonium salicylates, lithium carboxylic acid salts, such as lithium salicylate, lithium 2-chlorobenzoate, 5-chlorolithium salicylate, and lithium 5-t-butyl salicylate, triazoles, and imidazoles. For example, the at least one catalyst can be present in an amount ranging from greater than 0.0005 percent by weight to 10 percent by weight, based on the total weight of the chemiluminescent composition, such as from 0.001 percent or greater by weight, from 0.005 percent or greater by weight, from 0.01 percent or greater by weight, from 0.05 percent or greater by weight, from 0.1 percent or greater by weight, from 0.25 percent or greater by weight, from 0.5 percent or greater by weight, from 1 percent or greater by weight, from 1.5 percent or greater by weight, from 2 percent or greater by weight, from 2.5 percent or greater by weight, from 3 percent or greater by weight, from 3.5 percent or greater by weight, from 4 percent or greater by weight, from 4.5 percent or greater by weight, from 5 percent or greater by weight, and from 7.5 percent or greater by weight. In addition, the at least one catalyst can be present in an amount ranging from 0.0005 percent by weight to less than 10 percent by weight, based on the total weight of the chemiluminescent composition, such as from 7.5 percent or less by weight, from 5 percent or less by weight, from 4.5 percent or less by weight, from 4 percent or less by weight, from 3.5 percent or less by weight, from 3 percent or less

by weight, from 2.5 percent or less by weight, from 2 percent or less by weight, from 1.5 percent or less by weight, from 1 percent or less by weight, from 0.5 percent or less by weight, from 0.25 percent or less by weight, from 0.1 percent or less by weight, from 0.05 percent or less by weight, from 0.01 percent or less by weight, from 0.005 percent or less by weight, and from 0.001 percent or less by weight. It is also intended that the amount of at least one catalyst can range between any of the numerical values listed above.

[052] In certain embodiments, the chemiluminescent composition according to the present disclosure can also comprise at least one carrier, i.e, solvent. Examples of the at least one carrier useful in the present disclosure include dimethyl phthalate, dibutyl phthalate, dioctal phthalate, butyl benzoate, acetyl triethyl citrate, triethyl citrate, ethylene glycol dibenzoate, glycerol tribenzoate, and propylene glycol dialkyl ether containing one to three propylene moieties and each alkyl group is independently a straight-chain or branched-chain alkyl group containing up to 8 carbon atoms. In certain embodiments, the carrier is chosen from dimethyl phthalate, triethyl citrate, ethylene glycol dibenzoate, glycerol tribenzoate, propylene glycol dialkyl ethers containing two propylene moieties such as dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether and dipropylene glycol di-t-butyl ether, dibutyl phthalate, butyl benzoate, propylene glycol dibenzoate, ethyl-hexyl diphenyl phosphate, and mixtures thereof.

[053] In certain embodiments, the at least one carrier is present in an amount ranging from 5 percent to 95 percent by weight, based on the total weight of the chemiluminescent composition. For example, the at least one carrier can be present in an amount ranging from greater than 5 percent by weight to 95 percent by weight, based on the total weight of the chemiluminescent composition, such as from greater than 10 percent by weight, from greater than 20 percent by weight, from greater than 30 percent by weight, from greater than 40 percent by weight, from greater than 50 percent by weight, from greater than 60 percent by weight, from greater than 70 percent by weight, from greater than 80 percent by weight, and from greater than 90 percent by weight. In addition, the at least one carrier can be present in an amount ranging from 5 percent by weight to less than 95 percent by weight, based on the total weight of the chemiluminescent composition, such as from less than 90 percent by weight, from less than 80 percent by weight, from less than 70 percent by weight,

from less than 60 percent by weight, from less than 50 percent by weight, from less than 40 percent by weight, from less than 30 percent by weight, from less than 20 percent by weight, and from less than 10 percent by weight. It is also intended that the amount of at least one carrier can range between any of the numerical values listed above.

[054] These systems are more properly illustrated by the following examples.

EXAMPLE 1 - Device that Disintegrates but does not Biodegrade

[055] Extrude into a tubular form a starch/polyolefin combination. Heat seal one end and fill with a typical chemical light oxalate solution (91.6% deputy phthalate, 8.4% CPPO, 0.19% BPEA). Float within the oxalate solution a sealed glass vial containing a typical chemical light activator solution (85% dimethyl phthalate, 10% t-butanol, 5% of 70% concentration hydrogen peroxide, 0.0085% sodium salicylate). Heat seal the remaining end. Flex to break the glass vial and light will result. Drop the device into water and it will soften and then dissolve. However, the polyolefin will remain and be unaffected over a long period of time (decades). Additionally, although not environmentally hazardous in small quantities, e.g. that found in a lightstick, the solvents, if released in large quantities may present environmental and toxicological problems as known marine pollutants (dibutyl phthalate) and possible endocrine disruptors (dimethyl phthalate). Neither has a particularly high bioavailability.

EXAMPLE 2 - Device that Disintegrates and Partially Biodegrades

[056] Extrude into a tubular form a polyvinyl alcohol/polyvinyl acetate combination. Heat seal one end and fill with a typical chemical light oxalate solution (91.6% dibutyl phthalate, 8.4% CPPO, 0.19% BPEA). Float within the oxalate solution a sealed glass vial containing a typical chemical light activator solution (85% dimethyl phthalate, 10% t-butanol, 5% of 70% concentration hydrogen peroxide, 0.0085% sodium salicylate). Heat seal the remaining end. Flex to break the glass vial and light will result. Drop the device into water and it will soften and then dissolve. With the addition of normal soil bacteria, the polyvinyl alcohol/polyvinyl acetate combination will be consumed (this PVA combination has the same bioavailability as cellulose in the normal environment). Although not environmentally hazardous in small quantities, e.g. that found in a lightstick, the solvents, if released in large quantities may present environmental and toxicological problems as known

marine pollutants (dibutyl phthalate) and possible endocrine disruptors (dimethyl phthalate). Neither has a particularly high bioavailability.

EXAMPLE 3 - Device that Disintegrates and Partially Biodegrades

[057] Extrude into thin sheet form a ketone carbonyl copolymer (vinyl ketone comonomer inserted into polyethylene). Thermoform it into a shallow cup with a lip. Drop into the cup a non-woven polyester felt pad or sheet and two sealed glass vials, one containing a typical oxalate component (91.6% dibutyl phthalate, 8.4% CPPO, 0.19% BPEA) and the other containing a typical activator component (85% dimethyl phthalate, 10% t-butanol, 5% of 70% concentration hydrogen peroxide, 0.0085% sodium salicylate). Heat seal a flat sheet of the ketone carbonyl copolymer onto the cup lip, forming a sealed container with the felt sheet and vials. Flex the entire unit, breaking the glass vials and allowing the liquids to mix and soak into the felt, creating light. Leave the light device outside where is can and will be exposed to sunlight (and in particular, UV light). The plastic container will degrade and disintegrate. It may reenter the food chain in a reasonable length of time. The felt sheet and the solvents released will not degrade quickly and present possible environmental and toxicological problems.

EXAMPLE 4 - Device that Disintegrates and Biodegrades

[058] Injection mold a tube and cap combination from a polyvinyl alcohol/polyvinyl acetate combination. Contain within (prior to sealing the tube and cap together) an oxalate component made with 8.4% CPPO, 0.19% BPEA, and 91. 41% of a 50/50 mixture of propylene glycol dibenzoate and acetyltributyl citrate. Float within this oxalate component a sealed glass vial containing 85% triethyl citrate, 10% t-butanol, 5% of 70% concentration hydrogen peroxide, and 0.0085% sodium salicylate. Seal the cap and tube together and flex to break the glass vial and allow mixing of the liquids. Light will result. The expired device may be buried in the ground (typical landfill disposal) or alternatively disposed of at sea, or the like. Naturally occurring bacteria will consume the polymer and the solvent combinations in a reasonable period of time (both the polymer and solvents have a bioavalability similar to cellulose).

[059] Biodegradable chemiluminescent chemical light systems are selected in accordance with the following criteria:

[060] Oxalate Solvent Selection Rules:

[061] 1. Select a general set of parameters or limiters that you wish or need to meet, i.e. a particular biodegradable characteristic such as comprising a biodegradable solvent with a bioavailability close to that of cellulose.

[062] 2. Select a class of solvents that meets the parameters set forth in Number 1.

[063] 3. Find members of this class of solvents that contain a carboxy-phenyl group. Solvents containing at least one carboxy-phenyl group within their structure can and will solvate the active chemical light ingredients (CPPO and fluorescers). Group the members in order of water miscibility so as to optimize the degree of CPPO solubility.

[064] 4. If the class of solvents does not contain any members with a carboxy-phenyl group but is still the best candidate to satisfy the parameters set forth in Number 1, then choose a second class of solvents that comes close to meeting the requirements of Number 1, is miscible in the class of solvents chosen in Number 3, has at least one member with a carboxy-phenyl group, and rank via water miscibility.

[065] 5. Make mixtures of the solvents chosen in Steps 3 and 4 with varying concentrations of each solvent. Blend into them different levels of CPPO and the individual fluorescers. CPPO solubility DECREASES with decreasing concentration of the solvent chosen in Step 4. The solvent chosen in Step 4 was deliberately chosen to optimize the degree of CPPO solubility of members of that group. The optimum combination of solvents, CPPO, and fluorescer will have to be determined empirically due to the differing absorption of the different colors of light by different solvents (a solvent that absorbs in the blue region of the spectrum will require a higher concentration of CPPO and blue fluorescer than a solvent that absorbs in the red end of the spectrum).

[066] Activator Solvent Selection Rules:

[067] 1. Return to the class of solvents chosen in Step 2 of the Oxalate Selection Rules.

[068] 2. From this class of solvents, find all members that have a miscibility in water effective to stabilize the peroxide component of the chemical light activator system.

[069] 3. If no members of the class of solvents chosen in Step 2 of the Oxalate Selection Rules has a miscibility in to effectively stabilize the peroxide component, then choose a second class of solvents that comes close to meeting the requirements of Number 1 from the Oxalate Selection Rules, is miscible in the class of solvents chosen in Number 2 of the Oxalate Selection Rules, and has member(s) that effectively stabilize the peroxide component.

[070] 4. Make mixtures of the solvents chosen in Steps 2 and 3 with varying concentrations of each solvent. Choose the blend that contains the highest concentration of the desired solvent (that chosen in Step 2 of the Oxalate Selection Rules) AND effectively stabilizes the peroxide component.

[071] In certain embodiments, the chemical light system comprises approximately 8.4% CPPO, 0.19% BPEA and 91.41% of a 50/50% mixture of propylene glycol dibenzoate and acetyltributyl citrate in said oxalate component and a mixture of approximately 85% triethyl citrate, 10% tbutanol, 5% of a 70% concentration hydrogen peroxide, and 0.0085% sodium salicylate in said peroxide component.

[072] It will be apparent to those skilled in the art that various changes may be made without departing from the scope of the disclosure and the disclosure is not to be considered limited to what is shown and described in the specification.

[073] The embodiments, methods, procedures and techniques described herein are intended to be exemplary and are not intended as limitations on the scope of the disclosure. Changes therein and other uses will occur to those skilled in the art which are encompassed within the spirit of the disclosure and are defined by the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A chemiluminescent light producing device comprising a biodegradable polyhydroxyalkanoate composition, said biodegradable polyhydroxyalkanoate composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial each containing one of at least one oxalate component and at least one peroxide component of said chemical light system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said polyhydroxyalkanoate outer containment device.

2. The chemiluminescent light producing device in accordance with claim 1, wherein said chemical system retained therein is biodegradable.

3. The chemiluminescent light producing device in accordance with claim 1, wherein the at least one oxalate component comprises at least one oxalate chosen from bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate; bis(2,4,5-trichlorophenyl)oxalate; bis(2,4,5-tribromo-6-carbohexoxyphenyl)oxalate; bis(2,4,5-trichloro-6-carboisopentoxyphenyl) oxalate; and bis(2,4,5-trichloro-6-carbobenzoxyphenyl) oxalate.

4. The chemiluminescent light producing device in accordance with claim 1, wherein the at least one peroxide component is chosen from hydrogen peroxide, sodium peroxide, sodium perborate, sodium pyrophosphate peroxide, urea peroxide, histidine peroxide, t-butyl hydroperoxide, peroxybenzoic acid, sodium percarbonate, and mixtures thereof.

5. A chemiluminescent light producing device comprising a polyhydroxyalkanoate composition that disintegrates so as to lose its physical form, said polyhydroxyalkanoate composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial

each containing one of at least one oxalate component and at least one peroxide component of said chemical light system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said polyhydroxyalkanoate outer containment device.

6. The chemiluminescent light producing device in accordance with claim 5, wherein said chemical system retained therein is biodegradable.

7. The chemiluminescent light producing device in accordance with claim 5, wherein the at least one oxalate component comprises at least one oxalate chosen from bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate; bis(2,4,5-trichlorophenyl)oxalate; bis(2,4,5-tribromo-6-carbohexoxyphenyl)oxalate; bis(2,4,5-trichloro-6-carboisopentoxyphenyl) oxalate; and bis(2,4,5-trichloro-6-carbobenzoxyphenyl) oxalate.

8. The chemiluminescent light producing device in accordance with claim 5, wherein the at least one peroxide component is chosen from hydrogen peroxide, sodium peroxide, sodium perborate, sodium pyrophosphate peroxide, urea peroxide, histidine peroxide, t-butyl hydroperoxide, peroxybenzoic acid, sodium percarbonate, and mixtures thereof.

9. A chemiluminescent light producing device comprising a polyhydroxyalkanoate composition that is photodegradable so as to lose its physical form, said polyhydroxyalkanoate composition forming an outer containment device enclosing at least one inner frangible vial, said outer containment device and said vial containing a chemical light system, said outer containment device and said vial each containing one of at least one oxalate component and at least one peroxide component of said chemical system, separately, said at least one oxalate component and said at least one peroxide component producing visible light when intermixed in said polyhydroxyalkanoate outer containment device,

wherein said polyhydroxyalkanoate composition comprises ultraviolet-sensitive components, whereby said ultraviolet-sensitive components photodegrade when subjected to ultraviolet light.

10. The chemiluminescent light producing device in accordance with claim 9, wherein said chemical light system retained therein is biodegradable.

11. The chemiluminescent light producing device of claim 9, wherein said UV sensitive components are chosen from ketone carbonyl copolymers, carbon monoxide copolymers or metal salts.

12. The chemiluminescent light producing device in accordance with claim 9, wherein the at least one oxalate component comprises at least one oxalate chosen from bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate; bis(2,4,5-trichlorophenyl)oxalate; bis(2,4,5-tribromo-6-carbohexoxyphenyl)oxalate; bis(2,4,5-trichloro-6-carboisopentoxyphenyl) oxalate; and bis(2,4,5-trichloro-6-carbobenzoxyphenyl) oxalate.

13. The chemiluminescent light producing device in accordance with claim 9, wherein the at least one peroxide component is chosen from hydrogen peroxide, sodium peroxide, sodium perborate, sodium pyrophosphate peroxide, urea peroxide, histidine peroxide, t-butyl hydroperoxide, peroxybenzoic acid, sodium percarbonate, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/029412

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K11/07 F21K2/06
ADD.

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)
C09K F21K

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 practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/042326 A1 (OMNIGLOW CORP [US]) 22 May 2003 (2003-05-22) claims; examples 1-4; table 1 page 8, line 13 - line 24	1-13
X	WO 2007/117231 A1 (CYALUME TECHNOLOGIES INC [US]) 18 October 2007 (2007-10-18) the whole document	1-13

☐ 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 application or patent 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	Date of mailing of the international search report
10 May 2012	22/05/2012

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/029412

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 03042326	A1	22-05-2003	AU	2002361635	A1	26-05-2003
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			EP	1478714	A1	24-11-2004
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			US	2003102467	A1	05-06-2003
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