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(54) Titre : SOLUTION CHIMILUMINESCENTE A BASE D'ACIDES TETRACARBOXYLIQUES DE PERYLENE DISUBSTITUES, DE LEURS DIANHYDRIDES ET DIIMIDES

(54) Title: CHEMILUMINESCENT SOLUTION BASED ON DISUBSTITUTED PERYLENE TETRACARBOXYLIC ACIDS, THEIR DIANHYDRIDES AND DIIMIDES

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Compositions adapted to be reacted with hydrogen peroxide to provide chemiluminescent light are disclosed wherein the fluorescent is selected from 1,7-disubstituted perylene-3,4-9, and 10-tetracarboxylic acids, their dianhydrides and diimides.

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(57) Abstract: Compositions adapted to be reacted with hydrogen peroxide to provide chemiluminescent light are disclosed wherein the fluorescent is selected from 1,7-disubstituted perylene-3,4-9, and 10-tetracarboxylic acids, their dianhydrides and diimides.

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CHEMILUMINESCENT SOLUTION BASED ON DISUBSTITUTED PERYLENE TETRACARBOXYLIC ACIDS, THEIR DIANHYDRIDES AND DIIIMIDES

FIELD OF THE INVENTION:

The present invention relates to the production of light by chemiluminescence and, more particularly, the use of specific fluorescent agents for this purpose.

BACKGROUND OF THE INVENTION:

The principle and the techniques for the production of chemiluminescent light are described in detail in U.S. Pat. No. 4,678,608.

Chemiluminescence is produced by a reaction in the liquid phase of an activator such as hydrogen peroxide with a fluorescent agent and an oxalate. Optionally, other secondary compounds can be present. In general, they are also fluorescent agents, which modify the characteristics of the emitted light.

Until now, there existed no simple means to produce orange chemiluminescent light which is satisfactory for the users. The prior art mixed yellow and red chemiluminescent light producing solutions to yield an orange colored light. The major drawback of this approach was that the color was blotchy, especially in a narrow environment, e.g. in a chemiluminescent glow necklace. Additionally, the two solutions would sometimes decay at different rates, leading to a shift in coloration with time, e.g. to yellow or red.

U.S. Patent No. 5,122,306 discloses a chemiluminescent solution based on substituted perylene for producing a red chemiluminescent light.

There exists a significant demand for orange

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chemiluminescent light. Orange is a color which is greatly appreciated by the public at large and the ability to produce a pleasing orange coloration via a chemiluminescent composition would be highly desirable.

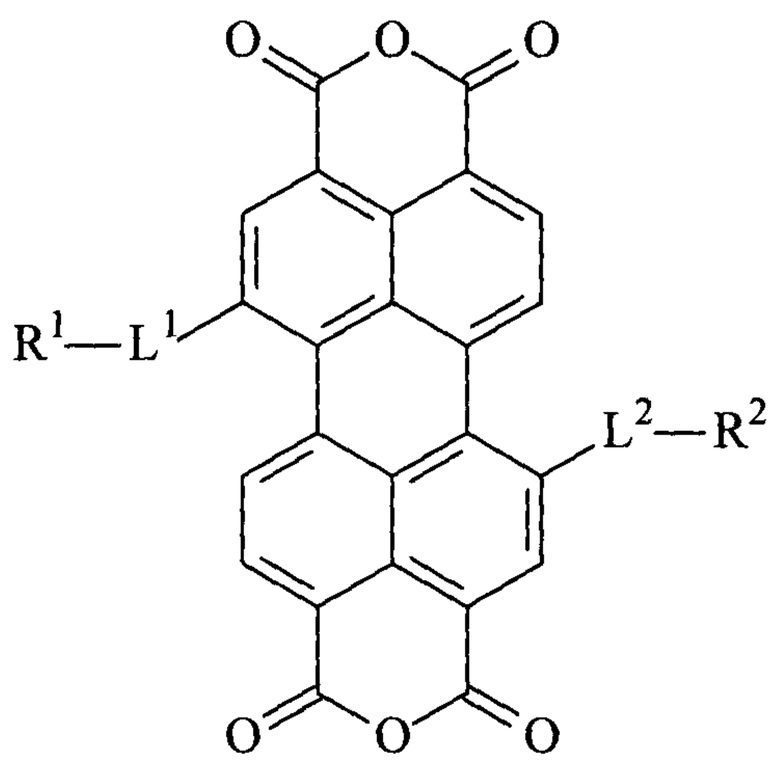
SUMMARY OF THE INVENTION:

It has now been observed unexpectedly that known fluorescent dyes which are soluble in organic solvents and, particularly, disubstituted perylene tetracarboxylic acids, their dianhydrides and diiimides, can be used advantageously to produce a chemiluminescent light, particularly an orange chemiluminescent light, which is particularly appreciated by the users and which differs from the colors produced in the prior art.

Accordingly, it is an objective of the instant invention to teach a composition adapted to be reacted with hydrogen peroxide to provide orange chemiluminescent light.

It is a further objective of the instant invention to teach a composition for providing chemiluminescent light wherein the fluorescer is selected from 1,7-disubstituted perylene-3,4,9,10-tetracarboxylic acids, their dianhydrides and diimides.

According to one aspect of the present invention, there is provided a composition for reaction with hydrogen peroxide to provide chemiluminescent light, wherein the composition comprising an oxalate compound and a 1,7-disubstituted perylene-3,4,9,10-tetracarboxylic dianhydride fluorescer compound having the formula:



wherein L^1 and L^2, independently of each other, are 1,2-ethylene, 1,2-ethenylene or 1,2-ethynylene; R^1 and R^2, independently of each other, are hydrogen or C_1-C_{30}-alkyl, whose carbon atom chain optionally is interrupted by at least one moiety selected from the group consisting of -O-, -S-, -NR^3-, -CO- and -SO_2- and which is optionally substituted once by a moiety selected from the group consisting of -$COOR^3$, -SO_3R^3, cyano and a 5- to 7-membered heterocyclic radical which is attached via a nitrogen atom and which optionally comprises one additional nitrogen atom, oxygen atom or sulfur atom and which is optionally aromatic; or substituted one or two times by hydroxyl, C_1-C_5-alkoxy, C_5-C_8-cycloalkyl or aryl, wherein R^3 is hydrogen or C_1-C_6-alkyl, and wherein the amount of said oxalate compound and said fluorescer compound is such as to provide orange light.

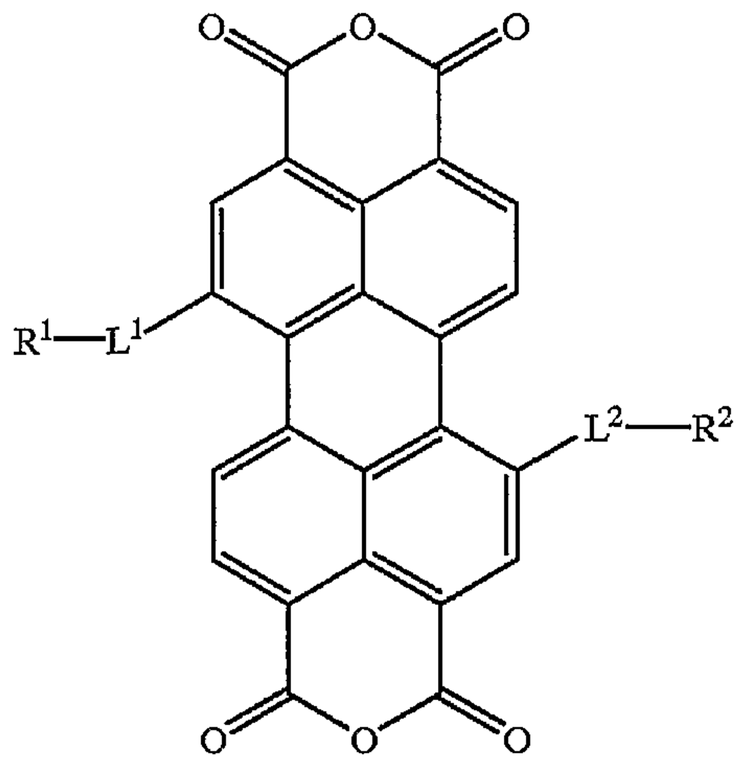
According to another aspect of the present invention, there is provided a method of producing orange chemiluminescent light which comprises adding to a composition as described herein, a solution of hydrogen peroxide.

Other objects and advantages of this invention will become apparent from the following description taken in conjunction with the accompanying drawings wherein are set forth, by way of illustration and example, certain embodiments of this invention.

DETAILED DESCRIPTION OF THE INVENTION:

The present invention relates to a composition adapted to be reacted with hydrogen peroxide to provide chemiluminescent light, said composition containing a 1,7-disubstituted perylene-3,4,9,10-tetracarboxylic

dianhydride compound having the general formula:



wherein L^1, L^2 independently of each other are 1,2-ethylene, 1,2-ethenylene or 1,2-ethynylene;

R^1, R^2 independently of each other are hydrogen or C_1-C_{30}-alkyl, whose carbon atom chain optionally is interrupted by at least one moiety selected from the group consisting of -O-, -S-, -NR^3-, -CO- and -SO_2- and/or which is optionally substituted once by a moiety selected from the group consisting of --$COOR^3$, -SO_3R^3, cyano or a 5- to 7-membered heterocyclic radical which is attached via a nitrogen atom and which optionally contains one additional nitrogen atom, oxygen atom or sulfur atom and which is optionally aromatic; or substituted one or two times by hydroxyl, C_1-C_5-alkoxy, C_5-C_8-cycloalkyl or aryl, R^3 being hydrogen or C_1-C_6-alkyl, the amount of said compound being such as to provide visible light.

Specific embodiments include compositions wherein L^1, L^2 are identical and are 1,2-ethenylene or 1,2-ethynylene and

R^1, R^2 independently of one another are hydrogen or C_1-C_{18}-alkyl which can be substituted by --$COOR^3$, hydroxyl or cyano. Additionally, specific heterocyclic radicals

are 4-morpholinyl, 1-pyrrolidinyl, 1-piperidyl or 4-piperidyl.

The above-mentioned compounds, their related tetracarboxylic acids, and the diimides of said acids are described in WO 97/22608, published June 26, 1997 and U.S. Patent No. 6,063,181, issued May 16, 2000. These patents also describe the preparation of analog derivatives. The preferred compound is sold under the trade name LUMOGEN PINK ED2222, and is known to be useful as a fluorescent dye For producing a pink light reflecting surface when compounded into various polymers. It has now been discovered that LUMOGEN PINK ED2222 will emit a true orange light, e.g. 580-585nm, when utilized as a fluorescer composition in chemiluminescent light producing solutions.

To produce chemiluminescent light, the compounds according to the present invention are used under the conditions already described in the literature, particularly in said U.S. Pat. No. 4,678,608. In general, one can use any known solvent or oxalate which can be used for the production of chemiluminescent light. The solvent can be an ester, aromatic derivatives or a chlorinated hydrocarbon. Preferably, phthalates are used, in particular dibutyl phthalate.

Oxalates, such as those described in U.S. Pat. Nos. 3,749,679 and 3,846,316 may be used to produce the chemical reaction to cause chemiluminescent light when mixed with the fluorescers described above, with bis (2,4,5-trichloro-6-carbopentoxylphenyl) oxalate being exemplary.

Substituted carbalkoxyphenyl oxalate are the preferred class of oxalates used herein the oxalate and perylene fluorescer each being used in sufficient quantity

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to cause chemiluminescent light, preferably in a 20-40:1 oxalate to
fluorescer, molar ratio.

Useful catalysts are disclosed in U.S. Pat. No. 3,775,336 in concentrations disclosed therein, and usually in the solvent
solution of the hydrogen peroxide.

The areas of application are well known and they include the production of useful objects, particularly signs, decorative objects, games and gadgets such as chemiluminescent necklaces, etc.. In such articles, the chemiluminescent light is produced by mixing a solution of an activator, in general oxygenated water (hydrogen peroxide), with a solution which contains the derivatives of disubstituted perylene and an oxalate diester. The article consists of, in its passive state, two compartments between which a communicating link was established at the time of use, for example as described in French Pat. No. 87 11296, for the case of flexible luminescent tubes.

The following example will illustrate the invention without limiting it.

Example 1

Prepare an Activator solution containing approximately 85 weight percent Dimethyl Phthalate, 10 weight percent t-Butanol, and 5 weight percent 70% hydrogen peroxide (as is). Catalyze with 0.0085 weight percent Sodium Salicylate.

Prepare an Oxalate solution with 86 weight percent Butyl Benzoate, 13.9 weight percent bis(2-carbopentyloxy-3,5,6-trichlorophenyl) oxylate (CPPO), and 0.1 weight percent LUMOGEN PINK ED2222.

Mix equal parts of the oxalate and activator solution. A strong orange colored light will be produced as the two are mixed, with a color exhibiting a wavelength of

approximately 585 nm.

Example 2

Prepare the activator solution as in Example 1.

Prepare an Oxalate solution as in Example 1 but increase the quantity of LUMOGEN PINK ED2222 from 0.1 weight percent to 0.5 weight percent.

Again mix equal parts of the oxalate and activator solutions. A strong orange-red colored light will be produced as the two are mixed, with a color exhibiting a wavelength of approximately 600 nm.

Example 3

Prepare the activator solution as in Example 1.

Prepare an Oxalate solution as in Example 1 but increase the quantity of LUMOGEN PINK ED2222 from 0.1 weight percent to 1.0 weight percent.

Again mix equal parts of the oxalate and activator solutions. A strong red colored light will be produced as the two are mixed, with a color exhibiting a wavelength of approximately 610 nm.

Example 4

Prepare an Oxalate solution with 85 weight percent Butyl Benzoate, 13.9 weight percent CPPO, and 1.0 weight percent LUMOGEN PINK ED2222.

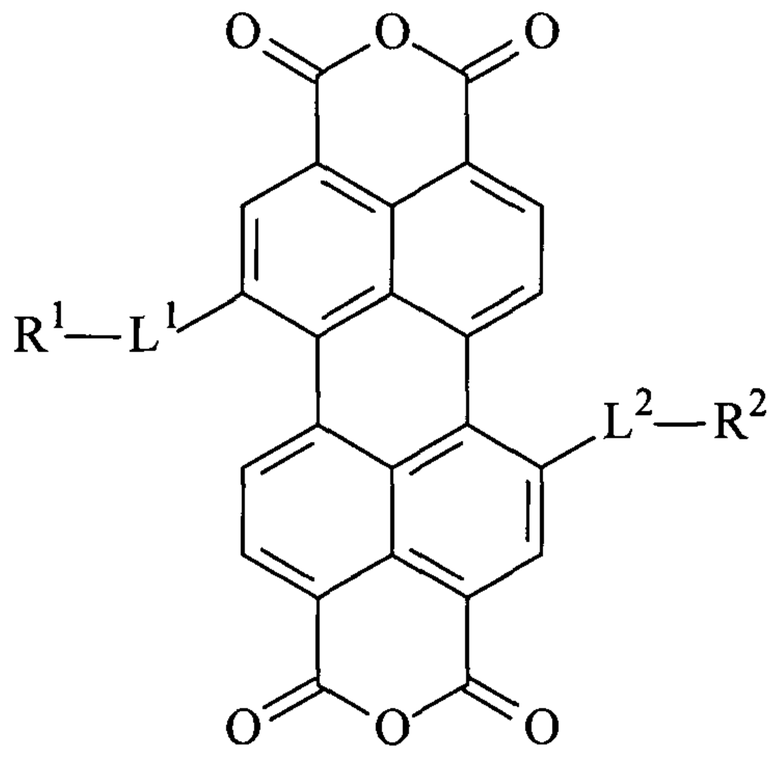
Prepare an Oxalate solution with 85 weight percent Butyl Benzoate, 13.9 weight percent CPPO, and 1.0 weight percent 1-chloro-9,10-bis(phenylethynyl) anthracene (CBPEA).

Store both at 20F for 24 hours. The CBPEA will crystallize out of solution.

It is to be understood that while a certain form of the invention is illustrated, it is not to be limited to the specific form or arrangement of parts herein described and shown. It will be apparent to those skilled in the art that various changes may be made without departing from the scope of the invention and the invention is not to be considered limited to what is shown and described in the specification and drawings.

CLAIMS:

1. A composition for reaction with hydrogen peroxide to provide chemiluminescent light, wherein the composition comprising an oxalate compound and a 1,7-disubstituted perylene-3,4,9,10-tetracarboxylic dianhydride fluorescer compound having the formula:



wherein L^1 and L^2, independently of each other, are 1,2-ethylene, 1,2-ethenylene or 1,2-ethynylene; R^1 and R^2, independently of each other, are hydrogen or C_1-C_{30}-alkyl, whose carbon atom chain optionally is interrupted by at least one moiety selected from the group consisting of -O-, -S-, -NR^3-, -CO- and -SO_2- and which is optionally substituted once by a moiety selected from the group consisting of -$COOR^3$, -SO_3R^3, cyano and a 5- to 7-membered heterocyclic radical which is attached via a nitrogen atom and which optionally comprises one additional nitrogen atom, oxygen atom or sulfur atom and which is optionally aromatic; or substituted one or two times by hydroxyl, C_1-C_5-alkoxy, C_5-C_8-cycloalkyl or aryl, wherein R^3 is hydrogen or C_1-C_6-alkyl, and wherein the amount of said oxalate compound and said fluorescer compound is such as to provide orange light.

2. A composition according to claim 1, wherein:

L^1 and L^2 are identical and are 1,2-ethenylene or 1,2-ethynylene; and

R^1 and R^2 independently of one another are hydrogen or C_1-C_{18}-alkyl which is optionally substituted by -$COOR^3$, hydroxyl or cyano.

3. A composition according to claim 1, wherein said heterocyclic radical is 4-morpholinyl, 1-pyrrolidinyl, 1-piperidyl or 4-piperidyl.

4. A composition according to any one of claims 1 to 3 further comprising a solvent for said fluorescer compound.

5. A composition according to claim 4, wherein the solvent is t-butylphthalate.

6. A composition according to any one of claims 1 to 5, wherein the oxalate compound is a substituted carbalkoxyphenyl oxalate.

7. A composition according to any one of claims 1 to 5, wherein the oxalate compound is bis(2,4,5-trichloro-6-carbopentoxylphenyl) oxalate.

8. A composition according to any one of claims 1 to 7, wherein the 1,7-disubstituted perylene-3,4,9,10-tetracarboxylic dianhydride fluorescer compound is the only fluorescer in the composition.

9. A method of producing orange chemiluminescent light which comprises adding to the composition defined in any one of claims 1 to 8, a solution of hydrogen peroxide.

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