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[54] **CHEMILUMINESCENT DEVICE**

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[51] **Int. Cl.** **F21v 9/16**

[58] **Field of Search** 240/2.25; 222/94; 53/30

[56] **References Cited**

UNITED STATES PATENTS

2,834,345	5/1958	Tabbert	222/94 X
3,068,154	12/1962	Majors	222/94 UX
3,286,835	11/1966	Crane, Jr.	53/30 X
3,520,471	7/1970	Faust	222/94 X
3,576,987	5/1971	Voight	240/2.25
3,584,211	6/1971	Rauhuf	240/2.25
3,764,796	10/1973	Gilliam et al.	240/2.25

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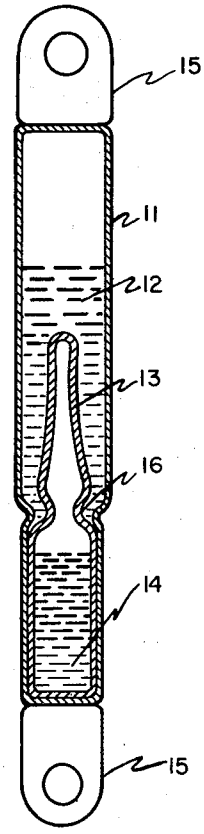
[57] **ABSTRACT**

Radiation cross-linked polyolefines are used to fabricate containment devices for chemiluminescent systems which utilize oxalate ester-fluorescer solutions as one component.

6 Claims, 2 Drawing Figures



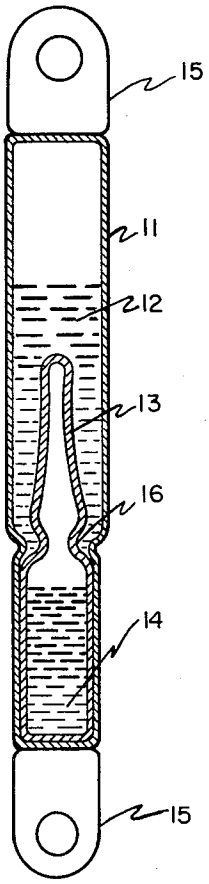


Fig. 1

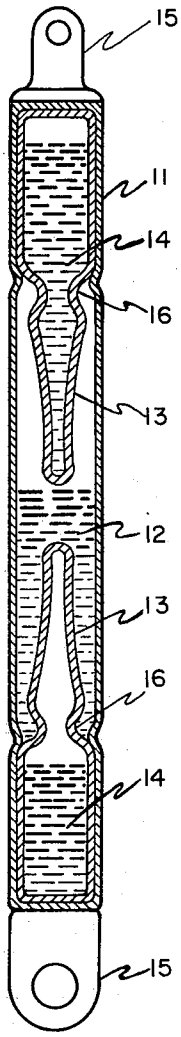


Fig. 2

CHEMILUMINESCENT DEVICE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to chemiluminescent devices. More particularly, this invention relates to containment devices or packages for chemiluminescent systems which utilize two or more components, one of which is an oxalate ester-fluorescer solution.

2. Description of the Prior Art

Chemiluminescent systems, i.e., systems which produce light when a chemical reaction takes place are known. One type of chemiluminescent system is a one component system which produces light when the single component comes into contact with oxygen from the air or the like. A second type of chemiluminescent system is one which produces light when two components come into contact with each other.

In order to be useful, chemiluminescent systems must be packaged or contained in some manner which permits them to remain inactive until it is desired to use them and then permits quick and easy activation. The most widely used prior art package or containment device for a two component system consists of a glass ampule holding one component sealed within a polyethylene container which, in addition, holds the second component. When it is desired to use the device, one merely presses inwardly on the outer polyethylene container to cause the inner glass ampule to rupture and permit the two components to mix. This device is simple and easy to operate. However, it has several drawbacks.

One serious drawback is that, when stored in conventional polyethylene, certain components of chemiluminescent systems tend to disintegrate quickly. More specifically, oxalate ester-fluorescer solutions tend to disintegrate quickly when stored in conventional polyethylene containers. An oxalate ester-fluorescer solution has a shelf life of only about 2 years at room temperature and less than about 2 weeks at 165° F when packaged in a conventional polyethylene container.

Another drawback of the above described package is that the inner glass ampule which floats freely in the solution contained by the outer polyethylene container is often hard to see. This makes it difficult, and sometimes impossible, to tell whether the device is ready for use or if the device has already been expended. It is also sometimes difficult to rupture the free floating inner glass ampule.

Another material from which the outer tube has been fabricated is Teflon FEP^R. Oxalate ester-fluorescer solutions exhibit long shelf lives when stored in Teflon FEP^R. However, Teflon REP^R has drawbacks in that it is expensive and difficult to fabricate.

SUMMARY OF THE INVENTION

It has now been found that irradiation cross-linked polyolefines are excellent materials for use in the fabrication of containment devices for chemiluminescent systems. The devices described herein solve the problems associated with devices which utilize Teflon FEP^R in that they are easy to fabricate and less expensive. They solve the problems associated with devices which utilize conventional polyethylene in that systems packaged in them can be stored at 165° F for considerably longer periods of time and in that one can easily determine whether they are expended or not. These and other advantages will become apparent from reading the following description of the preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a cross sectional view of a containment device for two component chemiluminescent systems according to this invention.

FIG. 2 is a cross sectional view of a containment device capable of containing either a two component or a three component chemiluminescent system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Going first to the drawing. FIGS. 1 and 2 depict the general physical appearance of two containment devices for chemiluminescent systems according to this invention. Whether one would choose the device of FIG. 1 or the device of FIG. 2 depends upon the particular system to be packaged and its intended use. This will become clear from the following discussion.

In FIG. 1, the numeral indicates an outer container fabricated from irradiation cross-linked polyolefin. The outer container 11 holds one component 12 of the chemiluminescent system. Component 12 is an oxalate ester-fluorescer solution. Sealed within the outer container 11 is a glass inner container 13 which contains a second component 14 of the chemiluminescent system. The second component 14 is a solution of hydrogen peroxide in an inert solvent. The ends 15 of the irradiation cross-linked polyolefin outer container are sealed by conventional heat sealing means and the glass inner container is fabricated with a constricted neck 16 to facilitate breakage when it is desired to mix the two components.

FIG. 2 depicts a device similar to that of FIG. 1 except that two glass inner containers 13, one at either end, are enclosed within the outer container 11. The numerals in FIG. 2 indicate parts similar to those indicated by like numerals in FIG. 1.

If one merely wishes to produce light by mixing two components of a chemiluminescent system, the device of FIG. 1 is adequate. On the other hand, the device of FIG. 2 allows one to do several things in addition to merely producing light. For example, if one wishes to quench the light producing reaction, one of the glass inner containers can be filled with a quenching agent and broken at the desired quenching time. If one wishes to change the intensity of the light produced, one of the glass inner containers can be used to contain a hydrogen peroxide solution with a low amount of catalyst and the other inner glass container may contain a relatively higher catalyzed hydrogen peroxide solution. The lowly catalyzed hydrogen peroxide, upon reacting with an oxalate-fluorescer system will produce low intensity, long duration light while the highly catalyzed solution will produce high intensity, short duration light. As another example, one of the inner glass containers may be filled with an extra amount of oxalate-fluorescer solution and broken when light produced from the breaking of the first container is about to expire, to increase the duration of the light. As still another example, the color of the light produced may be varied by filling one glass inner container with an oxalate ester-fluorescer solution which is different from that contained by the outer radiation cross-linked polyolifin container.

The material from which the outer container **11** in either of the two devices shown in FIGS. **1** and **2** is fabricated is critical. As stated in the description of the prior art, certain materials have been tried and found wanting for various reasons. The irradiation cross-linked polyolefin outer containers used in the practice of the present invention are fabricated from prestressed irradiation cross-linked polyolefines which exhibit a "memory effect" such as those whose preparation and properties are described in chapter IX (pp. 385–494) of Volume XV of *Radiation Chemistry of Polymer Systems* written by Adolphe Chapiro and published by Interscience Publishers of New York and London in 1962. The polyolefin of the container may be polyethylene, polypropylene or a mixture of the two. Heat shrinkable tubing is fabricated by subjecting prestressed conventional polyolefin tubing to either beta or gama radiation for a short period of time. The shrinkable polyethylene described on pages 441–442 of the above-cited reference is particularly suitable for use in practicing this invention.

To fabricate a device of the type shown in FIG. **1**, a sealed glass inner container which holds a suitable hydrogen peroxide solution is placed within a length of radiation cross-linked polyethylene tubing which has been heat sealed at one end. The radiation cross-linked outer tubing is then locally heated to cause it to shrink around the glass container and rigidly fix the glass container in place. Oxalate ester-fluorescer solution is then poured into the outer container and, finally, the second end of the radiation cross-linked polyolefin tube is heat sealed closed.

From the above description with regard to the device of FIG. **1**, it will be apparent to those skilled in the art that a device of the type depicted in FIG. **2** may be fabricated in a similar manner with the exception that two glass inner containers are placed and sealed into the radiation cross-linked polyolefin outer container rather than one.

The glass from which the inner containers of this invention are fabricated is preferably neutral or only very slightly basic. Pyrex glass, which is only slightly basic, and commercially available neutral glasses are suitable. The oxalate ester-fluorescer solution is in contact with the outer surface of the glass inner containers and tends to decompose if the surface of the glass is too basic. Also, the hydrogen peroxide solution within a glass inner container may decompose if the surface of the glass which contains it is too basic.

Examples of oxalate esters suitable for use in the practice of this invention are bis (2, 4, 5 - trichloro-6-carbopentoxyphenyl) oxalate and bis (2, 4, 5 - trichloro-6-carbobutoxyphenyl) oxalate.

Examples of fluorescers suitable for use in the practice of this invention are 9, 10 - bis(phenylethynyl) anthracene and rubrene.

The oxalate ester and fluorescer are dissolved with heating in a solvent such as dibutylphthalate for use. The ester and fluorescer may be dissolved in the solvent in an oxygen free atmosphere, i.e., for example in a glove box containing a nitrogen atmosphere. The solution also may be placed and sealed into a containment device in an oxygen free atmosphere. Utilization of an oxygen free atmosphere will increase the light output by approximately 15 percent. A solution containing 0.15 M oxalate and 0.003 M fluorescer in dibutylphthalate has been found to be preferable. However, a range of from 0.1 M to 0.3 M for the oxalate and of from 0.003 M to 0.01 M for the fluorescer is suitable.

The inert solvent for hydrogen peroxide may be a tertiary alcohol such as t-butyl alcohol or 3-methyl-3-pentanol. Also, a mixture of 20 volume percent of t-butyl alcohol with 80 volume percent dimethylphthalate has been found to be a suitable solvent for hydrogen peroxide. A concentration of from 1 to 1.5 M for the hydrogen peroxide is preferable but a range of from 0.5 M to 3 M is suitable.

Devices are preferably fabricated so as to contain about 3 volume units of the oxalate ester solution per 1 volume unit of the hydrogen peroxide solution.

It is usually desirable to dissolve a catalyst such as sodium salicylate or sodium trifluoroacetate in the hydrogen peroxide solution. If no catalyst is included, a device will give a long light output but the light output will be relatively inefficient. A concentration of from about 0.0001 M to about 0.01 M is preferred for the catalyst. As mentioned above, increasing the catalyst content increases the intensity but shortens the duration of the light produced.

Where it is desirable to use a device such as that depicted in FIG. **2** and fill one of the glass inner containers with a quencher, any primary or secondary amine, whether aromatic such as pyridine or aliphatic such as diethyl amine, will work as a suitable quencher.

The fact that the devices of FIGS. **1** and **2** have the glass inner containers held rigidly in place by means of locally shrunk outer container is of importance in this invention. As noted in the description of the prior art, free floating inner containers are often hard to see. This, in addition to making them hard to locate if one wishes to determine whether or not the device has been expended, sometimes leads to difficulty in rupturing the inner container. The devices of the present invention, on the other hand, are easily operated because the fixed inner container(s) can not slide back and forth and resist crushing.

In tests comparing devices of the type described herein with similar devices utilizing conventional polyethylene as the outer container, it has been found that, under room temperature storeage conditions, the devices of this invention can be used effectively to produce light three years after they have been prepared whereas devices utilizing conventional polyethylene fail or are unsatisfactory after 2 years. Under 165° F storeage conditions, devices with conventional polyethylene fail after about 2 weeks whereas devices utilizing radiation cross-linked polyethylene still operate satisfactorily after three months. It can, accordingly, be seen that the use of radiation cross-linked polyethylene is a great improvement over the use of conventional polyethylene.

What is claimed is:

1. A chemiluminescent device comprising:

a. a breakable glass inner container having sealed within a solution of hydrogen peroxide, said inner container having a constricted neck to facilitate breakage thereof; and

a flexible outer container fabricated from radiation cross-linked polyolefin having sealed within a solution of an oxalate ester and a fluorescer, said solution of oxalate ester and fluorescer and said outer container encompassing said breakable inner container, a portion of said outer container being

shrunk inwardly around a portion of said breakable inner container to hold said inner container rigidly in place, and said outer container being heat sealed closed at both ends thereof.

2. A chemiluminescent device according to claim 1 wherein, additionally, a second breakable glass inner container having a constricted neck to facilitate breakage thereof and having a component of a multi-component chemiluminescent system sealed within it is rigidly held in place within said outer container by means of a portion of said outer container being shrunk inwardly around a portion of said second breakable inner container.

3. A chemiluminescent device according to claim 2 wherein said second breakable inner container has a quenching material selected from the group consisting of primary and secondary amines sealed within it.

4. A chemiluminescent device according to claim 2 wherein said second inner container has hydrogen peroxide sealed within it.

5. A chemiluminescent device according to claim 2 wherein said second inner container has a solution of oxalate ester and fluorescer sealed within it.

6. In the method of fabricating a chemiluminescent device which comprises sealing at least one closed breakable container which contains a component of a chemiluminescent system within an outer container which contains another component of the chemiluminescent system, the improvements which reside in fabricating the closed breakable container with a constricted neck to facilitate breakage thereof, fabricating the outer container from radiation cross-linked polyolefin, shrinking a portion of the outer container around a portion of the closed breakable container to hold the closed breakable container rigidly in place and permanently heat sealing the outer container closed at both ends thereof.

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