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[54] **CHEMILUMINESCENT LIQUID DISPENSING OR DISPLAY CONTAINER**
7 Claims, 4 Drawing Figs.

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[51] **Int. Cl.** **F21k 2/00**
[50] **Field of Search** 240/2.25; 102/37.8; 161/196; 250/71; 222/94, 136, 541; 195/103.5, 54

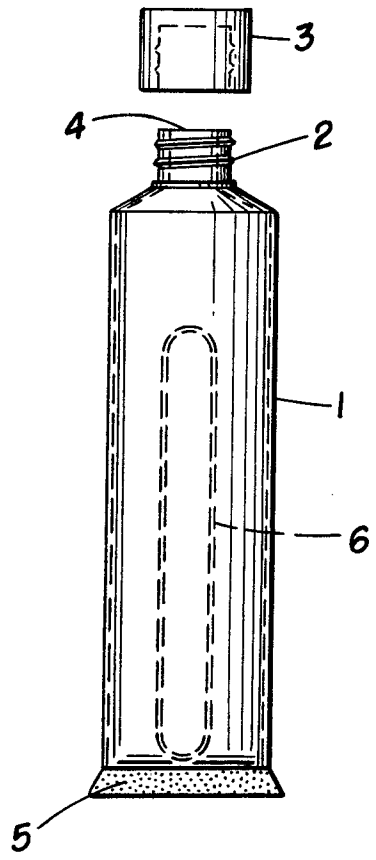
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Primary Examiner—Samuel S. Matthews
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ABSTRACT: A device for providing chemiluminescent light from a chemical reaction of suitable compounds in the presence of a fluorescent compound, said device being both a self-contained light unit and a chemiluminescent dispensing unit. Bending the flexible, light-transmitting outer tube containing one chemiluminescent component breaks a frangible inner container holding a second component, allowing the substances to react. The luminescent reaction product may be dispensed and used as a luminescent marker or held in the closed device for use as an illumination wand.



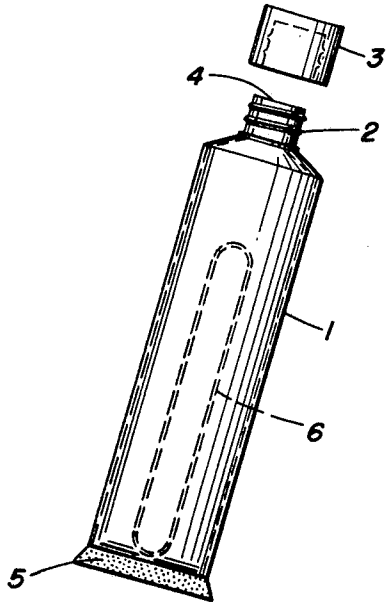


FIG. 1

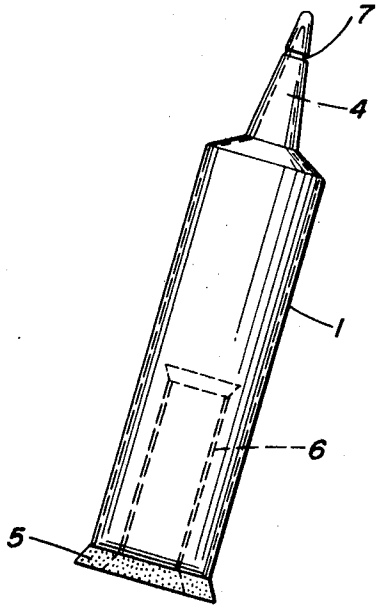


FIG. 2

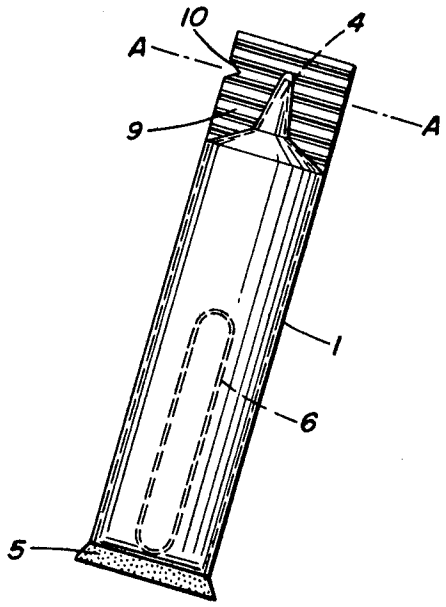


FIG. 3

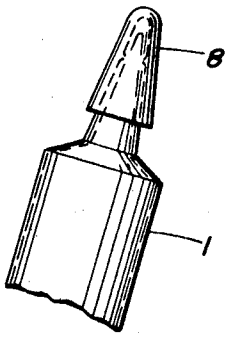


FIG. 4

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CHEMILUMINESCENT LIQUID DISPENSING OR DISPLAY CONTAINER

This invention relates to systems and devices for providing chemiluminescent light incorporating chemical components which react chemically and provide excitation for a fluorescent compound. The invention more particularly relates to systems and devices whereby the reactive components are maintained in a nonreactive condition until light is desired, the systems incorporating means to bring said components into a reactive condition and means to display the resultant light.

Under certain circumstances, it is desirable to have a source of visible light which is not electrically activated. Light can be provided by chemical systems, wherein the luminosity is solely the result of chemical reaction without provision of any electrical energy. Such light is known as chemiluminescent light.

Chemiluminescent light may be useful where there is no source of electricity. For example in emergencies where sources of electrical power have failed, a chemiluminescent system could provide light. Since the system requires no externally generated source of energy, devices can be made small and highly portable. Moreover, chemiluminescent light is cold light and can be used where the heat of conventional illumination is not desired. It is also useful where electrical means could cause a fire hazard, such as in the presence of inflammable agents. Chemiluminescent light is also effective under water since there are no electrical connections to short out. Thus it may be seen that chemiluminescent light can have many useful applications.

A principal object of the present invention is to provide systems and devices incorporating chemiluminescent components for the provision of chemiluminescent light.

A further object of this invention is to provide means for containing chemically reactive chemiluminescent components in a nonreactive condition and means to combine said components when desired to provide chemiluminescent light.

A further object is to provide a self-contained, highly portable chemiluminescent lighting device having all chemical components therein and in which the light is displayed and from which it may be dispensed.

Another object is to provide a chemiluminescent lighting device which is inexpensive to make, easy to activate and highly effective.

Another object of the invention is to provide an illuminated wand having a chemiluminescent lighting system.

These and other objects of the invention will become apparent as the description thereof proceeds.

This invention comprises a device for the storage and subsequent admixture and display or dispensing of a multicomponent chemiluminescent system. The device consists essentially of an elongated, transparent or translucent flexible outer tube and a rigid or rupturable, breakable inner container or tube within the outer tube. The inner tube may be free or fixed within the outer tube. The inner tube is filled (wholly or in part) with one component of a two-component chemical lighting system. The outer tube is filled with the second component. The outer tube is permanently sealed at one end and provided with a dispensing closure at the other.

To operate the device, the outer, flexible tube is bent causing the inner breakable tube to fracture and thus mix the two components and initiate light production. The outer translucent tube thus becomes a lighted wand for display purposes. If desired, all or part of the chemiluminescent mixture may be dispensed by opening the closure at one end of the outer tube.

It is clear that two or more inner tubes could be employed to store separately the components of a three or multiple-component chemical lighting system.

The chemiluminescent system of this invention thus comprises the device as described accommodating the admixture of at least two chemiluminescent components and providing for the admixture in the device of at least two chemiluminescent components comprising either (a) a component containing a chemiluminescent compound and a second component containing a hydroperoxide compound, either or both components containing a diluent, or (b) a dry solid component containing both a solid chemiluminescent compound and a solid hydroperoxide compound and a second component comprising a solvent for said solid chemiluminescent compound and said solid hydroperoxide compound. Any other necessary ingredients for the production of chemiluminescent light, or for lifetime control, or for intensity improvement, or for storage stabilization must of course either be included in one of the two system components or included as additional components. In particular with the preferred oxalic-type chemiluminescent compounds of this invention, a fluorescent compound must be included in the system.

The preferred chemiluminescent light is obtained in this invention by the reaction of a hydroperoxide with a chemiluminescent composition which, in combination, comprises a chemiluminescent compound selected from the group consisting of (1) an oxalic-type anhydride of the type disclosed and claimed in the copending application, Ser. No. 485,920, now U.S. Pat. No. 3,399,137, which is hereby incorporated by reference, (2) an oxalic-type amide of the type disclosed and claimed in copending applications, Ser. Nos. 520,052, now U.S. Pat. No. 3,442,815, and 547,782, now abandoned, which are hereby incorporated by reference, (3) an oxalic-type O-acylhydroxylamine of the type disclosed and claimed in copending application, Ser. No. 547,761, now abandoned, and (4) an oxalic-type ester disclosed and claimed in application Ser. No. 491,896, now abandoned, in the presence of a fluorescer compound, and a solvent. Other suitable chemiluminescent compounds are 3-aminophthalhydrazide, 3,4,5-triphenylimidazole, 10,10'-dialkyl-9,9'-biacridinium salts, and 9-chlorocarbonyl-10-methylacridinium chloride. The latter is disclosed and claimed in copending application, Ser. No. 427,459, now U.S. Pat. No. 3,352,791. All of the foregoing provide chemiluminescence when reacted with a hydroperoxide compound in the presence of a base. Other chemiluminescent materials are described by K. D. Gunderman, Angew. Chemie, Int. Ed., 4, 566/1965.

The preferred chemiluminescent compound of this invention is an oxalic-type ester selected from the group consisting of (a) an ester of an oxalic-type acid and an alcohol characterized by acid ionization constant in water greater than 1.3×10^{-10}, and (b) a vinyl ester of an oxalic-type ester. Similarly, in a preferred embodiment thereof, the alcohol would be an aromatic alcohol substituted by a substituent characterized by a positive Hammett sigma value. The preferred species of oxalic-type esters include bis(substituted-phenyl)oxalate, such as bis(2-nitrophenyl)oxalate, bis(2,4-dinitrophenyl)oxalate, bis(2,6-dichloro-4-nitrophenyl)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(2,5-dinitrophenyl)oxalate, bis(2-formyl-4-nitrophenyl)oxalate, bis(pentachlorophenyl)oxalate, bis(1,2-dihydro-2-oxo-1-pyridyl)glyoxal, bis-N-phthalmidyl oxalate. The preferred subspecies is bis(2,4,6-trichlorophenyl)oxalate.

The peroxides employed in the components of this invention may be any hydroperoxide compound. Typical hydroperoxides include t-butylhydroperoxide, peroxybenzoic acid, and hydrogen peroxide. Hydrogen peroxide is the preferred hydroperoxide and may be employed as a solution of hydrogen peroxide in a solvent or as an anhydrous hydrogen peroxide compound such as perhydrate of urea (urea peroxide), perhydrate of pyrophosphate (sodium pyrophosphate peroxide), perhydrate of histidine (histidine peroxide), 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 peroxide concentration may range from about 15 molar down to about 10^{-15}, preferably about 3 molar down to about

10^{11} molar. The ester of this invention may be added as a solid or in admixture with a suitable solid peroxide reactant or in a suitable diluent, or alternatively dissolved directly in a solution containing the peroxide reactant.

Typical diluents, which additionally may be used in conjunction with the necessary diluent of this invention, are those which do not readily react with a peroxide such as hydrogen peroxide, and which do not react with an ester of oxalic acid.

Where a solvent is employed with the hydroperoxide-containing component of this invention said solvent can be any fluid which is unreactive toward the hydroperoxide and which accommodates a solubility of at least 0.01 *M* hydroperoxide. Typical solvents for the hydroperoxide component include water; alcohols, such as ethanol or octanol; ethers, such as diethyl ether, diamyl ether, tetrahydrofuran, dioxane, dibutyldiethyleneglycol, perfluoropropyl ether, and 1,2-dimethoxyethane; and esters, such as ethyl acetate, ethyl benzoate, dimethyl phthalate, dioctylphthalate, propyl formate. Solvent combinations can, of course, be used such as concentrations of the above with aromatic anisole, tetralin, and polychlorobiphenyls, providing said solvent combination accommodates hydroperoxide solubility. However, when oxalic-type chemiluminescent materials are used, strong electron donor solvents such as dimethyl formamide, dimethyl sulfonide, and hexamethylphosphoramide should not, in general, be used as a major solvent component.

Where a solvent is employed with a component containing the chemiluminescent material any fluid can be used providing said fluid solubilizes at least 0.01 *M* concentration of the chemiluminescent material and is unreactive toward the chemiluminescent material. Typical solvents include ethers, esters, aromatic hydrocarbons, chlorinated aliphatic and aromatic hydrocarbons, such as those cited in the preceding paragraph. For oxalic-type chemiluminescent compounds, hydroxylic solvents such as water or alcohols and basic solvents such as pyridine should not be employed since such solvents used in general, react with and destroy oxalic-type chemiluminescent compounds. Solvent combinations may, of course, be used but such combinations when used with oxalic-type chemiluminescent compounds should not include strong electron donor solvents.

When a component comprising a solid chemiluminescent compound and a solid hydroperoxide is used, the solvent or solvent composition comprising the second component may vary broadly. Said solvent, however, should preferably dissolve at least 0.02 *M* concentrations of both, the hydroperoxide and the chemiluminescent compound, and for oxalic-type chemiluminescent compounds, strong electron donor solvents should be avoided as major solvent components.

The fluorescent compounds contemplated herein are numerous; and they may be defined broadly as those which do not readily react on contact with the peroxide employed in this invention, such as hydrogen peroxide, likewise, they do not readily react on contact with the chemiluminescent compound.

A fluorescent compound is required for light emission when the prepared oxalic-type chemiluminescent compound of the invention is employed. For other types of chemiluminescent compounds a fluorescer is not required but may be used to shift the wavelength of emitted light toward the red region of the spectrum so as to change the color of emitted light. Fluorescent compounds for use with oxalic-type chemiluminescent compounds should be soluble in the reactive solvent at least to the extent of 0.0001 moles per liter.

Typical suitable fluorescent compounds for use in the present invention are those which have a spectral emission falling between 330 millimicrons and 1,000 millimicrons and which are at least partially soluble in any of the above diluents, if such diluent is employed. Among these are the conjugated polycyclic aromatic compounds having at least three fused rings, such as anthracene, substituted anthracene, benzanthracene, phenanthrene, substituted phenanthrene, naphthacene, substituted naphtharene, pentacene, substituted pentacene, and the like. Typical substituents for all of these are phenyl, lower alkyl, chlorine, bromine, cyano, alkoxy (C_1-C_{16}), and other like substituents which do not interfere with the light-generating reaction contemplated herein.

Numerous other fluorescent compounds having the properties given hereinabove are well known in the art. Many of these are fully described in "Fluorescence and Phosphorescence," by Peter Pringsheim, Interscience Publishers, Inc., New York, New York 1949. Other fluorescers are described in "The Color Index," Second Edition, Volume 2, The American Association of Textile Chemists and Colorists, 1956, pp. 2907—2923. While only typical fluorescent compounds are listed hereinabove, the person skilled in the art is fully aware of the face that this invention is not so restricted and that numerous other fluorescent compounds having similar properties are contemplated for use herein.

A fluorescent oxalic-type ester, such as the oxalic acid ester of 2-napthol-3,6,8-trisulfonic acid, does not require a separate fluorescent compound to obtain light. Other typical fluorescent oxalic acid esters include esters of oxalic acid (1) 2-carboxyphenol, (2) 2-carboxy-6-hydroxyphenol, (3) 1,4-dihydroxy-9,10-diphenylanthracene, and (4) 2-naphthol. Thus, a reactant including a fluorescent oxalic-type ester would thereby include at least one fluorescent compound.

It has been found that the molar (moles per liter of diluent) concentrations of the major components of the novel composition herein described may vary considerably. It is only necessary that components be in sufficient concentration to obtain chemiluminescence. The ester of oxalic acid molar concentration normally is in the range of at least about 10^{14} to 5 molar, preferably in the range of at least about 10^{13} to about 1 molar; the fluorescent compound is present in the range from about 10^{15} to 5, preferably 10^{14} to 10^{11} molar and the diluent must be present in a sufficient amount to form at least a partial solution of the reactants involved in the chemiluminescent reaction. If the ester is liquid, it may serve as either the sole diluent or a partial diluent.

The ingredients of the composition of this invention may be admixed in a single stage of admixing or in a sequence of steps of admixing the separate ingredients.

The wavelength of the light emitted by chemiluminescence of the compositions of this invention, i.e., the color of the light emitted, may be varied by the addition of any one or more energy transfer agents (fluorescers) such as the known fluorescent compounds discussed at length above.

The wavelength of the light emitted by the composition of this invention will vary, depending upon the particular fluorescent component employed in the reaction.

Additionally, it has been found that the superior intensity of chemiluminescence is obtained when the final mixture producing the luminescence is maintained at a temperature of between about −40° C. and 75° C., preferably between about 20° C. and 50° C. However, temperature is not critical and the luminescence of Applicant's process is not limited to these ranges.

The lifetime and the intensity of the chemiluminescent light obtained with the preferred oxalic-type chemiluminescent compounds of this invention can be regulated by the use of certain regulators such as:

1. By the addition of base to the chemiluminescent composition. Both the strength and the concentration of the base are critical for purposes of regulation.

2. By the variation of hydroperoxide. Both the type and the concentration of hydroperoxide are critical for the purposes of regulation.

3. By the addition of water.

4. By the addition of a catalyst which changes the rate of reaction of hydroperoxide with the oxalic-type ester. 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 those accelerators of copending

application, Ser. No. 577,595, now abandoned, and decelerators of copending application, Ser. No. 577,615, now abandoned.

While acids are not in general accelerators for oxalic-type chemiluminescent reactions it should be noted specifically that acids are accelerators for the oxalic amide chemiluminescent compounds of copending application, Ser. No. 547,782, now abandoned.

More specifically, the advantages obtained by the corporation of a catalyst of Ser. No. 577,595 may be obtained in conjunction with the objects of this present invention, by employing, according to the copending application, an ionized salt having a cation selected from (a) an organic quaternary cation selected from the group consisting of ammonium, arsenic and phosphorous, and (b) alkali metal having an atomic weight above 22, the salt of said cation preferably being soluble in an organic solvent and preferably being characterized by a property of forming cation-aggregates when reacted with the oxalic-type ester and a hydroperoxide. One of the advantages is the fact that an excessive amount of the chemiluminescent agent may be employed whereby a higher quantum yield may be obtained when the ionized salt is employed, in contrast to systems not employing the accelerator whereby such systems would be limited to a much lower maximum concentration of chemiluminescent agent which would continue to increase rather than decrease the total quantum yield of chemiluminescent light.

Similarly, within the scope of the present invention is the concurrent employment of one or more decelerators either alone in the composition of this invention, or in conjunction with one or more of the accelerators discussed in the preceding paragraphs. By employing one of the accelerators of the preceding paragraph, it would be possible to employ a greater total concentration of the chemiluminescent agent while concurrently it would be possible to employ a decelerator which would prolong the period during which the light of high intensity is obtained from the chemiluminescent reaction. Such decelerators set forth in the copending application, Ser. No. 577,615, now abandoned, include for example a compound such as oxalic acid.

When oxalate-type chemiluminescent compounds are used in a solution component it may be desirable to include a stabilizing agent such as those described in copending application, Ser. No. 614,397.

The chemical compounds, components and their reactions for providing chemiluminescent light are described in copending, commonly assigned applications, Ser. Nos. 442,802, now U.S. Pat. No. 3,329,621; 442,818, now Pat. No. 3,425,949; and those previously mentioned, and as such they do not form a part of the present invention.

In this invention, the reactive components are stored in a multiple compartment container device having a minimum of two compartments, wherein the separate components may be brought into contact to produce the reaction which provides chemiluminescent light to be displayed in said container. When either the chemiluminescent compounds, hydroperoxide, or both are fluid, they must be in separate compartments. The diluent and fluorescent compounds can be in either of these two compartments. If the chemiluminescent compounds, hydroperoxide and fluorescent compounds are dry powdered solids, they may be kept together in one compartment with the diluent in the other compartment. The components in each compartment are brought together by pressure on the outer tube to break the inner container, and the combined components may be dispensed as a chemiluminescent light mixture or used as a source of light in the transparent container. The light mixture may be dispensed directly from the container onto any surface by means of the closure in one end of the outer tube, thus providing visible light on the surface.

The invention may be better understood by reference to the drawings in which FIG. 1 shows one outer flexible tube for one embodiment of the chemiluminescent light device, with a screw cap closure and a rigid inner tube. FIG. 3 shows one embodiment of the device with a sealed, tear tip closure. FIG. 4 shows a friction fit cap for the break tip of FIG. 2.

Referring to FIGS. 1 and 2, the device comprises a flexible tube 1 party threaded at 2 to receive a threaded cap 3 to close opening 4 of tube 1. The opposite end of tube 1 is sealed at 5 by a heat seal or other suitable means. A sealed inner, rigid tube 6 contains one chemiluminescent component, such as a hydrogen peroxide solution and a fluorescer. Tube 1 is filled with the other component of the chemiluminescent system, previously described, for example the chemiluminescent compound in a diluent.

Tube 1 is a flexible transparent or translucent material, having sufficient rigidity to maintain a shape, but sufficiently thin to be readily flexible, such as low density polyethylene; high density polyethylene; Teflon FEP®Nylon 6; Nylon 6,6; Nylon 6,10; polyester; polyacrylonitrile; polyvinylidine fluoride; polypropylene; and the like.

It will be clear to those skilled in the art that blends and laminates of the above can be used.

The thickness of the tubing will be from about 10 to 30 mils depending on the material. Polyethylene (low density) is preferred with a thickness of from about 15—20 mil.

Tube 6 may be a rigid, breakable or frangible material such as glass, or a relatively brittle thermoset resin, e.g., thin wall bakelite or other suitable material and need not be transparent or translucent.

Alternatively tube 6 may be a rupturable pod formed from any of the plastics used for tube 1. If tube 6 is of the same material as tube 1, it is preferably of less thickness so as to rupture readily under pressure. The pod 6 may be heat sealed, or sealed by any other suitable means. In addition, pod 6 could be aluminum foil, or a laminate of polyethylene and aluminum foil, the aluminum foil being on the outer side. It will therefore be obvious that pod 6 can be of any material, so long as it is inert to the solution put in it, and to the solution in tube 1. While the wall areas of tube 1 are fairly thin, so as to be flexible as pointed out previously, the closure area is somewhat thicker for the threaded and breakoff tip types. Tube 1 could be molded so as to produce an integral thicker tip. On the other hand, tube 1 could be made from sections of extruded tube and separate molded tips which are heat sealed to the tubular section.

To activate the device and provide light, tube 1 is flexed sufficiently to break tube 6, allowing its contents to admix with that of tube 1 to bring about the chemiluminescent reaction and to obtain a chemiluminescent light mixture within tube 1 and provide chemiluminescent light emission visible through tube 1. The device may thus be used in this form as a source of light. If desired, cap 3 may be removed and some or all of the light mixture may be dispensed through opening 4 to provide a glowing mark on any surface. In the device shown in FIG. 2, opening 4 is within a breakoff tip breakable at a scored point 7 for example. The inner container can be a heat sealed pod 6, sealed into the seal 5 of tube 1. A friction fit cap 8 may be used for the breakoff tip, as shown in FIG. 4.

As shown in FIG. 3, the dispensing end of tube 1 may also be heat sealed as shown at 9. This is done in such a manner that a dispensing nozzle area 4 remains. A notch 10 is sealed area 9 makes it possible to tear tube 1 along the line represented by chain line A–A, thus providing the dispensing nozzle at 4.

Caps 3 and 8 may be formed of any plastic or other material inert to the chemiluminescent solutions.

The device may have more than one breakable tube 6, so that more than two chemiluminescent components may be kept separated. Such a system is useful where rate regulators such as acidic or basic materials may be used in the reaction.

The color of the light emission will depend on the type of fluorescent compound and its spectral response. However, the visible color could be varied by using a colored plastic for tube 1.

The invention provides a device for providing visible light whenever and wherever desired, independent of conventional electrical lighting methods and without the hazards and limitations of electrical lighting. The chemiluminescent lighting systems can be especially useful in emergency situations where all other forms of lighting have failed. The systems do not have the fire of ignitable lighting devices such as candles, gas, or oil lights.

It will be readily apparent that the chemiluminescent device is not confined to emergency lighting, however. It can be used at any time where a cold, safe illuminating means is desired. It is also useful to provide illumination where electrical illumination is unavailable. The device is highly portable and can be hand held for signalling.

While certain specific embodiments and preferred modes of practice of the invention have been describe, it will be understood that this is solely for illustration, and that various changes and modifications of the invention may be made without departing from the spirit of the disclosure or the scope of the appended claims.

I claim:

1. A chemiluminescent light device comprising an outer flexible, light transmitting tube means and a sealed inner breakable tube means enclosed within said outer tube means, a chemiluminescent component in each of said tube means, said outer tube being sealed at one end, and dispensing closure means the other end of said outer tube; said components being capable of reaction upon admixture to provide chemiluminescent light.

2. The device of claim 1, wherein said inner tube means comprises more than one tube.

3. A device of claim 1, wherein the closure means for the outer tube means comprises an opening and a removable cap therefor.

4. The device of claim 3, wherein said cap is threaded.

5. The device of claim 3, wherein said cap is a friction fit.

6. The device of claim 1, wherein said closure device is a heat sealed tear spout.

7. The device of claim 1, wherein said closure device is a sealed breakoff tip.