

FIG. 1 FIG. 2 FIG. 3 FIG. 4

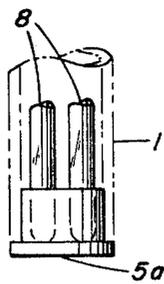


FIG. 5

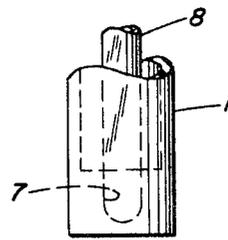


FIG. 6

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CHEMICAL LIGHTING DEVICE TO STORE, INITIATE AND DISPLAY CHEMICAL LIGHT

This application is a continuation-in-part of our previous application Ser. No. 674,296, filed Oct. 10, 1967, now abandoned.

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 flammable 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.

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 of a multicomponent chemiluminescent system. The device consists essentially of an elongated, transparent or translucent flexible outer tube and a ridged, breakable inner tube which runs parallel to the outer tube and which preferably is joined to the outer tube, or relatively fixed at its ends with respect to the inner 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 capped at both ends with a closure which may contain a recess which fits around the inner tube to hold it in place and which, if desired, may serve as a closure for at least one end of the inner tube. Alternatively, the inner tube may be sealed separately and attached to the outer tube at the ends or along the longitudinal side in any convenient way.

To operate the device, the outer, flexible tube is bent causing the inner inflexible 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.

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, which is hereby incorporated by reference, (2) an oxalic-type amide of the type disclosed and claimed in copending applications, Ser. Nos. 520,052 and 547,782, which are hereby incorporated by reference, (3) an oxalic-type O-acyl-hydroxylamine of the type disclosed and claimed in copending application, Ser. No. 547,761, and (4) an oxalic-type ester disclosed and claimed in application, Ser. No. 491,896, 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. 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-phthalimidyl oxalate. The preferred subspecies is bis(pentachlorophenyl)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} molar, preferably about 2 molar down to

about 10^{12} 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, dibutyl-diethyleneglycol, 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 naphthacene, pentacene, substituted

pentacene, and the like. Typical substituents for all of these are phenyl, lower alkyl, chlorine, bromine, cyano, alkoxy (C_1-C_{10}), 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, N.Y. 1949. Other fluorescers are described in "The Color Index," Second Edition, Vol. 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 fact 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-naphthol-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 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 5°C . However, temperature is not critical and the luminescence of Applicants' 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, and decelerators of copending application, Ser. No. 577,615.

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.

More specifically, the advantages obtained by the incorporation 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 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, 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; 442,818, 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 reactive components are brought together to provide chemiluminescent light.

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,

FIG. 2 shows the inner, rigid tube,

FIG. 3 shows one embodiment of an assembled device,

FIG. 4 shows the method of activation of the device.

Referring to FIGS. 1 and 2, the device comprises a flexible tube 1 partly threaded at 2 to receive a threaded plug 3 to close opening 4 of tube 1. A second plug 5 is provided to close opening 6 at the opposite end of tube 1 by a press fit. Both plugs 3 and 5 have a bore 7 for receiving a tube 8 of a rigid, breakable material.

In FIG. 3, the assembled device is shown, with tube 8 fitted in plugs 3 and 5, which are in turn fitted into openings 4 and 6 of tube 1, holding tube 8 substantially parallel to the longitu-

dinal axis of tube 1 and relatively fixed with respect to the ends of tube 1. Tube 8 is filled with one component of the chemiluminescent system, previously described, for example the chemiluminescent compound in a diluent.

Tube 1 is filled with the second component, described previously, such as a hydrogen peroxide solution and a fluorescent compound.

Tube 1 is a flexible, transparent or translucent material, having sufficient rigidity to maintain a shape, such as polyethylene, polypropylene, teflon and the like. Tube 7 is a rigid, breakable or frangible material such as glass, or a relatively brittle thermoset resin, e.g., thin walled bakelite or other suitable material and need not be transparent or translucent. Plugs 3 and 5 may be any suitable material such as plastic or wood. Plastics are particularly suitable in view of their ease of fabrication.

To activate the device and provide light, tube 1 is flexed slightly as shown in FIG. 4. Tube 7, which is rigid, has its ends fixed in parallel relation to plugs 3 and 5 in recesses 7 is bent and broken at a number of points 9 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.

As shown in FIG. 5, the device may have more than one breakable tube 8, 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.

It will be obvious that the construction of the inventive device may be varied so long as the basic requirements are maintained. For example, tube 8 could be open at one end and a recess 7 could be the means for closing it. In addition, one end of tube 1 could be molded closed with a recess 7 as shown in FIG. 6. Moreover, tube 8 could be fitted within tube 1 in any suitable manner, so long as its ends are relative fixed with respect to the ends of 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 described, 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.

We claim:

1. A chemiluminescent light device comprising an outer flexible, light transmitting tube means and an inner rigid, breakable tube means, substantially coextensive with said outer tube means, a chemiluminescent component in each said tube means, means to close said tube ends, and means to maintain said inner tube means relatively fixed with respect to said outer tube means.

2. The device of claim 1 comprising a pair of concentric tubes.

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

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4. The device of claim 1 wherein the means for closing the outer tube means comprise plugs fitted to the ends thereof.
5. The device of claim 4 wherein said plugs are provided

with recesses into which the ends of the inner tube means fit.
6. The device of claim 5 wherein said recesses comprise the closing means for the ends of the inner tube means.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,576,987 Dated May 4, 1971

Inventor(s) Heinz Kurt Walter Voight and Robert Lee Myers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 46 delete " $1.3 \times 10 \text{ahl}^{10}$ " and insert -- 1.3×10^{-10}

Col. 2, line 75 delete " 10^{15} " and insert -- 10^{-5} ---.

Col. 3, line 1 delete " 10^{12} " and insert -- 10^{-2} ---.

Col. 4, line 31 delete " 10^{14} " and insert -- 10^{-4} ---.

Col. 4, line 32 delete " 10^{13} " and insert -- 10^{-3} ---.

Col. 4, line 34 delete " 10^{15} " and insert -- 10^{-5} ---.

Col. 4, line 34 delete " 10^{14} " and insert -- 10^{-4} ---.

Col. 4, line 34 delete " 10^1 " and insert -- 10^{-1} ---.

Col. 4, line 52 delete " 20°C. " and insert -- -20°C. ---.

Col. 4, line 52 delete " 5°C. " and insert -- 50°C. ---.

Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents