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CHEMILUMINESCENT PERAMINOETHYLENE POSITIONED
WITHIN A BRITTLE CAPSULE
Original Filed Sept. 23, 1965

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Fig. 1.

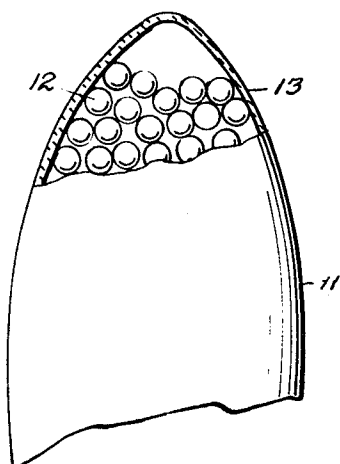


Fig. 2.

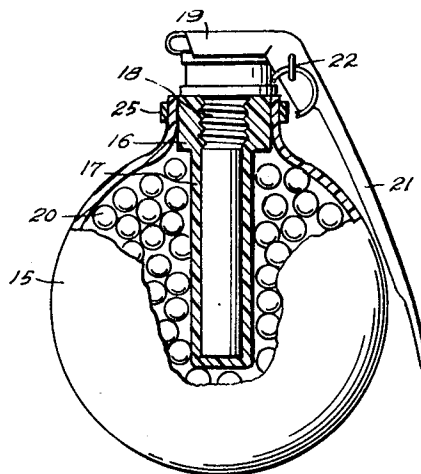
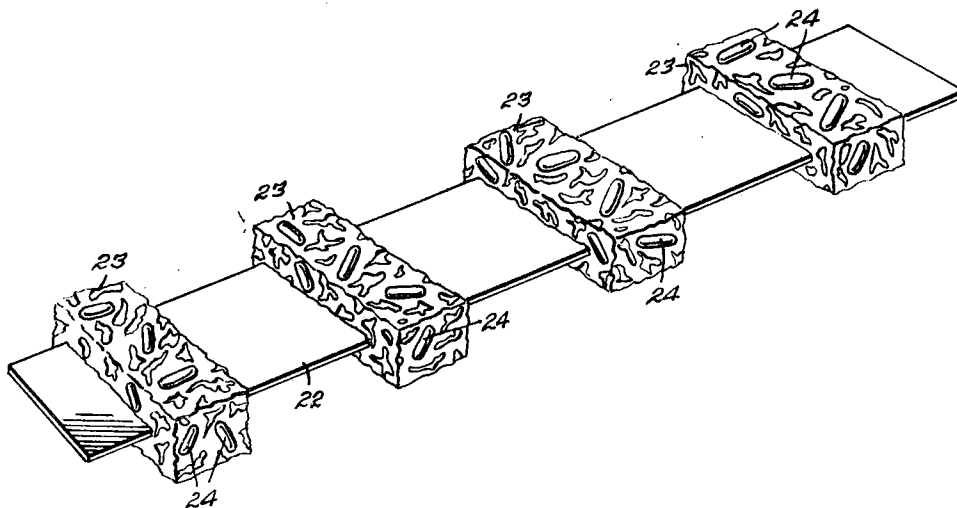


Fig. 3.



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3,515,070

CHEMILUMINESCENT PERAMINOETHYLENE POSITIONED WITHIN A BRITTLE CAPSULE

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Continuation of application Ser. No. 490,780, Sept. 23, 1965. This application May 15, 1968, Ser. No. 729,475
Int. Cl. F42b 13/36, 13/40, 27/00
U.S. Cl. 102—60

4 Claims

ABSTRACT OF THE DISCLOSURE

A chemiluminescent marker having a brittle air-impermeable capsule containing a chemiluminescent peraminoethylene therein, whereby on the application of a stress of brittle capsule shatters thereby releasing the chemiluminescent peraminoethylene material.

This application is a continuation of application 490,780, filed Sept. 23, 1965, now abandoned.

The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention relates to improvements in chemiluminescent materials and their applications in light-emitting devices. More particularly, it relates to a novel chemiluminescent marker of improved stability and capable of instant activation to produce a visible glow at night.

Highly reactive compounds such as the peraminoethylenes display the unusual property of emitting blue-green light when oxidized by air. This fluorescence phenomenon is observed even when traces of air come in contact with these compounds. In view of this reactivity, the prospects of storing, handling or incorporating them in marker devices were very limited considering the effort which would be required to preserve them in sealed containers and to handle them in an inert atmosphere.

This invention utilizes the chemiluminescent peraminoethylenes in a form which safeguards them from air oxidation and other unwanted chemical action, thus obviating previous requirements for sealed containers and inert atmospheres. Furthermore, the invention not only enables these highly reactive compounds to be handled and stored with considerable ease, but it also provides a stable filler which may be variously utilized as a light source by restoring it to full luminescent reactivity at the command of the user.

The present chemiluminescent marker may find substantial utility alone or in combination with various devices which are made luminiferous or even visible at night. The marker may be applied to rescue work and employed in field and aerial operations during warfare. In the present more stable and inert form, chemiluminescent materials are now utilized as fillings for munitions or projectiles in which said materials are propelled on distant terrain and activated upon impact to become a luminescent marker to help guide other projectiles and missiles on a visual target.

It is therefore an object of the present invention to provide chemiluminescent compounds and compositions in a chemically resistant form but which can be readily activated to resume their light-emitting property.

Another object of the invention is to provide a novel filling for projectiles and other munitions to project, disseminate and activate said filling as a luminescent marker.

A further object is to provide a trail marker which is set into operation by an unsuspecting intruder.

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A still further object is to provide a luminescent marker for air drops at night, in which said marker is initially inactive but which becomes actively luminescent at the time of use.

These and other objects and advantages of the invention may best be understood from the following description reference being had to the accompanying drawing wherein:

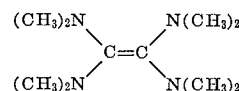
FIG. 1 shows the forward portion of a projectile partly in section to expose the novel filling therein which becomes a luminescent marker after the projectile has been fired and delivered;

FIG. 2 is an elevation view of a hand grenade partly in section to expose the chemiluminescent marker; and

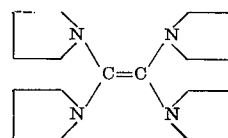
FIG. 3 is a perspective view of a novel marker showing a plurality of chemiluminescent strips.

Chemiluminescent compounds and compositions are now provided according to this invention in the form of an air-impermeable capsule protected from air-oxidation by a suitable encapsulating or shell material. The peraminoethylenes, which are exemplified by the following liquids of high chemiluminescent reactivity:

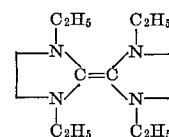
Tetrakis (dimethylamino) ethylene, structurally represented by



Tetrakis (N-pyrrolidiny) ethylene, structurally represented by



and 1,1'-3,3'-tetraethyl-Δ^{2,2'}-bi (imidazolidine), structurally represented by



are encapsulated by a shell of polymer or a gel-forming material, said shell being characterized by low oxygen permeability and complete inertness to the enclosed liquid. A polymeric material which may be used for this purpose is polyvinyl alcohol (PVA) being both an effective oxygen barrier and chemically inert to the peraminoethylenes and their oxidation products. Gelatin is also effective as the shell wall as long as water and high humidity are avoided. Water resistance and other properties of a gelatin capsule can be further improved by applying a surface coating on the dry capsule. Additionally, a chemical treatment of capsules has been found advantageous to increase brittleness whereby the capsules may be crushed more easily.

The encapsulation of a reactive liquid, such as tetrakis (dimethylamino) ethylene and solutions thereof in mineral oil sold under the trademark Nujol are effectively protected against air when PVA was used as the shell material and hardened by air material. The capsules produced are free-flowing and are substantially free of liquid exudation even under long term storage. The capsules can be left standing in air without loss of activity as evidenced by their luminescence on crushing.

Various encapsulating techniques known in the art may be employed to form the capsules of the present inven-

tion. Encapsulation may be achieved, for example, by machinery which passes gel ribbons between a set of heated dies that clamp the ribbons together to form a bag. The liquid is fed from a tube directly into the bag, and the filled bag is then clamped by another set of dies that form the bag into spheres. In effect, two hemispheres of gel ribbons are heat sealed around a droplet of liquid.

Another encapsulation process that has been found suitable for the production of the present capsule provides for a simultaneous extrusion of a solution of the polymer and the fill liquid through outer and inner concentric orifices, respectively, the polymer solution surrounding and encapsulating the fill liquid. The capsules are then allowed to fall through a hot gas tower to dry the capsular wall. Alternately, the capsules may be gelled or hardened in a coagulating bath which is then followed by rinsing and drying. This technique is described in detail in "Basic Studies of the Southwest Research Institute Encapsulation Process" by F. E. Massouth, W. E. Hensel, Jr., and W. W. Harlowe, Dec. 30, 1962, Southwest Research Institute, San Antonio, Tex.

Capsules containing chemiluminescent peraminoethyl- enes may be prepared in various sizes and shapes. Smaller encapsulated forms have been prepared in the range of 500-1680 microns in diameter. Larger capsules up to $\frac{3}{16}$ inch diameter have also been prepared utilizing longer drying towers and improving the rate of hardening the polymer. Larger capsules may be prepared from coagulating baths whereby the polymer may be hardened more readily. A coagulation bath which is most effective for hardening PVA and gelatin capsules comprises a cuprammonium hydroxide treating bath. The treating solution is prepared from 5 parts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 24 parts concentrated ammonium hydroxide, 1.6 parts sodium hydroxide and 14.6 parts of water by weight. Capsules left in the coagulating bath for a few minutes will produce cross linking resulting in a hardened, insolubilized capsular wall.

Thus, the cuprammonium hydroxide treatment may be used to impart brittleness to capsules whenever ease of crushing is desired. As will be mentioned later in the specification, specific applications of the encapsulated marker require a more brittle type capsule which can be readily crushed or broken when stepped upon or when dropped from a certain height. The coagulation and consequently hardening of the capsular wall may be modified by varying the concentration of the sodium hydroxide in the bath solution, decreasing the concentration of sodium hydroxide therein or diluting said solution will cause a decrease in the rate of hardening.

The cuprammonium hydroxide bath hardens a relatively thin skin surrounding the capsules, leaving the remainder of their capsular wall in a relatively fluid state. If the capsules remain stationary in the hardening bath and during drying, the liquid filler will penetrate some parts of the fluid wall leaving a part of the capsular wall extremely thin and relatively weak. This off-centering of the capsules may be avoided by agitating them in the hardening bath and by tumble-drying them following the bath treatment.

Soft gelatin capsules of the type used in preparing pharmaceutical products may also be employed for encapsulating the present chemiluminescent compounds. Capsules of $\frac{1}{4}$ inch or more can be prepared from a gelatin composition containing glycerine and water. For maximum storage stability the dry gelatin wall should have a thickness of about 7.5 mils or more. Increases in thickness result in more resistant capsules, but the capsules become more difficult to crush. Gelatin capsules filled with active chemiluminescent liquid are sufficiently stable; light emissions are not observed in these capsules, even after 5 months of storage. When the capsules were opened the liquid filler was still active and emitted light for a considerable time.

Improved brittleness and ease of crushing can be achieved in gelatin capsules by maintaining the glycerine

content and wall thickness as low as possible. Soft gelatin capsules are obtained from a composition containing 39.75% gelatin, 25.75% glycerine and 34.50% water by weight. Capsules of medium hardness are obtained from a composition containing 41.50% gelatin, 22.50% glycerine and 36.00% water. A considerably harder capsule will be provided in a composition of 45.00% gelatin, 16.00% glycerine and 39.00% water by weight.

As noted previously, brittleness in capsules may be achieved by coagulating baths. Gelatin capsules treated in a cuprammonium hydroxide solution become more brittle and are more easily crushed. Gelatin capsules may be surface coated by shellac or other resin to become resistant to water and high humidity atmospheres. Several coatings may be applied until a high water resistance is obtained. Shellac-coated capsules which had received at least four individual coatings of white shellac and had been dried thoroughly after each coating displayed no swelling when they were allowed to soak in water for more than 4 hours.

In applying the present encapsulated compounds to various emergency situations and to military use, rescue workers and service personnel may handle the present chemiluminescent compounds and compositions as an inert filler to be loaded into or combined with munitions, signaling devices, visible targets, air drops, etc. A target area may be conveniently designated and pin-pointed by means of the present marker. Emergency landing areas may be marked and visibly identified without the need for electrical equipment. Air strips may be made to glow along the entire area or landing strips may be outlined at regular intervals with the present marker. The very reactive 1,1',3,3'-tetraethyl $\Delta^{2,2'}$ -bi (imidazolidine) which fumes and chemiluminesces brightly may be used to obtain low-visibility identification of the terrain.

Turning now to the drawing for a clearer explanation of ways in which the invention may be used, there is shown in FIG. 1 the forward portion of a conventional projectile 11 in which capsules 12 of chemiluminescent composition are loaded into the nose section 13 thereof. The nose is formed of a fracturable metallic or ceramic composition which will be shattered to bits on impact. The enclosed capsules will be crushed and released in a relatively small area, thus the high concentration of active capsules will produce a vivid glow in the target area. If less brittle capsules are employed, they may survive the impact, in which case their activation will be delayed and luminescence will be initiated over a longer period of time.

In the embodiment shown in FIG. 2, a hand grenade 15 is provided with a detonator or burster (not shown) which explodes and scatters capsules 20 over a wider area. The grenade is formed of a rubber bulb 15 into which circular head 16 of a closed cylindrical well 17 is inserted and bound tightly by hand 25. A burster, such as the M201A1, is inserted in well 17 and screwed into the threaded portion 18 of the head. The closed well isolates the burster from possible contamination of a leaking capsule. The grenade is kept safe in handling by the safety pin 22 which holds the lever 21 in place. The grenade is activated by grasping the bulb and lever together in one hand removing the safety pin; as the grenade is thrown the lever flies off lifting cover plate 19 which activates the firing mechanism (not shown). The detonation will break up the capsules thus disseminating active chemiluminescent material.

In a further embodiment, a streamer or ribbon marker may be provided, such as the one shown in FIG. 3. Streamers of folded cloth, felt pads, gauze, cellulose foam and the like are provided with capsules of chemiluminescent material retained in the structure. The capsules may be retained by folding them in cloth strips, sewing them into pockets or by putting into foamy layers. In the illustrated embodiment, a plurality of rectangular foamy sections 23 are slitted to form convenient mounting means

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on strip 22. Potted in each foam are capsules 24 containing chemiluminescent liquid. The capsules are broken by striking or exerting pressure on the foam; the liquid released saturates the foam thus providing a large concentration of chemiluminescent material. Capsules placed in polypropylene felt may be strung at intervals on streamers. These streamers may then be used as parachute bundle markers for air delivery at night. The streamers are tied to the bundle and the capsules are broken prior to release from the aircraft.

From the foregoing, it will be apparent that the present invention provides an improved chemiluminescent marker which is a convenient filler for munitions and in perimeter defense. The marker may be sown on the ground and remains inert until stepped upon. Signaling and identification devices may be conveniently formed and stored until ready for use.

We wish it to be understood that we do not desire to be limited to the exact ingredients or manner of utilization shown and described, in that obvious modifications will occur to a person skilled in the art.

We claim:

1. A projectile including in a fractionable cone section thereof, brittle, air-impermeable capsules composed of a material selected from the group consisting of polyvinyl alcohol and gelatin, said capsules containing therein a chemiluminescent peraminoethylene.

2. A hand grenade comprising a casing, a well positioning a detonator therein, firing means in association with said detonator, brittle, air-impermeable capsules positioned in said casing, said capsules containing therein a chemiluminescent peraminoethylene therein, a lever

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holding said firing means away from said detonator and a safety pin for holding said lever in the locked position.

3. A chemiluminescent marker comprising a porous fabric strip, a plurality of brittle, air-impermeable capsules positioned in said strip, said capsules containing therein a chemiluminescent peraminoethylene.

4. A chemiluminescent marker comprising a brittle, air-impermeable capsule composed of a material selected from the group consisting of polyvinyl alcohol and gelatin, having a chemiluminescent peraminoethylene contained therein selected from the group consisting of tetrakis (dimethylamine) ethylene; tetrakis (N-pyrrolidiny) ethylene, and 1,1',3,3'-tetraethyl 1- $\Delta^{2,2'}$ -bi (imidazolidine).

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102—64; 252—301,2