United States Patent [19]

Griffith et al.

[11] **3,835,782**

[45] **Sept. 17, 1974**

[54] **PRODUCT AND METHOD**

[75] Inventors: **George L. Griffith**, Coopersburg; **Donald W. Edwards**, Lehighton, both of Pa.

[73] Assignee: **Commercial Solvents Corporation**, New York, N.Y.

[22] Filed: **Sept. 22, 1972**

[21] Appl. No.: **291,171**

[52] **U.S. Cl.** ..... **102/27 R**

[51] **Int. Cl.** **C06c 5/04**

[58] **Field of Search** 102/27

[56] **References Cited**

UNITED STATES PATENTS

3,474,730	10/1969	Sheeran	102/27
3,712,222	1/1973	Richardson et al.	102/27

Attorney, Agent, or Firm—Morton, Bernard, Brown, Roberts & Sutherland

[57] **ABSTRACT**

An explosive device including means permitting identification of the explosive source or manufacturer even following detonation, and a method of identifying the source or manufacturer of an explosive device even after detonation thereof. A luminescent material is added to the explosive device having a non-thermal emission of electromagnetic radiation upon excitation which uniquely identifies the source or manufacturer of the explosive. The luminescent material may be pulverized and mixed with the explosive material within the device. Alternatively, the luminescent material may be added to the exterior of the explosive device. Following detonation of the explosive device, the area around the detonation is activated or excited, and the luminescent material is identified from the resulting luminescent radiation.

23 Claims, No Drawings

PRODUCT AND METHOD

The present invention pertains to explosive devices. More particularly, the present invention pertains to a method of identifying the source of explosive devices even after detonation of the explosive and to explosive devices including means enabling identification of the source of the explosive even after detonation thereof.

Explosive devices are often used in illegal manners to harm, and even kill, persons, to damage property, for instance, to make openings in buildings, permitting unlawful access to property, and the like. Following such explosions, the police and other authorities must attempt to identify the responsible persons. If the source of the explosive device can be determined, this frequently aids in identifying and apprehending the responsible persons. Generally, such explosions are of a strength which essentially completely destroys the explosive device, including both the explosive material and its container. Consequently, little or no identifiable evidence is available from which the source of the explosive device can be determined.

In one aspect, the present invention is a method of identifying the source of an explosive device utilized in an explosion after detonation of that explosive. In another aspect, the present invention is an explosive device incorporating a luminescent material which, following explosion of explosive device, enables its detection through luminescent radiation. Different manufacturers or sources of explosive devices can thus incorporate luminescent materials which emit different electromagnetic wavelengths so that, by identifying the wavelength of the luminescent radiation, the manufacturer or source of the explosive can be identified.

Upon excitation, luminescent materials emit visible or invisible electromagnetic radiation unaccompanied by high temperatures. The excitation of the materials may be by other electromagnetic radiation, by charged particles, or by chemical change. Most commonly, luminescent materials which are excited by electromagnetic radiation, particularly ultraviolet radiation (long wave and short wave) are employed. Generally, luminescent materials are fluorescent, that is, materials from which emission of luminescent radiation stops upon cessation of supplying the excitation energy, or phosphorescent, that is, materials from which emission of luminescent radiation continues for at least about 10^{-8} second after the source of excitation is removed. Luminescent radiation is generally a narrow bandwidth radiation such that upon excitation not only the presence of a luminescent material, but also usually the identity of the material can be ascertained. Often the luminescent radiation is in the infrared, visible, or ultraviolet portion of the electromagnetic radiation spectrum. Often, with luminescent materials which provide a visible emission, the unaided eye can detect and identify the material. With invisible radiations from such luminescent materials, instruments are required for detection and identification.

Luminescent materials may be crystalline or liquid; however, crystalline materials are preferred for application in the present invention. Normally liquid phase luminescent materials may be employed by, for instance, coating a particulate substrate material with the liquid. The luminescent materials may be inorganic or organic and may occur naturally or may be synthetically produced. Admixtures of luminescent materials

may be employed. Such admixtures may, for instance, have luminescent materials which respond to different forms of excitation energy, for example, one material may be excited by ultraviolet radiation and another material may be excited by infrared radiation. Also, an admixture may contain two or more luminescent materials which respond to essentially the same form of excitation energy. Thus, if one component is masked by the surroundings, another component may still be identifiable and the manufacturer of the explosive device can be ascertained. The use of two or more luminescent materials may also provide more flexibility and combinations to assist in the marking and identification of explosives.

Exemplary of luminescent material operable in this invention are naturally occurring luminescent materials including scheelite ($CaWO_4$), willemite (Zn_2SiO_4), calcite ($CaCO_3$), scapolite ($(Na_2Ca)_4Al_3$ $(Al_2Si)_3$. $Si_6O_{24}(Cl, Co_3, SO_4)$), sphalerite (ZnS), rhodochrosite ((Fe, Cs, Mg, Zn) $MnCO_3$) and other naturally occurring fluorescent oxides, halides, carbonates, and the like. Synthetic samples of these naturally occurring materials and other combinations may be prepared and may fluoresce when properly doped with selected impurities. Examples of synthetic luminescent materials are strontium orthophosphate, calcium halophosphate, zinc sulfide, zinc sulfide-cadmium sulfide, and the like provided with proper activator metals. Activator metals which have been employed are, for example, tin, antimony, manganese, the rare earths such as europium, yttrium, cerium, samarium, etc., and the like. Other inorganic luminescent materials are derived from the rare earths. For example, samarium nitrate, dysprosium nitrate, and the like. Solid organic compounds such as stibene, naphthalene, anthracene, and phenanthrene exhibit luminescent properties as do some organic dyes and the like. The luminescent material should be selected such that it achieves or retains luminescent properties after detonation of the explosive. High temperature explosives generally require more stable luminescent materials than explosives providing less severe conditions, when the luminescent material is admixed with the explosive material. If the explosive material is provided on the explosive device, for instance, in the label, thermal stability is less of a concern.

In accordance with the present invention, luminescent material is incorporated in the explosive device by, for instance, admixing it with the explosive material or incorporating it into or coating it on the material employed for the container of the explosive charge. For instance, the luminescent material can be deposited on the exterior of the explosive device container by, for example, sprinkling the luminescent particles onto the container which has previously been coated with an adhesive such as clear polyurethane. The luminescent material may be admixed with, for instance, molten wax into which the explosive is dipped to form a container. Plastic explosive device containers may be formed with luminescent particles therein. Further, the luminescent material may be incorporated into the ink with which markings on the explosive device label are printed.

The amount of luminescent material should be sufficient to result in the presence of detectable luminescent material subsequent to detonation of the explosive device. Generally, when detecting traces of the luminescent material by the unaided eye, the luminescent

material should be provided in an amount generally less than about 2, for sake of convenience, preferably at least about 0.025, more preferably 0.05 to 1, percent by weight. The amount required depends upon several factors, for example, the intensity of the luminescent radiation, the particle size, the number of particles in the explosive device, the strength of the explosive device, where the luminescent particles are incorporated in the explosive device and how they will be distributed upon detonation, and the like. Thus, less than 0.025 percent luminescent material may be sufficient for a low powered explosive device whereas greater than 2 percent luminescent material may be required when employing a high energy explosive. Generally, when the luminescent material is provided on the explosive container in, for example, a printed label, or when the material is incorporated in the explosive container, less luminescent material will be required than if it is in admixture with the explosive powder. For instance, concentrates as low as about 0.01 or less weight percent luminescent material may be operable. Other means of luminescent particle detection and identification may require different relative amounts of luminescent particles.

The luminescent material should be provided in a particle size sufficiently large that detection and identification can be made. When employing visual means of detection, generally, the average particle size of the luminescent material after detonation should be at least about 40 microns, preferably larger than about 50 microns, in diameter. With larger particle sizes, the number of particles which can be incorporated into the explosive device is limited. Generally, the luminescent material should have an average particle size of less than about 2000, preferably less than 1000 or 800, microns in diameter. Easy detection and identification of smaller particle sizes, e.g., about one micron or more, may be possible when employing a detection and identification means other than the unaided eye.

It may be desirable to provide a mixture of large and small particle size luminescent materials to assist the recovering of samples for analysis for identification of the manufacturer of the explosive. For example, a portion of the luminescent material may be of a particle size of about +100 −200 mesh (U.S. Sieve Series). This luminescent material may be visually identifiable by excitation with ultraviolet radiation. Thus after an explosion, the investigating authorities may comb the area with ultraviolet lamps to visually detect the location of the large particle size luminescent materials. The remaining portion of the luminescent material may not be easily visibly detectable or may require other means of excitation. Upon locating the large particle size luminescent material, samples may be collected from surrounding surfaces, and the collected material may be analyzed in a laboratory having the appropriate detection equipment for identifying the manufacturer of the explosive from the luminescent material.

This invention is operable with essentially all explosive devices. Various types of explosives include gaseous, liquid, and solid explosives. The explosives may be of high energy such as ammonium nitrate, dynamites, trinitrotoluene, nitrocarbon nitrates, and the like, or relatively low energy explosives such as black powder. A further discussion of explosives can be found in the *Encyclopedia of Chemical Technology*, Second Edition, Volume 9, pages 581 to 719.

The following examples further illustrate the invention:

EXAMPLE I

A sample of franklinite zinc ore, obtained from Franklin, New Jersey, is comminuted and screened through a 40 mesh screen (U.S. Sieve Series). The iron-containing franklinite particles are removed with a magnet and a ten gram sample of the remaining ore is mixed with only one kilogram of a forty percent ammonium dynamite, nitrostarch base, explosive powder, hereinafter designated as 4OWR powder. A ten gram sample of this mixture detonated in a test cannon (Seiple Test Lab Ballistics Pendulum Cannon). When the cannon is subsequently checked with ultraviolet light, particles of the luminescent material can be visibly detected as light pale green:

EXAMPLE II

Two weight percent of the above ore is admixed with 4OWR powder and formed into one-and-one-fourth inch by eight inch stick of explosive. The stick is then suspended within a clean, empty 55 gallon drum and detonated. Under ultraviolet light, particles of the ore are visibly detected by their light pale green color on pieces of the drum.

EXAMPLE III

About 0.25 weight percent PI phosphor is mixed with sixty percent ammonium, nitrostarch base, explosive powder, herein after referred to as 6OWR powder, and detonated as a one-and-one-fourth inch by eight inch stick in a barrel as in Example II.

PI phosphor is a sulfide-based phosphor obtainable from the United States Radium Corporation. The phosphor can be detected under ultraviolet light. The phosphor is exceptionally fine and more difficult to identify by the visible eye after explosion than is the luminescent material in Examples I and II.

EXAMPLE IV

About 0.5 weight percent PI phosphor is mixed with 6OWR powder and detonated as in Example IV. The results are substantially the same as in Example III.

EXAMPLES V – XI

One weight percent of the following phosphors, obtainable from the United States Radium Corporation, are added to samples of a standard 4OWR powder, and the resulting mix is checked by the naked eye for detection of visible emissions upon excitation of the luminescent material by short and long wave ultraviolet radiation, both before and after detonation as in Example II, with results indicated below:

		SHORT WAVE (ABOUT 1500 to 2600A)		LONG WAVE (ABOUT 3600 to 3700A)	
Ex.	Type	Before Detonation	After Detonation	Before Detonation	After Detonation
V	Radelin Phosphor Zn Silicate; Mn; GS-115	Yes	No	Yes	No

Ex.	Type	SHORT WAVE (ABOUT 1500 to 2600A) Before Detonation	SHORT WAVE (ABOUT 1500 to 2600A) After Detonation	LONG WAVE (ABOUT 3600 to 3700A) Before Detonation	LONG WAVE (ABOUT 3600 to 3700A) After Detonation
Helecon Phosphorescent Pigment					
VI	2304 (zinc sulfide-cadmium sulfide base)	Yes	No	Yes	No
VII	2315 (zinc sulfide-cadmium sulfide base)	Yes	No	Yes	No
VIII	2330 (zinc sulfide base)	Yes	No	Yes	No
IX	2330* (zinc sulfide base)	No	No	No	No
Helecon Fluorescent Pigment					
X	2210	Yes	No	Yes	No
XI	2330**	Yes	No	Yes	No

* Unfired
** Overs From 200 Mesh (USSS) Screening

The inability to detect the luminescent material after detonation is due to the inability of the unaided eye to detect the emission.

EXAMPLES XII - XVIII

About 0.5 weight percent of the following phosphors is added to samples of a standard 4OWR powder, and the resulting mix is checked under a 100 power microscope for detection of visible light emissions under excitation as in Examples V - XI with results as indicated below. Of those which could be detected with both short wave and long wave ultraviolet radiation after detonation, the short wave radiation produces more easily detectable results.

Example	Type	SHORT WAVE (ABOUT 1500 to 2600A) Before Detonation	SHORT WAVE (ABOUT 1500 to 2600A) After Detonation	LONG WAVE (ABOUT 3600 to 3700A) Before Detonation	LONG WAVE (ABOUT 3600 to 3700A) After Detonation
Radelin Phosphor					
XII	Zn Silicate; Mn; GS-115	Yes	Yes	Yes	No
Helecon Phosphorescent Pigment					
XIII	2304	Yes	Yes	Yes	Yes
XIV	2315	Yes	Yes	Yes	No
XV	2330	Yes	Yes	Yes	Yes
XVI	2330*	No	No	No	No
Helecon Fluorescent Pigment					
XVII	2210	Yes	Yes	Yes	No
XVIII	2330**	Yes	Yes	Yes	Yes

* Unfired
** Overs From 200 Mesh (USSS) Screening

EXAMPLES XIX - XL

Samples of the following phosphors are added to samples of powder and formed into one-and-one-fourth inch by eight inch stick, and the resulting mixes are detonated in the vicinity of a steel plate dirtied with the following contaminants, with results, using a X100 microscope as indicated below under short wave ultraviolet light:

Example	Type	CONTAMINANT Oil	Grease	Gasoline	Human Waste
Radelin Phosphor					
XIX-XXI	Zn Silicate; Mn; GS-115	No	No	No	
Helecon Phosphorescent Pigment					
XXII-XXV	2304	Yes	Yes	Yes	Yes
XXVI-XXVIII	2315	Yes	Yes	Yes	
XXIX-XXXI	2330	Yes	Yes	Yes	
XXXII-XXIV	2330*	No	No	No	
Helecon Fluorescent Pigment					
XXXV-XXXVII	2210	Yes	Yes	Yes	
XXXVIII-XL	2330**	Yes	Yes	Yes	

* Unfired
** Overs From 200 Mesh (USSS) Screening

EXAMPLES XLI - XLV

Examples XII to XVIII, the luminescent materials are sprinkled onto the shell of an explosive which is then coated with a polyurethane clear finish. The results are more easily detected under aide of microscope than when the phosphors are mixed with the explosive powder, as in Examples XII - XVIII.

Example	Type	SHORT WAVE (ABOUT 1500 to 2600A) Before Detonation	SHORT WAVE (ABOUT 1500 to 2600A) After Detonation	LONG WAVE (ABOUT 3600 to 3700A) Before Detonation	LONG WAVE (ABOUT 3600 to 3700A) After Detonation
Radelin Phosphor					
XLI	Zn Silicate; Mn; GS-115	Yes	Yes	No	
Helecon Phosphorescent Pigment					
XLII	2304	Yes	Yes	Yes	
XLIII	2315	Yes	Yes	Yes	
XLIV	2330*	No	No	No	
Helecon Fluorescent Pigment					
XLV	2210	Yes	Yes	Yes	
XLVI	2330**	Yes	Yes	Yes	

* Unfired
** Overs From 200 Mesh (USSS) Screening

EXAMPLES XLVII - L

Limestone is ground to +20 − 40 mesh (U.S. Sieve Series) mixed to a two weight percent level with a 4OWR powder into a one-and-one-fourth inch by eight inch stick, and exploded in a barrel and onto brick, steel plate and wood in the barrel. The luminescent material can not be detected under short or long wave ultraviolet radiation by eye following detonation. It appears that the limestone deflected off the harder materials such as steel and embedded within the shorter materials such as wood.

EXAMPLES L - LIII

Brown willemite is ground to +20 − 40 mesh (U.S. Sieve Series), mixed to a two weight percent level with 4OWR powder into a one-and-one-fourth inch by eight inch stick, and exploded in a barrel and onto brick, steel plate and wood in the barrel. The luminescent material is detectable in every instance by eye upon short or long wave ultraviolet excitation, with the luminescent material being more easily detected on barrel pieces and steel plate.

EXAMPLE LIV

Each of two rare earths, samarium nitrate and dysprosium nitrate, are mixed with 4OWR powder at the 200 part per million by weight level and tested as in Example II. Following explosion of the mixture, the detected particles are too sparse for positive identification by the unaided eye.

The above examples illustrate the invention and show its breadth. Although the present invention has been described with reference to preferred embodiments and specific examples, numerous modification could be made, and still the result would be within the scope of the invention.

What is claimed is:

1. An explosive device comprising an explosive material and a luminescent material making-up less than about 2 percent by weight of the explosive device such that prior to detonation of the explosive device the luminescent material is not readily detectable under ambient light while following detonation of the explosive device the luminescent material is detectable upon excitation by a nonvisible excitation radiation.

2. An explosive device of claim **1** in which the luminescent material is present in an amount of from about 0.025 to about 2 percent.

3. An explosive device of claim **2** in which the luminescent material is present in an amount of from about 0.05 to about 1.0 percent by weight.

4. An explosive device of claim **1** in which the luminescent material is added to explosive material in the explosive device.

5. An explosive device of claim **1** in which the luminescent material is coated on the exterior of the explosive device.

6. An explosive device of claim **5** in which the luminescent material is sprinkled onto the exterior of the explosive device and covered with a polyurethane clear finish.

7. An explosive device of claim **1** in which the luminescent material is incorporated into the container of the explosive.

8. An explosive device of claim **1** in which the luminescent material is a fluorescent material.

9. An explosive device of claim **1** in which the luminescent material is a phosphorescent material.

10. A method of identifying the source of an explosive device following detonation thereof comprising:

prior to detonation adding to the explosive device a luminescent material which upon excitation by a non-visible radiation has a known electromagnetic emission uniquely associated with the explosive device source;

subsequent to detonation of the explosive device radiating the area surrounding the detonation with the non-visible excitation radiation;

detecting the electromagnetic emission of the luminescent material in the radiated area; and

associating the electromagnetic emission with the explosive device source.

11. The method as claimed in claim **10** in which the luminescent material is added by mixing luminescent material with explosive material and forming the mixture into the explosive device.

12. The method of claim **10** in which the luminescent material is incorporated in the explosive device by depositing luminescent material on the exterior of the explosive device.

13. The method of claim **12** in which the luminescent material is sprinkled onto the exterior of the explosive device and covered with a polyurethane clear finish.

14. The method of claim **10** in which the luminescent material is less than about 2 percent by weight of the explosive device.

15. The method of claim 14 in which the luminescent material is in an amount of from about 0.025 to 2.0 percent by weight of the explosive device.

16. The method of claim 15 in which the luminescent material is in an amount of from about 0.05 to 1.0 percent by weight of the explosive device.

17. The method of claim 10 in which subsequent to detonation of the explosive device the area surrounding the detonation is radiated with ultra-violet radiation.

18. The method of claim 10 in which the luminescent material is phosphorescent.

19. The method of claim 10 in which the luminescent material is fluorescent.

20. An explosive device of claim 1 in which at least two luminescent materials are employed.

21. An explosive device as claimed in claim 1 in which the average particle size of the luminescent material is about 40 to 2000 microns.

22. An explosive device of claim 16 in which the average particle size of the luminescent material is about 50 to 1000 microns.

23. A method of identifying the source of an explosive device having incorporated therein a luminescent material which upon excitation by a non-visible excitation radiation has a known electromagnetic emission uniquely associated with the explosive device source, said method comprising:

subsequent to detonation of the explosive device radiating the area surrounding the detonation with the non-visible excitation radiation;

detecting the electromagnetic emission of the luminescent material in the radiated area; and

associating the electromagnetic emission with the explosive device source.

* * * * *

Notice of Adverse Decision in Interference

In Interference No. 99,183, involving Patent No. 3,835,782, G. L. Griffith and D. W. Edwards, PRODUCT AND METHOD, final judgment adverse to the patentees was rendered Oct. 28, 1976, as to claims 1, 2, 3, 4, 8, 9, 20, 21 and 22.

[*Official Gazette February 1, 1977.*]

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,835,782

DATED : September 17, 1974

INVENTOR(S) : GEORGE L. GRIFFITH and DONALD W. EDWARDS

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

IN THE CLAIMS:

Claim 22, Column 10, line 1, "device of claim 16", should be -- device of claim 21 --.

Signed and Sealed this

thirtieth Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks