Patented May 6, 1947

2,420,286

UNITED STATES PATENT OFFICE

2,420,286

CHEMILUMINESCENT COMPOSITIONS

Harold T. Lacey and Henry E. Millson, Plainfield, and Frederick H. Heiss, Martinsville, N. J., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application March 3, 1943, Serial No. 477,856

5 Claims. (Cl. 252—188.3)

1

This invention relates to a method of and composition for temporarily generating diffused light. More particularly, the invention relates to a novel composition which when moistened is capable of generating visible light and which can be used at night to fix temporarily a designated position at the water surface.

Various conditions under which it is important to be able to mark a position at or near the surface of a body of water frequently occur. For example, in navigation, particularly in the air, it is highly desirable to be able to fix a position on the water surface in order to enable a drift measurement to be made. By day this is easily done, as by dropping a small quantity of some floating substance such as an oil or an oil-treated metal powder onto the surface. At night, however, the problem is not so readily solved since the marker must be illuminated.

Again, an airplane pilot when preparing to land on the water, particularly in an emergency, needs some means of accurately estimating his height above the surface. This is a factor ordinarily not readily determinable at night except at established airports where adequate illumination can be produced. Still another important example is in the case of ship or plane wreck survivors afloat on life rafts, buoys and the like who wish to call attention to their position to planes which may be searching for them at night.

In time of war, other occasions arise. Unarmed ships or planes, for example, often desire to mark the position where an enemy submarine was seen for the benefit of approaching armed craft. Again it is often desirable to designate temporarily a landing area for the use of friendly sea planes so that they may have an indication of the best position and be able to estimate elevation. Under war time conditions the temporary nature of the markings is particularly important since the use of permanent installations or apparatus would enable the enemy to take advantage of the same information intended for friendly planes.

Another limitation imposed in wartime is that the light must be visible only for a limited distance. This requires that the light be diffused in order to prevent it from throwing a beam visible for a considerable distance. Ordinarily, it also requires that the intensity be limited so as to be visible only for a fixed distance. For example,

2

it would not be advisable to mark a plane-landing area in such a way that it is visible not only to the friendly craft but also to enemy craft at considerable higher altitude. Again, in small-boat landing operations, a source of light adequate to enable the boats to maintain formation without advertising their presence to the enemy is necessary.

Battery-operated electrical devices have been suggested for these various purposes. In some cases they have worked well. However, such devices are subject to certain inherent drawbacks in actual use. Primarily, the batteries required are heavy, so that the devices are not easily transported. Nor, are they particularly reliable since the charge usually is gone at the most inconvenient times and places. Where they must be used under wet conditions the batteries require extreme care to prevent unexpected short circuits. If storage batteries are to be used, there is the problem of renewing the charge. Where the devices must be thrown overboard the cost is an appreciable consideration.

There is, therefore, an existing demand for some means, temporarily self-illuminating and adapted to be used for these purposes. Preferably, also they should be small and of light weight so as to be easily portable; relatively cheap and simple to manufacture so as to be made readily obtainable; and simple to use so as to be capable of use without any special preparation. It is the object of the present invention to provide such a means whereby the various requirements are readily met.

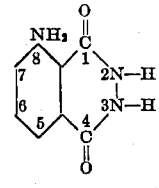
In general the objects of the present invention are accomplished by the manufacture of a chemical composition having incorporated therein dry materials which react when wet to produce chemiluminescent light. Such compositions may be made by preparing the reactive ingredients in powdered form and incorporating them with other materials which will bind the powder into a solid mass and if necessary, insure their floating on the water surface.

Chemiluminescent materials per se are not new. For example, it has been known for some time that when any one of a number of materials are reacted in solution with a powerful oxidizing agent, the resultant reaction temporarily produces a so-called "cold" or chemiluminescent light.

However, the use of such solutions for the purposes of the present invention would not only be impractical because of the difficulty in preparing and/or transporting the solutions but also because a light generated by pouring such solutions on a body of water would be entirely too evanescent.

An important feature of the present invention is that the materials are used in a solid form so as to increase the duration of the period during which light is generated. The composition may be used as a powder, in flake form or as large pieces such as blocks, lumps or tablets. The physical state has a direct effect on the duration of the light produced since the larger pieces dissolve more slowly. Various additions also may be made to the composition whereby the duration of the reaction may be regulated.

The compositions of the present invention may incorporate any of a number of materials which generate the desired light under the influence of an oxidizing agent. Among the better compounds adapted for the purposes are such materials as the 3- and 4-amino-phthalhydrazides the 3-amino derivative, for example, being represented by the following formula:



and their nitro, hydroxy and acyl derivatives, particularly the acetyl derivatives; various substituted benzhydrazides; Luzigenin salts (N,N'-dimethyl-biacridylium dinitrate) and the like. The 3-amino-phthalhydrazide is perhaps the easiest to prepare and most readily available and for that reason is preferable although the invention is by no means intended to be so limited.

An active oxidizing agent is required to react with the hydrazides or the like which constitute the principal component of the composition. Preferably it should be a stable solid, readily soluble in water and readily decomposed in solution either to generate oxygen or to a compound which will generate oxygen. One of the better compounds for this purpose is sodium perborate since it is cheap, available and gives excellent results. However, the invention is not necessarily so limited. Any of the water-soluble perborates may be used. Other compounds which are useful include the water-soluble perchlorates, persulfates and hypochlorites.

Most of the solid compounds used as oxidizing agents in the present invention rely for their utility on the formation of hydrogen peroxide which occurs when they are wetted. Therefore a compound which will accelerate the decomposition of the hydrogen peroxide so formed to nascent oxygen is generally found to be useful. Sodium ferricyanide is particularly well suited for use for this purpose. However, the invention is not so limited since other soluble ferricyanides as well as such materials as sodium or potassium hypochlorite and most of the water-soluble copper and cupro-ammonium salts may be used in a similar manner.

It is possible to intensify further the luminescence by increasing the rate of oxidation. Among other materials useful for this purpose are the peroxidases, dried blood, casein, manganese dioxide and small amounts of colloidal platinum,

haemine, and a salicylic-aldehyde-ethylenediimine ferric chloride complex. Such a procedure, however, will shorten the duration of the lighted period unless larger amounts of the other materials are used.

The reaction is carried out in an alkaline medium. It is therefore usually desirable to incorporate a considerable proportion of a solid material having a strongly alkaline reaction. Trisodium phosphate is excellently well suited for the purpose because of its relatively low hygroscopicity. However, the invention is again not intended to be so limited. Other compounds which can be used with normally satisfactory results include for example the sodium or potassium meta silicates, caustic soda and the like.

While most of the oxidizing reagents require an alkalinity at least that produced by trisodium phosphate, if a suitable accelerator is present some will work satisfactorily at lesser pH's. Notable among these accelerators is the salicylic-aldehyde- ethylenediimine ferric chloride complex set forth above. The light produced by this mixture is less intense but requires air and therefore in practical applications is most useful in those compositions to be used on the surface of the water.

As was pointed out above, use may be made of the material in powdered form although to do so is not particularly convenient. The powdered form is the quickest acting and therefore must be more carefully stored and used. Powder is also more difficult to use successfully because of its tendency to spread. Particularly if it must be dropped from any appreciable height it is likely to be blown away by the wind. Unless an intense light of short duration is required, it is preferable that the composition be made up into flakes, tablets, cakes of other pieces of larger size. For this purpose a binding agent is usually necessary.

The type of binding agent used largely determines the luminescent life of the material after contact has been made with the water. Water-insoluble waxes such as paraffin, carnauba or Japan wax prolong the active life at the expense of the brightness. On the other hand, water-soluble waxes, such as the well-known alkylene oxide polymers, such as are commercially available under the trade-name "Carbowax," enable the production of a tablet which gives off an intensely bright light, but only for a relatively short period of 3 to 5 minutes of useful luminescence. By properly combining the water-soluble and water-insoluble waxes in different proportion the intensity and duration of the glow produced when the material is wetted may be varied over quite a wide range.

Variations in the duration of the glow can be further controlled by other means. For example, a larger piece of material, being less readily moistened, has a longer life than a small piece. A more definite control however may be made by partially coating one or more of the soluble chemically-active ingredients with a material which alters its rate of solution. When the solution rate is to be decreased, a material which is but slowly dissolved or which swells in the presence of water should be used. An excellent substance for this purpose is ordinary commercial gelatine. Other materials such as gelatine glue, fish glue, dextrose, shellac, gum arabic, gum tragacanth, albumen and various water-soluble cellulose derivatives such as methyl cellulose and the like also are suitable for the purpose.

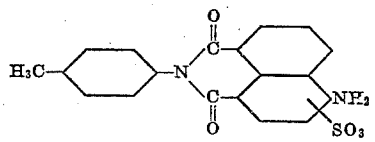
In other cases, particularly where it is desirable to quickly activate a large quantity of reagent so as to create an intense glow, materials may be added which increase the rate at which one or more of the components will dissolve. This can be readily accomplished in most cases by the use of a wetting agent. A number of these are commercially available. Among others, Aerosol OT and Aerosol OTC, commercial reagents containing dioctyl sodium sulfosuccinate, were found to give excellent results.

Another method of controlling the duration of the reaction where the material need not be placed on the water, is to regulate the amount of moisture which is applied to the composition. This method is particularly applicable where the material is to be placed in a holder of some type and used as a signal light. An excellent example of this use occurs in connection with the small boat landing operations which were mentioned above. The materials may be placed in a holder having a window facing in the proper direction. By regulating the application of water, the reaction rate and thereby the intensity and duration of the light may be controlled.

By properly regulating the various components and control means, the duration of the light may be controlled at will. The lighted period was lengthened from the few seconds obtained where the materials were mixed by combining solutions of the reagents to as long as 10–15 hours. Similarly the intensity and thereby the limit of visibility may be adjusted. The light may be controlled so as to be visible for only a few feet or as much as a thousand feet or more in accordance with the demands of the use to which it is put.

Since the compositions with which the present invention is concerned will in many cases have but very little utility unless they can be floated on the surface of the water, various ingredients may be advantageously incorporated in the composition to insure buoyancy. Cork dust, for example, is one such material and is found to give an excellent product. Products of good properties can be made using other buoyant agents such as wood flour and fibrous materials such as methyl cellulose. The latter is particularly useful since it not only increases the buoyancy of the solid material, but is also translucent and can be utilized, as pointed out above, to regulate the rate of solution and thereby the rate of reaction. It has still further advantage which it shares with the other gelatinous types of binders in that it ensnares gaseous products of the reaction such as nitrogen and excess oxygen and thereby aids in keeping the material afloat.

Chemiluminescent light produced by derivatives of phthalic acid hydrazide is normally a greenish-blue in color. This color may be varied by the addition of suitable dyestuffs. Yellows and reds may be supplied by suitable fluorescent dyes such as for example Sulfo Rhodamine B (CI–748). A greenish-yellow light may be produced by the addition of a small amount of Uranine (CI–766) or Brilliant Sulfo Flavine, a dyestuff having the structural formula



An orange color light may be made by mixtures of a yellow and red fluorescent dye. Other blues

and greens may be produced by the addition of water-soluble dyestuffs which do not fluoresce such as Brilliant Indo-Cyanine G, Milling Green CR (CI-735), Alizarine Cyanine Green CG (CI–1078) and the like. The properties of the resultant composition may be altered also by using various salts of these dyestuffs since the sodium, potassium, calcium, barium salts and the like have varying degrees of solubility.

The addition of fluorescent materials such as uranine is particularly interesting. Not only does the addition of the fluorescent material change the normal blue-green light to another shade but in some cases it also intensifies the light. The addition of small amounts of uranine, for example, may actually increase the apparent intensity of the generated light by as much as five hundred per cent. This is probably due to the change in the wave-length of the light to a band more readily perceptible to the average eye as is set forth in the copending application for U. S. Letters Patent of Lacey and Millson, Serial No. 477,855, filed of even date.

Certain precautions should be observed in storing the compounded materials. Since the chemiluminescence is generated by the reaction in the presence of water, the materials must be kept dry. This, however, is readily accomplished by storing the materials in air and moisture tight containers. This is true whether the material is in powder, flake or solid form. In solid or tablet form the material may be conveniently handled since a large number of pieces of a size suitable for instant use may be packed and transported in a convenient size package or can.

The invention will be more fully explained in connection with the following examples which are meant to be illustrative only and not by way of limitation. The parts are by weight unless otherwise noted.

Example 1

A mixture containing the following ingredients:

	Parts
3 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Potassium ferricyanide	5.0
Trisodium phosphate	5.0

was prepared by thoroughly grinding each of the ingredients and drying them at 40° C. When dry the ingredients were blended in a powder mill. A sample of the blended powder when placed on water gives a greenish-blue light.

Example 2

20 parts of monosodium dipotassium ferricyanide was added to 5 parts of water in which 1.25 parts of gelatine had been dissolved. The resultant mixture was dried at 70° C. and ground to a fine powder. 20 parts of trisodium phosphate was mixed with 4 parts of water in which 1 part of albumen had been dissolved. This mixture was also dried at 70° C. and ground to a fine powder. The materials after this treatment were blended with the other components to form a mixture of

	Parts
3 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Monosodium dipotassium ferricyanide (gelatine treated)	5.5
Trisodium phosphate (albumen treated)	5.5

A sample of the resultant product placed on water gave the same greenish-blue light as was obtained in Example 1 but for a considerably longer period of time.

Example 3

To a sample of the blended mixture of Example 2 was added 1 part of uranine to give a mixture of the following composition:

	Parts
3 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Monosodium dipotassium ferricyanide (gelatine treated)	5.5
Trisodium phosphate (albumen treated)	5.5
Uranine	1.0

A sample of this mixture when placed on water gives a green-yellow light of approximately five times the visual intensity of that obtained with the mixture of Example 2.

Example 4

A mixture of the following components:

	Parts
3 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Potassium ferricyanide	5.0
Trisodium phosphate	5.0
Cork dust	2.0

was made by drying and grinding each of the ingredients and blending them together. The resultant mixture was treated with a solution containing the following ingredients:

	Parts
Paraffin	0.75
Carbon tetrachloride	5.0
Mixed hexanes	9.0

After thorough mixing the resultant paste was pressed into cakes approximately ⅛ inch thick and the volatile solvents evaporated.

Example 5

A mixture of the following components:

	Parts
3 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Potassium ferricyanide	5.0
Trisodium phosphate	5.0
Methyl cellulose, 4000 cps. viscosity	10.9

was made by drying and grinding each of the ingredients and blending them together. The resultant mixture was treated with a solution containing the following ingredients:

	Parts
Paraffin	0.9
Carbon tetrachloride	4.3
Mixed hexanes	28.0

After thorough mixing the resultant paste was pressed into cakes approximately ⅛ inch thick and the volatile solvents evaporated.

Example 6

A mixture of the following components:

	Parts
Sodium perborate	1.9
Trisodium phosphate	5.0
Potassium ferricyanide	5.0
Dioctyl sodium sulfo succinate 10% and dextrose 90%	0.3

was prepared by drying the ingredients separately at 40° C. and then grinding them for 2 hours in a ball mill. The mill was opened and 1 part of approximately 90% 3-amino-phthalhydrazide was added and the mixture ground for an additional 15 minutes. The material was removed from the mill and thoroughly blended with

	Parts
Methyl cellulose 15 cps	10.5

and a binder solution consisting of:

Paraffin	1.0
Carbon tetrachloride	16.0
Mixed hexanes	6.0

The resultant mixture was pressed into a cake approximately ¼ inch thick and the volatile solvents evaporated.

Example 7

A mixture of the following components:

	Parts
4 - amino - phthalhydrazine (approximately 93%)	1.0
Sodium perborate	1.9
Potassium ferricyanide	5.0
Trisodium phosphate	5.0
Methyl cellulose 15 cps	14.5

was made by drying and grinding each of the ingredients and blending them together. The resultant mixture was treated with a solution containing the following ingredients:

	Parts
Ethylene oxide polymer, such as Carbowax #4000 or #1500	2.18
Carbon tetrachloride	31.00

After thorough mixing the resultant paste was pressed into cakes approximately ⅛ inch thick and the volatile solvents evaporated at 40° C.

Example 8

A mixture of the following components:

	Parts
3 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Potassium ferricyanide	5.0
Trisodium phosphate	5.0
Methyl cellulose 400 cps	14.5

was made by drying and grinding each of the ingredients and blending them together. The resultant mixture was treated with a solution containing the following ingredients:

	Parts
Ethylene oxide polymer (Carbowax #4000)	1.0
Ethylene oxide polymer (Carbowax #1500)	1.0
Carbon tetrachloride	32.0

After thorough mixing the resultant paste was pressed into cakes approximately ⅛ inch thick and the volatile solvents evaporated at 40° C.

Example 9

A mixture of the following ingredients:

	Parts
4 - amino - phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Potassium ferricyanide	5.0
Sodium metasilicate	5.0
Methyl cellulose	14.5

was prepared by first drying them separately at 40° C. and then grinding them together. A binder solution containing the following ingredients:

	Parts
Ethylene oxide polymer (Carbowax #4000)	1.83
Paraffin	1.35
Carbon tetrachloride	31.00

was added and the composition thoroughly mixed and passed through two rollers fitted with doctor blades. This treatment pressed the composition into flakes about $\frac{1}{16}$ inch thick from which the volatile solvent was evaporated at 40° C. care being taken to handle the flakes as little as possible until they were dry so as to avoid breaking.

Example 10

A sample of the flakes prepared according to Example 9 was treated by spraying them with 20 parts of a solution of 3 parts of dioctyl sodium sulfo succinate (Aerosol OT) dissolved in 100 parts of carbon tetrachloride. The volatile solvent was then evaporated.

Example 11

A mixture of the following ingredients:

	Parts
3-amino-phthalhydrazide (approximately 90%)	5.0
Sodium perborate	10.0
Monosodium dipotassium ferricyanide	25.0
Trisodium phosphate	30.0
Uranine	5.0

was prepared according to the procedure of Example 9 and mixed with the following ingredients:

	Parts
Methyl cellulose 15 cps	75.0

Binder solution consisting of:

Paraffin	2.0
Ethylene oxide polymer (Carbowax 4000)	11.0
Carbon tetrachloride	190.0

The wet mass was converted into flakes as in Example 9 and the flakes dried and blended with 13 parts of a mixture containing 10% dioctyl sodium sulfo succinate and 90% dextrose (Aerosol OTC).

Example 12

20 parts of monosodium dipotassium ferricyanide was treated with gelatine according to the procedure of Example 2 and used to make up a mixture of the following ingredients:

	Parts
3-amino-phthalhydrazide (approximately 90%)	1.0
Sodium perborate	1.9
Monosodium dipotassium ferricyanide (gelatine treated)	5.5
Trisodium phosphate	5.0
Uranine	1.0

each of which was dried separately and then compounded with the following:

	Parts
Methyl cellulose 15 cps. viscosity	21.0

Binder solution consisting of:

Paraffin	0.75
Carbowax (#4000)	10.5
Carbon tetrachloride	41.5

The composition was thoroughly mixed and pressed into a cake approximately ⅛ inch in thickness and the volatile solvents evaporated at 40° C.

Example 13

A mixture of the following ingredients:

	Parts
3-amino-phthalhydrazide	82
Uranine	82
Sodium bicarbonate	41
Sodium perborate	164
Sodium carbonate	412
Salicylic-aldehyde-ethylenediimine ferric chloride	13

was prepared by drying the sodium bicarbonate and sodium perborate at 35–40° C. and the other ingredients at 50° C. This mixture was then thoroughly mixed with 1060 parts of methyl cellulose and 1978 parts of a binder solution containing 540 parts of an ethylene oxide polymer (Carbowax 4000), 38 parts of paraffin and 1400 parts of carbon tetrachloride. The resulting wet pulp was placed in frames and compacted into flat mats after which the volatile solvents were evaporated by heating the mixture to about 40° C. When floated on water the mat produced a light of good intensity and long duration. The mats also gave a good light when suspended in air and wetted with a fine water spray.

Example 14

350 parts of methyl cellulose were ground to a fine powder in a high speed hammer-mill. This powder was used to make up a mixture of the following ingredients:

	Parts
3-amino phthalhydrazide	82
Uranine	82
Sodium bicarbonate	41
Sodium carbonate	412
Sodium perborate	164
Salicylic-aldehyde-ethylenediimine-ferric chloride	13
Methyl cellulose	350

The sodium perborate was dried previously to the mixing operation at 35–40° C. and the other ingredients at about 50° C. The compounded mixture was placed in containers with porous, high-wet-strength paper faces. Water entering through these faces activated the mixture and gave a good light of long duration which was visible through the porous paper faces.

Example 15

After thoroughly drying the various ingredients a mixture having the following proportions:

	Parts
3-amino-phthalhydrazide (approximately 93%)	5.0
Sodium perborate	10.0
Monosodium dipotassium ferricyanide	25.0
Trisodium phosphate	30.0
Uranine	5.0

was prepared, mixed and ground. The powder was then compacted into tablets on a tableting machine. A large tablet was placed in a vessel of water which was slowly irrigated with a slow stream of water. It was found that the life could be extended by adding various amounts of methyl cellulose which had been thoroughly dried and ground before the mixture was tableted.

Any of a number of different methods of using the material may be employed without departing from the scope of the invention. Perhaps the

simplest is to drop the material directly on the surface of the water. This may be modified in various ways. For example, it may be placed inside water-soluble capsules of gelatine, methyl cellulose and the like, the materials being activated after the capsule is dissolved. By using a plurality of capsules of different solubilities, their contents may be activated in succession thereby prolonging the lighted period. Or, the capsules may be replaced by water-insoluble containers having openings normally closed by water-soluble material. Again the openings in the container may be closed with a removable closure, such as an adhesive strip or the like, which can be readily removed before dropping the container on the water. In other cases, a small explosive charge may be included so as to break the container and spread the contents over a considerable area. Again, a plurality of containers may be used, detonated in succession so as to prolong the illuminated period. If so desired, the materials may be mixed with an oil and poured on the water. Another example, the use of a holder, with a directional window, in which the material can be placed and water added to it, has been noted above.

We claim:

1. Solid material adapted to be placed upon and supported by the surface of a body of water whereby a portion of its contents dissolves in the water and reacts to produce chemiluminescent light, the portion which dissolves consisting essentially of an intimate mixture of dry powdered material which when dissolved in water and oxidized gives off chemiluminescent light, a powdered water-soluble material which generates nascent oxygen when wetted, and the remainder of the composition comprising particulate material incorporated in the mixture, whereby its buoyancy is increased and a sufficient amount

of a binder to produce a unitary material at the temperature of the water upon which it is to be used.

2. A composition according to claim 1 characterized in being formed into a single unitary mass.

3. A composition according to claim 1 characterized in being formed into particulate flakes.

4. A composition according to claim 1 characterized in that the binder comprises a water-insoluble wax.

5. A composition according to claim 1 characterized in that the binder comprises a water-soluble wax-like alkylene oxide polymer.

HAROLD T. LACEY.
HENRY E. MILLSON.
FREDERICK H. HEISS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,035,267	Fleischman	Mar. 24, 1936
2,120,430	Rieche	June 14, 1938
2,338,719	Holt	Jan. 11, 1944
2,142,291	Solski	Jan. 3, 1939
2,274,252	Tanberg	Feb. 24, 1942
2,236,513	Bradshaw	Apr. 1, 1941
2,275,979	Molnar	Mar. 10, 1942

OTHER REFERENCES

Tamamusi—in Naturwissenschaften, vol. 28, pp. 722–3 (1940)—Abstracted in Chem. Abstracts, vol. 35, p. 4286 (1941). (Copy in Div. 6.)

Stoss and Brauch in J. Org. Chem., vol. 3, pp. 385–404 (1938), abstracted in Chem. Abstracts, vol. 33, p. 3697 (1939). (Copy in Div. 6.)