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LIGHT SOURCE COMPRISING PERAMINOETHYLENES ON POROUS PARTICULATE SUPPORTS

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U.S. Cl. 252—188.3 11 Claims

ABSTRACT OF THE DISCLOSURE

Oxyluminescent light sources of some renewability comprising inert, solid, particulate supports capable of being crushed underfoot and of about 0.05–0.5 inch average particle size, e.g., vermiculite or urethane foam, impregnated with a tetrakis(disubstituted-amino)ethylene, e.g., tetrakis(dimethylamino)ethylene.

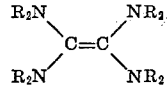
DESCRIPTION OF THE INVENTION

This invention relates to light sources. More particularly, it relates to oxyluminescent light sources.

New types of light sources are desired for various emergency purposes. In particular, light sources that remain serviceable for an indefinite period of time, that are easy to handle, and that generate adequate light immediately on demand are especially desired for various military applications. For example, light sources suitable for perimeter defense in military operations and as emergency lights are especially desired.

A novel light source especially useful in the above-mentioned and other applications is now provided by the present invention. This novel light source comprises porous, inert, solid supports of about 0.05 to 0.5 inch average particle size (diameter) impregnated with a tetrakis(disubstituted-amino)ethylene oxyluminescent material.

Preferably the oxyluminescent compositions of this invention comprise a porous, inert, solid support of about 0.05 to 0.2 inch average particle size, with the support amounting to 5–50% of the total weight of the composition, the support being impregnated with an impregnating agent comprising 10–100%, by weight, of at least one tetrakis(disubstituted-amino)ethylene of the formula



and 90–0% of an inert liquid carrier. The R's in the above formula are the same or different, and are monovalent alkyl or cycloalkyl of up to 10 carbon atoms each, divalent alkylene joined to the other R attached to the same nitrogen to form a 3–5 membered monoaza heterocycle, and divalent alkylene joined to an R attached to a second nitrogen to form a 3–7 membered diaza heterocycle.

These oxyluminescent compositions are stable for indefinite periods of time when enclosed in containers that are impermeable to oxygen or air. The impregnated porous particles do not flow together or adhere to each other on storage and hence are readily transferable from one container to another, and can be spread manually or mechanically over the particular surface to be lighted, without special pumps or pressurized dispensers being necessary. When the particles are placed on the ground or on other porous surfaces, they do not soak in. Those compositions in which the particles are impregnated with a waxy or other high-viscosity formulation of the peraminoethylene oxyluminescent material emit light for a time when first exposed to air, but only the oxyluminescent material near the outside surface of the particles is consumed or quenched. If during the next several hours the particles are crushed, new surfaces are formed and the particles again emit light.

Another superior property of the compositions of this invention is their ability to retain open channels for air or oxygen to circulate throughout all the particles in the container. Thus when light is desired and air is admitted to a container filled with the impregnated particles, the air circulates through the spaces between the particles and the oxyluminescent reaction proceeds throughout the entire mass of particles. This characteristic is particularly advantageous for compositions to be used as emergency light. In this application, containers having at least one transparent side or area can be filled with the impregnated particles, and, when air is admitted, light is immediately emitted. Light can be liberated repeatedly many times in this way before the oxyluminescent material is exhausted or quenched by reaction products.

The oxyluminescent particulate compositions of this invention are prepared by impregnating with a tetrakis (disubstituted-amino)ethylene of the formula given above a porous, solid support of average particle size (diameter) between about 0.05 and 0.5 inch and which is inert to the oxyluminescent material and other ingredients of the composition. Preferably the oxyluminescent material is dispersed in an inert liquid solvent, carrier, or thickening agent. The porous support should be deaerated before it is impregnated with the oxyluminescent composition and the impregnation step should be carried out in an inert atmosphere free of oxygen, e.g., in an atmosphere of an inert gas such as nitrogen.

A preferred way of removing air from the porous support consists in placing the porous solid in a container capable of being heated and of being evacuated, and subjecting the particles to a vacuum of about 1 mm. mercury at a temperature of about 25–100° C., then flushing the container and its contents with an inert gas, e.g., nitrogen. This evacuation and flushing with inert gas is repeated until the particles are free of atmospheric oxygen.

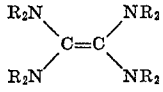
After the air is removed from the porous supports, the tetrakis(disubstituted-amino)ethylene, preferably blended with a solvent, carrier, or thickening agent such as mineral oil, petrolatum, natural paraffin wax, low molecular weight polymers, and the like, in the proportions specified above, is uniformly mixed with the porous particles. In some cases it is desirable to heat the mixture to a moderate temperature, e.g., 50–100° C., while mixing, to facilitate the uniform impregnation of the particles with the oxyluminescent composition.

After a uniform mixture is obtained, the container is filled with nitrogen to a pressure of one atmosphere. The particles are cooled (if they have been heated), while being maintained in an atmosphere of an inert gas, e.g., nitrogen, to protect them from oxygen. The composition is then stored in containers that are substantially impermeable to oxygen.

A wide variety of porous, solid supports are useful in the compositions of this invention. Any porous solid having an average particle size (diameter) between about 0.05 and 0.5 inch, and which is inert to the oxyluminescent material or its reaction products, can be used. It is important in obtaining compositions that remain particulate and permit adequate circulation of air to use particles having an average diameter of at least 0.05 inch. Smaller sized particles do not permit adequate air circulation when it is desired to produce light. In addition when exposed to air in thin layers, they oxyluminesce rapidly and emit light only for a limited time. They cannot be revived by crushing underfoot as can larger particles and hence are not useful in perimeter defense to discourage personnel from entering selected areas. Particles greater than 0.5 inch diameter are operable, but for

economic reasons they are not preferred. Specific examples of suitable porous supports include particles of expanded siliceous materials available commercially, e.g., vermiculite, and the material known commercially as "Perlite," pumice and other volcanic spongy rocks, glass frits, and solid organic and inorganic foams, having an average particle size of the range specified above.

The oxyluminescent materials operable in the compositions include the tetrakis(disubstituted-amino)ethylenes of the formula



wherein the R's have the meanings defined hereinbefore. Specific oxyluminescent compounds of this type include

tetrakis(dimethylamino)ethylene,
tetrakis(N-pyrrolidinyl)ethylene,
1,1',3,3'-tetramethyl-$\Delta^{2,2'}$-bi(imidazolidine),
1,1',3,3'-tetraethyl-$\Delta^{2,2'}$-bi(imidazolidine),
1,1'-diethyl-3,3'-dimethyl-$\Delta^{2,2'}$-bi(imidazolidine),
1,1',3,3'-tetramethyl-$\Delta^{2,2'}$-bi(hexahydropyrimidine), and
tetrakis(dimethylaminomethyleneamino)ethylene.

The tetrakis(dimethylamino)ethylene can be prepared by reaction of dimethylamine with chlorotrifluoroethylene as described in J. Am. Chem. Soc. 72, 3646 (1950). The other tetrakis(disubstituted-amino)ethylenes of the above general formula and the bis(disubstituted-amino)hydrocarbyloxymethanes intermediate thereto can be prepared by reaction of the requisite basic secondary amine and any amide acetal, i.e., any disubstituted-amino-dihydrocarbyloxymethane in accord with the following stoichiometery:

(1) $R_2NCH(OR')_2 + R''_2NH \longrightarrow R''_2NCH(OR')_2 + R_2NH$

(2) $R''_2NCH(OR')_2 + R''_2NH \longrightarrow (R''_2N)_2CHOR' + R'OH$

(3) $2(R''_2N)_2CHOR' \xrightarrow{\Delta} (R''_2N)_2C{=}C(NR''_2)_2 + 2R'OH$

wherein the R's, which can be alike or different, are monovalent alkyl or cycloalkyl radicals, generally of no more than eight carbons each, which can be together joined (in a divalent radical) to form with the intervening nitrogen a heterocycle of from three to seven ring members; the R's, which can also be alike or different, or together joined, are monovalent (or divalent) alkyl, aryl, aralkyl, alkaryl, or cycloalkyl radicals, generally of no more than eight carbons each, and when together joined, form with the two oxygens and intervening carbon a 1,3-dioxaheterocycle of from five to seven ring members; and the R'''s, which can also be alike or different or together joined, are monovalent (or divalent) alkyl or cycloalkyl hydrocarbon or oxa- and/or azahydrocarbon radicals of no more than eight carbons each, each nitrogen carrying no more than one methyl group and, in the case of the divalent radicals, no more than 6 carbons per divalent radical. In any event, when the two R'''s are together joined, they form with the indicated amine nitrogen a monoazacarbocycle, an oxaazacarbocycle, or a diazacarbocycle of from three to seven ring members. This process is described in greater detail in the Winberg U.S. Pat. 3,239,519.

As indicated previously, the oxyluminescent materials used in the compositions of this invention are preferably used with an inert non-quenching solvent or carrier, i.e., a material which does not extinguish the oxyluminescence of the tetrakis(disubstituted-amino)ethylene. Suitable solvents of this type include the liquid hydrocarbons such as n-hexane, decane, Decalin, triisobutylene, cetane, tetrapropylene, n-octadecane, 1-octadecene, purified kerosenes, white gasolines, or the more viscous hydrocarbons such as mineral oil and the like; soft or hard, solid or semisolid hydrocarbons such as paraffin wax or petrolatum; non-quenching synthetic oils such as silicone oils, polyalkylene glycols and diesters; non-quenching, preferably essentially hydrocarbon esters such as ethyl acetate; non-quenching hydrocarbon ethers such as tetrahydrofuran, diethyl ether, dimethyl ether, and the like.

The oxyluminescent compositions can also include compatible non-quenching organic thickening agents. Examples of such agents include organic polymers such as the hydrocarbon polymers, e.g., polyisobutylene, polypropylene, polyethylene, and the like; non-quenching polyesters, e.g., poly(vinyl acetate) and the like; non-quenching polyethers such as poly(tetramethylene oxide) and the like; non-quenching olefin/ester copolymers such as ethylene/vinyl acetate copolymers and the like.

DESCRIPTION OF PREFERRED EMBODIMENTS

The compositions of this invention are illustrated in further detail in the following examples.

EXAMPLE 1

A glass vessel filled with vermiculite of of particle size 2–20 mesh but mainly 4–12 mesh and having a bulk density of about 0.067 g./ml. is evacuated and flushed with nitrogen several times. One-third volume of tetrakis-(dimethylamino)ethylene is added. This corresponds to about 4.2 parts of liquid per part of vermiculite by weight. Light is emitted from the particles for several minutes, due to residual air. In several hours there is little change in the color of the excess liquid. In time, all of the liquid is absorbed by the vermiculite particles.

Another preparation is carried out similarly except that the liquid tetrakis(dimethylamino)ethylene is added under vacuum and the vessel is returned to atmospheric pressure by introducing nitrogen. The liquid is absorbed completely by the solid. Three days later the vessel is opened to air. The contents begin to glow at once. Some of the particles are placed on a table in the atmosphere and they emit light for 30–60 minutes. These particles emit more light later after they are crushed.

EXAMPLE 2

A transparent vessel is filled with 6–12 mesh vermiculite and it is then flushed with nitrogen and evacuated several times. While still evacuated, 4/15 volume of mineral oil and 1/3 volume of tetrakis(dimethylamino)ethylene are added. The composition contains by weight 11.4% vermiculite, 40% oil and 48.6% of the peraminoethylene. The vessel is filled with nitrogen and stoppered. Six times during the day the vessel is opened to the air for a few seconds and then closed. Each time the particles glow brightly for several minutes. During the succeeding month the vessel is similarly opened briefly and closed again at least 14 times. Light is emitted each time for several minutes.

EXAMPLE 3

Vermiculite of 4–6 mesh particle size is soaked in molten petrolatum, drained, and then heated for 10 minutes at 60–80° C. Another portion of vermiculite is rendered water resistant by soaking a few minutes in a silicone-containing preparation known commercially as "Silgon Glass Glaze," drained, dried at room temperature, and baked 30 minutes at 110° C. Each of these two treated portions of vermiculite is placed in a vessel and alternately flushed with nitrogen and evacuated. To each portion there is added 2/15 volume of tetrakis(dimethylamino)ethylene which corresponds to 1.7 parts per part of vermiculite by weight. The liquid peraminoethylene is absorbed slowly. After storage for one day, the vessels are opened to the air and the contents of each glow strongly. When the particles are placed on water, they float and glow for several minutes. The particles emit light when they are stirred. This behavior differs from that of untreated vermiculite particles containing absorbed tetrakis (dimethylamino)ethylene. In this latter instance, the light emission of untreated particles soon is quenched when they are placed on water.

EXAMPLE 4

One part, by weight, of 4–6 mesh vermiculite is impregnated under vacuum with a mixture of 1.9 parts of mineral oil and 1.1 parts of tetrakis(dimethylamino)ethylene. The particles are placed in stoppered glass containers having all sides but one silvered or covered with shiny metal foil. Air is admitted to the containers for a few seconds and the particles glow for several minutes. These containers containing impregnated vermiculite are useful as emergency lights. They can be used to read printed material, maps and instrument panels at night or in dark areas.

EXAMPLE 5

Nine and seven tenths parts by weight of 12 mesh expanded siliceous material, known commercially as "Perlite," is impregnated with 28.7 parts of a molten composition prepared by blending 22 parts, by weight, of a high melting, microcrystalline petroleum wax, 2.4 parts of a purified natural paraffin wax, and 4.3 parts of tetrakis(dimethylamino)ethylene. The impregnation is carried out with mild heating (below 100° C.) and tumbling under nitrogen. Three days later an aliquot of the impregnated granules glows in air for at least one-half hour. Four hours later the light emission is rekindled by crushing the particles in air.

EXAMPLE 6

Thirty-five parts by weight of 6.8 mesh expanded siliceous material, known commercially as "Perlite," is impregnated as in Example 5 with a composition consisting of 44.0 parts of high melting, microcrystalline petroleum wax, 4.8 parts of purified natural paraffin wax, and 17.2 parts of tetrakis(dimethylamino)ethylene. A portion of the impregnated granules glows blue-green strongly in air in a darkened area, and after three hours the granules are still glowing. Still later when the essentially "dead" granules are crushed under foot, the glow is revived. Part of the material clings to the shoe and is tracked about, and causes the shoe to glow. Even after the granules are exposed to air for six hours, light emission is revived by crushing under foot. Because of its oxyluminescence the material transferred to the shoe can be seen easily from more than 100 feet away at night, even in the presence of some extraneous light.

EXAMPLE 7

Porous particles of the expanded siliceous material known commercially as "Perlite" amounting to 10,500 cc. volume (about 1544 g.) and having a particle size of 8–16 mesh are alternately evacuated and flushed with nitrogen to remove air. While petrolatum (1,505 g.) and tetrakis (dimethylamino)ethylene (510 g.) are melted together and mixed uniformly with the granular particles at a temperature of about 70° C. After the particles are uniformly impregnated, they are cooled under nitrogen to room temperature and stored in closed containers. When air is admitted, the granules emit light.

EXAMPLE 8

Sixteen parts by weight of deaerated molten petrolatum is mixed under nitrogen with 6 parts of 1,1',3,3'-tetraethyl-$\Delta^{2,2'}$-bi(imidazoline). The still molten mixture is added under a vacuum of about 1 mm. Hg to 10.2 parts of deaerated 6–8 mesh expanded "Perlite" granules. The mixture is tumbled for several minutes with mild heating at about 60–80° C. Nitrogen is admitted to the container and after cooling, the product is bottled under nitrogen. When an aliquot is contacted with air, it emits light for several minutes. Even after the particles stand in air for 22 hours, they emit a yellow light when crushed.

EXAMPLE 9

Four parts by weight of a polymeric urethane open-cell foam having a bulk density of 1.5 lbs. per cubic foot is subdivided to a particle size of about ⅛"–¼" diameter.

It is deaerated and impregnated under a vacuum of about 1 mm. Hg with a molten solution of 52 parts of petrolatum and 18 parts of tetrakis(dimethylamino)ethylene. After tumbling with mild heating at about 60° C. for a few minutes, nitrogen is admitted to a pressure of one atmosphere and tumbling is continued while the temperature is lowered to 25° C.

When an aliquot of the product is exposed to air, it emits a relatively high intensity, green-yellow light for several minutes. The light emission falls off until after seven hours it is barely visible in a darkened area to the partly adapted eye from a distance of a few feet. At the end of seven hours the relatively soft and almost gel-like particles resume glowing at a moderate level when crushed. Even after an exposure of 23 hours many of the particles can be revived by crushing although the intensity of the emitted light is less than that from similarly exposed and crushed particles of Example 6.

EXAMPLE 10

Two parts of polycaprolactam foam having a bulk density of about 1.7 lbs. per cubic foot is subdivided to roughly cubical particles ⅛"–¼" on a side. The particles are evacuated, flushed with nitrogen, reevacuated and contacted with a molten mixture of 23 parts of petrolatum and 8.1 parts of tetrakis(dimethylamino)ethylene at about 50–60° C. The mixture is tumbled for a few minutes, pressured with nitrogen to one atmosphere and allowed to cool to room temperature. The impregnated particles are "dry" and entirely free flowing. When exposed to air, the particles emit relatively intense, blue-green light. The intensity of the emission diminishes with time until at the end of two hours it is relatively low. After five hours the light emission is too low to be seen at once in a dark area, but if the particles are crushed, the light emission is revived moderately.

When another two-part portion of the polycaprolactam foam particles of the type used in Example 10 are impregnated in a similar manner with a molten mixture of 48 parts of petrolatum and 17 parts of tetrakis(dimethylamino)ethylene, not quite all of this molten composition is absorbed by the particles. The excess formulation on the outside of the particles causes the particles to stick together to some extent.

The critical nature of the lower limit of 0.05 inch particle size of the porous, particulate supports in the compositions of this invention is shown by the following experiment.

Eight parts by weight of deaerated molten petrolatum is mixed under nitrogen with 3 parts of tetrakis(dimethylamino)ethylene. The still molten mixture is added under a vacuum of about 1 mm. Hg to 5 parts of 50–60 mesh expanded "Perlite" (particle size 0.017–0.0098 inch) with tumbling for about 15 minutes at about 60° C. The mixture is cooled to room temperature and nitrogen is admitted to the vessel. When an aliquot is exposed to the air, it glows strongly at first, but the light emission falls off rapidly until it is essentially absent at the end of an hour. The light emission can be revived only slightly by crushing after an exposure of one hour, just barely after an exposure of three hours and not at all after an exposure of seven hours.

The above mixture can be said to be inoperable for such uses as perimeter defense in military operations where the object is to spread the material on the ground so that unfriendly forces can be detected when they come in contact with it and expose fresh surfaces to air. The reason that it is inoperable in this case is that the particle size of the support for the active formulation is too small. Because of the small particle size there is rapid and complete exposure of the active composition to air and the oxyluminescent reaction occurs only in the first part of a multihour exposure to air.

As indicated above, the oxyluminescent compositions of this invention are useful for certain military applica-

tions. One such use is the spreading of the impregnated porous particles on the ground in areas to be protected. The particles serve as a means of warning when personnel or vehicles pass over that particular area of ground at night. After the original light emission from the particles spread on the ground ceases, the particles remain in position. When feet of people passing over the ground or wheels of vehicles traversing the ground strike the particles and crush them, some of the oxyluminescent composition is transferred to the shoes of the personnel or to the wheels of the vehicles and emits light. Movements of the feet and vehicle wheels then become visible, due to the presence of the chemiluminescent compositions on them. In this particular use, impregnated particles having a size of 0.1–0.5" diameter are preferred.

The impregnated particles are also useful for loading into shells, grenades, etc., whereby the oxyluminescent particles can be spread over isolated areas by bursting of the shells and grenades.

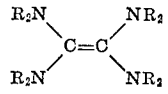
Containers having at least one transparent side filled with the impregnated compositions of this invention are especially useful as emergency lights. The amount and duration of light emitted can be controlled by controlling the amount of air or oxygen admitted to the particles in the containers. It is also possible to use the containers of impregnated particles as intermittent sources of light by adding small amounts of oxygen or air to the impregnated particles periodically. In this type of use, the luminescence can be turned on and off repeatedly until the tetrakis (disubstituted-amino)ethylene oxyluminescent material is completely consumed or quenched by the reaction products.

Since obvious modifications and equivalents in the invention will be evident to those skilled in the chemical arts, I propose to be bound solely by the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A light source which comprises a porous, inert, solid particulate support of about 0.05 to 0.5 inch average particle size impregnated with an oxyluminescent material comprising a tetrakis(disubstituted-amino)ethylene.

2. An oxyluminescent light source which comprises a porous, inert, solid particulate support of about 0.05 to 0.2 inch average particle size and impregnated with an oxyluminescent impregnating agent, said agent comprising 10–100% by weight of a tetrakis(disubstituted-amino) ethylene of the formula



wherein the R's are selected from the group consisting of monovalent alkyl and cycloalkyl of up to 10 carobns, divalent alkylene joined to the other R attached to the same N to form a 3–5 membered monoaza heterocycle and divalent alkylene joined to an R attached to a second N to form a 3–7 membered diaza heterocycle, and 0–90% of an inert liquid, said support amounting to 5–50% of the weight of the light source.

3. A light source of claim **1** wherein the tetrakis(disubstituted-amino)ethylene is tetrakis(dimethylamino) ethylene.

4. A light source of claim **2** wherein the support is vermiculite of 2–20 mesh particle size.

5. A light source of claim **2** wherein the active component of the impregnating agent is tetrakis(dimethylamino)ethylene.

6. A light source of claim **2** wherein the support is a polymeric urethane open-cell foam subdivided to a particle size of ⅛"–¼" diameter.

7. A light source of claim **2** wherein the support is a polycaprolactam foam.

8. A light source of claim **2** wherein the support is 6–16 mesh expanded siliceous material and the active component of the impregnating agent is 1,1',3,3'-tetraethyl-$\Delta^{2,2'}$-bi(imidazolidine).

9. An oxyluminescent article useful for perimeter defense in military operations which comprises a particulate solid, porous, inert, 6–8 mesh expanded siliceous support impregnated with a composition consisting essentially of a high melting, microcrystalline petroleum wax, purified natural paraffin wax, and tetrakis(dimethylamino)ethylene.

10. An oxyluminescent article suitable for use on water which comprises particulate solid silicone-treated vermiculite of particle size 2–20 mesh on which is absorbed tetrakis(dimethylamino)ethylene.

11. Oxyluminescent articles comprising solid, inert, porous granules, 0.1–0.5 inch in diameter, impregnated with tetrakis(dimethylamino)ethylene, said graules being further characterized by having their light emission revived by crushing under foot.

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STEPHEN J. LECHERT, JR., Primary Examiner

U.S. Cl. X.R.

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