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CHEMILUMINESCENT COMPOSITION CONTAINING SURFACTANT

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ABSTRACT OF THE DISCLOSURE

Compositions capable of emitting light when exposed to air consisting of emulsions of an oxyluminescent tetrakis(disubstituted-amino)ethylene in aqueous alkali containing non-ionic, anionic, cationic or amphoteric surfactants.

FIELD AND BACKGROUND OF THE INVENTION

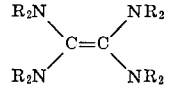
This invention relates to emergency light sources. More particularly, it relates to chemiluminescent compositions that are useful as emergency light sources to aid rescue operations on the sea.

Chemiluminescent compositions that provide emergency light have recently been described. These compositions have included oxyluminescent materials alone or dissolved in organic solvents and optionally containing organic or inorganic thickening agents. Also, various articles or devices employing such oxyluminescent compositions have been described. These hitherto known compositions and devices are useful in various applications but are not as effective as desired for use in certain rescue operations on the sea.

SUMMARY AND DETAILS OF THE INVENTION

Novel light sources especially useful for rescue operations at sea are provided by the present invention. The compositions of this invention comprise emulsions of oxyluminescent tetrakis(disubstituted-amino)ethylenes in aqueous alkali containing a surfactant, i.e., a surface-active agent. These emulsions are more stable on storage than similar compositions containing no surfactant. When selected emulsions are placed on water and exposed to air, they produce a higher intensity of light and maintain their light emission for longer times than control compositions containing no alkali or surfactant. Furthermore, selected oxyluminescent emulsions remain in a relatively small area when placed on water and do not spread out excessively.

The tetrakis(disubstituted-amino)ethylenes used as active oxyluminescent ingredients in the emulsions of this invention include the tetrakis(disubstituted-amino)-ethylenes of the formula



wherein the R's are the same or different and are monovalent alkyl or cycloalkyl of up to 10 carbon atoms, 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. Specific oxyluminescent compounds of this type include

tetrakis(dimethylamino)ethylene (TMAE),
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-aminodihydrocarbyloxymethane in accord with the following stoichiometry:

1. $R_2NCH(OR')_2 + R''_2NH \longrightarrow R''_2NCH(OR')_2 + R_2NH$
2. $R''_2NCH(OR')_2 + R''_2NH \longrightarrow (R''_2N)_2CHOR' + R'OH$
2. $2(R''_2N)_2CHOR' \xrightarrow{\Delta} (R''_2N)_2C{=}C(NR''_2)_2 + 2R'OH$

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-dioxa-heterocycle 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 U.S. Pat. 3,239,519.

The oxyluminescent tetrakis(disubstituted-amino)-ethylene can be used by itself in the emulsions or it can be dissolved in a water-insoluble, inert, non-quenching solvent or carrier, i.e., a material which does not extinguish the oxyluminescene of the tetrakis(disubstituted-amino)ethylene, to form the organic phase of the emulsion. Suitable solvents of this type include the hydrocarbons such as n-hexane, decane, Decalin, triisobutylene, cetane, tetraisobutylene, n-octadecane, 1-octadecene, purified kerosenes, white gasolines, or the more viscous hydrocarbons such as mineral oil and the like, or solid or semisolid hydrocarbons such as paraffin wax; and non-quenching synthetic oils such as silicone oils.

The organic phase of the emulsions can also include compatible non-quenching, organic or inorganic, thickening agents. Examples of suitable non-quenching thickening agents include non-reducible, non-coordinating inorganic oxides, preferably in colloidal dispersion, such as silica, alumina, zinc oxide, and the like; organic non-quenching polymers such as the hydrocarbon polymers, e.g., polyisobutylene, polypropylene, polyethylene, and the like; non-quenching polyesters, e.g., polyvinyl acetate and the like; non-quenching polyethers such as polytetramethylene oxide and the like; non-quenching olefin/ester copolymers such as ethylene/vinyl acetate copolymers and the like.

The aqueous phase of the emulsions of this invention is composed of aqueous solutions of alkali metal hydroxides, i.e., aqueous solutions of lithium, sodium, potassium, rubidium, or cesium hydroxides. The concentration of alkali

metal hydroxide in the aqueous solution can range from 2% to 40%, by weight, of the aqueous phase. Alkali concentrations of 5–20% are preferred for compositions that are to be floated on water. Emulsions in which the aqueous phase contains 40% of alkali give exceptionally brilliant luminescence at 30-minute exposure when impregnated on paper.

The surfactants useful in the emulsions of this invention include non-ionic, anionic, cationic and amphoteric types. The surfactants that are especially useful have hydrocarbon moieties containing from about 8 to about 22 carbon atoms. The particular surfactant employed in any particular composition will depend on whether an oil in water (O/W) or a water in oil (W/O) emulsion is desired and whether an emulsion that foams is desired. Specific surfactants that are operable include the following: non-ionic surfactants such as ethylene oxide reaction products with cetyl alcohol and octylphenol; anionic types such as the sodium sulfonates of saturated and unsaturated hydrocarbons having 8–22 carbon atoms; cationic types such as N-dodecyldiethanolamine, alkyltrimethylammonium chlorides in which the alkyl moiety has 12–18 carbon atoms; and the amphoteric type such as the N-alkyl and C-alkyl betaines in which the alkyl substituents have 10–12 carbon atoms.

These surfactants are employed in the emulsions of this invention in proportions ranging from about 1% to 15% of the weight of the tetrakis(disubstituted-amino) ethyleneoxyluminescent material. When the concentration of surfactant is based on the total weight of the emulsion, the surfactant can range from about 0.2% to about 5.0% of the total weight of the emulsion.

EMBODIMENTS OF THE INVENTION

The emulsions of this invention and their preparation are illustrated in further detail by the following examples in which proportions of ingredients are expressed in part by weight unless otherwise noted.

Example 1

A water-in-oil (W/O) emulsion is prepared under a nitrogen atmosphere from 8.8 parts of a commercial surfactant of the formula $RN(C_2H_4OH)_2$ in which the RN residue is derived from coconut oil amine, a solution of 86 parts of tetrakis(dimethylamino)ethylene (TMAE) in 123 parts of acid-washed mineral oil as the oil phase and 133 parts of 10% aqueous sodium hydroxide as the aqueous phase. The emulsion is agitated ultrasonically by means of a 110-watt Branson Sonifier for about one minute. The emulsion is milky in appearance, essentially colorless, and is reasonably stable. A clear upper layer that separates in several days can be redispersed readily by shaking. An aliquot of the emulsion produces a bright chemiluminescence when spread on glass fiber paper in air. When another aliquot of the emulsion is placed on water, it remains in relatively small area without spreading excessively and emits blue-green light of good brightness for well over an hour. Thereafter the light fades slowly, but even after 15 hours the emulsion is seen to be still emitting light.

When a single-phase control composition (A) comprising 224 parts of tetrakis(dimethylamino)ethylene dissolved in 88 parts of acid-washed mineral oil is placed on water in the same manner as in the above example, it emits light well at the start. However, it is far less persistent than that from the emulsion, and by the end of one hour the luminescence has essentially faded out.

Another control composition (B) is prepared by emulsifying a mixture identical to that of Example 1 except that the aqueous phase is composed of 120 parts of water instead of sodium hydroxide solution. The emulsion (W/O type) is light yellow in color and is less stable than the emulsion of Example 1. In one day it separates to such an extent that about one-half of its volume exists as a clear upper layer. The composition redisperses on shaking. When an aliquot is placed on water, it emits light well for a few minutes, but the light emission diminishes more rapidly than does that of the emulsion of Example 1.

The relative stability and performance of the emulsion of Example 1 and that of emulsion Control B are illustrated as follows:

Stability.—After standing several weeks, both emulsions separate, but the lower layer of Control B is dark yellow while that of Example 1 is colorless. Both redisperse on shaking, whereas Control B separates almost completely again in a few minutes. The emulsion of Example 1 shows no sign of separating again until about 90 minutes later.

Performance.—Equal volumes of the two emulsions at an age of 15 weeks for Example 1 and 9 weeks for Control B are placed on water, glass, and paper, respectively, and observed. At the start, Example 1 is brighter in all cases and Control B is yellower. At the end of 15 minutes, the two emulsions on glass and on paper are about equal in brightness although Control B has spread more and is yellower. On water, the emulsion of Example 1 is much brighter and does not spread as much as Control B. Although the control has spread more than the emulsion of Example 1, its still luminous area is less than that of Example 1. At the end of 0 minutes, the emulsion of Example 1 is much brighter than that of Control B on all substrates. The control exposed on water is almost dark. At 75 minutes, Control B is dark in all cases except for a few dim spots scattered over the surface of the emulsion. The emulsion of Example 1 is still of medium brightness on glass and somewhat less bright on water and paper. After 3 hours' exposure, Control B on glass is dark, but the emulsion of Example 1 is still emitting light although at a relatively low level as seen by the eye.

Example 2

An emulsion (O/W type) is prepared as in Example 1 using 8.8 parts of a 25% aqueous solution of actodecyltrimethylammonium chloride as a surfactant, 86 parts of tetrakis(dimethylamino)ethylene in 88 parts of acid-washed mineral oil as the oil phase, and 178 parts of 10% aqueous sodium hydroxide as the aqueous phase. The resulting emulsion has a relatively high stability. On standing for a day, only about 3 parts of a milky lower layer separates. When an aliquot of the emulsion is placed on water, it emits little light at the start, presumably because the oil phase is the internal one and air does not readily diffuse into it to react with the tetrakis(dimethylamino) ethylene. However, the light emission builds up with time. One hour later it is bright and two hours later it is still of medium brightness. This type of behavior is advantageous in those circumstances where a delayed action is desired in relatively inaccessible, dangerous, or otherwise sensitive locations.

Example 3

An emulsion is prepared similar to that of Example 2 except that a 25% aqueous solution of dodecyltrimethylammonium chloride is used as the surfactant. This emulsion behaves in a manner similar to that of Example 2 and, in addition, foams on shaking although, at first, the foam does not emit much light. When it is exposed to air, the light emission biulds up to a moderate level as the foam slowly collapses. Light emission continues for over two hours.

Examples 4–16

Additional emulsions are prepared from the ingredients specified in Table I below using only hand agitation. Remarks concerning pertinent features of the emulsions are included in the right-hand column of the table.

TABLE I

Ex. No.	Surfactant	Percent of TMAE [1]	NaOH solution Percent	NaOH solution Parts	Mineral oil (parts)	TMAE [1] (parts)	Other	Remarks
4	8.4 parts 25% aqueous solution of $C_3H_7-CH=C(C_2H_5)-CH_2SO_3Na$	7.0	15	84		30		Foamy emulsion.
5	8.8 parts stearic acid	10.2	10	171		86	86 parts triisobutylene	W/O, thick. Glows well on paper.
6	8.8 parts cetyl alcohol-ethylene oxide reaction product (1:2.5).	10.2	10	171		86	do	W/O. Bright emission on water.
7	6 parts octylphenol-ethylene oxide reaction product (1:5).	10.7	10	111	114	56		W/O. Good light emission on water for over one hour.
8	do	10.7	10	111		56	101 parts 5% high mol. wt. polyisobutylene in acid-washed kerosene.	W/O, very stable. No separation in several days.
9	6 parts 75% aqueous paste of sodium sulfonate of C_{20}-C_{22} hydrocarbons.	8.0	10	111	114	56		W/O. Good light emission on water for over 1 hour.
10	6 parts 25% aqueous solution of C_{10} C-alkyl-betaine amphoteric agent.	2.7	10	111	114	56		O/W. Same light emission as Ex. 9. Excellent foam former.
11	6 parts 25% aqueous solution of C_{12} N-alkylbetaine amphoteric agent.	2.7	10	111	114	56		O/W. High foaming emulsion.
12	6 parts ethylene oxide reaction product of a phosphated alcohol.	10.7	10	111	114	56		O/W. Delayed action light emission on water. Brighter than Control A at 3 hrs.
13	6 parts aluminum stearate	10.7	10	111	114	56		W/O. Extremely stable W/O emulsion. No separation in several days.
14	Same as Ex. 10	3.5	10	67	62	43	5 parts 200 mesh CaO	Less foam at start than Ex. 10, but both foam and emulsion more stable than those of Ex. 10.
15	Same as Ex. 12	14.0	10	67	62	43	do	Very stable. Essentially no separation in one day. Good light emission on water for over 90 minutes.
16	Same as Ex. 10	3.5	10	67	62	43	2 parts polyethylene (melt index, 22) ground to <20 microns.	Less foam but emulsion more stable than Ex. 10.

[1] TMAE=tetrakis(dimethylamino)ethylene.

Examples 17–21

Additional emulsions of the W/O type are prepared under nitrogen using hand agitation. Each emulsion contains 86 parts of tetrakis(dimethylamino)ethylene and 123 parts of acid-washed mineral oil. The surfactant is 8.8 parts of the $RN(C_2H_4OH)_2$ of Example 1 in all cases except one of the controls (D). The additional components of these emulsions are listed in Table II.

TABLE II

	NaOH solution Percent	NaOH solution Parts	Finely divided solid
Example Number:			
17	5	126	None.
18	10	133	Do.
19	20	146	Do.
20	40	172	Do.
21	10	133	2 parts polyethylene (melt index, 22) ground to 20 microns.
Control:			
C	0	120	I.e., water alone without NaOH.
D	86 parts of TMAE in 123 parts of mineral oil only		

Aliquots of the above compositions are tested on water as follows (the light emitted is measured with a sensitive photometer):

TABLE III

	Brightness, foot lamberts 5 min.	15 min.	30 min.	60 min.	90 min.	Remarks
Example number:						
17	0.52	0.46	0.23	0.19	0.15	
18	0.40	0.38	0.31	0.25	0.18	
19	0.67	0.40	0.38	0.33	0.23	Maintains original area of emission better than the others.
21	0.80	0.52	0.46	0.28	0.23	
Controls:						
C	0.40		0.25	0.14	0.09	Spreads badly.
D	0.43	0.25	0.23	0.22	0.23	

The caustic-containing emulsions out perform the control emulsion C in brightness. In addition, they spread less on the water and maintain their original blue-green emission better instead of yellowing badly as does control emulsion C. The emulsion of Example 21, containing finely divided polyethylene, which serves as an emulsion stabilizer, gives the best results of all.

The single-phase control D, although not as bright as the emulsions of Examples 17–21, during the first part of the emission, maintains its brightness well for at least 90 minutes. It projects much of its light downward, whereas the emulsions do not. Hence it would not be desirable for use in rescue operations in shark-infested areas. The emulsion of Example 20 (containing 40% sodium hydroxide solution as the aqueous phase) is too dense for floating on water, but it produces a more brillant emission than any of the others during the first 30 minutes when applied to paper.

I claim:

1. An oxyluminescent composition comprising an emulsion of a tetrakis(disubstituted-amino)ethylene of the formula $(R_2N)_2C=C(NR_2)_2$, wherein the R's can be the same or different and are selected from a group consisting of monovalent alkyl and cycloalkyl of up to 10 carbon atoms, 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, in aqueous alakali metal hydroxide solution containing at least one member of the group consisting of non-ionic, anionic, cationic and amphoteric surfactants having hydrocarbon moieties of from 8 to 22 carbons.

2. A composition of claim 1 wherein the tetrakis(di-substituted-amino)ethylene is tetrakis(dimethylamino) ethylene and the concentration of the alkali metal hydroxide in the aqueous solution ranging from 2% to 40%, by weight, of the aqueous phase.

3. A composition of claim 1 in which the tetrakis(di-substituted-amino)ethylene is dissolved in a water-insoluble, inert, non-quenching solvent or carrier to form the organic phase of the emulsion, said solvent or carrier being selected from the group consisting of hydrocarbons and non-quenching synthetic oils.

4. A composition of claim 1, especially adapted for floating on water, wherein the alkali metal hydroxide concentration of the aqueous phase is from 5 to 20% by weight.

5. A composition of claim 1 wherein the surfactant is present in the emulsion in an amount by weight of from about 1 to 15% based on the tetrakis(disubstiutted-amino) ethylene.

6. A composition of claim 1 wherein the surfactant is present in the emulsion in an amount from about 0.2 to about 5% based on the total weight of the emulsion.

7. A composition of claim 1 wherein the surfactant is an ethylene oxide reaction product with cetyl alcohol or with octylphenyl.

8. A composition of claim 1 wherein the surfactant is a sodium sulfonate of a saturated or unsaturated hydrocarbon having 8–22 carbon atoms.

9. A composition of claim 1 wherein the surfactant is an alkyltrimethylammonium chloride in which the alkyl moiety has 12–18 carbon atoms.

10. A composition of claim 1 wherein the surfactant is an N-alkyl or C-alkyl betaine in which the alkyl substituent has 10–12 carbon atoms.

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