United States Patent

Maeder et al.

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[45] **May 30, 1972**

[54] SCINTILLATION COUNTING COMPOSITION CONTAINING OXDIAZOLE

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[22] Filed: **June 9, 1969**

[21] Appl. No.: **832,881**

Related U.S. Application Data

[62] Division of Ser. No. 577,168, Sept., 1966, abandoned.

[52] **U.S. Cl.**.....**252/408,** 250/83, 252/301.2, 260/93.5, 260/309, 356/98

[51] **Int. Cl.**.....**C07d 85/54,** G01t 1/204

[58] **Field of Search**.....252/408, 301.2; 260/93.6, 307, 260/309, 144; 250/83, 83.6; 356/98

[56] **References Cited**

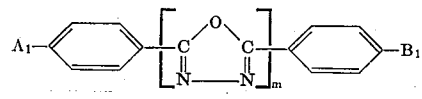
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[57] **ABSTRACT**

The invention relates to a composition of matter for counting atomic disintegrations of radioactive material which is accompanied by emission of β-rays which contains an oxdiazole compound of the formula



wherein A_1 is a branched chain alkyl, B_1 is hydrogen, phenyl, lower alkyl, or lower alkoxy, and m is 1 or 2. The counts per minute emitted by the material dispersed in the scintillation liquid are measured with a suitable instrument such as a liquid scintillation spectrometer.

8 Claims, No Drawings

SCINTILLATION COUNTING COMPOSITION CONTAINING OXDIAZOLE

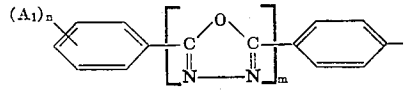
CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of Ser. No. 577,168, filed Sept. 6, 1966, and now abandoned.

The present invention relates to the use of selected oxdiazole derivatives for scintillation counting methods in atomic disintegrations.

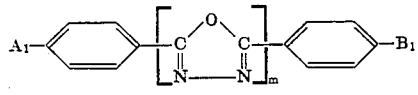
While a number of oxdiazole derivatives have already been proposed for use in scintillation counting, especially in liquid systems, these compounds do not satisfy fully all the requirements they should satisfy. This refers above all to a high energy transfer at an extremely short extinction time combined with a low absorption coefficient for self-quenching and with a high solubility in the solvents or solvent systems preferably employed in liquid scintillation counting methods. An adequate chemical stability (stability towards the action of light and towards acids and alkalies) is moreover a precondition for their suitability anyway.

It has now been found that a small selection of certain oxdiazole derivatives satisfy all of these requirements. According to this invention there are thus used oxdiazole derivatives comprising the structural element

(1) 

—in which A_1 represents an alkyl group which contains three to seven carbon atoms and at least one chain branching, and m and n each is 1 or 2 (n meaning that A_1 represents one or two substituents)—as scintillator substances.

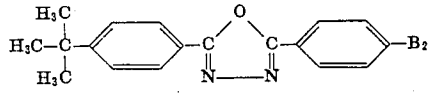
Primarily, there are used in this invention oxdiazole derivatives of the formula

(2) 

in which A_1 represents an alkyl group which contains three to seven carbon atoms and at least one chain branching, and B_1 represents a hydrogen atom, a phenyl group, an alkyl group having one to seven carbon atoms, which may be branched, or a lower alkoxy group, and $m = 1$ or 2—as scintillation substance for use in liquid scintillation counting.

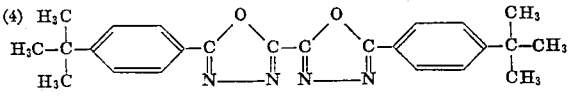
The scintillation liquids concerned are characterized in that they contain as solvent benzene or an alkylbenzene which is liquid at room temperature or a dioxane+naphthalene+water mixture and 0.01 to 5 percent by weight (referred to the total weight of the scintillation liquid) of an oxdiazole derivative of the formula (2).

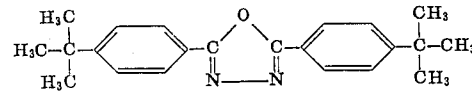
Of special importance within the scope of this invention is the use of oxdiazole derivatives of the formula

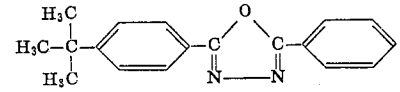
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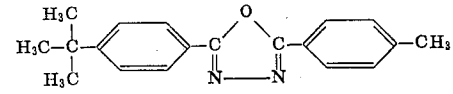
—in which B_2 represents a tertiary butyl group or a phenyl group—in liquid scintillation counting methods. In this case the scintillation liquids contain preferably toluene as solvent and 0.01 to 5 percent by weight (referred to the total weight of the scintillation liquid) of an oxdiazole derivative of the formula (3).

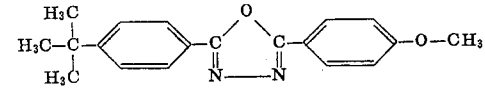
As examples from the above-mentioned types of oxdiazoles the following compounds may be mentioned:

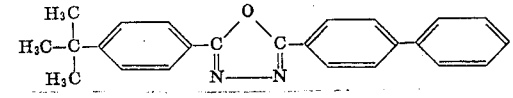
(4) 

(5) 

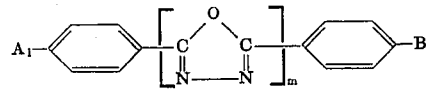
(6) 

(7) 

(8) 

(9) 

From the foregoing it will be realized that the use of the said scintillation substances is of special importance to liquid scintillation counting methods in conjunction with certain solvent systems. Thus, this invention further includes a method of counting atomic disintegrations accompanied by the emission of β-rays, by means of the liquid scintillation method in predominantly aromatic hydrocarbons as scintillator solvents, characterized in that the scintillation liquid used is a solution of an oxidazole of the formula



(in which A_1, B_1 and m have the above meanings) in benzene, or in an alkylbenzene liquid at room temperature, in a mixture of methanol+toluene, methylcellosolve+naphthalene+toluene or dioxane+naphthalene+water.

The specific oxdiazoles mentioned in connection with the liquid scintillation counting method described above are even as such scintillators that satisfy all above-mentioned requirements. In addition, they may also be used as so-called primary solutes in the narrower sense, that is to say as a primary substance activated to emit light by an energy-rich radiation released by an atomic disintegration; these primary substances are combined with the usual secondary solutes, that is to say substances distinguished by an emission of longer wavelength. Such suitable secondary solutes are, for example, 1,4-di-[2-(5-phenyloxazolyl)]-benzene, 1,4-di-[2-(4-methyl-5-phenyloxazolyl)]-benzene and 1,4-di-(4'-isopropylstyryl)-benzenes. Furthermore, they may be combined with neutron capture solutes, gamma conversion solutes, further solvent additives, gels, suspending assistants or solubilizers. The counting method used may, of course, be either an internal or an external method.

Suitable solvents for the liquid scintillation counting method are above all aromatic hydrocarbons that are liquid at room temperature (provided no solvent combination is used) such, for example, as benzene, toluene, a xylene, ethylbenzene, 1,3,5-triethylbenzene, cumene, a cymene, phenylcyclohexane, also ethers such as anisole, dioxane, 1,2-dimethoxyethane; non-aromatic hydrocarbons such as cyclohexane, heptane and the like; or finally solvent mixtures such as toluene+methanol and possibly water, toluene+ethanol, naphthalene+dioxane, naphthalene+toluene and possibly water, naphthalene+dioxane+water, methylcellosolve+naphthalene+toluene and possibly water, naphthalene+tributylphosphate or other commercial mixtures of aromatic hydrocarbons recommended for these purposes.

The concentration of the oxdiazole derivatives to be used in the present process may principally vary within wide limits which are defined or restricted by practical considerations. For example in the lower region it must be chosen so that an adequate transmission to the photomultiplier is ensured, whereas the upper region is delineated by the appearance of visible absorption of the self-quenching. Though thus, for example, for the preparation of stock solutions (which are suitably diluted for use) concentrations of 10 percent or higher are quite acceptable, the working concentrations most suitable for actual practice range approximately from 0.1 to 3 percent, preferably from 0.4 to 2 percent (all percentages are by weight, referred to the total weight of the solution).

Apart from toluene, preferred solvent systems are the systems toluene+methanol (1:1) with the addition of about 2 percent of water, methylcellosolve+toluene+naphthalene (40:60:8) with addition of up to 4 percent of water, dioxane+toluene+naphthalene (40:60:8) with up to 10 percent of water, or toluene+methanol+ethanolamine (50:44:6). The composition of the solvent system depends above all on the nature of the substrate or of the isotope to be counted. For isotope counting there are, for example, most frequently used C^{14}, H^3, S^{35}, P^{32}, Fe^{59}, Fe^{55}, I^{125} and I^{131}.

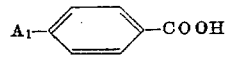
The technical advance residing in the oxdiazoles to be used in this invention is especially the fact that they represent as such scintillators that can be used by themselves (that is to say without a secondary solute) which not only satisfy all other requirements to a great extent but above all also display excellent solubility properties such as the hitherto known highest grade scintillators of the oxdiazole series did not possess. This is especially true of the particularly good solubility in transparent solvents having a high flash point.

In addition to the range of applicability described above the oxdiazoles defined above may be used quite generally wherever the task involved is the transformation of an energy-rich radiation into measurable light.

An important sphere of application is, for example, their use for so-called plastics scintillators. In this use the scintillator may be homogeneously dispersed in the polymers concerned (polymerizate, polycondensate or polyadduct) before proceeding to the final shaping operation (casting, drawing, moulding, injection moulding or the like), and the whole is then shaped. According to another possibility the scintillator is added to the starting materials used in the manufacture of the polymer, thus for example to the monomers, before polymerization, whereupon the whole is polymerized (examples: polystyrene, polyvinyltoluene). Further variants of the use of the above-mentioned scintillators result readily from the conventional operations practized in this technique.

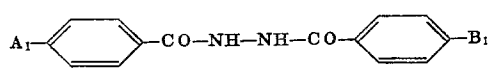
The oxdiazoles to be used in the present process can be manufactured by known methods, for example

a. by reacting 2 mols of a carboxylic acid

(10) 

or of an ester thereof with 1 mol of hydrazine in the presence of a phosphoric acid whose water content is inferior to that of orthophosphoric acid (especially polyphosphoric acid); this method is particularly suitable for synthesizing symmetrical oxdiazoles, that is to say those in which $A_1 = B_1$, or

b. by treating a diacylhydrazine of the formula

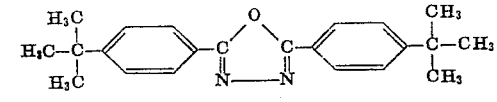
(11) 

(for $m = 1$ according to formula [2]) with a non-sulphonating dehydrating agent or

c. by reacting an imidoether upon a suitable carboxylic acid hydrazide at an elevated temperature in the presence of a solvent.

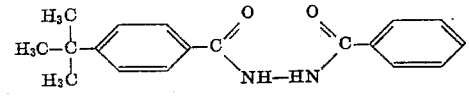
Unless otherwise indicated, parts and percentages in the following manufacturing instructions and examples are by weight.

A. 10.0 Parts of hydrazine hydrate are stirred dropwise at 50° C into 400 parts of polyphosphoric acid (83% P_2O_5), with the temperature rising to about 80° C. Then 71.2 parts of para-tertiary butylbenzoic acid are added and while excluding air the temperature is raised within 30 minutes to 125° C. The batch is stirred for 8 hours at 125° to 130° C, whereupon a clear, colorless solution forms. After cooling to about 50° C, the whole is vigorously stirred into 1,000 parts of cold water, the precipitated reaction product is suctioned off and washed with water until the washings run neutral to congo red. After drying, there are obtained 66.7 parts (= 100 percent of theory) of 2,5-bis-[4'-para-tertiary butylphenyl-(1')]-1,3,4-oxdiazole of the formula

(5) 

as an almost colorless powder which melts at 135° to 136°C. After recrystallization from ethanol+water (7:1) it forms colorless flakes melting at 139° to 141°C.

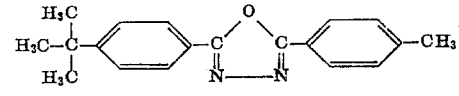
B. 29.6 parts of the diacylhydrazine of the formula

(12) 

are brought to the boil in 150 parts by volume of freshly distilled thionylchloride within 1 hour while being stirred, and the whole is then refluxed for 2 hours, whereupon a clear, pale-yellow solution forms. The excess thionylchloride is then distilled off, first under atmospheric pressure and then under vacuum. The residue is triturated with ice water, whereupon it solidifies; it is filtered off, washed with water until the washings run neutral and dried, to yield about 27.6 parts (= 99.3 percent of theory) of 2-[4'-tertiary butylphenyl-(1')]-5-phenyl-1,3,4-oxdiazole of the formula (6) as a colorless powder which on recrystallization from ethanol+water (3:1) forms colorless flakes; it melts at 98° on 99° C and displays in an ethanolic solution three absorption maxima at 288 mμ (ε = 30,400), 238 mμ (ε = 7,550) and 232 mμ (ε = 7,350). Solubility in 100 ml of ethanol at 20°C: 4.00 grams.

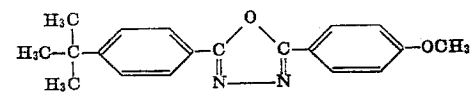
The following 1,3,4-oxdiazole derivatives are accessible by the method described above:

a. 2-[4'-tertiary butylphenyl-(1')]-5-[4''-methylphenyl-(1'')]-1,3,4-oxdiazole of the formula

(7) 

in colorless, fine crystals from ethanol+water (7:2). Melting point: 111° to 112°C. Solubility in 100 ml of ethanol at 20°C: 2.92 grams. Ultraviolet absorption in ethanol, maxima at 291 mμ (ε = 31,000) and 242 mμ (ε = 8,650).

b. 2-[4'-tertiary butylphenyl-(1')]-5-[4''-methoxyphenyl-(1'')]-1,3,4-oxdiazole of the formula

(8) 

Colorless, fine crystals from ethanol, melting at 162.5° to 163.5°C. Solubility in 100 ml of ethanol at 20°C: 0.605 gram. Ultraviolet absorption in ethanol, λ_{max} 298 mμ (ε = 32,000) and 249 mμ (ε = 6,100).

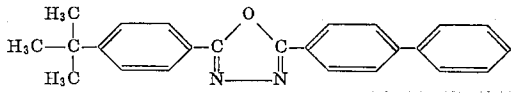
c. 2,5-bis-[4'-tertiary butylphenyl-(1')]-1,3,4-oxdiazole of the formula (5) (see above).

C. A mixture of 212 g of diphenyl-4-carboxylic acid hydrazide and 2 liters of anhydrous ortho-dichlorobenzene is stirred at room temperature, then 197 g of 4-tertiary butylbenzoylchloride and 81 ml of anhydrous pyridine are added; the thick paste is heated within 1 hour to 100° to 105°C and stirred at this temperature for 1 hour. Within a further hour the reaction mixture is then heated to 140° to 145°C, whereupon an almost complete solution is obtained. 90 ml of thionylchloride are then dropped in within 45 minutes at 140° to 145°C, whereupon a turbid solution forms which is stirred on for 15 minutes after the dropwise addition is complete.

The bulk of the solvent is then evaporated under vacuum and 1 liter of ethanol is dropped in so that the reaction mixture is kept at the reflux temperature, whereupon a crystalline precipitate soon forms which is suctioned off at room temperature, and the filter cake is washed with alcohol and dried, to yield 295 g of a greyish, crystalline powder melting at 135° to 136°C.

Crystallization from n-propanol with the aid of active carbon furnishes 240 g of the compound of the formula

(9)



in the form of colorless prisms melting at 136° to 137°C. $C_{22}H_{22}ONB2$ (mol. weight: 354.43)

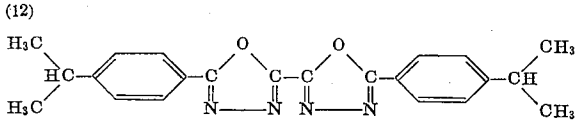
calculated:	C 81.32	H 6.26	N 7.90%
found:	81.27	**6.14**	**7.92%**.

D. 5.2 Grams of oxalic acid dihydrazide and 10 ml of anhydrous pyridine are added at 40° to 50°C to a solution of 14.5 g of 4-isopropylbenzoylchloride in 200 ml of anhydrous ortho-dichlorobenzene. In the course of 2 hours the reaction mixture is heated to 130° to 135°C, whereupon a thinly liquid paste is obtained. Within 30 minutes at 130° to 135°C 20 ml of thionylchloride are dropped in, whereupon a clear solution forms which is stirred for another 15 minutes at this temperature and then allowed to cool.

The excess thionylchloride and the solvent are then almost completely evaporated under vacuum. The residue is stirred with 100 ml of methanol, whereupon a light-brown, crystalline precipitate is obtained which is suctioned off and washed with methanol.

Two recrystallizations from alcohol in the presence of bleaching earth furnish 7 g of the bis-oxdiazolyl compound of the formula

(12)



in the form of small colorless needles melting at 175° to 176°C. $C_{22}H_{22}O_2N_4$ (mol. weight: 374.45)

calculated:	C 70.57	H 5.92	N 14.96%
found:	70.65	**5.91**	**14.84%**.

In the following examples all measurements were recorded in counter tubes poor in potassium with the use of a liquid scintillation spectrometer TRI-CARB model Ex-2, makers Messrs. Packard Inst. Comp. Inc., Ill.

EXAMPLE 1

20 ml each of a solution of 5 g of the compound of the formula (9) and of the formula (5) in 1 liter of toluene are introduced into a counter tube and mixed with 1 ml of a solution of benzoic acid marked with C^{14} having an activity of 0.01 microCurie. The counter tube is inserted into the counter and the counts per minute (= cpm) are counted. At a high-voltage of 900 Volts and a calibration from 100 to 600 there are recorded 13,630 cpm for compound (9) and 13,200 for compound (5).

EXAMPLE 2

20 ml each of a solution of 5 g of the compound of the formula (9) and of the formula (5) in 1 liter of toluene are introduced into a counter tube, and 0.1 ml of toluene marked with H^3, having an activity of 0.01 microCurie, is added. At a high-voltage of 1,100 Volts and a calibration from 100 to 600 there are recorded 6,600 cpm for the compound (9) and 5,930 cpm for the compound (5).

EXAMPLE 3

20 ml each of a solution of 10 g of the compound of the formula (9) and of the formula (5) in 1 liter of toluene are mixed in a counter tube with 1.0 ml of an ethanolic solution of 1-butyl-3-(para-tolylsulphonyl)-urea marked with S^{35}. The activity added is 0.01 microCurie. The counter tube is then inserted in the counter and the counts per minute are counted. At a high-voltage of 900 Volts and a calibration from 100 to 600 in the measuring channel there are recorded 13,200 cpm for compound (9) and 12,950 cpm for compound (5).

EXAMPLE 4

20 ml of a solution of 10 g of the compound of the formula (9) in a mixture of 400 ml of methylcellosolve, 80 g of naphthalene and 600 ml of toluene are introduced in a small measuring cylinder, and 0.5 ml of water marked with H^3, having an activity of 0.01 microCurie, is added. At a high-voltage of 1,200 Volts and a calibration from 100 to 600, 2,200 counts per minute are counted.

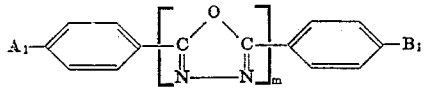
EXAMPLE 5

A mixture of 1 g of 2-[4'-tertiary butylphenyl-(1')]-5-biphenylyl-1,3,4-oxdiazole of the formula (9) and 100 g of vinyltoluene distilled twice under 11 mm Hg pressure (mixture of the ortho, meta and para isomers) is introduced into a Pyrex glass tube of 25 mm diameter which is fused at one end. The tube is repeatedly evacuated to a pressure of 0.1 mm Hg and scavenged with pure nitrogen. Finally, the tube is once more evacuated to 0.1 mm Hg pressure and the tube is fused at the other end. The tube is then heated within 2 hours in a furnace to 110°C while ensuring by carefully revolving it that the compound of the formula (9) is completely dissolved. To polymerize the batch in the tube it is maintained for 24 hours at 110°C, then heated for 24 hours at 130°C and for 48 hours at 140°C. The following cooling and detensioning phase at 75°C takes 81 hours. When the batch has cooled to room temperature, the resulting transparent polymer core is recovered by smashing the glass tube. To measure the relative count rate the core is turned down to a diameter of 20 mm, sawn up into discs 10 mm thick, and these discs are polished. The measure of the light output is the relative amplitude (RPH) of the counts produced by the Cs^{137} conversion electrons. For counting a Philips 56 AVP photomultiplier with a ratio 2,2-paraphenylene-bis-(5-phenyloxazole) : terphenyl of 1.30 (photomultiplier characteristic) is used. The counting standard used is the commercial plastics scintillator NE 102 A (makers Nuclear Enterprises Ltd.) whose RPH value is taken as equal to 1.00. The plastics scintillator according to this invention displays an RPH value of 1.10. A plastics scintillator prepared in identical manner from polyvinyl-toluene, which contains 2 percent of the compound of the formula (9) and

0.1 percent of 2-[4'-biphenylyl-(1')]-6-phenyl-benzoxazole, gives the high RPH value of 1.23.

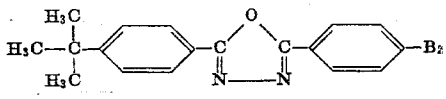
What is claimed is:

1. A composition of matter for scintillation counting containing a solvent selected from the group consisting of benzene, or an alkylbenzene that is liquid at room temperature and a dioxane+naphthalene+water mixture and 0.01 to 5 percent by weight, referred to the total amount of scintillation liquid, of an oxdiazole derivative of the formula



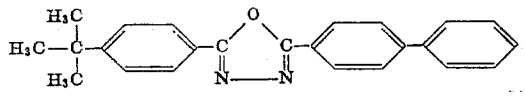
in which A_1 represents an alkyl group containing three to seven carbon atoms and at least one chain branching, and B_1 represents a member selected from the group consisting of hydrogen atom, a phenyl group, and an alkyl group which contains one to seven carbon atoms and may be branched or a lower alkoxy group, and *m* is a whole number from 1 to 2.

2. A composition of matter for scintillation counting according to claim 1 containing a solvent toluene and 0.01 to 5 percent by weight, referred to the weight of the whole liquid, of an oxdiazole derivative of the formula

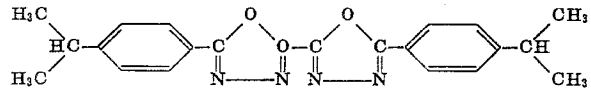


in which B_2 represents a member selected from the group consisting of a tertiary butyl group and a phenyl group.

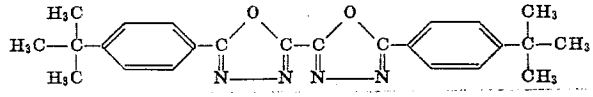
3. A composition of matter according to claim 1 containing as oxdiazole derivative the compound of the formula



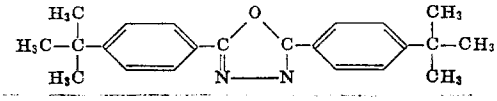
4. A composition of matter according to claim 1 containing as oxdiazole derivative the compound of the formula



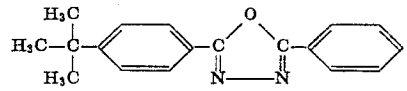
5. A composition of matter according to claim 1 containing as oxdiazole derivative the compound of the formula



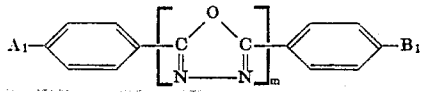
6. A composition of matter according to claim 1 containing as oxdiazole derivative the compound of the formula



7. A composition of matter according to claim 1 containing as oxdiazole derivative the compound of the formula



8. A composition of matter for scintillation counting method substantially consisting of a polymeric material which contains at least one compound of the general formula



in which A_1 represents an alkyl group which contains three to seven carbon atoms and at least one chain branching; B_1 represents a member selected from the group consisting of a hydrogen atom, a phenyl group, an alkyl group which contains one to seven carbon atoms and a lower alkoxy group, and *m* stands for a whole number from 1 to 2.

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