

(12) UK Patent Application (19) GB (11) 2 101 460 A

- (21) Application No **8202566**
(22) Date of filing **6 Jul 1981**
(43) Date of issue
12 Jan 1983
(51) **INT CL³**
(As given by ISA)
G01T 1/04 1/10
(52) Domestic classification
H5R 6
(56) Documents cited by ISA
US, A, 2844465
US, A, 3710109
US, A, 2676887
US, A, 2528496
US, A, 2441561
US, A, 3226233
US, A, 2664511
US, A, 3068178
US, A, 3666683
US, A, 3010908
US, A, 2877169
US, A, 2877167
US, A, 2877166
N, Radiat. Phys. Chem.
Vol 9, No 4-6, pages 737-
747
(58) Field of search by ISA
US 250/474, 461R
252/408, 600, 301.17
96/82, 89, 90R, 90PC
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(54) Radiochromic liquid solution

(57) A solution of a leucocyanide dye in a clear polar solvent with enough organic acid added to make the solution at least slightly acidic which is sensitive to small dosages of ionizing and ultraviolet radiation and responds by permanently changing color. Up to one half of the solution by

weight can be replaced by a second solution of an aromatic solvent and an organic fluor. Another modification of the invention is a solution of a leucocyanide dye in a clear polar solvent having an aromatic group, an organic fluor, and enough organic acid to make the solution at least slightly acidic.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ³: G01T 1/04, 1/10</p>	<p>A1</p>	<p>(11) International Publication Number: WO 82/00527 (43) International Publication Date: 18 February 1982 (18.02.82)</p>
<p>(21) International Application Number: PCT/US81/00920 (22) International Filing Date: 6 July 1981 (06.07.81) (31) Priority Application Number: 172,250 (32) Priority Date: 25 July 1980 (25.07.80) (33) Priority Country: US (71) Applicant: BICRON CORPORATION [US/US]; 12345 Kinsman Road, Newbury, OH 44065 (US). (72) Inventors: CULP, Randolph, A.; 4967 South Sedgewick Road, Lyndhurst, OH 44124 (US). NOAKES, John, E.; 4295 Barnett Shoals Road, Athen, GA 30605 (US). (74) Agents: SOPKO, Jeffrey, J. et al.; Pearne, Gordon, Sessions, McCoy & Granger, 1200 Leader Building, Cleveland, OH 44114 (US).</p>		<p>(81) Designated States: CH, DE, DK, GB, JP, NL, SE. Published <i>With international search report</i></p>
<p>(54) Title: RADIOCHROMIC LIQUID SOLUTION</p>		
<p>(57) Abstract</p> <p>A solution of a leucocyanide dye in a clear polar solvent with enough organic acid added to make the solution at least slightly acidic which is sensitive to small dosages of ionizing and ultraviolet radiation and responds by permanently changing color. Up to one half of the solution by weight can be replaced by a second solution of an aromatic solvent and an organic fluor. Another modification of the invention is a solution of a leucocyanide dye in a clear polar solvent having an aromatic group, an organic fluor, and enough organic acid to make the solution at least slightly acidic.</p>		

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RADIOCHROMIC LIQUID SOLUTION

This invention relates to a radiochromic liquid solution which is particularly sensitive to radiation from wave lengths of between .005 Angstroms and 3900 Angstroms and which, upon exposure to such radiation, responds by permanently changing from a clear solution to a colored solution.

The above wave lengths include ultraviolet radiation, gamma ray radiation, and X-ray radiation. There are a number of devices which respond to radiation from the above wave lengths. One device measures ultraviolet radiation and provides a color indicator for use when a person has been exposed to too much sunlight, as disclosed in U.S. Patent 3,449,572. Other devices measure, by color indicators, the exposure to gamma ray and X-ray radiation for persons who work around equipment which emits such radiation, as disclosed in U.S. Patents 2,848,625; 3,657,538; and 3,899,677. Still other devices measure the exposure to nuclear radiation, as disclosed in U.S. Patents 3,461,288 and 4,001,587.

The problem with most such devices and compounds is that they are not sensitive enough. In monitoring the exposure of personnel during a nuclear war or nuclear disaster, for instance, readings have to be provided in a range of from about 20 rads to about 1000 rads. A "rad" is a unit of absorbed radiation dosage equal to the delivery of .01 joules per kilogram of human body material. A dosage of 1000 rads is lethal. A dosage of 600 rads can be lethal to perhaps fifty per cent of the population exposed to the dosage. A dosage of 200 rads is not lethal. It is obviously important to be able to measure these various dosages accurately, and

there are such devices, but they are laboratory-type instruments which require a special reader or which require a special power supply to charge them and keep them charged.

The object of the present invention is to provide a radiochromic liquid which responds to radiation from ultraviolet wave lengths and below, including X-rays and gamma rays, which is particularly sensitive to low exposures of radiation from such wave lengths and which does not require a separate reader or power supply. Other objects and advantages will become apparent from the following description of the invention.

In accordance with our invention, we dissolve relatively large amounts of a hydrophobic leucocyanide dye in a clear polar organic solvent ultrasonically and add small amounts of an organic acid to act as a sensitizer and stabilizer to make a radiochromic liquid which responds to photons between .005 Angstrom and 4000 Angstroms in proportion to the integrated intensity of the exposure.

The leucocyanide dyes come as a crystalline powder and are described in U.S. Patents 2,441,561; 2,528,496; 2,676,887; and 2,877,167. They can be dissolved in a monomer and then polymerized into a solid plastic or they can be dissolved in a suitable liquid medium and kept in solution. In either event, when they are exposed to ultraviolet or ionizing radiation, they change from the clear or "leuco" state into the colored state. In suitable conditions, the change is permanent. Even the crystalline powder will change color when exposed to ultraviolet or ionizing radiation, but it does this more slowly than when dissolved in solution or suitably incorporated into a polymer. Prior to our invention, these dyes were believed to be of low radiation sensitivity and were used to measure high doses of radiation, from about 1000 rads up to over 10 megarads.

The leucocyanide dyes for use in the present invention can be any hydrophobic, substituted aminotriphenyl methane leucocyanide dye. We prefer blue, violet, or green dyes because those colors can be discerned by most persons, that is, fewer persons are color-blind to them.

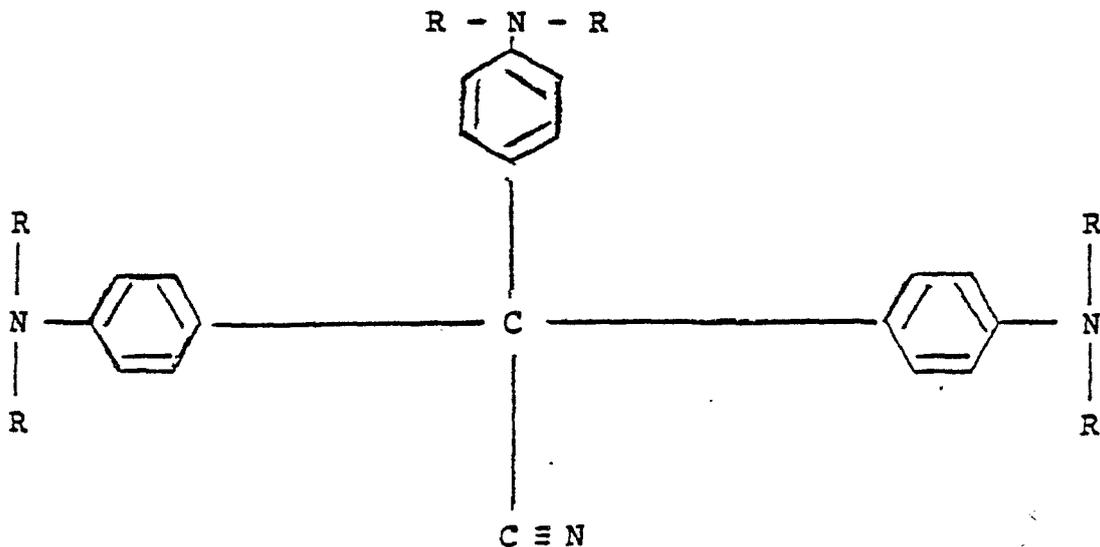
The preferred dyes are:

- pararosaniline cyanide
- hexa(hydroxyethyl) pararosaniline cyanide
- new fuchsin cyanide
- crystal violet cyanide.

Other suitable dyes are:

- malachite green cyanide
- brilliant blue cyanide
- methyl green cyanide
- helvetia green cyanide
- seto-glaucine cyanide.

The leucocyanide dyes for use in accordance with the present invention may be represented by the following basic formula:



The R groups may be one of a hydrogen atom, an alkyl group of less than eight carbon atoms, such as methyl, ethyl, propyl, or butyl groups, or a hydroxyethyl group. The R groups may be the same or may be different in the positions shown in the formula. Also, the amino groups in the para position on the phenyl groups can be replaced by a hydrogen atom.

The dyes are dissolved in a polar solvent, which should be clear so that when the dye is dissolved, the solution is clear or at least has a minimum of background coloration. Preferably, the solvent should be free of hydroxy groups. We prefer solvents with relatively high polarities of at least about 5 debye units. The higher polarity solvents facilitate dissolving greater amounts of dye therein. Also, they seem to enhance the sensitivity of the dye in the color change reaction.

The solvents should stay liquid down to below at least about 20° C., and should not boil or vaporize at temperatures below about 80° C. Cost and availability are other obvious considerations.

The concentration of the dye in the polar solvent should be at least about 1 to 25 per cent by weight, and preferably about 1 to 10 per cent by weight, which in most instances is approaching or about at the saturation point. We prefer, and try to obtain, relatively high concentrations of dye in the polar solvent.

The compounding and formulation must take place in a room which is filtered to keep out ultraviolet light and all other wave lengths of less than 4000 Angstroms. The dye solution must also be kept in containers which filter out ultraviolet light. Preferably, the solution is bubbled with nitrogen.

Means must be found to facilitate dissolution of the dyes in the solvent, because you are approaching the saturation limits of the dye in the solvent. The dyes cannot be heated in order to dissolve them in the solvent because the heat activates them and they tend to change to their colored state. They therefore have to be dissolved in the solvent in amounts which approach their saturation point by ultrasonic vibration. The powdered dye is poured into a beaker of solvent and the beaker subjected to ultrasonic vibration until, by visual inspection, one may determine that all of the dye has been dissolved in the solvent.

After the dye has been dissolved in the solvent, we add small amounts of an organic acid sensitizer and stabilizer. Acid sensitizes the dye so that it responds to radiation from wave lengths under 4000 Angstroms and then, once it has responded and effected a color change, stabilizes the dye so that it does not revert back to the clear color form.

When a solvent/dye system goes from clear to color as a result of radiation, it loses some of its acidity. One purpose of the organic acid is to make sure that the system stays on the acid side and that there are acid groups available for reaction with the dyes so that the color change is stabilized.

Suitable polar solvents are: triethyl phosphate; dimethyl sulfoxide; dimethyl formamide; vinyl pyrrolidone; tributyl phosphate; trioctyl phosphate; and trichloroethyl phosphate.

The preferred organic acid sensitizers and stabilizers are: acetic acid; citric acid; carboxylic and benzoic acid.

Other acids which we contemplate using in addition to those already mentioned are:

tartaric acid
phthalic acid
salicylic acid
maleic acid.

The organic acids should dissolve in the solvent in which they are employed, and should be free of water.

The amount of the organic acid should be enough to make the solution slightly acidic with a pH of 5 to 7 and stabilize the color change.

The following examples illustrate this aspect of our invention.

EXAMPLE I

From a stock supply of highly purified hexahydroxy ethyl pararosaniline cyanide dye, we weighed out accurately 7g of dye, which was then placed into 100 ml of high purity or reagent grade triethyl phosphate in an amber-coated flask to filteractinic ultraviolet light. The dye was then ultrasonically dissolved until the solution was clear. To this was added 0.1 ml of glacial acetic acid, which resulted in solution pH of 6. The solution was bubbled with nitrogen after the acid was added to eliminate gaseous oxidants within the mixture that could have confounding effects on the system.

The above solution was then irradiated with gamma rays from a cobalt 60 source to provide an exposure of 100 rads. The solution turned pale blue.

EXAMPLE II

From a stock supply of high purity new fuchsin cyanide dye, 10g of dye was dissolved ultrasonically in 100 ml reagent grade dimethyl sulfoxide until a clear solution appeared. Then 0.1 g of benzoic acid was added to give a pH of 5.5.

The above was irradiated with ultraviolet radiation from a hydrogen continuum lamp for 60 seconds. The liquid changed to a deep red color.

In accordance with a modification of our invention, we have discovered that we can dissolve an organic fluor or scintillator in an aromatic solvent, such as benzene, toluene, or xylene, dilute the aforesaid leucocyanide dye/polar solvent/organic acid solutions by up to one-half by volume, and still have an excellent, sensitive radiochromic liquid.

A wave shifting and concentration of radiant energy takes place so that, in this combination, a smaller amount of dye becomes just about as effective as a larger amount in the combination of the foregoing examples.

The aromatic solvent absorbs X-ray and gamma ray radiation, and emits radiation at around 3000 Angstrom wave lengths. The fluor, in turn, picks up the emissions from the aromatic solvent and emits photon energy in the 3000-3800 Angstrom wave length range, which is a range to which the leucocyanide dyes are very sensitive. These photons, in turn, are absorbed by the leucocyanide dye in the polar solution to change its color.

The wave lengths at which the aromatic solvent and fluor absorb and emit radiation should be matched, bearing in mind that one is dealing with peaks and bands over which these materials act, and not precise numbers. Of course, the closer the peak at which the aromatic solvent emits is matched with the peak at which the fluor absorbs, and the like, the more efficient the system becomes.

Suitable fluors are those which absorb radiation at around 3000 Angstroms and emit at around 3850 Angstroms.

Suitable fluors are the various oligophenylenes, oxazoles, thiazoles, or oxadiazoles with two to six or more benzene rings such as PPO, PBD, PBBO, NPO, and NOPON and the like, in which P is used for phenyl, N for naphthyl, B for biphenyl, O for oxazole, and D for the oxadiazole group.

Suitable aromatic solvents are those which absorb radiation below 2000 Angstroms and emit at around 3000 Angstroms.

The fluor is dissolved in the aromatic solvent in amounts approaching the saturation point so as not to exceed the saturation point when mixed with the polar solvent.

EXAMPLE III

4 grams of hexahydroxyethyl pararosaniline cyanide dye was dissolved in 50 ml reagent grade triethyl phosphate ultrasonically. It was then acidified with .05 ml glacial acetic acid to give a pH of 6. 0.3 grams of PPO was dissolved in 50 ml reagent grade benzene. The two solutions were mixed together.

The mixed solution was then exposed to gamma rays from a cobalt 60 source to provide a total exposure of 100 rads.

The solution changed to a pale blue color determined by unaided visual observation. The color approached the intensity of that of Example I, which contained about twice the amount of dye.

In a still further modification of our invention, we can provide a polar solvent which also has an aromatic ring

in it which responds to X-ray and gamma ray radiation like the aromatic solvent previously disclosed. To this solvent may be added a leucocyanide dye, an organic acid, and a fluor. The advantage of this system is that it eliminates the need for separate solvents for the dye and, for the fluor, provides an energy transfer means for direct photon activation of the dye, and solubilizes the dye.

Polar aromatic solvents for hydrophobic leucocyanide dyes possessing one or more aromatic groups may be a compound such as triphenyl phosphate.

The compounds used in accordance with our invention should be free of impurities. The dyes, in particular, should be pure. Impurities in the dyes will give objectionable background coloration or flush. While the commercially available solvents, organic acids and secondary fluors are usually relatively pure and can often be used as is without additional purification, the purity of the ingredients in the system must be kept in mind. In working with these materials, one can never tell when an impurity will act as a screener or otherwise upset the response of the system.

We should note that solutions made in accordance with our invention respond to two general classes of radiation, namely, ultraviolet radiation, and radiation from gamma rays and X-rays and the like at the lower end of the spectrum which is also ionizing radiation. Ultraviolet radiation starts at 3900 Angstroms and goes down to 100 Angstroms. The ionizing radiation is in the range of from about 300 Angstroms down to .005 Angstroms.

Radiochromic solutions made in accordance with the present invention respond to photons or wave lengths between .005 Angstroms up to 3900 Angstroms by changing color, as is well known. For gamma and X-rays, these solutions respond to exposures of from about 20 rads up to 1000 rads. For ultraviolet, the threshold of response is in the range of about 5

millijoules per square centimeter. The response to radiation is cumulative. If a person receives 100 rads one day and 300 rads the next day, the radiochromic dye solutions of the present invention give a response of 400 rads. In other words, radiochromic solutions made in accordance with the present invention respond in proportion to the integrated intensity of the exposure.

As should be apparent to those skilled in the art, there are a number of applications and uses for the radiochromic liquids of our invention. They can be incorporated in dosimeters and carried about by persons working with X-rays or gamma radiation. They can be made up in sealed ampoules with tissue or bone equivalencies and placed on or within a critical area of the human body in order to determine precise dosage for radiation therapy. They can be used by persons with sensitive skin working in bright sunlight who wish to avoid excessive exposure to ultraviolet radiation. They can be attached to foodstuffs to record sterilizing radiation. Troops exposed to nuclear radiation can carry simple dosimeters having a solution made in accordance with our invention and, by noting color change alone in the field, will be able to estimate their exposure.

It will be understood that in accordance with the provisions of the patent statutes, variations and modifications of the compositions disclosed herein may be made without departing from the spirit and scope of the invention.

Having thus described our invention, we claim:

1. A radiochromic liquid comprising 100 parts by weight of a polar solvent, at least 4 parts by weight of a hydrophobic leucocyanide dye dissolved in such solvent, and enough organic acid to make the solution acidic, said dye being in its colorless state.

2. A radiochromic liquid in accordance with claim 1, in which the solvent is one of:

triethyl phosphate,
 dimethyl sulfoxide,
 dimethyl formamide,
 2-ethoxy ethanol,
 vinyl pyrrolidone;
 tributyl phosphate,
 trioctyl phosphate,
 trichloroethyl phosphate;

the dye is one of:

pararosaniline cyanide,
 hexahydroxyethyl pararosaniline cyanide,
 new fuchsin cyanide,
 crystal violet cyanide,
 formyl violet cyanide,
 malachite green cyanide,
 brilliant blue cyanide,
 methyl green cyanide,
 helvetia green cyanide, and
 seto-glaucine cyanide;

and the organic acid is one of:

acetic acid,
citric acid,
salicylic acid,
carboxylic acid,
benzoic acid,
tartaric acid,
phthalic acid, and
maleic acid.

3. A radiochromic solution in accordance with claim 1, in which the solvent is triethyl phosphate, the dye is hexahydroxyethyl pararosaniline cyanide and the acid is glacial acetic acid.

4. A radiochromic solution in accordance with claim 1, in which up to half of the solvent/dye solution by weight is replaced by a solution of an aromatic solvent and an organic fluor, the absorption and emission characteristics of said aromatic solvent and a fluor being matched to each other and to the dye so as to retain the sensitivity of the solution and measure radiation at levels below 2000 Angstroms.

5. A radiochromic solution comprising a hydrophobic leucocyanide dye, an organic polar solvent with an aromatic group, an organic fluor, and an organic acid, the dye being dissolved in the solvent and there being enough organic acid to make the solution acidic.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 81/00920

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. Cl ³ G01T 1/04, 1/10
 US Cl 252/408,600 250/474

II. FIELDS SEARCHED

Minimum Documentation Searched ⁴

Classification System	Classification Symbols
US	250/474, 461R 252/408,600, 301.17 96/82, 89, 90R, 90PC

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	US, A, 2,844,465, PUBLISHED 22 August 1958, CHALKLEY	1-5
X	US, A, 3,710,109, PUBLISHED 09 January 1973, CHALKLEY	1-3
X	US, A, 2,676,887, PUBLISHED 27 April 1954, CHALKLEY	1-3
X	US, A, 2,528,496, PUBLISHED 07 November 1950, CHALKLEY	1-5
X	US, A, 2,441,561, PUBLISHED 18 May 1948, CHALKLEY	1-5
X	US, A, 3,226,233, PUBLISHED 28 December 1965, AGRUSS	4,5
X	US, A, 2,664,511, PUBLISHED 29 December 1953, MOOS	4,5
X	US, A, 3,068,178, PUBLISHED 11 December 1962,	4,5
A	KALLMANN ET AL US, A, 3,666,683, PUBLISHED 30 May 1972, MAEDER ET AL	4,5
A	US, A, 3,010,908, PUBLISHED 28 November 1961, BRODERICK ET AL	4,5
A	US, A, 2,877,169, PUBLISHED 10 March 1959, CHALKLEY	1-3
A	US, A, 2,877,167, PUBLISHED 10 March 1959, CHALKLEY	1-3

⁶ Special categories of cited documents: ¹⁵

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹

13 OCTOBER 1981

Date of Mailing of this International Search Report ¹

19 OCT 1981

International Searching Authority ¹

ISA/45

Signature of Authorized Officer ¹⁹

Teddy S. Gron

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 2,877,166, PUBLISHED 10 March 1959, CHALKLEY	1-3
A	N, RADIAT. PHYS. CHEM., VOLUME 9, NO. 4-6, ISSUED 1977, HUMPHERYS, K.C., ET AL, PAGES 737-747.	1-4

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers _____, because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹⁴

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

- The additional search fees were accompanied by applicant's protest.