United States Patent [19]

Groff

[11] **3,843,939**

[45] **Oct. 22, 1974**

[54] **METHOD AND APPARATUS FOR MODULATING LIGHT WITH A MAGNETIC FIELD**

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[73] Assignee: **E.I. du Pont de Nemours and Company**, Wilmington, Del.

[22] Filed: **May 3, 1972**

[21] Appl. No.: **249,802**

[52] **U.S. Cl.** **332/7.51**, 252/301.2, 350/160

[51] **Int. Cl.** **H01s 3/10**

[58] **Field of Search** 332/7.51; 252/301.2, 301.3, 252/188.3; 350/160; 307/88.3

[56] **References Cited**

UNITED STATES PATENTS

3,656,835 4/1972 Johnson et al. ..... 350/160 R

OTHER PUBLICATIONS

Nickel, "Energy Transfer from Absorbed Dye Molecules to Anthracene Single Crystal", 1969, pg. 27–30, Chem. Phys. Letter 4(1).

Primary Examiner—T. H. Tubbesing
Assistant Examiner—N. Moskowitz

[57] **ABSTRACT**

Delayed fluorescence due to triplet-triplet exciton annihilation in crystalline host materials sensitized with certain dyes (such as anthracene sensitized with Rhodamine B) is modulated by magnetic fields in a more useful manner than conventional delayed fluorescence, and can be used to measure magnetic fields, including spatially modulated fields such as those produced by recorded magnetic tapes. The dyestuffs must be employed in the absence of fluorescence quenching agents and the chromophoric group must be free of atoms having an atomic number greater than 9.

9 Claims, 4 Drawing Figures

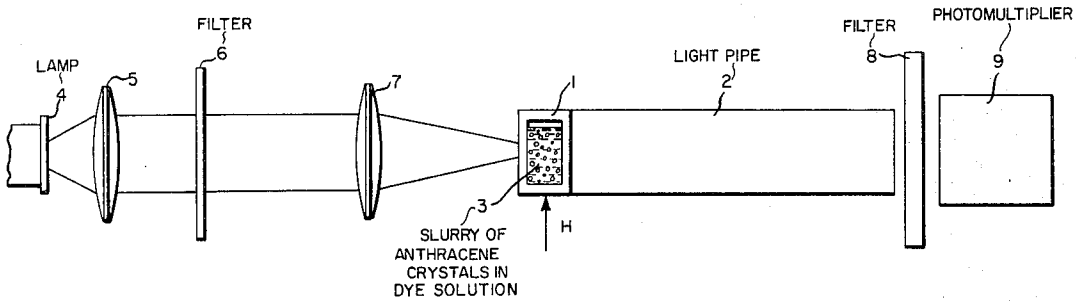


FIG. 1

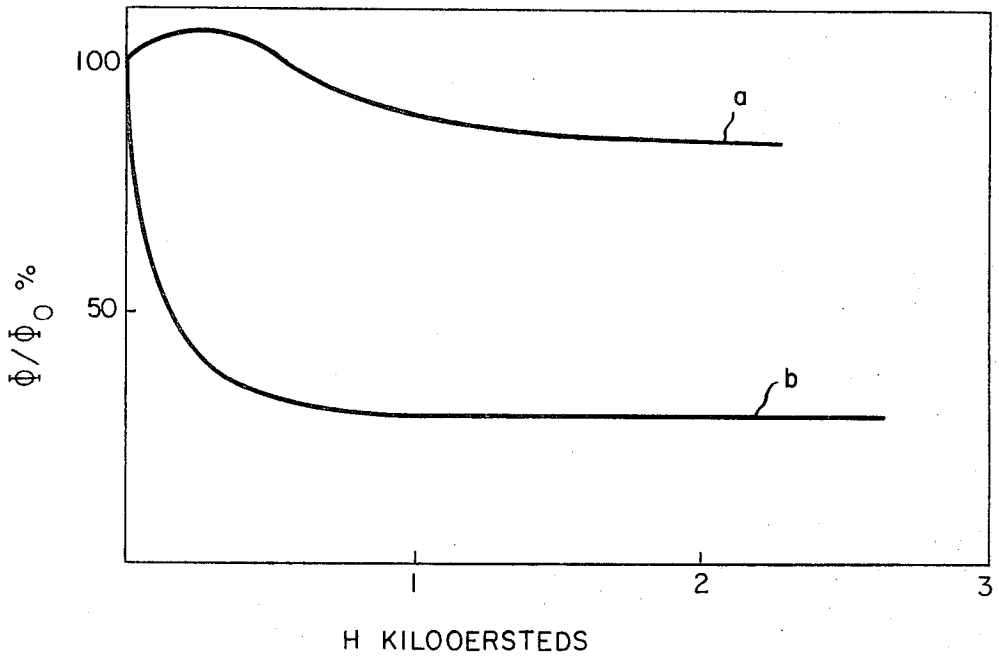
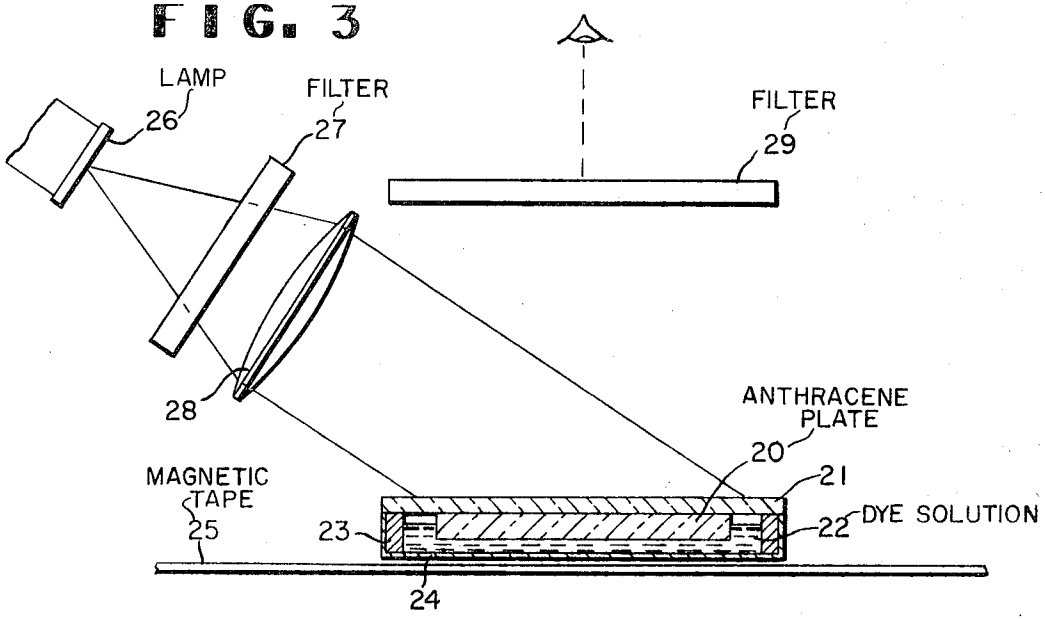

100
50
Φ/Φ_0 %
a
b
1
2
3
H KILOOERSTEDS

FIG. 3


LAMP
26
FILTER
27
FILTER
29
28
ANTHRACENE PLATE
20
21
MAGNETIC TAPE
25
23
22
DYE SOLUTION
24

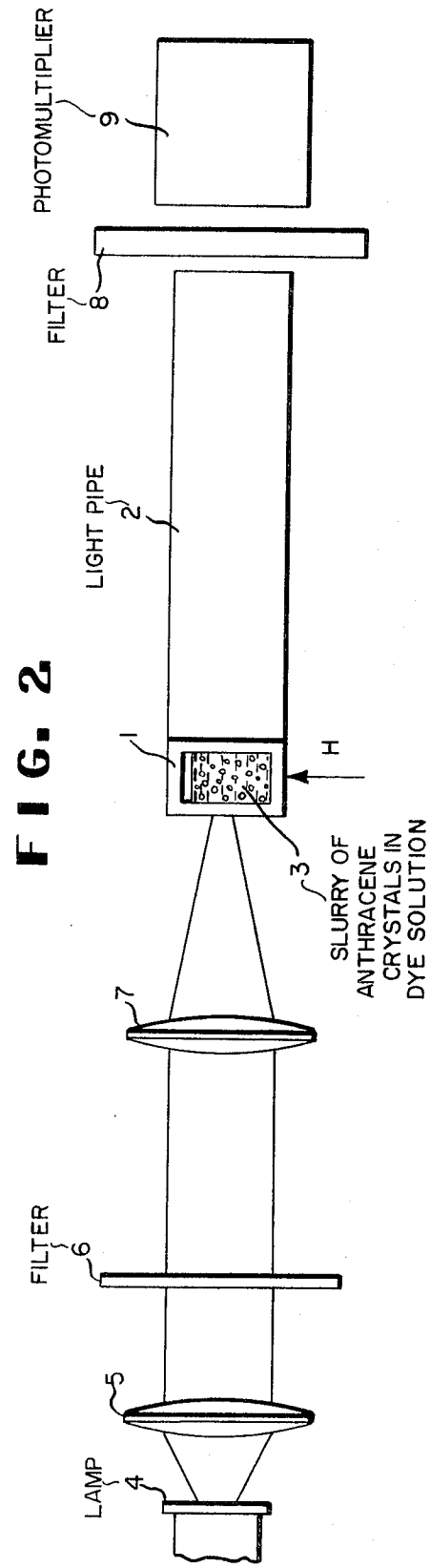

PHOTOMULTIPLIER
9
FILTER
8
LIGHT PIPE
2
1
H
3
SLURRY OF ANTHRACENE CRYSTALS IN DYE SOLUTION
7
FILTER
6
5
LAMP
4

FIG. 2

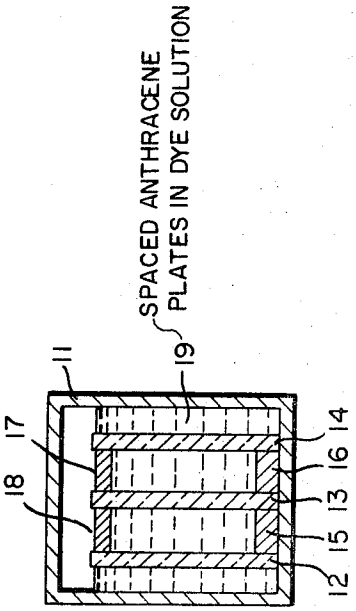

SPACED ANTHRACENE PLATES IN DYE SOLUTION
19
11
17
18
14
16
13
15
12

FIG. 2A

METHOD AND APPARATUS FOR MODULATING LIGHT WITH A MAGNETIC FIELD

FIELD OF THE INVENTION

This invention relates to a process of producing light modulated spatially and/or temporally by a magnetic field.

BACKGROUND OF THE INVENTION

The present invention utilizes dye-sensitized delayed fluorescence in crystalline materials such as anthracene, which is believed to result from triplet-triplet exciton annihilation.

An exciton in a crystal or region of a crystal is an internally mobile, electronically excited state which can internally transport energy but not charge. A triplet exciton is one in which the electronically excited state in question bears one unit of spin (arising from two unpaired electrons). Excitons, once created in a crystal, do not persist indefinitely, but decay by a monomolecular process characterized by a lifetime τ. In the case of triplet excitons, the energy given up in this monomolecular decay process can either appear as heat or as light (phosphorescence).

In some crystals, triplet excitons can also disappear by a second, bimolecular, process, termed mutual annihilation, in which a pair of excitons meet and combine their energy to yield a single, higher energy singlet exciton (one with zero spin, i.e., all electrons paired). This singlet exciton, which normally has a much shorter lifetime than the triplet exciton, subsequently disappears with emission of light. The light produced in this manner is usually termed "delayed fluorescence" to distinguish it from the more usual "prompt fluorescence" which results when the singlet exciton is produced directly by absorption of light.

Crystals in which triplet excitons can be created can be classified according to whether they show phosphorescence, delayed fluorescence, or both. These classes of crystals are discussed in more detail below.

The process of mutual annihilation of triplets leading to delayed fluorescence and the process of phosphorescent emission from triplets can take place in fluid systems as well as in crystals. In the former case the triplets involved are simply triplet states of molecules rather than excitons. In the following the term "triplet" will refer to a triplet exciton for crystalline substances.

The exciton and methods for its production have been studied extensively, both theoretically and experimentally. See, for example, Dexter and Knox, *Excitons*, Interscience Publishers, Inc., New York (1964), and Knox in Solid State Physics, Academic Press, New York, Suppl. 5 (1963). The triplet-triplet annihilation process is discussed in some detail by R. G. Kepler, J. C. Caris, P. Avakian and E. Abramson, Phys. Rev. Letters, 10, 400 (1963) and by P. Avakian and E. Abramson, J. Chem. Phys. 43, 821 (1965). The process of triplet-triplet annihilation in fluid systems is described by C. A. Parker, *The Triplet State*, A. B. Zahlan, Ed., pp. 353–359, The University Press, Cambridge (1967). Generally, excitons are produced by absorption of electromagnetic radiation, the delayed fluorescence resulting from triplet-triplet annihilation occurs at a shorter wavelength than that of the exciting radiation and is thus readily detected. Means for creating triplets by injecting charge carriers have also been described.

Johnson and Merrifield, U.S. Pat. application Ser. No. 853,183, filed Aug. 26, 1969, now U.S. Pat. No. 3,656,835 disclose a method whereby the intensity of electromagnetic radiation (i.e. delayed fluorescence) resulting from the decay of triplets in an unsensitized material changes according to the variation in the strength of the applied magnetic field. The method utilizes the discovery that the emitted radiation increases to a maximum when an increasing magnetic field is applied, and on further increasing the magnetic field, decreases, reaching a constant value at high fields (c. 4,000 oe). In the above application triplets were excited throughout crystals by exposure to exciting radiation or by injection of holes and electrons with suitable electrodes. The radiation is emitted by the triplet annihilation process throughout the crystal, possibly modified by quenching process at the faces of the crystal.

It is also known that delayed fluorescence can be induced in suitable crystalline materials using dye sensitization wherein electromagnetic radiation is absorbed by the dye and transferred to the surface of the crystal in the form of triplet excitons. The process is highly efficient and emission is largely confined to a small volume of the crystal near the surface in contact with the sensitizer. The volume depends on the particular crystal face exposed, and the relative mobility of the triplet excitons along different directions in the crystal, i.e., the rate of decay and intensity of the delayed fluorescence will differ markedly depending on which crystal plane the triplets are generated by sensitization.

The effect of dye sensitization on materials capable of producing delayed fluorescence, henceforth referred to as triplet materials, has been studied extensively in the art. B. Nickel, et. al., Chem. Phys. Letters 4, 27 (1969) discuss the sensitizing action of dye molecules adsorbed on anthracene crystals. See also B. Nickel et al., Chem. Phys. Letters 9, 555 (1971).

Surprisingly it has been discovered that when delayed fluorescence is induced by certain dye sensitizers in the absence of agents which quench the fluorescence of the dye molecules themselves, the delayed fluorescence is modulated by magnetic fields in a new and more useful manner than heretofore.

SUMMARY OF THE INVENTION

This invention comprises a method of producing electromagnetic radiation modulated in accordance with a magnetic field which comprises

a. contacting at least one surface of a crystalline material in which triplet excitons can be generated with a sensitizing dye free of fluorescence quenching agents for dye fluorescence,

b. illuminating said surface with exciting radiation absorbed by said dye sensitizer whereby triplet excitons are generated in said crystalline material,

c. applying said magnetic field to said surface, and

d. detecting electromagnetic radiation emitted by said crystalline material.

This invention also includes apparatus for practising the method of this invention.

THE DRAWINGS AND DETAILED DESCRIPTION OF THE INVENTION

This invention will be better understood by reference to the drawings which accompany the specification. In the drawings:

FIG. 1 shows the dependence of emitted electromagnetic radiation from triplet-triplet annihilation in a crystalline material such as anthracene and magnetic field inducing (a) the normal effect, and (b) the anomalous effect produced according to the present invention.

FIG. 2 illustrates apparatus which can be employed to modulate light with a magnetic field.

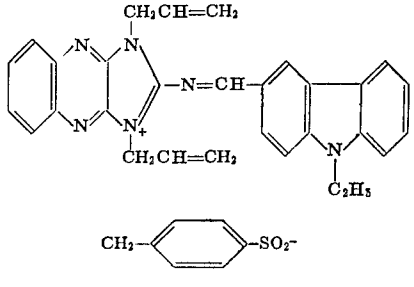
FIG. 2A shows another form of detecting device using plates of the host crystal.

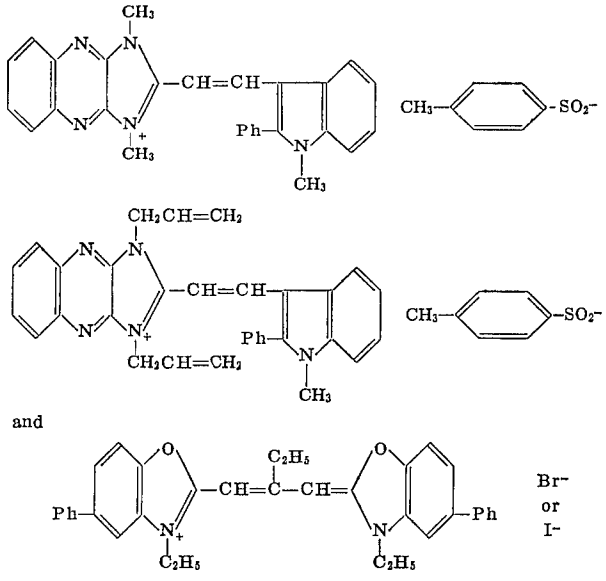
FIG. 3 shows a device to convert a pattern of magnetization on a magnetic tape to an optical image.

Referring now to the drawings: FIG. 1 shows the magnetic field dependence for electromagnetic radiation generated by triplet-triplet annihilation in anthracene for the normal and the newly discovered anomalous case. Curve a shows the normal field dependence observed: with increasing magnetic field the intensity of the emitted radiation increases about 5 percent at a field of about 200 oe, and thereafter decreases to a value about 10 to 20 percent below the initial or zero field value. The anomalous field dependence obtained with dye sensitization according to the present discovery is shown by curve *b*. The intensity of the light emitted by triplet-triplet annihilation decreases monotonically with increasing field to approach a level about 70 percent below the initial or zero-field value. Thus for small magnetic fields, of the order of 100 oe, such as those generated at the surface of a conventional magnetic audio tape having recorded signals, the relative change of light intensity with increase in magnetic field is approximately linear, and of substantially greater magnitude than in the case of the normal effect.

In addition to a more useful type of modulation, sensitized delayed fluorescence provides additional advantages for modulating light with a magnetic field: the output at zero field is very much greater than that obtained with other means of excitation. Further, the radiation is emitted in a thin layer of the crystal close to the surface, which renders the effect particularly suitable for detecting spatially modulated magnetic fields such as images recorded on magnetic tape.

As noted above, not all dye-sensitized excitation of triplets excitons in crystalline systems exhibit the newly discovered anomalous field dependence. Thus Rhodamine B, Rhodamine 6G, pyronine B, ethyl red and cyanine dyes such as:





and

have been found to sensitize delayed fluorescence and produce the anomalous field dependence of the present invention.

Other crystalline host materials which exhibit sensitized delayed fluorescence and anomalous field dependence with Rhodamine B sensitization, and are believed to exhibit the same with the equivalents thereof, are 1,8-dichloroanthracene, 2-chloroanthracene and 9,10-diphenylanthracene.

On the other hand many dyestuffs which will sensitize delayed fluorescence do not produce the anomalous field dependence of curve (b) of FIG. 1 but rather the conventional field dependence of curve (a). All such dyestuffs examined have been characterized by the presence of heavy atoms in the chromophore-containing moiety, i.e., atoms having an atomic number greater than 9, which are believed to act as internal fluorescence quenching agents for dye fluorescence. External quenching agents should also be absent, although the effect is less sensitive to such agents external to the chromophoric group. Sensitized delayed fluorescence exhibiting anomalous field dependence is converted to the conventional field dependence by such agents.

In this connection it should be noted that fluorescence quenching agents may be present in commercial dyestuffs either as accidental impurities or as agents as added by the manufacturer to the commercial formulation to inhibit fluorescence. Such commercial dyestuffs are not useful in the present invention even though nominally appropriate.

The sensitizing dye must be in contact with the organic crystal. Preferably the crystal or at least the face of the crystal which is to be sensitized is contacted with a solution of the dye in a solvent which does not dissolve the crystal. For this purpose, water is preferred. Only very small dye concentrations are required, generally of the order of 10^{-6}M. Thus for anthracene an excellent sensitizing solution is a 2×10^{-6}M solution of Rhodamine B in 0.1 M $NaHSO_3$ [B. Nickel, H. Staerk and W. Weller, Chem. Phys. Letters 4, 27 (1969)].

The anomalous magnetic field effect is not confined to the above materials, but can be observed in any suitable organic crystal exhibiting sensitized delayed fluorescence including

1. Materials exhibiting delayed fluorescence but not phosphorescence such as 9,10-diphenyl anthracene, 9,9'-bianthryl, phenanthrene p-terphenyl, trans-stilbene, tetracene and 2-methyl pyrene, 1,8-dichloroanthracene, and 2-chloroanthracene

2. Materials showing both phosphorescence and delayed fluorescence: anthracene, 4,5-iminophenanthrene and 4,5-methylenephenanthrene.

The sensitizing dyes will vary with the particular crystal selected. Generally good sensitizing dyes have closely spaced triplet-singlet levels and further have those levels approximately equal to the triplet level of the host crystal which is to be sensitized, as taught by Nickel et al. loc. cit.

Delayed fluorescence occurs in a very thin layer of the crystal adjacent the face excited by the sensitizer. The thickness of the layer appears to depend on the rate of diffusion of the excitons within the crystal and to be different for different crystal structures and for different crystal faces of a given crystal structure. Thus in anthracene it is known that triplet excitons diffuse in the *ab* plane more readily than in the c* direction perpendicular thereto, accordingly when anthracene is excited by sensitization on an *ab* face (which is readily obtained by cleaving or by vapor growth) the emitted light is emitted from a thinner layer of the crystal than when the crystal is cut perpendicular to the *ab* plane.

It is believed that the delayed fluorescence arises from triplet-triplet exciton annihilation at the surface of the host crystal. In view of the effect of fluorescence quenching agents on otherwise operable dyestuffs it is possible that the singlet state of the exciting dye is involved in the excitation process.

In the light of the above, the form of the host crystalline material can be selected to fit the desired end use. Thus for applications such as the conversion of magnetic images recorded on magnetic tape to corresponding patterns of light, plates of the host crystal can be employed which can be of any convenient thickness, but need be only a few micrometers in thickness, the surface adjacent the magnetic tape being sensitized. When the utmost sensitivity is required, and spatial conditions permit, the crystal plates can be stacked in a spaced stack and immersed in the sensitizing solution of dye. A slurry of finely ground host crystalline material in the dye sensitizing solution can be employed.

Also, the sensitized host material can be dispersed in a hardenable composition such as gelatin or an epoxy resin, either as a self-supporting sheet or deposited on a flexible transparent substrate such as as sheet of poly-(ethylene terephthalate) or a rigid transparent substrate such as glass.

The radiation employed to excite the sensitizer dye and hence the host crystal should have a wavelength at or close to the absorption maximum of the dye. The radiation emitted is of substantially shorter wavelength than the exciting radiation and is readily separated therefrom by suitable filtering of the exciting and the emitted light.

The light can be directed on the sensitized crystal host material by conventional optical means including lens systems, light pipes and the like, and the emitted radiation likewise can be imaged or directed to a suitable detector.

A device utilizing the effect of delayed fluorescence to modulate light by a magnetic field is shown in FIG. **2.** In FIG. **2** a small optically transparent cell **1** is mounted on a light pipe **2.** The cell contains a slurry of a finely powdered host crystal such as anthracene in a solution **3** containing the sensitizing dye, such as Rhodamine B. A light source **4** such as a Xenon lamp provides light which is collimated by lens **5** and then passes through filters **6** to produce light having a wavelength of about 570 mμ, close to the absorption maximum of the Rhodamine B. The light from the filter **6** is focused onto the anthracene slurry **3** contained in cell **1** by a lens **7.** Delayed fluorescence and exciting light emerging from the cell is conveyed by the light pipe **2** to filter **8** which removes all of the exciting radiation while permitting the blue light from the delayed fluorescence of the anthracene to pass. Light passing the filter **8** is detected by a photomultiplier **9** equipped with suitable power supplies (not shown) and means to measure the output thereof such as an amplifier and recorder (also not shown).

In the absence of a magnetic field the photomultiplier measures the blue light produced by triplet annihilation. On application of a magnetic field, indicated in FIG. **2** by an arrow labelled H, the emerging light is decreased with increasing field as described hereinabove in connection with FIG. **1.** Thus the output of the photomultiplier is a measure of the magnetic field and will record variations of the same with time.

In place of the cell **1** containing a slurry of a fine powder of the host crystal in an aqueous solution of the sensitizing dye, one or more plates of anthracene or other host crystal can be employed as shown in FIG. **2***a*. In FIG. **2***a* a cell **11** contains an assembly of plates of the host crystal **12, 13, 14** separated by spacers **15, 16, 17** and **18** to permit access to liquid **19** containing the sensitizing dye to the faces of the plates. Such a cell will usually be employed with incident exciting light normal to the face of the plates.

FIG. **3** is a device for observing the spatial modulation of a magnetic field such as that produced by a pattern of magnetization impression on a magnetic recording member such as magnetic tape. In FIG. **3** a host crystal, for example a plate of anthracene **20** is cemented to a transparent support **21** such as a sheet of glass. A solution of the sensitizing dye **22** is maintained in contact with the face of crystal **20** in a cell formed by spacer **23** and plate **24** which should be of a non-magnetic material, although transparency is not required. The assembly is placed on a magnetic tape **25** having a recorded pattern of magnetization.

Exciting light is provided by a lamp **26,** a filter **27** to remove radiation outside the wavelength region required for excitation and a lens **28** which are arranged to obliquely illuminate crystal **20** through the support **21.** The crystal **20** is observed through a filter **29** to eliminate the exciting radiation while transmitting shorter wavelength light, due to delayed fluorescence. A pattern of light is observed corresponding to the pattern of magnetization on the magnetic tape. If desired the light emerging from the crystal **20** can be filtered then imaged on a video detector such as an image orthicon or a plumbicon.

In place of the crystal of anthracene **20** and the cell required to contact the same with a dye there can be employed a dispersion of microcrystals of anthracene on the like dispersed in a hardenable binder such as gelatin which has been sensitized by addition of the sensitizing dye to the gelatin, or by prior exposure of the

crystals to an aqueous solution of the sensitizer so that the dye is adsorbed thereon. The gelatin is then coated on a suitable substrate and hardened.

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

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

1. Method of producing electromagnetic radiation in accordance with a magnetic field which comprises

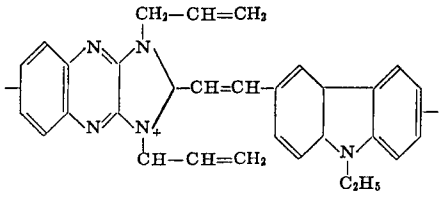
a. contacting at least one surface of a crystalline material in which triplet excitons can be generated with a sensitizing dye free of fluorescence quenching agents for dye fluorescence,

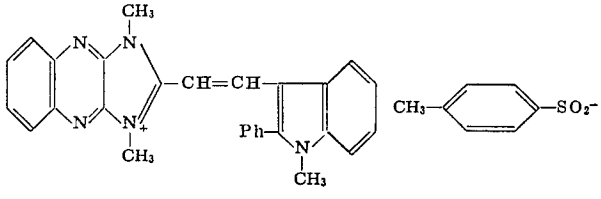
b. illuminating said surface with exciting radiation absorbed by said sensitizing dye whereby triplet excitons are generated in said crystalline material,

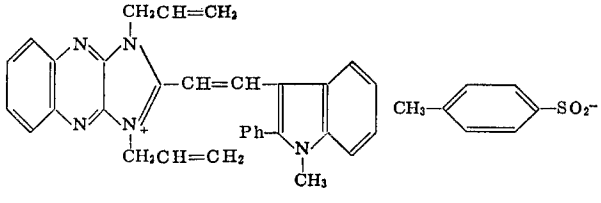
c. applying said magnetic field to said surface; and

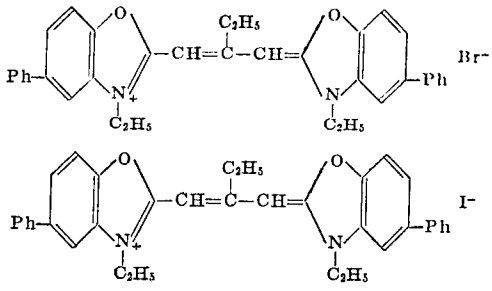
d. detecting electromagnetic radiation emitted by said crystalline material whereby essentially maximum decrease in the intensity of emitted electromagnetic radiation is achieved at magnetic fields less than 1,000 oe.

2. Method of claim **1** wherein said crystalline material is anthracene, 1,8-dichloroanthracene, 2-chloroanthracene, or 9,10-diphenylanthracene and said sensitizing dye is Rhodamine B, Rhodamine 6G, pyronine B, ethyl red,









3. Method of claim **2** wherein said crystalline material is anthracene.

4. A device comprising

fluorescent means comprising at least one crystal of a substance in which triplet excitons can be created, and a dye sensitizer in contact with at least one face of said crystal capable of transfering energy to said crystal upon illumination with exciting radiation and free of fluorescence quenching agents for said dye fluorescence,

means to apply said exciting radiation to said face, whereby triplet excitons are created in said crystal and decay with emission of delayed fluorescence,

means to apply a magnetic field to said face whereby the delayed fluorescence is modulated, and

means to detect said delayed fluorescence whereby essentially maximum decrease in the intensity of emitted electromagnetic radiation is achieved at magnetic fields less than 1,000 oe.

5. Device of claim **4** wherein said fluorescent means is a slurry of finely powdered crystals in which triplet excitons can be created in an aqueous solution of said dye sensitizer.

6. Device of claim **4** wherein said fluorescent means is at least one crystal plate of a substance in which triplet excitons can be created.

7. Method of claim **6** wherein said means to apply a magnetic field is a magnetic recording member having a pattern of magnetization imposed thereon.

8. Device of claim **4** wherein said fluorescent means is a dispersion of microcrystals of a substance in which triplet excitons can be created in a hardened binder, said microcrystals having a dye sensitizer absorbed thereon.

9. Device of claim **7** wherein said means to apply a magnetic field is a magnetic recording member having a pattern of magnetization imposed thereon.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,843,939

DATED : October 22, 1974

INVENTOR(S) : Ronald Parke Groff

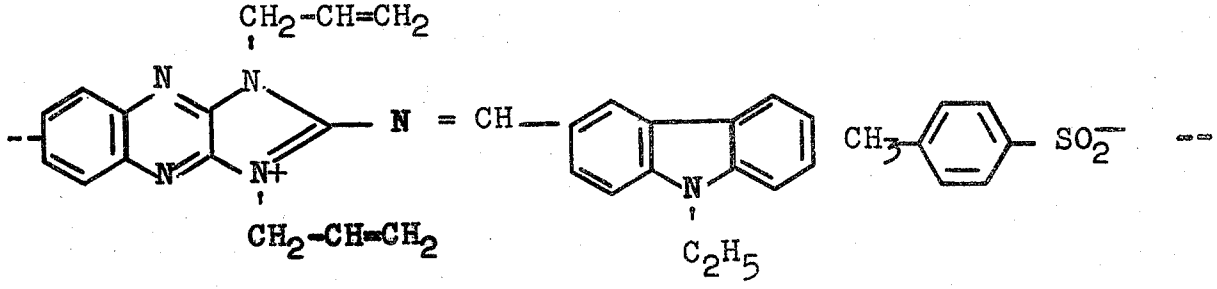
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 5, line 51 - change the second "as" to --a--;

Col. 6, line 65 - "on" should be --or--;

Col. 7, line 10, claim 1 - after "radiation" insert --modulated--;

Col. 7, line 30, claim 2 - the formula should read



Col. 8, line 5, claim 2 - after the first formula insert --or--.

Signed and sealed this 15th day of July 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

UNITED STATES PATENT OFFICE

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Col. 7, line 10, claim 1 - after "radiation" insert --modulated--;

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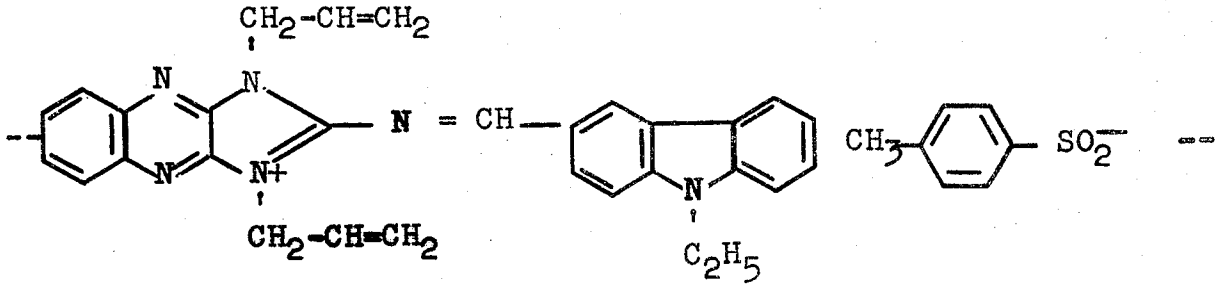

Col. 8, line 5, claim 2 - after the first formula insert --or--.

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(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks