

[54] FORMATION OF VISIBLE AND/OR FLUORESCENT IMAGES

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 764,313, Oct. 1, 1968, abandoned.

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[51] Int. Cl......G11c 13/04, G11c 11/42

[58] Field of Search 250/71 R, 71 T; 117/1, 93.3, 117/33.5 R; 346/135; 96/45.1; 252/301.2, 301.3; 340/173 LS, 173 CC

[56] References Cited**OTHER PUBLICATIONS**

Badger, Structures and Reactions of the Aromatic Compounds, Cambridge Univ. Press, London, 1954, 364-377.

Mouneu et al., Compt. issued 186 (1928). p. 1166-1168.

Southern et al., J. Chem. Soc., 1960, 4340-4346.

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Attorney—Charles J. Fickey

[57] ABSTRACT

Method of processing information by the use of derivatives of aromatic compounds which do not fluoresce, but which may be converted to fluorescent compounds by the action of heat or short wave ultraviolet radiation, and reconverted to the original non-fluorescent form by longer wavelength ultraviolet radiation.

8 Claims, No Drawings

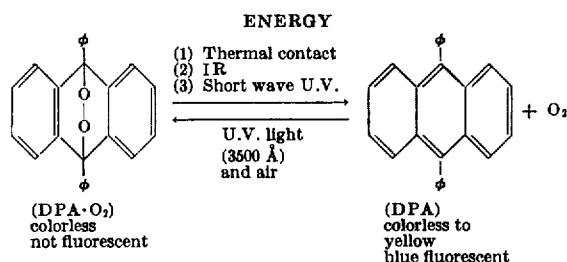
FORMATION OF VISIBLE AND/OR FLUORESCENT IMAGES

This application is a continuation-in-part of application Ser. No. 764,313, filed Oct. 1, 1968, now abandoned.

This invention relates to a new method of forming detectable information. It more definitely relates to the formation of images which are fluorescent under ultraviolet radiation, by the application of suitable energy to aromatic polycyclic compounds which are not fluorescent.

Numerous imaging systems are known based on the thermal or photo conversion of chemical compounds from one color to a different color or from a colorless state to a colored form. Most of these methods are mainly permanent conversions, i.e., the compounds once exposed to radiation and converted in form, cannot be returned to their original form. Moreover, most such systems depend on a visible change in form so that they are only useful where the final image can be left in its permanent form and position.

We have now found that images may be formed by the application of suitable energy to polycyclic aromatic type compounds, such as endoperoxides, according to the following equation, using 9,10-diphenyl anthracene as an example:



Some endoperoxides are fluorescent and the fluorescence and color and intensity will change with irradiation. The images which are formed are fluorescent and detectable under suitable long wave ultraviolet radiation and may or may not be visible. The process is also reversible, so that the fluorescent image may be erased, and a new image formed. This cycle may be performed any number of times.

The endoperoxide compounds may be incorporated with numerous substrates and matrixes such as paper or various plastics, by coating, impregnation or compounding. Excellent results can be obtained with only from about 0.05 to 0.1 mg. of the active compound per square centimeter of paper surface.

A large variety of fluorescent colors can be achieved depending on the specific aromatic endoperoxide or other aromatic employed. Such colors range from blue (9,10-diphenyl-anthracene) to orange (rubrene).

The requisite energy for the conversion of the endoperoxides and formation of images may be applied in different ways. It may be done by the physical contact of a hot die to the substrate incorporating the endoperoxide. In this instance, the die will have the shape of the desired image. A temperature of from about 20° to 200° C., preferably 150° to 200° C., is suitable. Images can be produced in from 1 to 3 seconds at

higher temperatures. The time and temperature will be variable depending on the substrate material and effect desired.

The substrate could also be irradiated by an imagewise pattern of infrared radiation, or short wave ultraviolet radiation of about 2,000 to 3,000 Å. wavelength. Energies of about **chemical joules/cm²** have been found adequate. The radiant source may be of various types providing ultra-violet or infra-radiation, including lamps, electric arcs, or ultra-violet and infrared lasers. The image can be formed in any well-known manner as by focusing a radiant beam, projecting a beam through a stencil, by use of moving mirror systems with lasers and the like. Other forms of radiation may also be used such as X-rays, electron bombardment, cathode rays, ionizing radiation, and the like. When infrared radiation is used, it is advantageous to incorporate infrared-absorbing agents such as charcoal, or chemical absorbers, with the aromatic polycyclic imaging compounds.

For reversing the process and erasing the image, the aromatic compound is irradiated with long wave ultraviolet light, most advantageously of 3,500 Å. wavelength, in the presence of air or oxygen to cause conversion of the aromatic compound to the original aromatic endoperoxide. The same types of irradiating sources may be used.

Although it has been indicated that a fluorescent image could be produced by application of energy in the form of heat, or infrared or ultraviolet radiation to the reducible aromatic compound, it will be readily apparent that an image could be created in the reverse manner. In this way, the aromatic compounds may be present on a substrate in the reduced state, i.e., the fluorescent state. Irradiation with a differential pattern of long wave ultraviolet (about 3,500 Å.) light in the presence of air or oxygen will bleach parts of the substrate to give a non-fluorescent image on a fluorescent back ground.

In all the imaging methods, the image can be any type of mark, signal, or intelligence, and be of either of the types conventionally known as positive or negative image. Moreover, it may simply consist of areas of varying fluorescent intensity. Since the present material has a further characteristic that the amount of detectable fluorescence is proportional to the amount of latent fluorescer which has been converted to the fluorescent state, the amount converted on any radiated area depends on the duration of time of exposure to the irradiating energy. The longer the time period is, the more latent fluorescer there will be converted per unit of exposed area and thus the more intense the fluorescence upon subsequent radiation and detection. This characteristic makes it possible to produce detectable, variable tone fluorescent radiation over a given area. This is much like the tone variation in a photographic negative or a magnetic sound tape. Thus the present invention could be used to prepare a sound tape by audio modulation of the radiant source. The sound is detectable by conventional fluorescent detection means coupled with audio output means by a suitable transducer. A sound track could be put on a movie film in the same manner, either beside the picture, or pointed directly on the film. A phonograph disc could be prepared and played by the same principal.

It will be obvious that the process may be used in various ways for imaging. For example a substrate may incorporate the aromatic compound and an image formed thereon. The image may be erased and a new image put on. If the initial endoperoxide and the image are colorless, a system is provided whereby information is not apparent to the ordinary observer, but is detectable under ultraviolet radiation when in the fluorescent form. Such a system would be useful for putting additional information on top of other information, which was ordinarily visible, for example, recognition codes or signals on microfilm or labels, and the like.

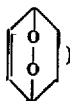
It is also possible to put the endoperoxide compounds onto a surface in a printed form, i.e., only in image areas and to activate them to the fluorescent form and reverse when desirable.

In some instances, the aromatic compounds of the invention will be colored in either one or the other form, and the process is sometimes irreversible depending on the substrate associated with the endoperoxide.

It will be obvious that many variations will be suggested within the purview of the process of this invention. For example, a printing ink could be made incorporating the endoperoxides of the invention. Thus, the present invention can be useful in coding all types of articles, for control, etc., data storage, acquisition and display, printing, coded inks, novelties, toys, and many other uses.

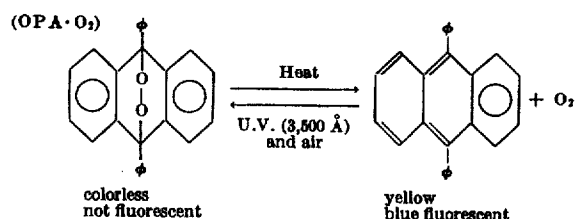
In general, any compound capable of forming an endoperoxide will work in this system as long as this endoperoxide is decomposable under the types of energy previously discussed, to a colored and/or fluorescent product.

Some of the names used in the literature to describe these cyclic peroxides include: transannular peroxides⁽²⁾, 1,4-peroxides⁽³⁾, photo-oxides⁽³⁾, photo-peroxides⁽³⁾, transannular epidioxides⁽⁴⁾, 1,4-epiperoxides⁽⁶⁾, aromatic peroxides (with or without numbers to indicate the positions involved, i.e., 9,10-dimethylantracene-9,10-peroxide⁽⁵⁾ or 9,10-dimethylantracene peroxide, also rubrene peroxide), endoperoxides⁽⁵⁾⁽⁷⁾ (or endoperoxides⁽¹⁾⁽⁸⁾), (also with or without numbers, i.e., 9,10-diphenylantracene-9,10-endoperoxide or 9,10-diphenylantracene endoperoxide) and dioxabicyclo systems⁽⁶⁾ (i.e., 5,6-dioxabicyclo[2.2.2]octene-2:



(see literature references below.)

For the reversible system, the heat generated image can be converted back to the endoperoxide. This is usually accomplished by U.V. light and air. Using 9,10-diphenylantracene endoperoxide as an example, the reactions are:



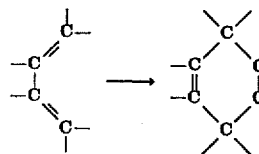
For the irreversible system, the heat generated image can not be converted back to the starting endoperoxide. Thus, the image produced by heating the endoperoxide may be an oxidation product (quinone, etc.) for other fluorescent decomposition product not capable of being converted to colorless and non-fluorescent material. Also, a normally reversible system can be made irreversible by preventing oxygen from reacting with the aromatic (see Table I).

Numerous aromatic endoperoxide compounds are disclosed in the following literature references:

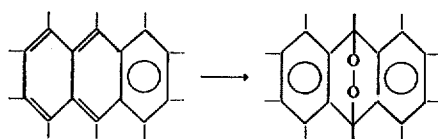
- 1A. Phenomenon observed in 1867 by Fritzsche using naphthalene. Fritzsche, *Compt. rend.*, 64, 1035(1867).
- 1B. E. McKeown and W. A. Waters, *J. Chem. Soc.*, 1040B(1966).
1. C. Moureu, C. Dufraisse and P. M. Dean, *Compt. rend.*, 182, 1440, 1584(1926). C. Moureu, C. Dufraisse and L. Girard, *Compt. rend.*, 186, 1027(1928).
2. W. Bergmann and M. J. McLean, *Chem. Revs.*, 28, 367(1941).
3. G. M. Badger, "Structure and Reactions of Aromatic Compounds", Cambridge Univ. Press, London (1954), Chap. 9, pp. 364-382.
4. Yu. A. Arbuzou, *Russ. Chem. Revs.*, 34, 558(1965).
5. E. J. Corey and W. C. Taylor, *J. Am. Chem. Soc.*, 86, 3881(1964).
6. C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, 86, 3879(1964).
7. E. G. E. Hawkins, "Organic Peroxides, Their Formation and Reactions", E. and F. F. Spon Ltd., London, 1961.
8. A. G. Davies, "Organic Peroxides", Butterworths, London, 1961.
9. Technical Report No. 3, "Chemiluminescent Material", Dec. 1, 1963-Feb. 29, 1964, ARPA No. 299 Amed. 3, Contract Nonr. 4200(00), Task NR 365-452, pp. 18, 19.

The initial endoperoxide may be prepared using U.V. light in the presence of air or oxygen^(1,2,3,4) (with or without a sensitizer), chemical synthesis^{(1)(8,6)}, or with active oxygen prepared by electrodeless discharge⁽⁵⁾.

A variety of compounds containing a 1,3-diene structure are known to give peroxides:



The most useful class of compounds for this invention is the aromatic acenes and their derivatives i.e., anthracene, naphthalene, pentacene, hexacene, etc.).



Additional aromatic endoperoxides within the scope of this invention are disclosed in "Organic Chemistry,

A Series of Monographs", Vol. 8, J. Hamer, ed., 1967, p. 299:

Anthracene Endoperoxides

- p. 374; ref. (3)
p. 385; ref. (2)
pp. 18, 19; ref. (9)
p. 369; ref. (3)

Tetracene Endoperoxides

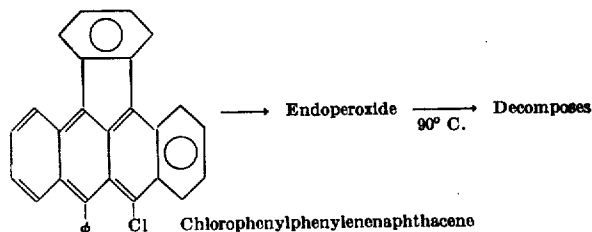
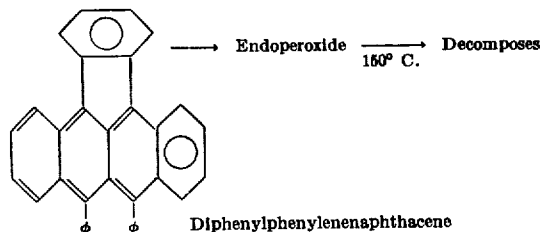
- p. 238; ref. (7)
p. 384; ref. (2)

Pentacene Endoperoxides

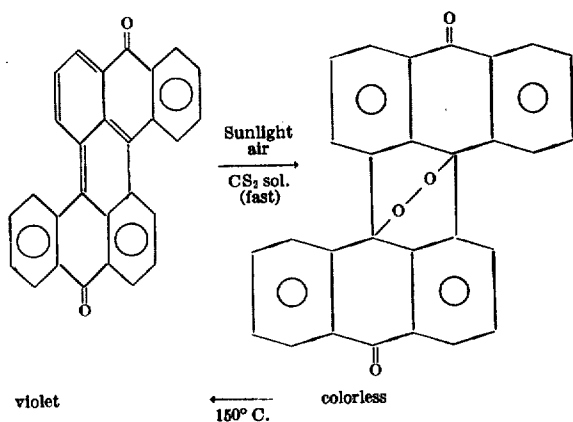
- p. 382; ref. (2) and p. 238; ref. (7)

Hexacene Endoperoxides — p. 367; ref. (3)

Larger polynuclear aromatic endoperoxides are known as follows:

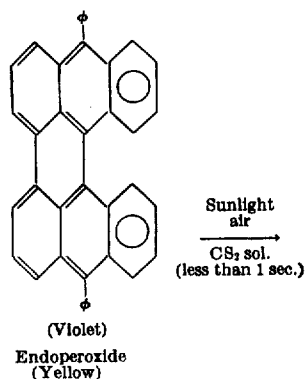


C. Dufraisse and M. T. Mellier, *Compt. rend.*, 215, 576 (1942).



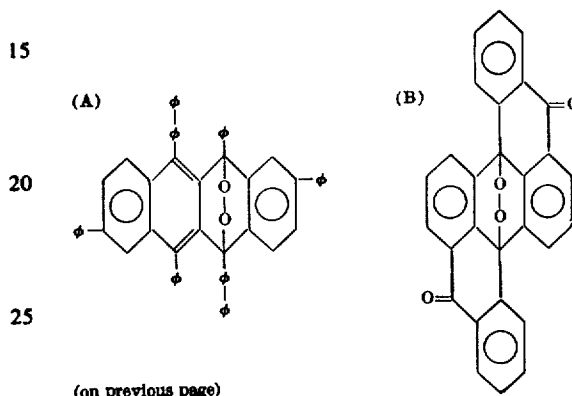
95% recovery of O_2
heterocordianthrone

C. Dufraisse and
M. T. Mellier,
Compt. rend., 215,
541 (1942).

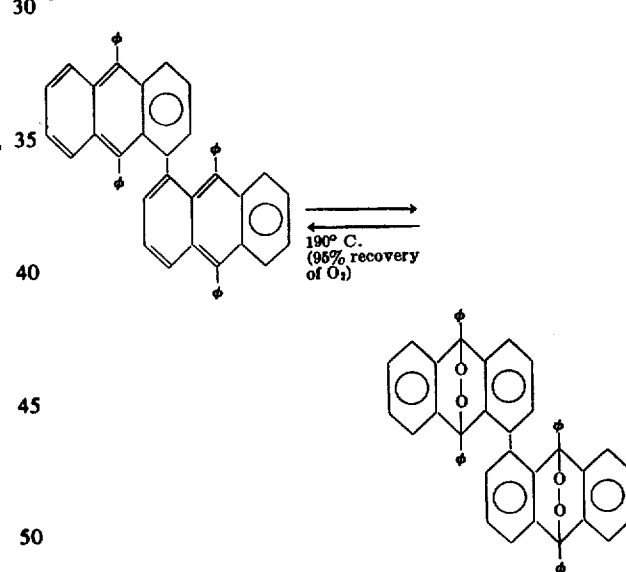


page 371 ref. (3);
p. 238; ref. (7) E. G. E. Hawkins,
"Organic Peroxides, Their Formation
and Reactions," E. and F. F. Spon
Ltd., London, 1961.

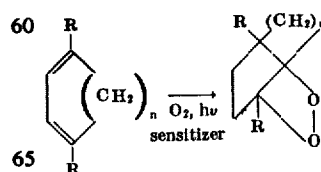
- 5 Other polycyclic hydrocarbons that can be converted to endoperoxides are: 1,2-benzoanthracenes, rubrene, naphthacene, 9,10-diphenylnaphthacene, 1,2,3,4-tetrahydro-9,10-diphenylnaphthacene, 9,11-diphenyl-10,12-bis-(biphenyl)naphthacene, 2,6,10,12-tetraphenyl-9,11-bis(biphenyl)naphthacene (A), 1,2,8,9-dibenzpentacene, heterocordianthrone (B), and the three isomeric p-toly-tetraphenylcyclopentadienols.



p. 239; ref. (7) and p. 370; ref. (3):

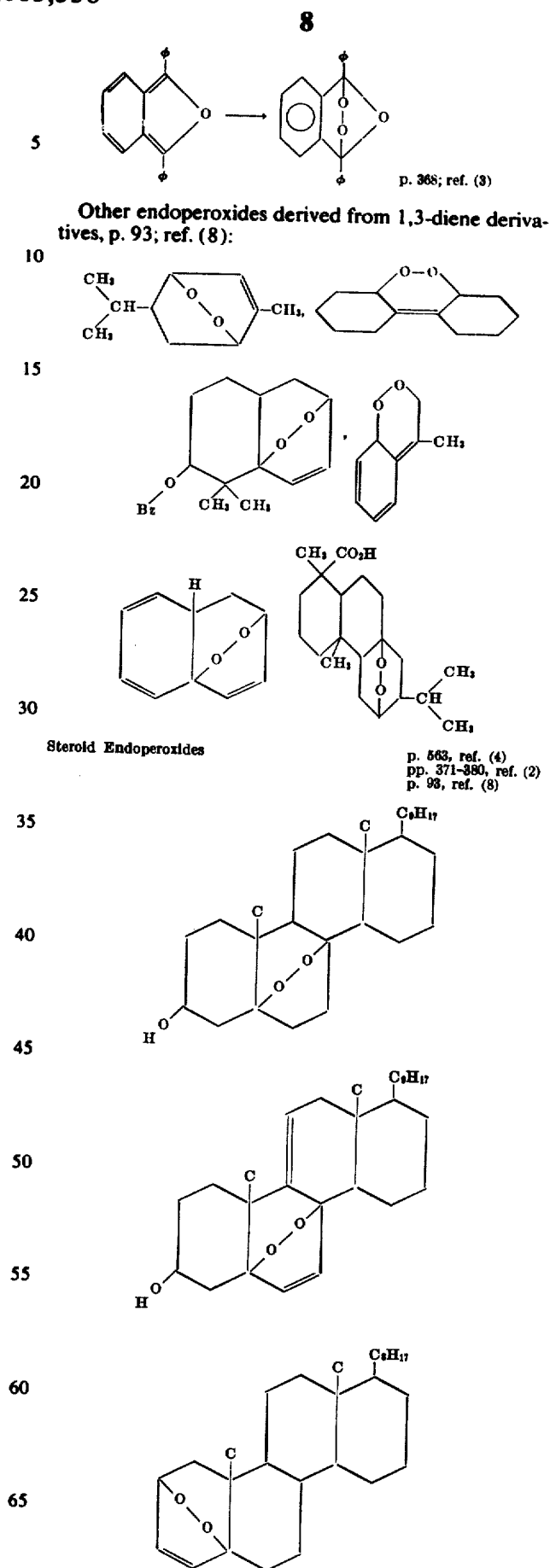
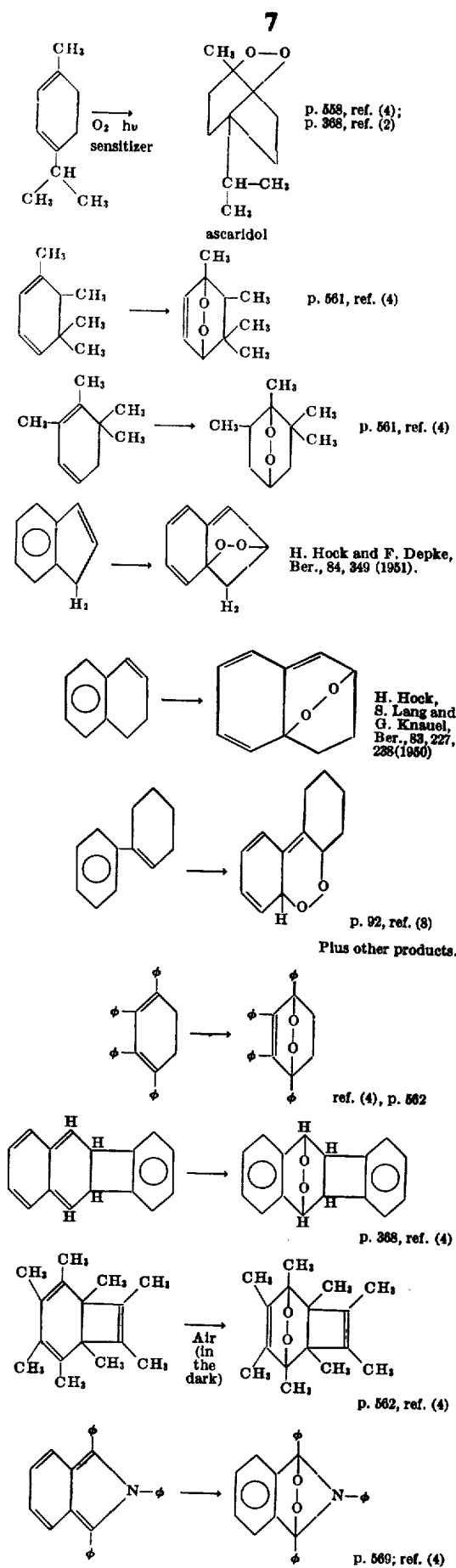


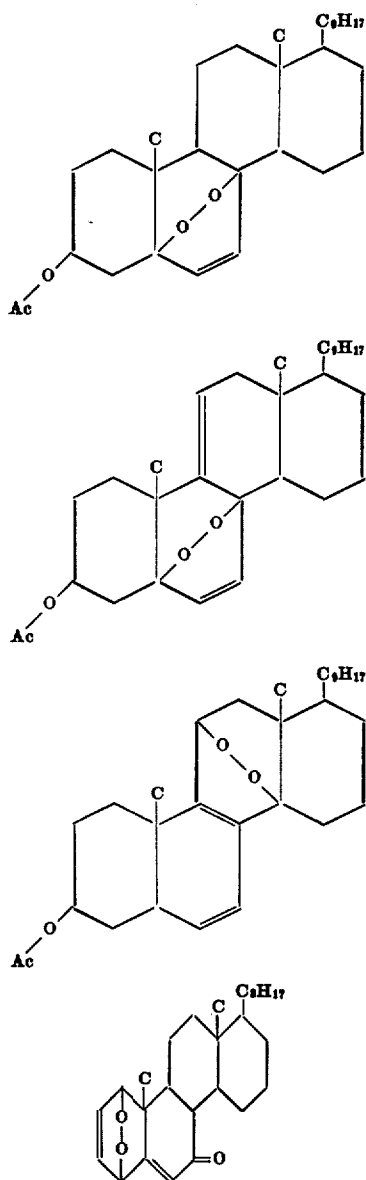
55 Bis-endoperoxide of 9,9',10,10',1,1'-anthryl. Endoperoxides obtained from 1,3-diene derivatives: (While the following cyclic peroxides are known, it is not known whether they will produce color or fluorescence upon heating.)



ref. (4)

(Heating this endoperoxide does give the starting 1,3-diene and oxygen.)





Also endoperoxides were prepared from: 24-methylcholesta-5,7-dien-3 β -ol, 3 β -acetoxy-24-methylcholesta-6,8(14), 9(11),22-tetraene, 3-acetoxy-2-methylcholesta-3,5,7,22-tetraene, 3-acetoxy-24-methylcholesta-3,5,7,9(11),22-pentaene, 3-acetoxy-5 α -pregna-6,8(14),9(11)-trien-20-one, 3 β ,21-diacetoxy-5 α -pregna-6,8(14),9(11)-triene-20-one, lumisteryl acetate, cholesta-5,7-diene-3 β -ol, 3 β -acetoxycholesta-5,7-diene, cholesta-5,7,24-trien-3 β -ol, cholesta-2,4-diene, cholesta-1,3,5-triene-7-one, androsta-5,7-diene-3,17-diol.

Other derivatives of polycyclic aromatic compounds may be useful provided they have an oxidized and a reduced state and are fluorescent in one such state, and are capable of being changed from one state to the other by the application of suitable energy. By oxidized and reduced state is meant a polycyclic aromatic compound having at least one ring with a diene structure which is capable of being converted to a monoene structure by 1,4 addition to the ring. The endoperoxides of anthracene are illustrative, as previously pointed out. In addition, halogen derivatives of anthracene would also be applicable, for example.

The following specific examples are given to illustrate the invention and are not intended to be limitative.

EXAMPLE I

The 9,10-diphenylanthracene endoperoxide (DPA-O₂) was prepared from commercially available 9,10-diphenylanthracene as follows:

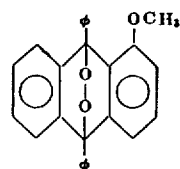
9,10-Diphenylanthracene Endoperoxide

Potassium hydroxide (12 g.) was added slowly one-half hour to 37 ml. of 30 percent hydrogen peroxide with stirring at ° C. (ice-water bath). A solution of 1.01 g. (3 mM) 9,10-diphenylanthracene in 50 ml. of chlorobenzene was added to the reaction vessel. The mixture was stirred gently, so that the boundary between the two liquid phases was not broken and bromine (5ml.) in chloroform (5 ml.) was added to the lower (aqueous-KOH-H₂O₂) phase through a capillary tube during a period of 4 hours. The organic phase was separated from the aqueous phase and washed with water. The organic solution was concentrated under reduced pressure to a yellow mud. This material was chromatographed on F-20 Alumina (eluted with 50:50 n-hexane:benzene). After recrystallization from n-hexane/benzene, 0.612 g. (55percent yield) of 9,10-diphenylanthracene endoperoxide and 0.277 g. (27percent recovered) 9,10-diphenylanthracene was obtained.

A solution of DPA-O₂ in an organic solvent (such as benzene) was allowed to dry on non-fluorescent paper to leave 0.05 mg. to 0.1 mg. of DPA-O₂ per square centimeter. An image was rapidly produced by applying a heated object of about 200° C. The images were bright blue fluorescent and had no visible color. If too hot an object or too long a contact time was used, then the image was transferred to the underlying substrate (paper). Higher concentrations of DPA-O₂ gave images which were yellow colored and blue fluorescent.

The images produced on paper coated with DPA-O₂ were bleached after 15 minutes to ½ hour exposure to 3,500 Å. ultraviolet light in air (Rayonet Photochemical Reactor). Also some fading of the blue fluorescent images was observed after 4 days in the direct afternoon sunlight. New images were produced on the above papers by reapplying the heated objects. One treated paper was carried through six cycles.

EXAMPLE II



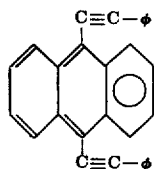
1-Methoxy-9,10-diphenylanthracene endoperoxide as described in C. Dufraisse, L. Velluz, R. Demuyne, Compt. rend. 215, 111(1942).

A benzene solution of this endoperoxide was allowed to dry on a piece of white, non-fluorescent paper to leave a colorless, non-fluorescent circle. Heated (150°-200° C.) objects (i.e., keys, metal with raised letters, etc.) developed blue-green fluorescent images (no visible color) when placed on the treated paper for less

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than a second. Higher temperatures or longer contact time caused the fluorescent (no visible color) images to be transferred to the material (paper) under the treated paper. These images were bleached in the Rayonet Photochemical Reactor at 3,500 Å. in 15 minutes. No new images could be developed by heated objects in the areas where the first images were. Good images were formed in areas where no first images were.

EXAMPLE III

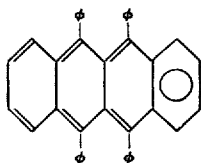


9,10-Bis(phenylethynyl)anthracene

A benzene solution of this compound was allowed to dry on a piece of white (non-fluorescent) paper to leave a slightly orange-colored and yellow-fluorescent circle. The endoperoxide was formed by irradiating the paper for 15 minutes in the Rayonet Photochemical Reactor at 3,500 Å. The yellow-green fluorescence was bleached but the paper was still slightly orange. Heated (about 200° C.) objects (keys, etc.) placed on this paper developed yellow-colored and yellow-green fluorescent images in about 1 second. The yellow-colored and yellow-green fluorescent images were also transferred to ordinary paper by using longer contact time (2-4 seconds) or higher temperatures. These images could be bleached by 3,500 Å. ultraviolet light but new images were difficult to produce on top of bleached images.

9,10-Bis(phenylethynyl)anthracene may be prepared as described by W. Ried, W. Donner and W. Schlegelmilch, Ber., 94, 1051 (1961).

EXAMPLE IV



Rubrene

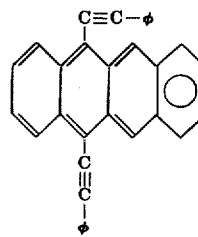
A benzene solution of rubrene was allowed to dry on white, non-fluorescent paper to leave a pink-colored and orange fluorescent circle. The pink color and orange fluorescence was bleached in two minutes by ultraviolet irradiation (3,500 Å.) in air (Rayonet Photochemical Reactor), thus forming the endoperoxide. When heated (about 200° C.) objects (keys, etc.) were placed on this bleached paper, a pink-colored and orange fluorescent image was formed in less than one second. These images were similarly bleached in a few minutes by ultraviolet irradiation (3,500 Å.) in air. Ordinary fluorescent laboratory light, also bleached the images slowly. The process was repeated three times on the same coated paper. Lower temperatures and/or shorter contact times of the heated objects produced only the orange fluorescent image (no visible color). These transformations can again be explained by the reversible formation of the endoperoxide.

Images were also transferred to an underlying sub-

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strate when hotter objects and/or longer contact times were used.

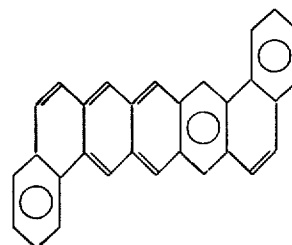
EXAMPLE V



5,12-Bis(phenylethynyl)tetracene

5,12-Bis(phenylethynyl)tetracene was prepared as follows: As disclosed in copending commonly assigned application Ser. No. 712,922, filed Mar. 14, 1968. A benzene solution of this compound was allowed to dry on a piece of white (non-fluorescent) paper to leave a dull gray and slightly orange fluorescent circle. Dilute concentrations of this compound on paper were almost colorless and slightly orange fluorescent. The endoperoxide was formed more easily on this paper since the orange fluorescence was bleached slowly in air by laboratory fluorescent light and more rapidly (5 to 10 minutes) in the Rayonet Photochemical Reactor at 3,500 Å. Heated (about 200° C.) objects (keys, etc.) rapidly (1-3 seconds) generated red visible colored and orange fluorescent colored images on this paper. If lower temperature objects were used, then only the orange fluorescent images were formed. These images were also transferred to untreated paper (as in the above cases) by using slightly hotter objects or longer contact time. The images were bleached in Rayonet Photochemical Reactor at 3,500 Å. in 15 minutes. This was a reversible system since one treated paper was carried through six cycles.

EXAMPLE VI



1,2,8,9-Dibenzpentalene, obtained commercially from L. Light & Co., Ltd., Colnbrook, England.

A benzene (or xylene) solution of this compound was allowed to dry on a piece of white, non-fluorescent paper to leave a colorless and non-fluorescent circle. Higher concentrations of the compound on paper were slightly purple colored and non-fluorescent. Ordinary fluorescent laboratory light caused formation of the non-fluorescent endoperoxide. The endoperoxides were also formed by ultraviolet radiation (3,500 Å., Rayonet) in 5 minutes. Heated (about 200° C.) objects (keys, etc.) rapidly (1-3 seconds) produced yellow fluorescent and colorless images. These images were bleached slowly by the fluorescent laboratory lights and in 5 minutes in the Rayonet Photochemical Reactor at 3,500 Å. to form the endoperoxide again. Heated objects again formed the fluorescent images on this

paper. As in the other cases, hotter objects or longer (2-4 seconds) contact time transferred the yellow fluorescent (no visible color) images to untreated paper or any substrate used under the treated paper.

The results of Examples I to VI are summarized in Table I.

EXAMPLE VII

Other aromatic derivatives (in addition to the endoperoxide) may be useful for imaging by heat or ultraviolet light. Thus, an attempt to prepare the endoperoxide of BPEA (9,10-bis(phenylethynyl)anthracene) using the procedure described for DPA-0₂ [E. McKeown and W. A. Waters, J. Chem. Soc., 1040B(1966)] gave a small amount of non-fluorescent material which had an infrared and mass spectrum indicating:

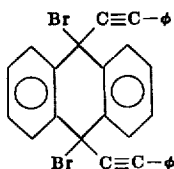


TABLE I.—AROMATIC ENDOPEROXIDES ON PAPER

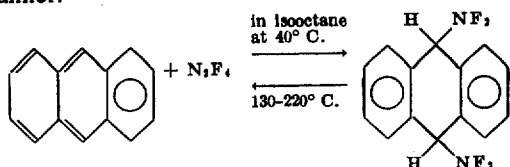
Endoperoxide of—	Initial appearance	Image formed by heat	Time for bleaching by 3,500 A. U.V.
I. DPA	Colorless, not fluorescent	Colorless, bright blue fluorescent	15 min.
II. BPEA	Almost colorless, not fluorescent	Yellow colored, yellow fluorescent	30 min.
III. BPET	Colorless (dilute), dull gray (concentrated), not fluorescent	Colorless or red, orange fluorescent	10 min.
IV. Rubrene	Colorless, weak fluorescence	Pink colored, orange fluorescent	2 min.
V. 1-methoxy-9,10-diphenylanthracene	do.	Colorless, blue-green fluorescent	10 min.
VI. 1,2,8,9-dibenzpentalene	Colorless, not fluorescent	Colorless, yellow-orange fluorescent	5 min.

A small amount of this material was dissolved in benzene and the solution allowed to dry on filter paper to leave a colorless and non-fluorescent circle. When a heated (about 200° C.) object was placed on the treated paper (about 1 second), a yellow-green fluorescent image was produced. Longer contact time caused the image to be transferred to the underlying substrate.

The images were bleached by 3,500 A. ultraviolet (10 minutes, Rayonet Photochemical Reactor) and yellowish fluorescent images regenerated by the heated objects.

A high molecular weight polyethylmethacrylate (PEMA) film containing a small amount of the above dibromo compound was weakly yellow colored and not fluorescent. Irradiation with 2,537 A. ultraviolet light (H100 A4/T Mercury lamp with pyrex envelope removed) for 1-2 minutes produced yellow colored and greenish fluorescent images in the film. Applying the heated (about 200° C.) objects also produced similar images in this film.

The following reactions are also useful in the same manner:



H. Cerfontain, J. Chem. Soc., 6602(1965).

THERMAL IMAGING OF PLASTIC FILMS CONTAINING AN AROMATIC ENDOPEROXIDE

EXAMPLES VIII TO XVI

Plastic films were prepared containing DPA-0₂.

All the films were solvent cast on glass microscope slides (except PVA). Each film of Examples VIII to XIII contained less than 40 mg. DPA-0₂ per gram of polymer. The films of Examples XIV to XVI contained compounds as indicated. The images were developed by applying a heated (150°-200° C.) key to the sample for approximately 1-2 seconds. All the samples became soft and sticky, and some (see Table II) became brown when too hot (>200° C.) an object was used. The bleaching studies were performed in the Rayonet Photochemical Reactor with 3,500 A. ultraviolet lamps.

EXAMPLE VIII

PEMA: High molecular weight polyethyl methacrylate, Elvacite 2042, DuPont Chemical Co. The films were cast from a mixture of toluene, methyl-ethyl ketone and ethanol. The imaging (by the heated key)

and bleaching (by 3,500 A. U.V.) was repeated three times on one area of the film.

EXAMPLE IX

CAB: Cellulose acetate butyrate, EAB-380-20, Eastman Chemical Co. The films were cast from acetone.

EXAMPLE X

VAGH: Bakelite, vinyl chloride-acetate copolymer with about 91 percent vinyl chloride. The films were cast from a mixture of acetone and methyl ethyl ketone.

EXAMPLE XI

PVC: Polyvinyl chloride. The films were cast from methylene chloride.

EXAMPLE XII

PVA: Polyvinyl alcohol, Elvanol 71-30, DuPont Chemical Co. The films were cast from a mixture of ethanol and water. An attempt to dry the film under reduced pressure gave large tough bubbles, which were cut into samples for testing.

EXAMPLE XIII

H-15 Acrylite: The films were cast from benzene.

EXAMPLE XIV

A clear, colorless and weakly fluorescent H-15 Acrylite film (American Cyanamid Co. polymethyl methacrylate) containing 6 percent by weight of 1-

methoxy-9,10-diphenylanthracene endoperoxide gave a colorless but good blue fluorescent image (and bubbles) when the heated key was applied.

EXAMPLE XV

A clear, weakly yellow colored and weakly blue fluorescent PEMA film containing 1 percent by weight BPET endoperoxide gave an orange-pink colored and orange fluorescent image (and bubbles), when the heated key was applied. This image was bleached after one day in the laboratory fluorescent lights. The initial endoperoxide was also prepared by exposing the PEMA-BPET film to the laboratory lights for four days.

EXAMPLE XVI

A clear, weakly yellow-colored and weakly blue fluorescent PEMA film containing 1 percent by weight rubrene endoperoxide gave a pink-colored and yellow-orange fluorescent image (and bubbles), when the heated key was applied. The image was bleached, and the endoperoxide prepared as described above for the perma-B BPET film.

The results of thermal imaging are illustrated in Table II for Examples VIII to XIII. As may be seen, the system can be reversible or irreversible depending on the plastic matrix.

IMAGING BY INFRARED IRRADIATION OF PEMA FILMS CONTAINING DPA-O₂

EXAMPLES XVII to XXII

All the films were prepared with high molecular weight polyethyl methacrylate (PEMA) of Example VIII and were cast on glass slides from a mixture of acetone, methyl-ethyl-ketone, toluene and ethanol. The infrared absorbers (Cyasorb IR-117 and Cyasorb IR-165) are products of American Cyanamid Company. All the tests were performed by holding the sample about 5 inches from a 250W, G.E. infrared bulb. The additives increased the sensitivity of the system to

infrared light in the following order: None <IR-117 <IR-165 <charcoal. Lower concentrations of the additives were still effective as sensitizers for this system.

5 The reversibility study was performed with Example XVIII. Thus, colorless but good blue fluorescent images were produced by irradiation for 1-2 minutes with the 250W, G.E. infrared light bulb (sample about 3 inches from the bulb). The images were bleached after 15-45 minutes irradiation with 3,500 A. U.V. light (Rayonet Photochemical Reactor). This process of imaging and bleaching was repeated 12 times. After this series, the film was still colorless (except for the black charcoal particles).

15 The results are shown in Table III.

An additional PEMA film containing 3 percent DPA-O₂ was cast from toluene, methyl-ethyl-ketone and ethanol and was clear, colorless and weakly fluorescent. When irradiated by infrared as above at 7 cm. for 2 to 5 minutes, a colorless but blue fluorescent image was produced.

IMAGING BY ULTRAVIOLET IRRADIATION OF FILMS CONTAINING DPA-O₂

EXAMPLES XXIII to XXIX

The films were the same ones as used in the thermal imaging in Example XIX, containing 20-50 mg. DPA-O₂ per gram of polymer. The 2,600 A. and 3,000 A. light was obtained from a 450W Xenon lamp in conjunction with a B & L Monochromator (No. 33-86-07) and water filter. The intensity of the light at 2,600 A. was 0.2 mW/cm² and at 3,000 A. it was 1.14 mW/cm². The 2,537 A. light was obtained from a 100 W mercury lamp (H100 A4/T with the Pyrex envelope removed). The 3,500 A. light was obtained with the Rayonet Photochemical Reactor using 3,500 A. bulbs. None of the images had any visible color (just the blue fluorescence).

40 The images produced in Examples XXIII to XXIX were bleached by 3,500 A. ultraviolet radiation.

TABLE II.—PLASTIC FILMS CONTAINING DPA-O₂

	Polymer	Initial appearance	Image developed by heat	Extent of bleaching by U.V.
VIII.....	PEMA.....	Clear, colorless non-fluorescent.....	Colorless, blue fluorescent (bubbles).....	2 hrs.: Completely bleached.
IX.....	CAB.....	Cloudy-white, non-fluorescent.....	Clear, colorless, blue fluorescent.....	2 hrs.: Almost bleached.
X.....	VAGH.....	Clear, colorless, non-fluorescent.....	Colorless, blue fluorescent*.....	2-3 hrs.: Some bleaching.
XI.....	PVC.....	Foamy, colorless, non-fluorescent.....	do*.....	2 hrs.: Only slightly bleached.
XII.....	PVA.....	Clear, colorless, non-fluorescent.....	Cloudy white, blue fluorescent*.....	2 hrs.: No bleaching.
XIII.....	II-15 Acrylite.....	do.....	Colorless, blue fluorescent (bubbles).....	3 hrs.: No bleaching.

*Too much heat caused the polymer to become brown.

TABLE III.—INFRARED IRRADIATION OF PEMA FILMS CONTAINING DPA-O₂

Example		½ min. irradiation	1 min. irradiation	3 min. irradiation
XVII.....	5% DPA-O ₂ ; clear, colorless and non-fluorescent.	No image.....	No image.....	Weak blue fluorescent image (no visible color.)
XVIII.....	5% DPA-O ₂ , 6% DARCO charcoal; colorless, non-fluorescent, translucent.	Weak blue fluorescent image (colorless).	Good blue fluorescent image (colorless).	Very strong blue fluorescent (colorless); also bubbled.
XIX.....	5% DPA-O ₂ , 10% IR-117; clear dark green, non-fluorescent.	No image.....	No image.....	Weak blue fluorescent and slightly brown colored image.
XX.....	5% DPA-O ₂ , 3% IR-117; clear, light green, non-fluorescent.	do.....	Weak blue fluorescent image (no additional visible color).	Good blue fluorescent and slightly yellow-brown colored image.
XXI.....	5% DPA-O ₂ , 10% IR-165; clear, dark brown, non-fluorescent.	do.....	No image.....	Blue fluorescent and slightly green-brown colored image.
XXII.....	5% DAP-O ₂ , 3% IR-165; clear, light brown, non-fluorescent.	Very faint blue fluorescent image.	Blue fluorescent image (no additional visible color).	Blue fluorescent and yellow-green colored image.

The results are shown in Table IV.

EXAMPLE XXX

A film containing 2.7 percent by weight of DPA-0₂ in H-15 Acrylite Molding Compound was prepared by allowing a methylene chloride solution to dry on a glass slide. The dried film was clear, colorless and only very weakly blue fluorescent. After irradiating the film for about 1 sec. with 2,537 A. ultraviolet light (same lamp as in Example XXVIII), a colorless but good blue fluorescent image was produced.

EXAMPLE XXXI

A film containing 2.3 percent by weight of DPA-0₂ in H-15 Acrylite Molding Compound was prepared by allowing an acetone solution to dry on a glass slide. The dried film was clear, colorless and only faintly blue fluorescent. After irradiating the film for about 1 second with 2,537 A. ultraviolet light (same lamp as above) a colorless but good blue fluorescent image was produced. A stronger blue fluorescent (and colorless) image was produced after 5 seconds ultraviolet irradiation at 2,537 A. The intensity of the blue fluorescent image was reduced after ½ hour irradiation at 3,500 A. (Rayonet Photochemical Reactor).

A second exposure to 2,537 A. ultraviolet light for 5 seconds increased the intensity of the blue fluorescence slightly. A blue fluorescent image still remained (only slightly reduced intensity) after 3 hours in 3,500 A. ultraviolet light (Rayonet Photochemical Reactor). A third exposure to 2,537 A. ultraviolet light for 5 seconds only slightly increased the intensity of the image. Again, the blue fluorescent image remained after 2-hour exposure to 3,500 A. ultraviolet light. A fourth exposure to 2,537 A. ultraviolet light for 5 seconds increased the intensity of the image only very slightly. Another 1½ hours of ultraviolet irradiation at 3,500 A. only caused a slight reduction in the intensity of

second with 2,537 A. ultraviolet light, a colorless but good blue fluorescent image was produced. The Examples XXX, XXXI, and XXXII show that the system is not dependent upon the solvent used to cast the film.

EXAMPLE XXXIII

A film containing 3 percent by weight of DPA-0₂ in high molecular weight polyethyl methacrylate (Elvacite 2042) was prepared by allowing a benzene-toluene-methyl ethyl ketone solution to dry on a glass slide. The dried film was clear, colorless, and only faintly blue fluorescent. After irradiating the film for about 1 second with 2,537 A. light, a colorless but very good blue fluorescent image was produced. Another colorless but good fluorescent image was produced by irradiating the film for 5 sec. with 2,537 A. ultraviolet light. This image was completely bleached after 15 minutes irradiation with 3,500 A. ultraviolet light (Rayonet Photochemical Reactor). This process of imaging and bleaching was repeated 21 times on the same area of the film. The resulting film was still colorless. This is an example of the reversible formation of colorless but blue fluorescent images by ultraviolet light.

EXAMPLE XXXIV

A film containing 6 percent by weight of 1-methoxy-9,10-diphenylanthracene endoperoxide in H-15 Acrylite Molding Compound was prepared by allowing a benzene solution to dry on a glass slide. The dried film was clear, colorless and faintly blue fluorescent. After irradiating the film for about 1 second with 2,537 A. ultraviolet light, a colorless but good blue fluorescent image was produced.

EXAMPLE XXXV

A film containing 10 percent by weight of DPA-0₂ in high molecular weight polyethyl methacrylate was

TABLE IV.—Ultraviolet Irradiation of Films Containing DPA-0₂

Example	Polymer and appearance	Image developed at 2,600 A.	Image developed at 3,000 A.
XXIII.....	High M. W. polyethylmethacrylate; Elvacite 2042; clear, colorless, and non-fluorescent.	5 min.: Good blue fluorescence. 10 min.: Stronger blue fluorescence.	5 min.: Fairly good blue fluorescence. 10 min.: Good blue fluorescence.
XXIV.....	Cellulose acetate butyrate; EAB 380-20; cloudy-white and non-fluorescent.	5 min.: Faint blue fluorescence. 10 min.: Good blue fluorescence.	5 min.: No image. 10 min.: Faint blue fluorescence.
XXV.....	Vinyl chloride-acetate copolymer; (≈91% vinyl chloride); VAGH; clear, colorless, non-fluorescent.	5 min.: Fairly good blue fluorescence. 10 min.: Stronger blue fluorescence.	5 min.: No image. 10 min.: Very faint blue fluorescence. 20 min.: Very faint blue fluorescence.
XXVI.....	Polyvinyl chloride; foam-like, colorless, nonfluorescent.	5 min.: Good blue fluorescence. 10 min.: Stronger blue fluorescence.	5 min.: No image. 10 min.: Faint blue fluorescence. 20 min.: Stronger blue fluorescence.
XXVII.....	H-15 Acrylite molding compound; clear, colorless, non-fluorescent.	5 min.: Very good blue fluorescence.	5 min.: Weak blue fluorescence. 10 min.: Good blue fluorescence.
		Image developed at 2,537 A.	Bleaching at 3,500 A.
XXVIII.....	High M. W. polyethylmethacrylate; Elvacite 2042; clear, colorless, and non-fluorescent.	1 sec.: Blue fluorescence. 5 sec.: Stronger blue fluorescence.	15 min.: Completely bleached.
XXIX.....	H-15 Acrylite molding compound; clear, colorless, non-fluorescent.	1 sec.: Blue fluorescence. 5 sec.: Stronger blue fluorescence.	3 hrs.: Not bleached.

the blue fluorescence of the image. The image was slightly yellow colored after all the above irradiations. Since the image could not be bleached, this is an example of a one-way system.

EXAMPLE XXXII

A film containing 3.4 percent by weight of DPA-0₂ in H-15 Acrylite Molding Compound was prepared by allowing a benzene solution to dry on a glass slide. The dried film was clear, colorless and only weakly blue fluorescent. After irradiating the film for about 1

prepared as described in Example XIII with the exception that this film was cast on 3 mil bond-coated Mylar. The dried film was clear, colorless, weakly blue fluorescent, and 1.5 mils thick. Five different colorless but blue fluorescent images were produced on this film by irradiation with 2,537 A. ultraviolet light for different lengths of time.

Image No. 1: 1-2 Seconds of exposure gave colorless and weakly blue fluorescent image.

Image No. 2: 5 Seconds of exposure gave colorless and stronger blue fluorescent image.

Image No. 3: 20 Seconds of exposure gave colorless and still stronger blue fluorescent image.

Image No. 4: 40 Seconds of exposure gave colorless and only slightly stronger blue fluorescent image.

Image No. 5: 1 Minute of exposure gave colorless and blue fluorescent image of same intensity as in No. 4.

Image No. 5 was completely bleached after 10 minutes of irradiation with 3,500 A. ultraviolet light. This image No. 5 (as well as all the other [Nos. 1 - 4]) remained colorless after the above irradiations.

EXAMPLE XXXVI

A benzene solution of DPA- O_2 was allowed to dry on paper to leave a colorless, non-fluorescent circle containing approximately 0.1 mg. DPA- O_2 per cm^2 . Irradiating the paper for 1-2 seconds with the 2,537 A. U.V. light at a distance of 5 inches (of Example XXVIII) gave a blue fluorescent and slightly yellow-colored image. The image was completely bleached after 15 minutes exposure to 3,500 A. U.V. light (Rayonet), and the cycle repeated four times.

While we have set forth certain specific embodiments and modes of practice of the invention, it will be understood that this is solely for the purpose of illustration and that various changes and modifications may be made without departing from the scope of the disclosure or spirit of the appended claims.

We claim:

1. A process which comprises applying a differential energy pattern to a member containing a polycyclic aromatic compound having an oxidized and reduced

state, said compound being fluorescent in one of said states, said energy being from between about 3×10^{-2} A. to 3.0×10^3 A. and between about 7×10^3 A. and 3×10^8 A. wavelength in the electromagnetic spectrum, said application being sufficient to form a differential pattern on said member.

2. The process of claim 1 wherein said polycyclic aromatic compound is an aromatic endoperoxide.

3. The process of claim 1 where said energy is thermal contact energy.

4. The process of claim 1 wherein said energy is actinic radiation.

5. The process of claim 4 wherein said actinic radiation is infrared radiation.

6. The process of claim 4 wherein said actinic radiation is short wave ultraviolet radiation.

7. The process of claim 1 wherein said energy applied is applied to the oxidized state and is sufficient for reduction so as to form a fluorescent pattern, and said pattern is erased by applying long wave ultraviolet radiation in the presence of air.

8. An information storage and retrieval process which comprises irradiating a substrate with a differential energy pattern of activating light, said substrate including a polycyclic aromatic compound having an oxidized and a reduced state, and being fluorescent in said reduced state, said compound being capable of being oxidized by long wave ultraviolet radiation, and reduced by short wave ultraviolet and lower, or infrared radiation, said energy used for irradiating being that which changes the state of said compound.

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