United States Patent [19]

Dorion

[11] **3,801,782**

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[54] **METHOD OF SELECTIVELY GENERATING FLUORESCENCE AND ITS SUBSEQUENT DETECTION**

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[22] Filed: **Jan. 27, 1972**

[21] Appl. No.: **221,470**

Related U.S. Application Data

[63] Continuation of Ser. No. 848,578, Aug. 8, 1969, abandoned, which is a continuation-in-part of Ser. No. 764,312, Oct. 1, 1968, abandoned.

[52] **U.S. Cl.** **250/271,** 250/461, 250/484

[51] **Int. Cl.** **G01n 21/00**

[58] **Field of Search** 204/158; 250/483, 484, 250/271, 458, 461

[56] **References Cited**

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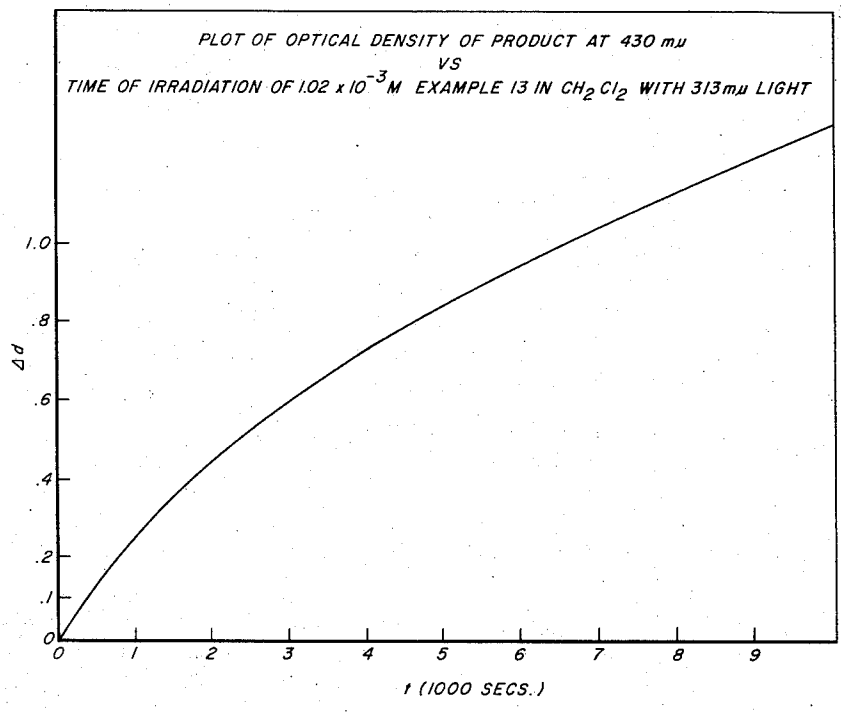
Primary Examiner—Archie R. Borchelt

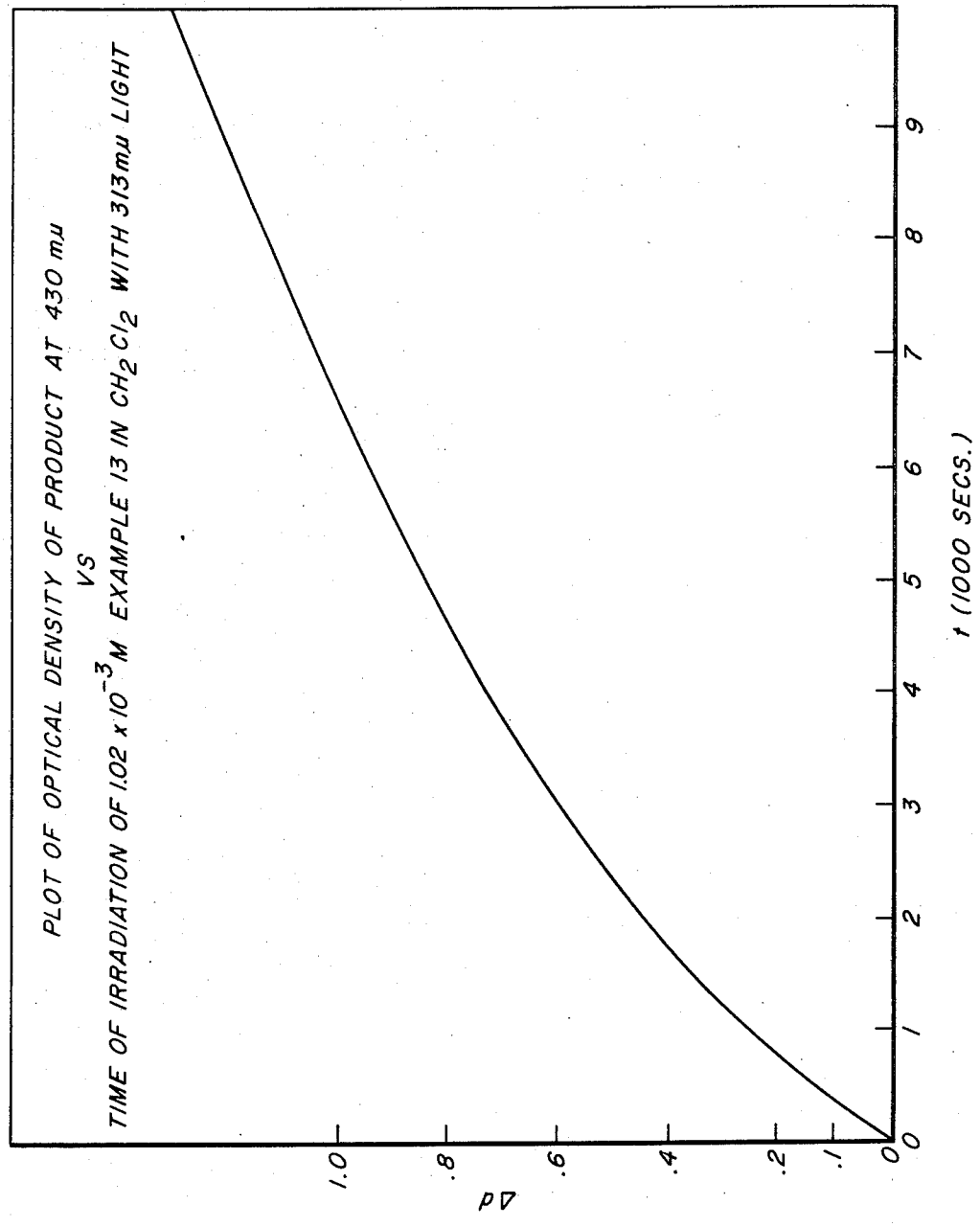
Attorney, Agent, or Firm—Charles J. Fickey

[57] **ABSTRACT**

A system for storage and retrieval of information comprising the use of a non-fluorescent material capable of photoconversion to a fluorescent material under light of a particular wavelength and which can be made to fluoresce, after such conversion, by stimulating light radiation of a longer wavelength. A fluorescent image may be formed and detected by the system.

9 Claims, 1 Drawing Figure




PLOT OF OPTICAL DENSITY OF PRODUCT AT 430 mμ
VS
TIME OF IRRADIATION OF 1.02 x 10⁻³M EXAMPLE 13 IN CH2Cl2 WITH 313mμ LIGHT
Δd
0
.1
.2
.4
.6
.8
1.0
t (1000 SECS.)
0
1
2
3
4
5
6
7
8
9

METHOD OF SELECTIVELY GENERATING FLUORESCENCE AND ITS SUBSEQUENT DETECTION

This application is a continuation of application Ser. No. 848,578, filed Aug. 8, 1969, which was a continuation-in-part of application Ser. No. 764,312, filed Oct. 1, 1968, both are now abandoned.

This invention relates to storage and retrieval of information by radiation and visual techniques. It more particularly relates to a system for forming a fluorescent image in a non-fluorescent material by radiation with light which converts the material to a fluorescent form and detecting the image with radiation of a different wavelength which does not convert the original compound, but which causes the fluorescent image form to emit light.

Information storage and recovery systems are of rapidly increasing importance in the present-day economy in view of the exponential rise in the number and complexity of the data which must be recorded and be retrievable to handle the increasing every-day business load, and to assist in scientific developments. Many optical systems, including those based on silver halide emulsions and the like, have contributed significantly to this development, largely because of the high packing density with good retrievable resolution inherent in such systems. Systems based on magnetic means, e.g., the well-known magnetic tape and magnetic ink check-printing systems, have likewise found great utility, largely because of the relative ease of handling and the relatively simple equipment involved, combined with, particularly in the case of the tapes, high reproducible fidelity. However, the optical systems are not as versatile as desired in that only a single image is normally recorded at any one bit, e.g., the developed Ag image. The same is true of the magnetic tape images where normally only the magnetic image is obtained at any one bit. This image can be made visual by a separate step, e.g., by dusting with iron powder. The magnetic ink images have the advantage of being both visually and magnetically sensible; however, these images suffer from a relatively low packing densiy.

A system for storing and retrieving information has now been discovered which comprises the following: a non-fluorescent material X capable of photoconversion to a fluorescent material Y, wherein Y has an absorption band of wavelength longer than the longest wavelength band of X, is irradiated with an information containing beam of light from an ordinary light source or a laser, etc. of such a wavelength to convert the image portion of material X to the fluorescent material Y. A longer wavelength stimulating light radiation is then applied to cause compound Y to fluoresce and thus display the image which can be detected visually or by suitable instrument. Thus material X may be considered as a fluorescer precursor. The radiant source may be of various types providing ultra-violet or infra-radiation including lamps, electric arcs, or ultra-violet and infra-red 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.

The time required for imaging will depend on the intensity of the radiation source, but is as low as nanoseconds to milliseconds to obtain detectable fluorescence emission.

It will be understood that information formed may be of any desired type, that is alphanumeric characters, code markings such as dots or lines, or pictorial information.

In the present invention, storage of information is rapid, accurate and dry, no fixing being required. Retrieval is rapid, exceptionally sensitive and accurate and is not accompanied by degradation. The inventive technique combines optical deposition of information, causing photochemical reaction in irradiated areas, thus allowing the fine resolution, with detection by fluorescence (more sensitive than absorption). As mentioned, no fixing is required where the fluorescer precursor is only sensitive to light of wavelength of less than the detecting beam of radiation. Moreover, it is possible to obtain high information density packing with the present invention.

The inventive method may be used to replace any process that employs change of optical density to change an electrical signal. This may include electronic storage and replay of sound and pictures, numerical data collection and retrieval, and the like; and to produce and validate cards, stamps, passes, and the like documents.

The fluorescer precursor X may be a colorless material, as may also the converted material Y. In this instance, the storage and retrieval may be unknown to all persons except those intended to have knowledge of the information storage. This could be used for placing information on passes or documents to be retained by one person and checked or authenticated by another such as in the case of a gate pass. An advantage of the present system is that any portion or entire cards or documents can be treated with fluorescer precursor material X, even over other information or images, after which particular information may be put on the treated part by light projection. It will be apparent therefore, that many cards may be produced, with individual information placed thereon at a later time, by conversion of the desired image portion to a fluorescent compound Y. Since the compounds are colorless in either state, space is saved in that the later information is printed over the original visible information. Detection is preferably, as previously indicated, by means of a longer wavelength light which stimulates the fluorescent form of the material. This stimulating radiation is of such a wavelength that it does not convert any of the remaining material X to material Y. Although this is the preferable mode of operation in order to prevent conversion of the background to the same state as the image by the detecting radiation, where the detection is relatively of short duration, this could be done by the same wavelength radiation as used to form the image.

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 to 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 printed directly on the film. A phonograph disc could be prepared and played by the same principal.

Although the intensity of fluorescence increases with exposure to radiation, detectable radiation has been obtained with a low intensity light source at as low as one millisecond and with a laser, imaging may be done in nanoseconds.

While the converted fluorescent information cannot be removed, it would be possible to insert new information by blotting an old word or number by converting it entirely to a fluorescent "bar", and creating another word or number adjacent thereto in fluorescer precursor material X. This, of course, is limited to the area of treatment with fluorescer precursor material X.

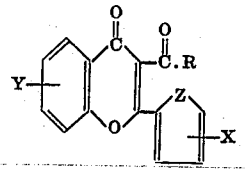
The fluorescer precursor material X may be coated on any desired substrate, or it may be incorporated in transparent or opaque plastic films. The substrate may be of any configuration, i.e., sheets, belts, discs, drums, three dimensional objects such as bottles, boxes, and the like. Techniques for this will be readily apparent to persons skilled in the art. It will be obvious that choice of materials may depend on the particular intended use.

The invention may be better understood by reference to the FIGURE. The FIGURE demonstrates the effect of increased exposure of compound X to short wave ultraviolet radiation on the fluorescent emission of product Y under longwave ultraviolet radiation. The FIGURE is in the form of a graph with the vertical axis representing optical density of product Y, i.e. fluorescence emission, under radiation at 430mμ., and the horizontal axis representing time of irradiation of compound X at 313mμ. The specific material X irradiated and converted that of subsequent Example 13, namely o-chlorophenyl-1-naphthyl ether, which is non-fluorescent, which upon irradiation with 313mμ light is converted to an entirely different chemical compound, benzo [b]-[2,1-d] furan which fluoresces under 340mμ light.

The fluorescer precursor material X may be any material which has the desired properties, that is it has a non-fluorescent form which absorbs light to be converted to a form in which it fluoresces under light of a longer wavelength than that used for conversion to the fluorescent form.

For this purpose, suitable compounds are as follows:

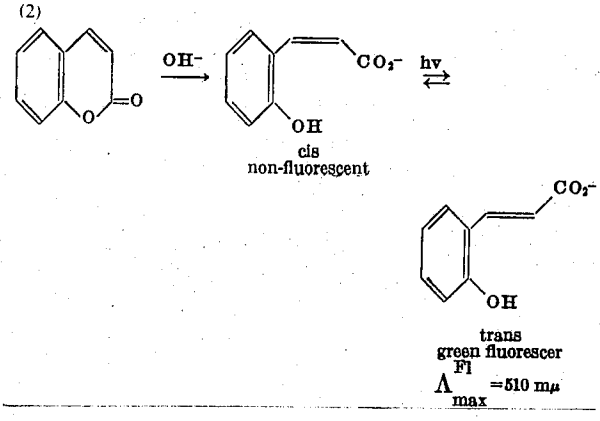
(1) 2-(2-furyl or thienyl)-3-acylchromones of the formula:



in which R is phenyl, lower alkylphenyl, lower alkoxyphenyl or furyl, X is a hydrogen or lower alkyl, Y is hydrogen, lower alkyl, lower alkoxy or furoyloxy and Z is oxygen or sulfur. The 2-thienyl compounds such as 2-(2-thienyl)-3-benzoylchromone, 2-(5-methyl-2-thienyl)-3-benzoylchromone and 2-(5-methyl-2-thienyl)- 3-anisoylchromone are included within the scope of the invention because their photolysis mechanism upon exposure to ultraviolet light is substantially the same as that of the 2-(2-furyl)-3-acylchromones.

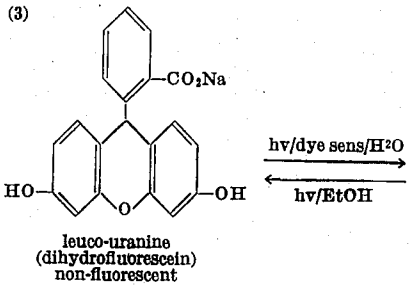
The preparation of these chromones is described in greater detail in copending, commonly assigned application Ser. No. 859,607, filed Aug. 8, 1969, which is a continuation-in-part of application Ser. No. 764,294, filed Oct. 1, 1968.

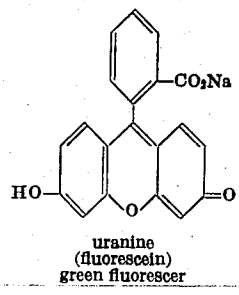
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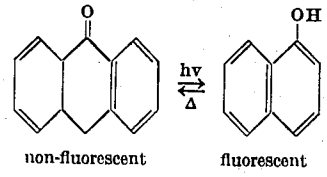
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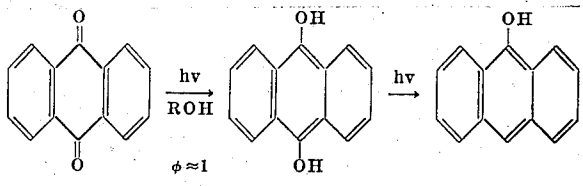


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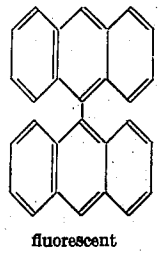


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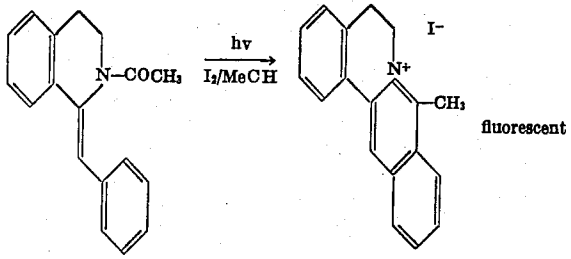


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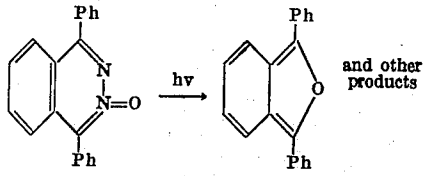


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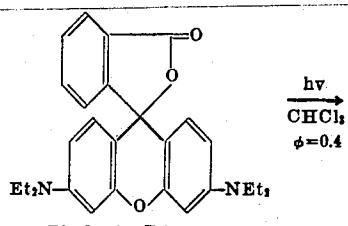
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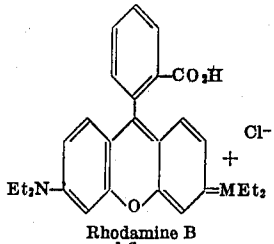
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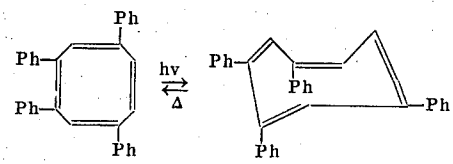
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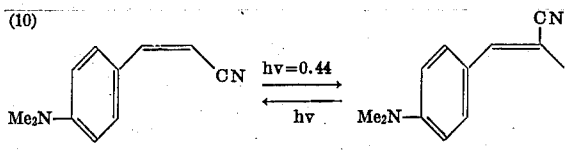
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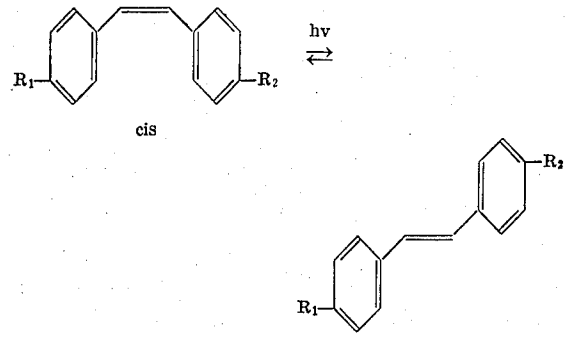
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$\lambda_{max.}^{Fl}$ =425 mμ, F.E.=0.11

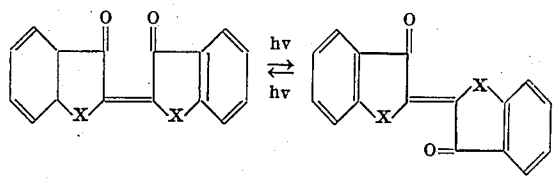
E. Lippert and W. Ludder, J. Phys. Chem., 66, 2430 (1962)

(11) Stilbenes



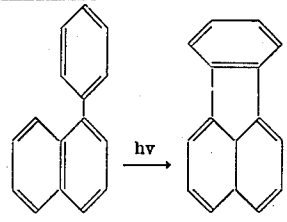
D. Schulte-Frohlinde, Ann., 615. 144 (1958) D. Schulte-Frohlinde, H. Blume and H. Gusten, J. Phys. Chem., 66, 2486 (1962) D. Gegion, F. A. Muszkat and E. Fischer, JACS 90, 3907 (1968)

(12) Indigo Dyes X=S or NH or NR



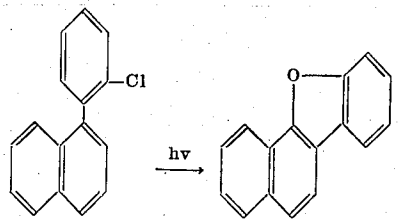
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blue fluorescer

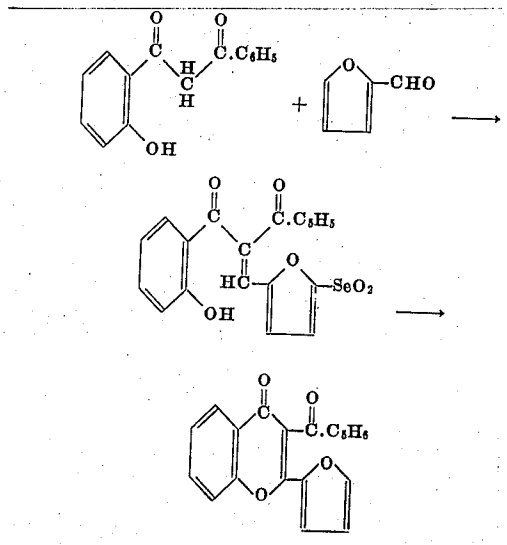
W. A. Henderson and A. Zweig, Tetra, Letters 625 (1969)

The invention will be further described and illustrated by the following specific examples which are representative of the wide variety of photosensitive chromones provided thereby.

EXAMPLE 1

3-Benzoyl-2-(2-furyl) chromone

An intermediate compound, 2-furfurylidene-1-(o-hydroxy-phenyl)-3-phenyl-1,3-propanedione is first prepared by condensing o-hydroxy-dibenzoylmethane with furfural. The intermediate may then be oxidized directly to the final product with selenium dioxide. The reactions are:



The o-hydroxy-dibenzoylmethane is prepared from o-benzoyloxyacetophenone as described in "Organic Syntheses", Vol. 32 (1952) page 74. A solution of 0.01 gram mole of this material, 0.011 gram mole of furfural and several drops of piperidine in 50 ml. of ethanol was refluxed for about 1 hour. The product which separated upon cooling was recrystallized from ethanol.

Calculated for $C_{20}H_{14}O_4$; C, 75.46; H, 4.43

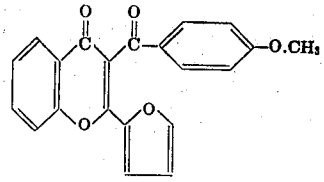
Found: C, 75.49; H, 4.45

A mixture of 320 mg. of this material and 220 mg. of selenium dioxide in 10 ml. of dioxane was refluxed for 6 hours, filtered, and the filtrate evaporated to dryness. The resulting solid was recrystallized from ethanol to five 310 mg. (97 percent yield) of 3-benzoyl-2-(2-furyl) chromone melting at 214.5°–215°C.

This product is both colorless and non-fluorescent. However, it is rearranged into a yellow colored compound exhibiting intense green fluorescence when its dilute solutions in methylene chloride are irradiated with 250–380 millimicron light.

EXAMPLE 2

3-(p-Anisoyl)-2-(2-furyl)chrome



The intermediate compound trans-3-(p-anisoyl)-2-(2-furyl)-4-chromanone is first prepared and is oxidized with selenium dioxide.

A solution in ethanol of 0.01 gram mole of o-hydroxy-p'-methoxydibenzoylmethane (W. Baker and F. Glockling, J. Chem. Soc., 1950, p. 2761) and 0.011 gram mole of furfural was refluxed for 1 hour and cooled and the product was recrystallized from a methanol-water mixture. A 59 percent yield of tan crystals was obtained melting at 136.5°–140°C. Analysis:

Calculated for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63

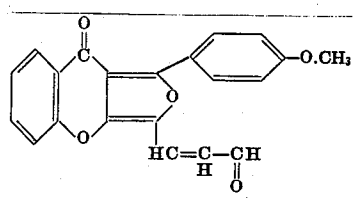
Found: C, 72.39; H, 4.64

330 Mg. of selenium dioxide was stirred into a solution of 480 mg. of this product in 15 ml. of dioxane and the mixture was refluxed for 6 hours. The product 3-(p-anisoyl)-2-(2-furyl) chromone, was obtained in 83 percent yield. Recrystallization from ethanol afforded cream colored crystals with a double melting point of 144°–6°C. and 172.5°–173.5°C.

EXAMPLE 3

Photolysis of 3-(p-anisoyl)-2-(2-furly) chromone

A solution of 16 mg. of the product of Example 2 in 900 ml. of methylene chloride in a quartz vessel was flushed with nitrogen for 30 minutes, stoppered, and irradiated in a reactor equipped with 16 bulbs having a peak light emission at 313 millimicrons. After 1.25 hours irradiation the solution was concentrated in vacuo and combined with the product solutions of other similar runs. The combined solutions were evaporated to near dryness, taken up in a 9:1 mixture of petroleum ether and ether, and chromatographed over a silica gel column. This was eluted with petroleum ether-ether mixtures containing progressively more diethyl ether. A series of intermediate fractions were combined, the solvent evaporated, and the residue was crystallized from a methylene chloride-cyclohexane mixture. It was a yellow-orange solid that fluoresced strongly in ultra-violet light. Analysis showed it to be a substituted furo-(3,4-b) chromone of the formula:



EXAMPLE 4

This Example shows the method for condensation of aldehydes with o-hydroxydibenzoylmethanes. In the general procedure, 2-furfurylidene-1-(o-hydroxyphenyl)-3-phenyl-1,3-propanedione; trans-3-(p-anisoyl)-2-(2-furyl)-4-chromanone; trans-3-(3,4,5-trimethoxybenzoyl)-2-(2-furyl)-4-chromanone; and trans-3-(p-anisoyl)-2- (5-methyl-2-furyl)-4-chromanone were prepared following the method of

Baker and Glockling, *J. Chem. Soc.*, 2579 (1962). This is the method used in Examples 4*a*, 4*b*, 4*c*, and 4*d*. A solution of 0.010 mole of the o-hydroxydibenzoylmethane, 0.011 mole of the aldehyde, and several drops of piperidine in 50 ml of ethanol was refluxed for 30 minutes to 2 hours. The product which separated upon cooling was recrystallized from ethanol.

EXAMPLE 4*a*

2-Furfurylidene-1-(o-Hydroxyphenyl)-3-phenyl-1,3-propanedione

Reaction of o-hydroxydibenzoylmethane with furfural afforded an 80 percent yield of **4***a*, mp 154.5°–159°; λ_{max}^{mull} 6.22 μ.

Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43
Found: C, 75.49; H, 4.45

EXAMPLE 4*b*

Trans-3-(p-Anisoyl)-2-(2-furyl)-4-chromanone

o-Hydroxy-p'-methoxydibenzoylmethane and furfural gave this compound in 59 percent yield, mp 127°–1-30°. Recrystallization from methanol-water afforded tan crystals, mp 136.5°–140°; μmax ^{mull} 5.97 , 6.03 μ. The nmr spectrum showed the aliphatic ring protons as a pair of doublets centered at τ3.94 and τ4.72 (J=10.5 Hz).

Anal. Calcd for $C_{21}H_{16}O_5$: C, 72.40; H, 4.63
Found: C, 72.39; H, 4.64

EXAMPLE 4*c*

Trans-3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl)-4-chromanone

This compound was obtained from 2-hydroxy-3', 4', 5'-trimethoxydibenzoylmethane and furfural. The yield was 65 percent, mp 114°–115.5°. Recrystallization from ethanol gave a mixture of crystalline modifications, mp 113.20–143°. Two further recrystallizations raised the mp to 129°–145°; λ_{max}^{mull} 5.86, 6.03 μ.

Anal. Calcd for $C_{23}H_{20}O_7$: C, 67.64; H, 4.94
Found. C, 67.91; H, 4.96

Solution infrared spectra ($CHCl_3$) of the low and high melting samples were identical.

EXAMPLE 4*d*

Trans-3-(p-Anisoyl)-2-(5-methyl-2-furyl)-4-chromanone

This compound was obtained from o-hydroxy-p'-methoxydibenzoylmethane and 5-methyfurfural in 81 percent yield; mp 134°–136.5°; λmax ^{mull} 5.92, 6.04 μ. The analytical sample separated as pale yellow needles, mp 137°–140°.

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01
Found. C, 72.98; H, 4.94

EXAMPLE 5

3-(3,4,5-Trimethoxybenzoyl)-2-(2-furyl)chromonone

Oxidation of the compound of Example 4*c* afforded a 94 percent yield of 3-(3,4,5-trimethoxybenzoyl)-2-(2-furyl)chromone, mp 160°–161.5°. The analytical sample was obtained as colorless crystals, mp 161°–16-2°, from ethanol.

Anal. Calcd for $C_{23}H_{18}O_7$: C, 67.97; H, 4.46
Found: C, 68.14; H, 4.47

EXAMPLE 6

3-(p-Anisoyl)-2-(5-methyl-2-furyl)chromone

A mixture of 1.81 g of the compound of Example 4*d* and 0.61 g of selenium dioxide in 40 ml of dioxane was refluxed for 6 hours to give 1.51 g (84%) of 3-(p-anisoyl)-2-(5-methyl-2-furyl)chromone, mp 167°–169°.

Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.32; H, 4.48
Found: C, 73.25; H, 4.35

EXAMPLE 7

3-(2-Furoyl)-2-(2-furyl)chromone

A mixture of 0.68 g (0.005 mole) of o-hydroxyacetophenone, 4.95 g (0.024 mole) of 2-furoic anhydride, and 1.5 g (0.015 mole) of triethylamine was heated at 175°–180° for 5 hours. The cooled black oil was treated with 1:1 methylene chloride-ether and the insoluble product was filtered. The filtrate was washed twice with 5% Na_2CO_3, dried, and evaporated and a second crop was crystallized in the same manner. One recrystallization of the combined crops from ethanol gave 0.83 g (54 percent) of 3-(2-furoyl)-2-(2-furyl)chromone, mp 212°–213°. A second recrystallization from methanol using charcoal afforded tan crystals, mp 214°–215°.

Anal. Calcd for $C_{18}H_{10}O_5$: C, 70.59; H, 3.29
Found: C, 70.73; H, 3.37

EXAMPLE 8

3-(2-Furoyl)-2-(2-furyl)-7-methoxychromone

A mixture of 0.83 g of o-hydroxy-p-methoxyacetophenone, 4.1 g of 2-furoic anhydride, and 1.5 g of triethylamine was heated at 150° for 6 hours and worked up as in the preceding example. 3-(2-furoyl)-2-(2-furyl)-7-methoxychromone was obtained as a tan solid; 0.36 g (21%), mp 234°–235°.

Anal. Calcd for $C_{19}H_{12}O_6$: C, 67.85; H, 3.60
Found: C, 67.37; H, 3.67

EXAMPLE 9

3-(2-Furoyl)-5-(2-furoyloxy)-2-(2-furyl)chromone

A mixture of 0.75 g of 2,6-dihydroxyacetophenone, 5.0 g of 2-furoic anhydride, and 1.5 g of triethylamine was heated at 160° for 4 hours. The resulting black solid mass was triturated with 2:1 methylene chloride-ether to give 1.85 g (80%) of 3-(2-furoyl)-5-(2-furoyloxy)-2-(2-furyl)chromone as light brown crystals, mp 252°–253°. Trituration with boiling methanol gave tan crystals of the same mp;λ_{max}^{mull} 5.75, 5.99, 6.12 μ.

Anal. Calcd for $C_{23}H_{12}O_8$: C, 66.35; H, 2.91
Found: C, 66.70; H, 2.98

EXAMPLE 10

Ultraviolet irradiation of dilute solutions in methylene chloride of the chromones of Examples 1–2 and 5–9 resulted in progressive generation of yellow colors accompanied by intense green fluorescence. This solvent was also substituted by others such as methanol, acetonitrile and benzene with essentially equivalent results. The solutions of the chromones, approximately 5 $\times 10^{-5}$ M, were irradiated with 240–400 mμ light from a 1,000 watt high pressure mercury arc.

EXAMPLE 11

A 10^{-2}N solution of 1-o-chlorophenylnaphthalene in benzene was irradiated with a 3,130 A. Hanovia 100 watt lamp with Corning No. 9863 and potassium chromate filter. The irradiated product was fluoranthene which gave a blue fluorescence.

EXAMPLE 12

o-Chlorophenyl-1-naphthyl Ether

In a 3-neck flask were mixed 95 g (0.75 mole) of o-chlorophenol and 35 g (0.75 mole) of pulverized potassium hydroxide. The mixture was stirred under nitrogen at 150 until the base was dissolved The mixture was cooled, and to it was added 100 g (0.50 mole) of α-bromonaphthalene and 1.2 g of activated copper bronze (United States Bronze Powder Works C-118 bronze powder). The whole was stirred vigorously under nitrogen and slowly heated to 190° at which temperature about 20 ml of water was distilled off. The mixture was further heated at 210° for 2 hours. Workup by extraction with aqueous potassium hydroxide and then water followed by distillation gave 14.7 g (16%) of o-chlorophenyl-1-naphthyl ether as a viscous, almost colorless oil, b.p. 138°–140°/0.04 mm. A small sample was further purified by g.l.c. for analysis.

Anal. Calcd for $C_{16}H_{11}OCl$:C, 75.46; H, 4.35; mol. wt. 254.

Found: C, 75.83; H, 4.41; m/e 254.

EXAMPLE 13

o-Chlorophenyl-1-naphthyl Ether

A solution of 200 mg of o-chlorophenyl-1-naphthyl ether as obtained in Example 12, in 300 ml of benzene, was bubbled with nitrogen in a quartz vessel. The solution was then irradiated with 254 mμ light in a Rayonet reactor for 18 hours. The resulting yellow solution was evaporated and the residue chromatographed on alumina. The appropriate fractions (110 mg. 65%) were combined, sublimed, and recrystallized 3 times from hexane and once from methanol to give 55 mg (32%) of benzo[b]naphtho-[2,1-d]furan, mp 102–103 (Liter. 103). This compound gave a blue fluorescence.

Determination of Yield and Quantum Yield

A solution of 25.5 mg of o-chlorophenyl-1-naphthyl ether in 10 ml of benzene was irradiated in a 1 cm ultraviolet quartz cell with 313 mμ light of known intensity. The rate of formation of benzo[b]-[2,1-d]furan was followed by observing the appearance of its long wavelength peak at 340 mμ. The quantum yield calculated therefrom was 3.2×10^{-3}.

A portion of the above solution diluted to 1/100 was irradiated in the same cell for 18 hours with 300 mμ light. The yield of benzo[b]-2[2,1-d]furan calculated from the size of the 340 mμ peak was 79 percent.

EXAMPLE 14

The compound of Example 2 was irradiated with 3,310 A. light in solutions of methylene chloride, benzene and acetonitrile at concentrations from 10^{-2} to 10^{-4}M. A fluorescent product was formed as in Example 3. The rate of product formation versus time of exposure is illustrated by the FIGURE. A detectable fluorescence is present after less than a second and the density increases with the time of exposure. Thus the storage of data in analog form is readily accomplished by suitably modulating the irradiating light.

The irradiating light can be modulated for a duration of exposure over different portions of the area treated with the fluorescer precursor compound to obtain information in analog form. A similar result could be obtained by modulating the irradiating light intensity over the treated area. The information is detechable with a suitable photocell coupled to a demodulation means to interpret the data.

While certain specific examples and preferred modes of operation have been set forth, it will be obvious that this is solely for illustration, and that various changes and modifications may be made in the invention without departing from the spirit of the disclosure and the scope of the appended claims.

I claim:

1. A method for processing information which comprises irradiating with an information containing beam of ultraviolet light not exceeding about 4,000 angstroms in wavelength, a substrate incorporating a fluorescer precursor compound which is non-fluorescent in its initial state, said compound being converted under said ultraviolet light of said information containing beam to a form in which it will fluoresce under stimulating untraviolet light, thereafter irradiating said converted compound with said stimulating light, and detecting the fluorescent emission.

2. The method of claim 1 wherein said fluorescer precursor compound is 2-(2-furyl)-3-acylchromone.

3. The method of claim 1 wherein said fluorescer precursor compound is a 2-(2-thienyl)-3-acylchromone.

4. The method of claim 1 wherein said stimulating light has a wavelength greater than said converting given wavelength.

5. The method of claim 1 wherein said fluorescer precursor is coated on a substrate.

6. The method of claim 1 wherein said fluorescer precursor is incorporated in a film which is the substrate.

7. The method of claim 1 wherein said fluorescer precursor is present as a coating on a substrate over information on said substrate detectable by visible light.

8. The method of claim 1 wherein said fluorescer precursor is applied to said substrate as the initial step of the imageing process.

9. The method of claim 1 wherein the intensity of said given wavelength light is varied to vary the fluorescence emission under said stimulating light.

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