

[54] **SPIRO(INDOLINE-2,2'-2H'-CHROMENE)PHOTOCHROMIC COMPOUNDS**

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[58] Field of Search.....260/326.11

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

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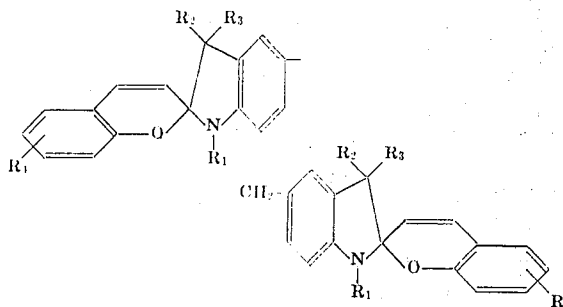
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[57] **ABSTRACT**

Photochromic compounds having the formula

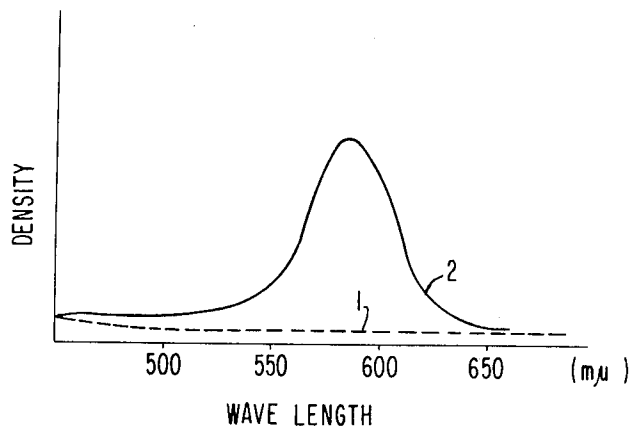


wherein R₁ is a member selected from the group consisting of an alkyl group, a substituted alkyl group, and an aralkyl group; wherein R₂ and R₃ each is a member selected from the group consisting of an alkyl group and a phenyl group; and, wherein R₄ is a member selected from the group consisting of an alkyl group, a nitro group, a halogen atom, an aldehyde group, an alkoxy group, a carboxyl group, and a carboxylic acid ester group; said alkyl group having from one to five carbon atoms are disclosed. The compounds are useful in recording media where their ability to change color on activation with ultraviolet light is advantageous.

2 Claims, 1 Drawing Figure

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1 SPIRO(INDOLINE-2,2'-2H'- CHROMENE)PHOTOCHROMIC COMPOUNDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to novel photochromic compounds and particularly to novel photochromic compounds having the characteristics of being activated by ultraviolet light and being deactivated by visible light.

2. Description of the Prior Art

Photochromism is a phenomenon in which a molecule or a complex compound changes its color when the compound is exposed to a mercury lamp enriched with ultraviolet rays or sunlight. That is to say, such compounds have stable electronic configurations, in the absence of activation, with their own specific spectral characteristics (in many cases, the unactivated compound is colorless). However, when the compound is irradiated with light of a specific wave length, the compound has a different absorption spectrum and is converted into a colored state. When the irradiation of the light is stopped, the compound reverts to the original state (usually a colorless state).

Photochromism is observed in inorganic compounds and organic compounds and further some compounds exhibit photochromism as liquids and other compounds exhibit it as solids.

Compounds showing such photochromism have recently been investigated actively and the fields of application have been enlarged. Among them, the utilization of such compounds as printing and photographic materials is an appropriate example of effectively utilizing the features of the compounds. More practically speaking, where a permanent recording of information is unnecessary, by using in the printing material a photochromic compound, as mentioned above, the information is recorded as an image for the necessary period of time. When the information becomes unnecessary, the image can be removed and the printing material can be used again.

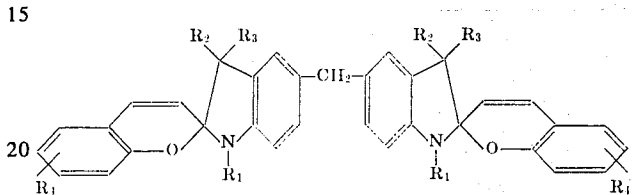
Moreover, photochromic compounds can further be utilized as ultra violet-absorbing glasses, curtains, display materials, and the like.

Although inorganic photochromic compounds have a high intensity and a repeating intensity to sunlight and ultraviolet rays, they have a disadvantage that the light response time thereof is long. Also, although conventional photochromic compounds have a short light

response time and a high density, they have the disadvantages that the light fastness thereof is weak and hence the repeating intensity is low. That is to say, compounds which are endowed with both advantages of the inorganic photochromic compounds and the organic photochromic compounds are rare.

SUMMARY OF THE INVENTION

Investigation directed to removing these faults of conventional photochromic compounds have resulted in the discovery that photochromic compounds represented by the following general formula have excellent properties:



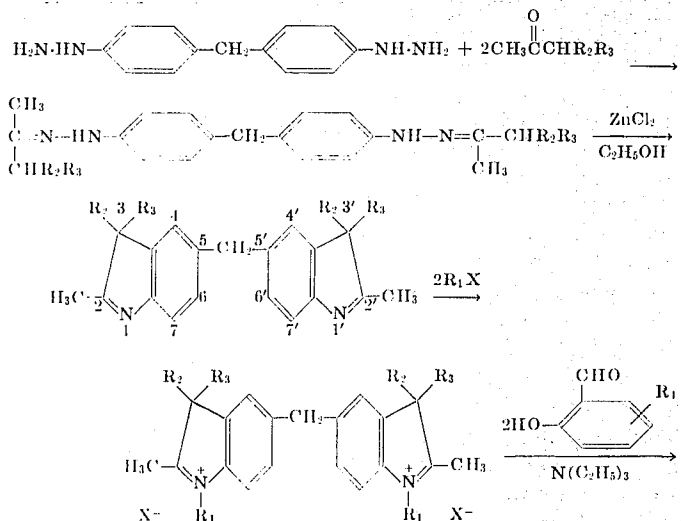
wherein R₁ represents an alkyl group, an alkyl group substituted with a substituent such as a cyano group, a hydroxyl group, a carboxyl group or an ethyl carboxylate or an aralkyl group; wherein R₂ and R₃ represent an alkyl group or a phenyl group; and R₄ represents an alkyl group, a nitro group, a halogen atom, an aldehyde group, an alkoxy group, a carboxyl group, or a carboxylic acid ester. Suitable alkyl groups have from one to five carbon atoms.

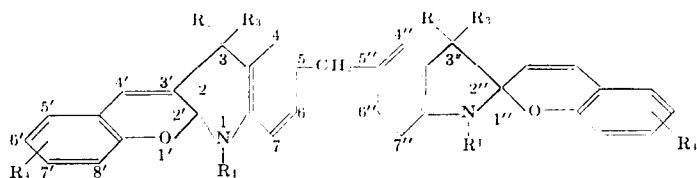
DETAILED DESCRIPTION OF THE INVENTION

That is, the compounds represented by the above general formula are colorless under ordinary conditions but when they are irradiated with ultraviolet light having wavelengths of from 2,000 to 4,000 Å, they are colored from blue to blue-purple and when they are placed in the dark, they retain the colored state for 10, 20, 30 or more days.

On the other hand, when the colored compounds are exposed to visible light of from 4,000 to 6,400 Å, the compounds are immediately converted into the original colorless state. Such coloring and discharging steps can be applied repeatedly to these photochromic compounds.

A general method of preparing the compound of the present invention is explained by the following reaction scheme:





The photochromic compounds of the present invention prepared as above are generally colorless or yellow compounds.

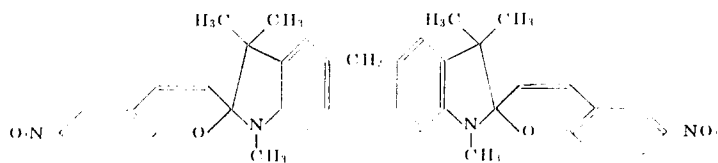
Each of the compounds mentioned above is dissolved in a solvent, at normal temperature, such as benzene, toluene, carbon bisulfide, chloroform, ethyl acetate, methyl ethyl ketone, acetone, methyl alcohol, ethyl alcohol, acetonitrile, tetrahydrofuran, dioxane, β -oxymethyl ethyl ether, (methyl cellosolve), morpholine and ethylene glycol to provide a colorless solution and when the solution is irradiated with ultraviolet light, the solution changes to a blue color.

Moreover, the compound of the present invention is dissolved in an ethyl acetate solution of polyvinyl acetate, an acetone solution of polymethyl methacrylate, an acetone solution of polyethyl methacrylate, a dimethylformamide solution of cellulose acetate, or a benzene solution of polystyrene, and the resultant solution is applied to a support such as a baryta-coated paper, a synthetic resin sheet such as a cellulose acetate sheet or a polyethylene terephthalate sheet followed by drying to provide a photochromic sheet. When the photochromic sheet thus prepared is irradiated with ultraviolet light, the sheet is colored blue to blue-purple and when the sheet thus colored is heated or exposed to visible rays after the ultraviolet irradiation, the sheet becomes colorless again. This process can be repeated numerous times.

Practical examples of photochromic materials utilizing the above mentioned compounds of the present invention are a photographic or printing photochromic material prepared by applying the aforesaid composition containing the photochromic compound of this invention to a high molecular weight compound film or a baryta-coated paper, an interior photochromic material prepared by applying the above-mentioned composition to a curtain or glass, a sun glass prepared by applying the composition to a lens or glass, and a photochromic material for use as a filter.

DESCRIPTION OF THE DRAWING

The accompanying drawing is a graph showing the change in the spectral characteristics of the compound having the following structure



in the graph the absorption spectrum 1 of the compound before irradiation with ultraviolet light and the absorption spectrum 2 thereof after the irradiation of ultraviolet rays are shown. In the experiment, Toshiba SHL-100 was used as the light source and benzene was used as the solvent.

EXAMPLE 1

In 15 ml. of ethyl alcohol were dissolved 0.7 g of

5,5'-methylene-bis(1,2,3,3-tetramethyl-indolenium-tosylate) and 0.4 g of 5-nitro-salicylaldehyde and the resultant solution was refluxed for 30 minutes.

The solution containing the reaction product was cooled to precipitate crystals, which were recovered by filtration and washed with ethyl alcohol. The crystals were recrystallized from a mixed solvent of ethyl alcohol and acetone to provide 0.5 g. of the crystal of 5,5'-methylene-bis[6'-nitro-1,3,3-trimethylspiro-(indoline-2,2'-2H'-chromene)] having a melting point of 120° to 122° C.

EXAMPLE 2

In 30 ml. of ethyl alcohol were dissolved 1.4 g. of 5,5'-methylene-bis(1,2,3,3-tetramethyl-indolenium-tosylate), 0.8 g. of 3-methoxy-5-nitro-salicylaldehyde, and 0.5 g. of triethylamine and the resultant solution was refluxed for 20 minutes.

The product solution was cooled to precipitate crystals, which were recovered by filtration and washed with ethyl alcohol. Then, the crystals were recrystallized from a mixture of ethyl alcohol and acetone to provide 1.1 g. of the faint green crystals of 5,5'-methylene-bis[6'-nitro-8'-methoxy-1,3,3-trimethylspiro-(indoline-2,2'-2H'-chromene)] having a melting point of 160° to 162° C.

EXAMPLE 3

In 30 ml. of ethyl alcohol were dissolved 1.4 g of 5,5'-methylene-bis(1,2,3,3-tetramethyl-indolenium-tosylate), 0.8 g. of 3-formyl-salicylaldehyde, and 0.5 g of triethylamine, and the resultant solution was refluxed for 20 minutes.

The product solution was cooled to precipitate crystals, which were recovered by filtration and washed with ethyl alcohol. Thereafter, the crystals were recrystallized from a mixture of ethyl alcohol and acetone to provide 0.9 g of the faint brown crystals of 5,5'-methylene-bis[8'-formyl-1,3,3-trimethylspiro-(indoline-2,2'-2H'-chromene)] having a melting point of 159° to 162° C.

EXAMPLE 4

In 30 ml. of ethyl alcohol were dissolved 1.1 g. of 5,5'-methylene-bis(1- β -hydroxyethyl-2,3,3-trimethyl-indolenium-bromide), 0.8 g. of 3-formyl-5-nitro-salicylaldehyde, and 0.4 g. of triethylamine and the solution prepared was refluxed for 20 minutes.

The product was cooled and the crystals precipitated were filtered and washed with ethyl alcohol. Thereafter, the crystals were recrystallized from a mix-

ture of an alcohol and tetrahydrofuran to provide 1.1 g. of the crystals of 5,5''-methylene-bis[6'-nitro-8'-formyl-1- β -hydroxyethyl-3,3-dimethylspiro(indoline-2,2'-2H'-chromene)] having a melting point above 300° C.

EXAMPLE 5

In 30 ml. of ethyl alcohol were dissolved 1.3 g. of 5,5''-methylene-bis(1- β -carboxyethyl-2,3,3-trimethyl-indolenium-bromide), 0.8 g. of 5-nitro-salicylaldehyde, and the solution thus prepared was refluxed for 20 minutes.

The product solution was cooled to precipitate crystals, which were recovered by filtration, washed with ethyl alcohol, and recrystallized from a mixed solvent of ethyl alcohol and tetrahydrofuran to provide 0.9 g. of the faint brown crystals of 5,5''-methylene-bis[6'-nitro-1- β -carboxyethyl-3,3-dimethylspiro(indoline-2,2'-2H'-chromene)].

EXAMPLE 6

In ethyl alcohol were dissolved 1.3 g. of 5,5''-methylene-bis(1- β -carboxyethyl-2,3,3-trimethyl-indolenium-bromide), 1.2 g. of 3,5-dibromo-salicylaldehyde, and 0.4 g. of triethylamine and the resultant solution was refluxed for 20 minutes.

The product solution was cooled to precipitate the crystals, which were recovered by filtration, washed with ethyl alcohol and then recrystallized from a mixed solvent of ethyl alcohol and acetone to provide 1.0 g. of the faint brown crystals of 5,5''-methylene-bis[6',8'-dibromo-1- β -carboxyethyl-3,3-dimethylspiro(indoline-2,2'-2H'-chromene)] having a melting point of 158° to 160° C.

EXAMPLE 7

In 30 ml. of ethyl alcohol were dissolved 1.4 g. of 5,5''-methylene-bis(1- β -ethoxycarbonylethyl-2,3,3-trimethyl-indolenium-bromide), 0.8 g. of 3-formyl-5-nitro-salicylaldehyde, and 0.4 g. of triethylamine, and the resultant solution was refluxed for 20 minutes.

The product solution was cooled to precipitate the crystals, which were recovered by filtration, washed with ethyl alcohol, and recrystallized from a mixed solvent of ethyl alcohol and acetone to provide 1.0 g. of the faint green crystal of 5,5''-methylene-bis[6'-nitro-8'-formyl-1- β -ethoxycarbonylethyl-3,3-dimethylspiro(indoline-2,2'-2H'-chromene)] having a melting point of 198° to 200° C.

EXAMPLE 8

A benzene solution, a toluene solution, and a tetrahydrofuran solution of the compound prepared in

was immediately colored blue and when the solution was placed in the dark, the color of the solution quickly became colorless.

Furthermore, a solution of 1 g. of the compound in 80 g. of a 15 percent polystyrene-benzene solution was applied to a polyethylene terephthalate film of 70 m μ in thickness in a dry thickness of 10 m μ and dried.

When a photographic negative film was closely placed on the photochromic layer of the film thus prepared and they were exposed to a mercury lamp, the exposed areas of the photochromic layer was colored into blue to provide a positive image. When the photochromic film was placed in the dark or heated, the image-bearing film was converted into the original colorless film.

EXAMPLE 9

A benzene solution of the compound prepared in Example 2 was colorless but when the solution was exposed to sunlight, it was colored blue and when the solution was placed in the dark, the solution became colorless. The coloring and discharging procedure could be repeated 10, 20, 30 times or more.

Then 1 g. of the compound was dissolved in 80 g. of a mixed solvent of 15 percent polyvinyl acetate and ethyl acetate and the solution was applied to a baryta-coated paper in a dry thickness of about 5 m μ . The light-sensitive paper prepared had the same properties as those of the light-sensitive film of Example 7, that is, when the light-sensitive paper was irradiated with ultraviolet light, the photochromic layer was immediately colored dark blue and when it was placed in the dark, the layer became colorless.

EXAMPLE 10

A tetrahydrofuran solution or a benzene solution of the compound prepared in Example 3 was colorless but when the solution was irradiated with ultraviolet light, the solution was immediately colored blue and when the irradiation was terminated, the solution quickly became colorless.

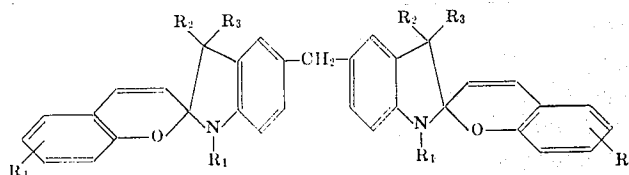
EXAMPLE 11

Each of the compounds prepared in Examples 4 to 7 was applied to a support in the same manner as in Example 8 and the light-sensitive materials prepared had almost the same properties as those of the light-sensitive material prepared in Example 8.

Besides the embodiments shown in the above examples, the compound of the present invention can be applied to a support or cast together with a sensitizer and a plasticizer.

What is claimed is:

1. A photochromic compound having the formula



Example 1 were all colorless and when each of the solutions was irradiated with a mercury lamp, the solution

wherein R₁ is a member selected from the group consisting of an alkyl group of from one to five carbon

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atoms, a substituted alkyl group of from one to five carbon atoms, whose substituents are selected from the group consisting of a hydroxyl group, a carboxyl group, and an ethyl carboxylate group; wherein R₂ and R₃ each is a member selected from the group consisting of an alkyl group of from one to five carbon atoms and phenyl; and, wherein R₄ is a member selected from the

group consisting of an alkyl group of from one to five carbon atoms, a nitro group, a halogen atom, formyl and methoxy.

5 2. A photochromic compound of claim 1 wherein the alkoxy group of R₄ is a methoxy group.

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