

[54] **PHOTORECORDING PROCESS AND  
PHOTORECORDING MEMBER**

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[22] Filed: **Feb. 18, 1972**

[21] Appl. No.: **227,636**

**Related U.S. Application Data**

[63] Continuation of Ser. No. 805,357, March 7, 1969,  
abandoned.

[52] U.S. Cl. .... **96/48 R, 96/90 PC**

[51] Int. Cl. .... **G03c 5/24**

[58] Field of Search ..... **96/48, 90 PC**

[56] **References Cited**

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[57]

**ABSTRACT**

A photochromic compound, particularly, spiropyran compound, is used for producing images. The difference of properties such as polarity and solubility between the colored species and the colorless species is utilized to produce the images and the spiropyran compound is maintained in a dense state to obtain a stable colored state.

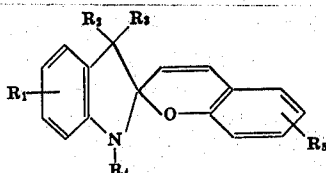
**7 Claims, No Drawings**

# PHOTORECORDING PROCESS AND PHOTORECORDING MEMBER

This is a Continuation of application Ser. No. 805,357 filed Mar. 7, 1969 now abandoned.

This invention relates to a photorecording process and photorecording member. More particularly, it relates to an improved photorecording process utilizing photochromism and a photorecording member comprising photochromic material.

The term "photochromism" is generally defined as a reversible color transformation caused when a material is exposed to a radiation. This color transformation is generally considered to be caused by isomerization, dissociation, oxidation, reduction or formation of an excited state etc. When the stimulation by a radiation is removed, the photochromic material reverts to its original state, and a reversible color transformation occurs by repeated stimulations. Efficiency in reverting to the original state of some materials is increased by the stimulation of radiation having a wave length different from that of a radiation capable of forming a colored species. One of the photochromic compounds preferred in this invention is a spiropyran compound which may be represented by the following general formula:



where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are as defined below, and it is considered that this compound is in a colored state when the C—O bond cleaves and it is in a colorless state when the C—O bond is closed. In other words, when the intrinsic absorption region of the spiropyran compound is stimulated by, for example, ultraviolet ray, it changes to a colored state having a new absorption at the visible region. This colored state continues for a certain period of time, but it reverts to the original state by stimulating the new visible region with light or heat. That is, this compound shows photoreversible photochromism. This invention is based on the principle that photochromic materials, particularly, spiropyran compounds and derivatives thereof, are in a colored state when the structure is in a cleavage state and in a form of zwitter ion, and the compounds at such state and form are of high polarity, of low solubility in a non-polar dispersion medium and in a dense state, and therefore, the colored state is stabilized.

According to this invention, the photochromic material is retained in a dense state at least at the colored state to stabilize the colored state, and further, the difference of solubilities of the colored species and the colorless species is utilized to separate these both species by dissolving and removing either the colored species or the colorless species. Thus, there is obtained an image of high resolving power in which the photochromic material is present only at the colored portion or the colorless portion.

An object of this invention is to provide a photorecording process producing a stable colored state.

A further object of this invention is to provide a photorecording process in which the colored state can be reverted to a color-eliminatable state by a chemical treatment.

5 A further object of this invention is to provide a photorecording process which can produce stable images of high contrast.

A further object of this invention is to provide a photorecording process and a photorecording member 10 which are useful for recording, storing, accumulation, amendment, elimination and layout of information in calculation, translation, communication, documentation and other various information treating mechanism.

15 A further object of this invention is to provide a photorecording process which comprises utilizing the remarkable difference of the polarity between the colored species and the colorless species and the difference of the solubility in various solvents, dissolving away either the colored species or the colorless species to produce images of high resolving power in which either the colored species or the colorless species is present.

20 A further object of this invention is to provide a photorecording member which comprises a dense state of photochromic material of stable colored state.

A further object of this invention is to provide a photorecording process in which the resulting colored image is of long life and of high quality, and if desired, 30 the elimination and the reuse are possible, and a photorecording member therefor.

A further object of this invention is to provide a photorecording member which gives red to black colored images having high degree of light absorption and high density of color and a photorecording method 35 therefor.

As mentioned above, this invention is based on a principle that photochromic materials, particularly, spiropyran compounds, are in a cleavage state at the colored state and are of high polarity and of low solubility in a non-polar dispersion medium and the colored species at the cleavage state is in a dense state. And a stable state of photochromic material is obtained at 40 least at the colored state. In this invention, a "dense state" in a colored state or in a colorless state is such a state that the colored species in the colored state or the colored species converted from the colorless species in case of the colorless state are coagulated and associated in the colored state and the absorption spectrum at the colored state is broader than that of the colored species when the colored species is present in a monomolecular state.

Preferable radiations used in this invention are  $\alpha$ -ray, 45  $\beta$ -ray,  $\gamma$ -ray, X-ray, ultraviolet ray, visible light, infrared ray etc.

As methods for retaining the photochromic material in the colored state at a dense state, there are mentioned, for example, a method which comprises applying uniformly a spiropyran compound to a self-supporting material, exposing the resulting photochromic layer to a radiation capable of color-forming to convert to the colored state, in which an appropriate dispersion medium is selected to utilize the low solubility of the colored spiropyran in the dispersion medium 50 during or after the exposure, whereby a dense state is formed to produce a stable colored state, and a method which comprises applying a radiation capable of color-

forming to a spiropyran compound existing in a dense state on a self-supporting material to obtain a stable colored state.

As methods for color-eliminating the colored state in a dense state formed as mentioned above in the photorecording process of this invention, there is mentioned, for example, a method which comprises dissolving the colored species away by using an appropriate dispersion medium, for example, polar solvent to convert to a colorless species which can be color-eliminated, color-converting the dissolved colored species which can be color-eliminated in accordance with the kind of the solvent, and applying a light of the absorption wave length range corresponding to that of the colored species or heat to the colored species to convert it to the colorless state.

In the photorecording process of this invention, images comprising only colored species or only colorless species may be obtained in order to have images of high contrast. In this process, there is utilized the difference in properties such as electrical, magnetical, chemical and other physical properties, due to the remarkable difference in the molecular structure between the colored species and the colorless species of photochromic material, particularly, spiropyran compound. More particularly, the remarkable difference of the solubility in solvent due to the marked difference of the polarity is advantageously utilized. In other words, it has been now found that the colorless species of spiropyran compound is in a ring-closure state and has low polarity so that it is soluble in a non-polar solvent while the polar colored species is in a form of zwitter ion and has high polarity so that it is soluble in a polar solvent, but not in a non-polar solvent.

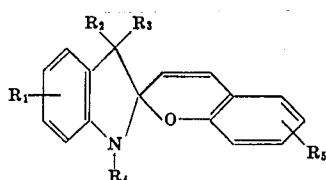
According to the present invention, the above-mentioned phenomena are utilized and a spiropyran compound is exposed to a radiation to color-form followed by treating the spiropyran compound with an appropriate solvent to dissolve and remove either the colored species or the colorless species producing the images. The color-converted colored species can easily revert to the colorless species by stimulating the colored species with a light having the absorption wave length range corresponding to that of the colored species or heat.

According to this invention, the above-mentioned features are utilized for carrying out the photorecording process more effectively.

The important components employed in the present invention are as follows:

- A. spiropyran compound
- B. dispersion medium
- C. solvent

A. Preferable spiropyran compounds employed in this invention are compound represented by the following general formula:



where  $R_2$ ,  $R_3$  and  $R_4$  are, similar or dissimilar, selected from the group consisting of hydrogen, alkyl and aryl;

and  $R_1$  and  $R_5$  are, similar or dissimilar, selected from the group consisting of nitro, alkoxy, hydroxy, carboxy, halo, carboalkoxy, alkyl, alkenyl, and aryl; and one or more of  $R_1$  and  $R_5$  may be attached to the respective six-membered ring, and the naphthopyran derivatives, the thiazole derivatives, and the oxazole derivatives etc. thereof.

Representative examples of the spiropyran compounds and the related compounds as mentioned above are:

- 1,3,3-trimethyl-6'-nitro-8'-allyl-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 1,3,3-trimethyl-5,6'-dinitro-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 1,3,3-trimethyl-7'-nitro-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 3-methyl-6-nitro-spiro-[2H-1-benzopyran-2,2'-(2'H-1'- $\beta$ -naphthopyran)],
- 1,3,3-trimethyl-8'-nitro-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 1,3,3-trimethyl-6'-methoxy-8'-nitro-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 1,3,3-trimethylindoline-8'-carboxybenzopyrlyspiran,
- 1,3,3-trimethyl-5-chloro-5'-nitro-8'-methoxy-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 1,3-dimethyl-3-isopropyl-6'-nitro-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 1-phenyl-3,3-dimethyl-6'-nitro-8'-methoxy-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 7'-nitro-spiro[xantho-10,2'-(2'H-1'-benzo  $\beta$  naphthopyran)],
- 3,3'-dimethyl-6'-nitro-spiro(2'H-1'-benzopyran-2,2'-benzothiazole),
- 3,3'-dimethyl-6'-nitro-spiro(2'H-1'-benzopyran-2,2'-benzothiazole),
- 3,3'-dimethyl-6'-nitro-spiro(2'H-1'-benzopyran-2,2'-benzo-oxazole),
- 1,3,3-trimethyl-6'-nitro-spiro(2'H-1'-benzopyran-2,2'-indoline),
- 6'-nitro-8'-methoxy-1,3,3-trimethylindolinobenzopyrlyspiran,
- 6'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 8'-allyl-1,3,3-trimethylindolinobenzopyrlyspiran,
- 8'-carboxymethoxy-1,3,3-trimethylindolinobenzopyrlyspiran,
- 8'-methoxy-1,3,3-trimethylindolinobenzopyrlyspiran,
- 6',8'-dinitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 7'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 8'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 6',8'-dibromo-1,3,3-trimethylindolinobenzopyrlyspiran,
- 6'-chloro-8'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 5-nitro-6'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 6'-nitro-8'-fluoro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 6'-methoxy-8'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran,
- 5'-nitro-8'-methoxy-1,3,3-trimethylindolinobenzopyrlyspiran, and
- 6'-bromo-8'-nitro-1,3,3-trimethylindolinobenzopyrlyspiran.

#### B. Dispersion medium

- 1. Liquid matrix

As examples of liquid matrix, the following are mentioned:

pentane, hexane, heptane, cyclohexane, dioxane, cyclohexene, carbon tetrachloride, decahydronaphthalene, xylene, toluene, benzene, carbon disulfide, ethylether, chloroform, ethyl acetate, trichlene, fluid paraffin, water, formaldehyde, furfural, acetonitrile, methanol, ethanol, acetone, n-propylalcohol, butanol, pyridine etc.

Furthermore, a mixture of these compounds may be also used.

## 2. Solid matrix

As examples of solid matrix, there are mentioned the following:

nitrocellulose, cellulose acetate, ethylcellulose, polyethylene, polystyrene, polyvinyl acetate, polyvinyl chloride, polyacrylonitrile, vinyl chloride, polymethylmethacrylate, gelatin, paraffin, and wax, etc;

oligomers known as low polymer having relatively lower degree of polymerization, and non-polymer organic compounds capable of forming a monomolecular layer film and not reactive with the spiropyran compounds.

It is desirable to select appropriately the solvent for the above-mentioned polymers and organic compounds.

## C. Solvent

As examples of solvent, the following are mentioned: water, formaldehyde, furfural, acetonitrile, methanol, ethanol, acetone, n-propyl alcohol, butanol, pyridine etc.

A mixture of these compounds may be also employed. Further, such solvent containing inorganic compound may be effectively used. As solvents of low polarity, benzene, toluene, xylene, cyclohexane, n-hexane, dioxane, and pentane are preferred. A mixture of these solvent also can be used. In the present invention, any solvent which can selectively dissolve or coagulate the colorless portion or the colored portion and shows different solubilities to these both portions may be used effectively.

The process for recording images in this invention is shown below.

1. Spiropyran compound is uniformly applied to a self-supporting material such as resin, glass, metal, paper, fiber, wood, ceramics and the like and then a radiation capable of color-forming such as ultraviolet ray and the like is applied to the layer containing the spiropyran compound obtained above to convert to the colored state. By selecting appropriately the dispersion medium in which the spiropyran compound is dispersed, the colored species resulting from applying the radiation to the colored compound coagulates, during or after the stimulation by the radiation, to a dense state due to the low solubility of the colored spiropyran compound formed in the dispersion medium.

2. A spiropyran compound is applied to a self-supporting material in a dense state and then exposed to a radiation capable of color-forming to convert the spiropyran compound in a dense state to a stable colored state. The method for forming a dense state of the colored species is further explained below. For example, a spiropyran compound is dissolved and dispersed in an appropriate dispersion medium and a radiation

capable of color-forming is applied thereto to convert to the colored state. By selecting an appropriate dispersion medium, the colored species can be formed as a dense state by utilizing the lowered solubility of the colored spiropyran during or after the stimulation of the radiation. And the spiropyran compound is dissolved in a solvent and the resulting solution is applied to the surface of a self-supporting material such as resin, glass, metal, paper, fiber, wood, ceramics and the like and dried. This procedure is repeated to convert the spiropyran compound to a dense state and then a radiation capable of color-forming is applied to convert to the colored state. Or a photochromic material is melted to form a layer in a dense state. The method for forming a photosensitive layer containing a photochromic material in a dense state in this invention is not limited to the above-mentioned methods, but other various methods may be used.

3. The colored state in a dense state as produced by the above-mentioned methods 1 and 2 is treated with a polar solvent to dissolve the colored species converting it to a color-eliminatable colored species, and when the dissolved color-eliminatable colored species is exposed to a light having an absorption wave length range of the colored species or heat, it reverts to the original colorless state. On the contrary, since the colorless state is in a state of low polarity, sharp images can be obtained by dissolving the colorless portions by using a non-polar solvent.

Further, the detailed explanation is given below.

1. A spiropyran compound is dissolved in a non-polar dispersion medium and the resulting mixture is applied to a self-supporting material such as resin, glass, metal, paper, fiber, wood, ceramics and the like to form a recording member. The resulting recording member is subjected to an image irradiation by a color-forming light such as ultraviolet ray while the dispersion medium is still present. Thus, a colored image is obtained by the colored species of the spiropyran compound. Since this colored species has low solubility in a non-polar dispersion medium, a coagulated matter of the colored species is formed and the colored state is retained in a dense state and is stable.

When the above-mentioned stable state is treated with a polar dispersion medium, a reversible process, i.e. color-elimination by light or heat.

2. A spiropyran compound is dissolved or dispersed in a non-polar high polymer of low dielectric constant. The resulting mixture is applied to a self-supporting material such as resin, glass, metal, paper, fiber, wood, ceramics and the like to form a recording member, or the above-mentioned mixture itself may form a self-supporting photosensitive matter. When this recording member is exposed to a color-forming light such as ultraviolet ray, a colored image is obtained by the formation of colored species of the spiropyran compound. This colored species becomes a coagulating state and the colored state is kept in a stable state. The treatment of the above-mentioned state by a polar dispersion medium accelerates the reversible process, i.e. the color-elimination by light or heat.

3. A spiropyran compound is applied to a self-supporting material such as resin, glass, metal, semiconductor, paper, fiber, wood, ceramics and the like to

form a photosensitive member. A radiation having sufficient energy to excite the spiropyran compound is applied to the resulting photosensitive member to convert an optional portion to the colored state. Or when the whole surface is first converted to a colored state, or with respect to a photosensitive member comprising a spiropyran compound already in a colored state, a radiation capable of color-eliminating is applied to color-eliminate selectively the optional portions and the images are produced. And a solvent is applied to the photosensitive member having the images formed as mentioned above to remove the colored portions or the colorless portions. The solvent used is that which can dissolve the portions to be removed. As the dissolving and removing methods, there are mentioned, for example, soaking the photosensitive member in an appropriate solvent, spraying the solvent onto the photosensitive member, and flowing away the portions to be removed with the solvent. When the colorless portions are dissolved away by the above-mentioned solvent treatment, colored images are produced. The above-mentioned colored state is gradually faded due to the intrinsic property of photochromic material. The faded colored state may be color-formed again by applying a radiation capable of color-forming thereto. Since photochromic material is present only at the image portions in the photosensitive member treated as above, a whole surface exposure is sufficient to color-form again, and it is not necessary to use a radiation of high resolving power. On the other hand, when the colored species is dissolved away, the pattern composed of colorless species can be converted to a colored state by applying a radiation thereto. The conditions in this case are similar to those in the above-mentioned case where colored portions are retained to form images and a whole surface exposure is effected.

The following examples are given by way of illustration and not limitation of this invention.

#### Example 1

1,3,3-Trimethylindolino-6'-nitrobenzopyrylsipran (50 mg.) was dissolved in 10cc. of toluene, and the obtained solution was uniformly applied to an art paper of about 80  $\mu$  thick, and when the coating was not yet perfectly dried, image exposure was given thereto at a distance of 20 cm from the light source for 60 seconds by using the ultraviolet ray obtained by passing the light from a 500w super high pressure mercury lamp (produced by Ushio Electric Co., Ltd) through Toshiba Glass Filter UV-D 25 (Trade name). Bluish purple image was first obtained, and then it was turned into black image gradually. The black image was not faded by ultraviolet ray or visible light at all. The black image could be retained stably for more than 9 months at room temperature. The bluish purple image had the absorption maximum at about 600 m $\mu$ , and when the image was turned to black and became a dense state, the absorption maximum was at 560 m $\mu$  and the absorption spectrum became broad. Next, when the black image was subjected to a wetting treatment by using ethyl alcohol, the black image was turned to reddish purple.

After the treatment, the same light source and Toshiba Glass Filter UV-39 (Trade name) was employed to remove the wave length shorter than 390m $\mu$ , and the irradiation of visible light was carried out at a distance of 20 cm. from the light source for 30 seconds, and the reddish purple image was erased.

#### Example 2

1,3,3-Trimethylindolino-6'-nitrobenzopyrylsipran  
70 mg.

Polystyrene 1.5 gr.

The above given ingredients were dissolved in 10 cc. of xylene, and the obtained solution was applied to a photographic ferro plate, and the resulting coating was dried to give a transparent film.

Thus obtained film was subject to ultraviolet ray irradiation by using a combination of Toshiba Glass Filter UV-D-25 and a 250 w super high pressure mercury lamp at the distance of 10 cm. from the light source for one minute, and it was turned into bluish black. No change was observed in this state even if further ultraviolet ray irradiation or the irradiation of visible light was carried out.

Thereafter the surface of the photosensitive matter was subjected to a wetting treatment by using acetone-trile and then to the visible light irradiation at a distance of 50 cm. for 1 minute by using a 250 w tungsten lamp, and the image was perfectly erased.

#### Example 3

1,3,3-Trimethylindolino-6'-nitrobenzopyrylsipran  
100 mg.

Paraffin 2 gr.

The above given ingredients were dissolved in 10 cc. of cyclohexane, and the resulting solution was applied to a two-sided art paper of 100  $\mu$  thick to prepare a photosensitive matter.

The resulting photosensitive matter was subjected to irradiation at a distance of 15 cm. from the light source for 1 minute by using Toshiba 100 w ultra high pressure mercury lamp, and thus the exposed portion was turned into black. The black product was not affected by ultraviolet ray or visible light. The black product could be retained stably at room temperature for more than 5 months.

Next, when the black state was subjected to a wetting treatment by using acetone, it was changed from black to reddish purple. After the treatment, the irradiation of visible light was carried out in the same manner as in Examples 1 and 2, and the reddish purple image was eliminated.

Thereafter, when the acetone was perfectly evaporated, the photosensitive matter reverted to the original state, i.e. it can be changed to a black state again by irradiation of ultraviolet ray.

#### Example 4

1,3,3-Trimethylindolino-6'-nitro-8'-methoxybenzopyrylsipran 100 mg.

Paraffin 1 gr.

The above given ingredients were dissolved in 10 cc. of trichlene, and the obtained solution was uniformly applied to an art paper of about 80  $\mu$  thick and dried to form a photosensitive matter.

Before the above prepared photosensitive matter was exposed to light, a wetting treatment was carried out by using cyclohexane, and then ultraviolet ray obtained by using a 250 w super high pressure mercury lamp and Toshiba Glass Filter UV-D 25 was irradiated at a distance of 10 cm. from the light source for 1 minute, and bluish green color appeared, and then it gradually turned into black.

The black state was not affected by ultraviolet ray or visible light.

Thereafter, wetting treatment was carried out by using methanol, and black state was turned into reddish purple.

After the treatment, color developed state was eliminated by irradiating visible light in the same manner as in Example 1.

The absorption maximum in bluish green state was at about 620 m $\mu$ , and as the light irradiation proceeded, the state changed to a black state having a broad absorption ranging from 500 m $\mu$  to 600 m $\mu$ . This black state was not faded by ultraviolet ray and visible ray. Then, the wetting treatment with methanol changed the black state to a reddish purple. After this treatment, it was subjected to irradiation of visible ray in a similar way to Example 1 above and the colored state was eliminated.

#### Example 5

1,3,3-Trimethylindolino-6'-nitro-8'-methoxybenzopyrylsipran (50 mg.) was dissolved in 10 ml. of benzene and a part of the resulting solution was spread over a glass plate (20 cm.  $\times$  30 cm.) held horizontally. The solvent in the spread solution was vaporized and the spreading was repeated five times in total to form a photochromic photosensitive layer. The resulting photosensitive layer was exposed to the ultraviolet ray obtained by passing a light from a 1 Kw super high pressure mercury lamp (manufactured by Ushio Electric Co., Ltd.) through a Toshiba Glass Filter UV-D25 at a distance of 15 cm. for 3 minutes. The exposed portion was changed to blue.

Then the following dissolving procedure was carried out.

1. The above photosensitive matter having images formed by the presence of the colored state and the colorless state was soaked in cyclohexane for 30 minutes to dissolve the colorless part away and retain the colored part. The above-mentioned colored part was color-eliminated with the passage of time, but when irradiation of ultraviolet ray was applied to the whole surface, it was colored as previously.

2. The photosensitive matter having images as in 1 above was subjected to a treatment of spraying methanol for 1 minute to dissolve the colored portion, and consequently only the colorless portion remained. After this treating, the whole surface of the photosensitive matter was exposed to an ultraviolet ray to be colored, and thus a normal image corresponding to the negative used as the pattern was obtained.

#### Example 6

A photosensitive layer was formed in the same way as in Example 5 by using 1,3,3-trimethylindolino-5-chloro-6'-nitrobenzopyrylsipran and was colored by a whole surface irradiation of ultraviolet ray. The resulting photosensitive layer was exposed through a negative to a visible light obtained by using a 500 w tungsten lamp and Toshiba Glass Filter VY-43 (Trade name) at a distance of 30 cm. for 1 minute. Thus, the exposed portion was color-eliminated and reverted to the colorless state. Then, a dissolving procedure as in Example 5 was effected, n-Hexane was used for dissolving the colorless portion while ethanol was used for dissolving the colored portion, and similar results was obtained.

#### Example 7

1,3,3-Trimethylindolino-8'-carboxybenzopyrylsipran (40 mg.) was dissolved in 10 ml. of ethanol and spread over a glass plate 6 times as in Example 5 to form a

photosensitive layer. This compound is originally red before exposed to a light and the red color is eliminated. This phenomenon is a reverse photochromism. The visible light source as used in Example 2 was used to apply an image-wise irradiation to the above-mentioned photosensitive matter. The exposed portion was color-eliminated to form images (positive-positive). The images were subjected to the treatment as described in Examples 1 and 2 to dissolve selectively the colored portion and the colorless portion.

What we claim is:

1. A photorecording process which comprises applying an imagewise radiation to a photosensitive layer comprising a spiropyran compound and a non-polar dispersion medium in an exposure amount and time duration sufficient to produce (1) an initial colored image in an unstable monomolecular colored state and thereafter (2) a stable colored species of low solubility adapted to form a stable colored image in a coagulated and associated stable colored state, said stable colored state unaffected by radiation and heat, wherein said stable colored state has a broader absorption spectrum when said initial monomolecular colored state.

2. A photorecording process which comprises applying a blanket irradiation of a radiation to a photosensitive layer comprising a spiropyran compound and a non-polar dispersion medium in an exposure amount and time duration sufficient to produce (1) an initial colored image in an unstable monomolecular colored state and thereafter (2) a stable colored species of low solubility adapted to form a stable colored image in a coagulated and associated stable colored state, said stable colored state unaffected by radiation and heat, wherein said stable colored state has a broader absorption spectrum then said initial monomolecular colored state, next wetting the surface of the colored photosensitive layer with a polar liquid dispersion medium to convert it to a color-erasable colored state, and then applying an imagewise irradiation by a radiation capable of erasing the color-erasable colored state to form an image.

3. A method for forming an image which comprises applying an imagewise irradiation by a radiation to a photosensitive layer comprising a spiropyran compound and a non-polar dispersion medium in an exposure amount and time duration sufficient to produce (1) an initial colored image in an unstable monomolecular colored state and thereafter (2) a stable colored species of low solubility adapted to form a stable colored image in a coagulated and associated stable colored state, said stable colored state unaffected by radiation and heat, wherein said stable colored state has a broader absorption spectrum then said initial monomolecular colored state, and then removing the colored species of the spiropyran compound at the colored portion of the resulting colored image using a polar solvent.

4. A photorecording process according to claim 1 in which the non-polar dispersion medium is removed by vaporization after imagewise exposure.

5. A photorecording process according to claim 1 in which after producing stable colored images by imagewise exposure, the colored image surface is wetted with a polar dispersion medium to convert the stable colored image to a color-erasable colored state.

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6. A photorecording process according to claim 5 in which the color-erasable state is erased by using a radiation, heat or a mixture thereof.

7. A method for forming an image according to claim

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3 in which the non-colored species of the spiropyran compound at the non-colored portion of the stable colored image is removed using a non-polar solvent.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,785,820 Dated January 15, 1974

Inventor(s) EIICHI INOUE, ISAMU SHIMIZU, ICHIRO ENDO, and

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

Enter on page 1, [30] Foreign Application Priority Data

March 12, 1968 Japan . . . . . 15988/1968

Column 4, line 23, "trimethylindoline" should be

--trimethylindolino--.

Column 5, line 2, "cyclchexene" should be --cyclohexene--

Column 5, line 53, "solored" should be --colored--.

Column 5, line 54, "colored" should be --spiropyran--.

Column 10, line 24, "when" should be --then--.

Signed and sealed this 29th day of October 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents