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3,667,949

IMAGEWISE PHOTOCHROMIC PROCESS UTILIZING SPIROPYRAN COMPOUNDS AND HALOGENATED HYDROCARBON PHOTOACTIVATORS

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No Drawing. Filed Mar. 6, 1969, Ser. No. 805,004

Claims priority, application Japan, Mar. 12, 1968,

43/15,712, 43/15,987

Int. Cl. G03c 1/52

U.S. Cl. 96—48

2 Claims

ABSTRACT OF THE DISCLOSURE

A stable colored image is obtained by using a spiropyran compound and an ionic compound in a coexistent state, applying image-wise radiation thereto.

The colored state can be eliminated by neutralizing the ionic compound.

Thus, the photochromic image formation can be repeatedly effected.

This invention relates to a photorecording method and a photorecording member for producing a stable photochromic colored state. More particularly, it relates to a process for forming a stable photoreversible state of spiropyran compounds by chemical treatment capable of color-forming or color-eliminating.

It is known that spiropyran compounds are converted to a colored state having new absorption at the visible region by stimulating the intrinsic absorption region of the spiropyran compounds with an ultraviolet ray. The resulting colored state continues for a certain period of time, but when it is stimulated by heat or the new visible absorption region is stimulated by a light, the colored state reverts to the original state. This is a photoreversible property.

Heretofore, processes for stabilizing and maintaining the colored state of photochromic materials have been known. For example, U.S. Pat. No. 3,341,330 discloses that a colored state obtained by irradiating a spiropyran compound with ultraviolet ray is treated with an acidic material such as hydrogen chloride to stabilize the yellow colored state and then, if desired, the color is eliminated by treating it with a basic material such as ammonia gas.

According to the present invention, spiropyran compounds having photochromic property are colored by treating with an acidic compounds or a basic compound or by an acid formed by irradiating a halogen compound with a radiation, and further, the colored state can be eliminated by irradiating a radiation having a wave length region different from that of the radiation used for color-forming. In addition, the colored state can be reverted to the original state by neutralizing the acid or the base used for color-forming.

An object of this invention is to provide a process for obtaining a stable colored state of a spiropyran compound and a process for converting the colored state to the colorless state.

A further object of this invention is to provide a recording member having a stable photoreversible property.

A further object of this invention is to provide an image of very high resolving power.

A further object of this invention is to provide a very simple recording method.

According to the present invention, the spiropyran compounds can be converted to the colored state by using an ionic substance existing together with the spiropyran compounds.

In this invention, "ionic substance" includes acidic materials and basic materials. The "existing together with" may mean a state of dispersion or a state of contacting the layers.

The color-forming mechanism is considered as follows, but the present invention is not limited by the following explanation of the mechanism.

The transformation from the colorless state to the colored state depends on the characteristic of the acidic compound, for example, when the acidity is higher than a certain value, the colored state appears, but an acid of very low acidity such as phenol and the like hardly gives a colored species of the spiropyran compound. The colored species obtained by applying a usual acid to the spiropyran in this invention is yellow to red. It is generally considered that the spiropyran compound is in a ring-open state in the colored state and the spiropyran compound in the colored state is in a "zwitter ion" form having both acidic and basic active centers. Thus, when the spiropyran compound is reacted with an ionic substance such as acid, the compound becomes a ring-open form by the action of acid and further, the interaction with the basic active center results in a stable colored state. When the colored state formed by the reaction with an acid or a colorless state formed by irradiating the colored state with a light (the colorless state can revert to the colored state by heat) is treated with a basic substance to neutralize the acidic substance, it can revert to the original state. In a similar way, when a spiropyran compound is reacted with an ionic substance, e.g. a base, it is changed to a ring cleavage state and results in a stable colored state by the interaction of the base with the acid active center.

When the colored state formed by the reaction with the base or the colorless state converted from the colored state by the irradiation of the absorption light is treated with an acidic substance to neutralize the basic substance to revert to the original state, i.e. a state before the color-forming occurs by contacting with the base.

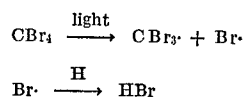
Furthermore, when the spiropyran compound is color-formed by the treatment with a solid acid or base, it is considered that the catalytic activity of the solid acid or base as well as the acidic or basic action contributes to the stabilization of the colored state.

The treatment with an ionic substance may be carried out by various ways, for example, coexistence of the spiropyran compound with the ionic compound, more particularly, maintaining the spiropyran compound and the ionic substance in a dispersion state or making one or both of them into a layer and contacting each other.

The H^+ used here is an acidic substance by which a spiropyran compound is color-formed.

Examples of H^+ used in this invention are inorganic acids, solid acids, organic acids which work directly, and halogen compounds which produce acids when exposed to light or other radiation.

With respect to the mechanism of the formation of acids from halogen compounds may be explained as follows. When a halogen compound is irradiated by light or other radiation, a halogen radical is produced and the free radical thus produced causes dehydrogenation to form an acid. In case of carbon tetrabromide, the reaction will proceed as shown below:



And then the isolation of halogen radical and the dehydrogenation occur repeatedly, and such chain reaction effectively produces the acid. It is considered that the acid

thus produced reacts with a spiropyran compound to color-form the spiropyran compound.

It has been now found that the colored state formed by the reaction of the acid produced by the chain reaction as above with a spiropyran compound is thermally stable and can be color-eliminated by irradiating an absorption visible light thereto. Further, the colored spiropyran compound resulting from the reaction with the acid as above can be reverted to the original state before reacting with the acid by neutralizing the colored spiropyran compound with a basic compound such as, for example, amines.

It has been also found that the colored spiropyran compound can be converted to a colorless state by applying a radiation such as visible ray. The radiation used in this color-eliminating step is that having a wave length range different from that of the radiation applied to the color-forming step. For example, a visible light is used. The resulting colorless state reverts to the colored state when the color-eliminating radiation is removed. This cycle of color-eliminating and color-forming can be effected repeatedly without fatigue.

When the spiropyran compound in the above-mentioned colored state or in the colorless state resulting from the above-mentioned irradiation by a radiation is treated with a basic compound, it reverts to the original colorless state, i.e. a state before the acid is formed by a radiation to convert the spiropyran compound to the colored state.

The above-mentioned cycle can be repeated starting from the colorless original state as far as the halogen compound is still present.

Further, the spiropyran compound at the colored state or at the colorless state formed by irradiation of an absorption visible light can be converted to the original state, i.e. a state before the compound is reacted with an acid, by neutralizing the acid with a basic compound such as, for example, amine compounds.

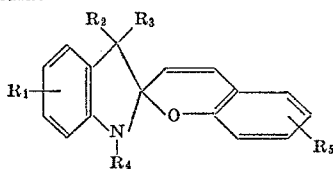
The compositions of the recording materials to be used in the present invention are classified into the following groups;

- (A) spiropyran compound
- (B) additive
- (C) binder
- (D) solvent

The above given ingredients are included in the recording material and in the system of recording of this invention.

These materials will be explained in detail in the following.

(A) Preferable spiropyran compounds employed in this invention are compounds 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.

(B) As the additives used in this invention, there are mentioned the following.

(1) Inorganic acid:

Representative inorganic acids used in this invention are, for example, hydrochloric acid, nitric acid, sulfuric acid, carbonic acid, phosphoric acid etc.

(2) Organic acid:

Representative organic acids used in this invention are, for example, sulfonic acids such as benzene sulfonic acid and the like, carboxylic acids such as acetic acid, propionic acid, lactic acid, malonic acid, oxalic acid, maleic acid, benzoic acid, phthalic acid, and the like.

(3) As the solid acids, Lewis solid acids are generally employed. Examples are shown below:

- (1) Natural clay minerals: acidic terra abla, clarite, bentonite, kaolin, fuller's earth, montmorillonite, floridine etc.
- (2) Solid acids: Those which are prepared by adhering sulfuric acid, phosphoric acid, or malonic acid on silica gel or alumina, Phosphoric acid with quartz sands as the carrier Calcined products of diatomaceous earth and phosphoric acid
- (3) Cation exchange resins
- (4) Silica-alumina, silica-magnesia, silica-boria, etc.
- (5) Inorganic chemicals: ZnO , Al_2O_3 , TiO_2 , CeO_2 , As_2O_3 , V_2O_5 , SiO_2 , Sb_2O_5 , $CaSO_4$, $MnSO_4$, $CuSO_4$, $NiSO_4$, $CoSO_4$, $CdSO_4$, $SrSO_4$, $MgSO_4$, $FeSO_4$, $BaSO_4$, $KHSO_4$, K_2SO_4 , $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, $Ca(NO_3)_2 \cdot 4H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $CaCO_3$, Zr phosphate, Ti phosphate, $AlPO_4$, $PbCl_2$, $HgCl_2$, $CuCl_2$, $AlCl_3$, $SnCl_2$, $CaCl_2$, $AgCl$, H_2WO_4 , $AgClO_4$, ZnS , CaS , $Mg(ClO_4)_2$, etc.

(4) As halogen compounds, the following are preferable:

CH_3Cl , CH_3Br , CH_3I , Cl_4 , CBr_3I , CCl_3I , $CHCl_2I$, $CHBr_2I$, CBr_4 , CCl_3Br , $CHCl_2Br$, CCl_4 , C_2Cl_6 , C_2H_5Cl , C_2H_5Br , C_2H_5I , $CH_3CH_2CH_2Cl$, $CH_3CH_2CH_2Br$, $CH_3CH_2CH_2I$, $(CH_3)_2CHCl$, $(CH_3)_2CHBr$, $(CH_3)_2CHI$,

$CH_3(CH_2)_3Br$, $CH_2=CHCl$, $CH_2=CHBr$

$CH_2=CHCH_2Cl$, $CH_2=CHCH_2Br$, $CH_2=CHCH_2I$ etc.

In addition to the above-mentioned polyhalogenated hydrocarbons, halogenated aromatic hydrocarbons also can be used.

(5) As basic compounds used in this invention, there are mentioned, for example, the following:

- (1) Inorganic bases such as sodium hydroxide, potassium hydroxide, calcium hydroxide and the like.
- (2) Amines such as ammonia, ethylamine, propylamine, butylamine and the like.
- (3) Salts of weak acids and strong bases such as potassium cyanide, sodium cyanide and the like.
- (4) As the solid base, Lewis solid base is generally used, and the following are the examples:
 - (a) Inorganic chemicals CaO , MgO , BeO , SiO_2 , ZnO , Na_2CO_3 , K_2CO_3 , $KHCO_3$, $(NH_4)_2CO_3$, $BaCO_3$, $KNaCO_3$, $Na_2WO_4 \cdot 2H_2O$, KCN etc.
 - (b) Those which can be obtained by adhering caustic soda on silica gel, or those which can be prepared by adhering caustic potash on alumina, etc.
 - (c) Anion exchange resin
 - (d) Nitrous oxide activated carbon, ammonia activated carbon, etc.

(C) As high polymers for binder, for example, the following are given.

(1) As high polymers of condensation type: polyamide resins, N-alkylpolyamide, polyimide, polypeptide, polyester resin, polycarbonate, resin, polyacid anhydride resins, polyether type resins, etc.

(2) As high polymers of polymerization type: aliphatic hydrocarbon type vinyl resin, aromatic hydrocarbon type vinyl resin (polystyrene type), vinyl alcohol type resin, nitrile resin, acryl resin, methacryl resin, etc.

As high polymers given above, the following are given as the examples; nitrocellulose, cellulose acetate, ethylcellulose, polyethylene, polystyrene, polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyacrylonitrile,

vinyl chloride, polymethyl methacrylate, gelatin, etc.

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In addition to the above, oligomer, or other monomer organic materials of excellent adherability can be used.

It is also possible to use synthetic photocolor forming materials chemically bonded to a high polymer or oligomer.

(D) As the organic solvents to be generally used in this invention, the following can be given as examples: benzene, toluene, xylene, cyclohexane, normal hexane, butyl alcohol, ethyl alcohol, isopropyl alcohol, dimethyl formamide, acetone, methyl alcohol, ethyl acetate, ethyl ether, pyridine, trichlene, quinoline etc.

The homologues of the above given organic solvents are also effectively used and water is also preferably used in this invention.

As the basic compounds used for converting to a colorless state, the following are, for example, mentioned: inorganic bases such as sodium hydroxide, potassium hydroxide and the like, amines such as ammonia, ethylamine, propylamine, butylamine and the like, and salts of weak acids and strong bases such as potassium cyanide, sodium cyanide and the like.

Regarding the structure of the recording member and the process employed in this invention are not restricted in the above given descriptions and the following examples.

This invention includes the structure of recording member prepared by applying the above described system to self-retaining materials such as resins, glass, metals, papers, fibers, wood, ceramics and other supports.

It is optional to apply the above given systems removed of the binder (generally chemically inactive carrier in resinous state) directly to a self-supporting material.

Examples of this invention are given below.

EXAMPLE 1

1,3,3-trimethylindolino-6'-hydroxy benzopyryl

spiran	-----mg--	25
Malonic acid	-----mg--	50
Polystyrene	-----g--	2

The above given ingredients were dissolved into 10 cc. of xylene, and the obtained solution was applied to a glass plate, and it was dried.

Thereafter, it was peeled off from the glass plate to produce a transparent film.

Thus obtained film was colored in yellow. The colored state of the obtained film was stable at a room temperature.

Next, visible light was applied thereto at the distance of 10 cm. from a light source for 60 seconds by using a 250 w. super high pressure mercury lamp (produced by Ushio Electric Co., Ltd.) and Toshiba Glass Filter UV-39 (trademark) and removing the wave length region shorter than 390 μ , and the colored state was perfectly eliminated.

The colorless state was thermally turned back to the original colored state before the color-elimination when allowed to stand at a room temperature.

The color-forming and color-eliminating process can be repeatedly carried out.

Moreover, it was possible to turn the colored state into colorless state by neutralizing the surface of the photosensitive matter with the mixture of 10% sodium hydroxide-alcohol-water solution through wetting process.

EXAMPLE 2

1,3,3-trimethylindolino-7'-hydroxybenzo-

pyrylspiran	-----mg--	100
Potassium hydroxide	-----mg--	100
Ethyl cellulose	-----g--	2

The above given ingredients were dissolved into 30 cc., of ethyl alcohol, and the obtained solution was uniformly applied to an art paper of 80 μ in thickness to form a recording matter. The recording matter was colored in yellow.

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The colored state was stable at a room temperature.

Next, the colored state was perfectly eliminated when irradiation of visible light was carried out at a distance of 20 cm., from the light source for 60 seconds by using a 250 w. ultra high pressure mercury lamp as the light source (produced by Ushio Electric Co., Ltd.) and Toshiba Glass Filter UV-39 to remove the wave length region shorter than 390 m μ .

The colorless state was thermally turned back to the original colored state before the color-elimination when allowed to stand at a room temperature, and the color developing and erasing process could be repeated. Moreover, the above mentioned colored state could be turned into colorless state by subjecting the surface of the photosensitive matter to a wetting process by using a mixture solution of 10% acetic acid-alcohol-water.

EXAMPLE 3

5 gr. of kaolin and 15 ml. of ethyl alcohol were sufficiently mixed for 5 minutes by using an ultrasonic wave stirrer, and then the mixture was uniformly applied to a one sided art paper (80 μ thick) in such a manner that the thickness of the coating became about 10 μ .

EXAMPLE 4

5 gr. of Japanese acid clay and 15 ml. of ethyl alcohol were sufficiently stirred for about 5 minutes by an ultrasonic stirrer and the resulting mixture was applied to a two-sided art paper of 80 μ thick to form a coating of 10 μ thick.

EXAMPLE 5

5 gr. of kaolin, 0.02 g. of ethyl cellulose, and 15 ml. of dioxane were sufficiently stirred for about 10 minutes by using an ultrasonic wave stirrer, and the resulting mixture was uniformly applied to an art paper (about 100 μ thick) in such a manner that the thickness of the coating could become about 15 μ .

EXAMPLE 6

5 gr. of bentonite and 15 ml. of ethyl alcohol were sufficiently stirred for about 5 minutes by using an ultrasonic stirrer and the mixture solution was uniformly applied to a 100 μ thick aluminum plate in such a manner that the thickness of the coating could become about 10 μ .

The solution prepared by dissolving 50 mg. of 1,3,3-trimethylindolino-6'-nitrobenzopyrylspiran into 10 cc. of toluene, was applied to the surfaces prepared in Examples from 3 to 6 in such a manner that the thickness of the coating could become from 1 to 2 μ , to form a photo-recording member.

It was also effective to add various kinds of binder materials to the above prepared compositions, if necessary.

The recording matters, having been prepared from the above given compositions, were colored as follows. In the case of Examples 3 and 5, the color was pink, and in the case of Example 4, it was reddish brown, and in the case of Example 6, it was dark orange.

The colored state was stable at a room temperature. Next, a tungsten lamp (250 w.) was used to carry out an exposure at the distance of 50 cm. for 60 seconds and the colored state was perfectly eliminated.

The colorless state was thermally turned back to the colored state that is the same as the color before the color is eliminated when stood at a room temperature.

On the other hand, when exposure was carried out for 60 seconds at the distance of about 30 cm. from the light source with the ultraviolet ray obtained by using a 500 w. ultra high pressure mercury lamp and a visible light cut filter [Toshiba Glass Filter UV-D25 (trademark)], the colorless state was turned back to the original colored state.

The above mentioned color forming and color eliminating processes could be repeated over again.

On the other hand, the deterioration caused by the continuous irradiation of visible light could hardly be observed.

EXAMPLE 7

1,3,3 - trimethylindolino - 6' - nitrobenzopyryl-spiran	mg--	50
Carbon tetrachloride	mg--	120
Ethylcellulose	gr--	2

The above given ingredients were dissolved in 15 ml. of dioxane and the resulting solution is applied to the surface of a glass plate and dried naturally in a dark place for 48 hours to form a transparent film of 75 μ in thickness. In the same way as in Example 1, ultraviolet ray is applied to the resulting photosensitive member through an image pattern. As the result of this procedure, the exposed portions are changed to yellow (absorption maximum: around 4200 A.). The photosensitive member is irradiated with a visible light obtained by using a tungsten lamp (500 W.) and Toshiba Glass Filter UV-39 (trademark) to eliminate the yellow color. When the photosensitive member is allowed to stand in a dark place for more than two hours, the portion exposed to ultraviolet ray reverted to yellow. The photosensitive member which yellow state was eliminated by a visible light irradiation was subjected to a wetting treatment with n-propylamine and in this case the colorless state was not reverted to a yellow colored state when allowed to stand in a dark place.

EXAMPLE 8

1,3,3 - trimethylindolino - 6' - hydroxybenzopyryl-spiran	mg--	30
Polystyrene	gr--	2
Iodoform	mg--	20

The above given ingredients were dissolved into 10 cc. of xylene, and the obtained solution was applied to a transparent glass plate, and after having it dried, it was peeled off to obtain a transparent film.

Thereafter, a 250 w. super high pressure mercury lamp (produced by Ushio Electric Company, Ltd.), and Toshiba Glass Filter UVD-25 were used to irradiate an ultraviolet ray of 365 m μ thereonto for 30 seconds at a distance of 10 cm. from the light source and the transparent film was turned into yellowish red color.

Thus obtained colored state was kept stable at a room temperature.

Next, a visible light was irradiated thereto by using Toshiba Glass Filter UV-39 together with the light from the above mentioned light source at the same distance for 60 seconds to remove the wave length below 390 m μ , and the colored state was perfectly eliminated.

The resulting colorless state is thermally reverted gradually to the colored state before the color-elimination when allowed to stand at room temperature. The color forming and color eliminating process can be repeated.

When the surface of the photosensitive member was treated with n-propylamine, the above mentioned colored state was turned back to the original state before the irradiation of ultraviolet ray.

EXAMPLE 9

1,3,3 - trimethylindolino - 8' - hydroxybenzopyryl-spiran	mg--	50
Carbon tetrabromide	mg--	50
Ethyl cellulose	gr--	3

The above given ingredients were dissolved into 10 cc. of dioxane, and the obtained solution was coated on a glass plate, and it was dried to produce a photosensitive matter.

Yellow color was obtained when treated in the same manner as in Example 8.

The photosensitive member surface was treated with an ethylamine-ethanol solution, the formed color was eliminated.

EXAMPLE 10

1,3,3 - trimethylindolino - 6' - nitrobenzopyryl-spiran	mg--	80
Hexachloroethane	mg--	40
Cellulose acetate	gr--	5

The above given ingredients were dissolved into 20 cc. of acetone, and the obtained solution was applied to an art paper of 80 μ thick uniformly to produce a recording paper.

Next, thus obtained recording paper was changed into yellow color when it was exposed to an ultraviolet ray having wave length of 365 m μ obtained by employing a 500 w. super high pressure mercury lamp and Toshiba Glass Filter UVD-25 at the distance of 10 cm. from the light source for one minute. The colored state thus obtained was kept stable. The colored state was eliminated by irradiating a visible light in the same manner as in Example 8.

Next, the above obtained colored state was reverted to the original state i.e. a state before the irradiation of ultraviolet ray was given, when the surface of the photosensitive matter was treated with a 10% alcohol solution.

EXAMPLE 11

Carbon tetrabromide	mg--	500
Polystyrene	gr--	2

The above given ingredients were dissolved in 10 cc. of xylene, and the obtained solution was applied to an art paper of 80 μ thick.

Thus obtained photosensitive matter was exposed to the ultra violet ray obtained by using a 500 w. ultra high pressure mercury lamp and Toshiba Glass Filter UV-DIA (trademark).

When the above obtained photosensitive matter was treated with a solution obtained by dissolving 100 mg. of 1,3,3-trimethylindolino-7'-hydroxybenzopyrylspiran in 10 cc. of ethyl alcohol, the exposed portion of the photosensitive matter was changed into yellowish red.

The colored state was eliminated when the colored photosensitive matter was irradiated with a 250 w. tungsten lamp at the distance of 50 cm. for 30 seconds.

EXAMPLE 12

(A)

Carbon tetrabromide	mg--	200
Ethanol	cc--	10

(B)

1,3,3 - trimethylindolino - 6' - nitrobenzopyryl-spiran	mg--	50
Alcohol	cc--	10
Gelatin	gr--	2
Water	cc--	10

The above given compositions A and B were respectively applied to a one-side art paper of about 80 μ thick uniformly to form the respective recording matters.

Image exposure was carried out to the recording matter comprising the composition A through a pattern for about one minute by using an ultraviolet ray obtained by using a super high pressure mercury lamp (500 w.) and Toshiba Glass Filter UVD2, and then the recording matter prepared from the composition B was wetted and closely contacted with the recording matter having the above given latent image for about five minutes. Thus, a yellow clear image was obtained.

Thereafter, the colored recording matter was exposed to a 250 w. tungsten lamp at the distance of 50 cm. for one minute, and the colored state eliminated.

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The structure of the recording matter and the process employed in the present invention are not restricted to the above given examples.

This invention includes the structure of photoreversible recording matter prepared by coating a self retaining material such as resin, glass, metal, paper, fiber, wood, porcelain, and the like with the mixture composed of a spriopyran compound, a halogen compound and a binder.

It is optional to apply directly the above given ingredients with no binder contained therein (generally a chemically inactive carrier in the form of resin) to a self-supporting material.

What is claimed is:

1. A photorecording process which comprises applying a blanket irradiation of ultraviolet radiation to a recording member composed of a spiropyran compound and a halogenated hydrocarbon compound capable of forming an acid when irradiated by an ultraviolet radiation, thereby color-forming the spiropyran compound, and then exposing the recording member thus colored to a light image having a wave length corresponding to the absorption region of the color-formed spiropyran compound to erase the color at the portion to which the light is applied thereby producing a photochromic colored image.

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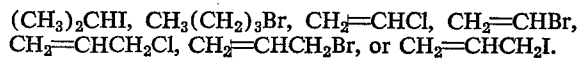
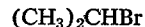
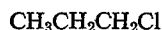
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2. A photorecording process according to claim 1 in which the halogenated hydrocarbon is CH_3Cl , CH_3Br , CH_3I , Cl_4 , CBr_3I , CCl_3I , CHCl_2I , CHBr_2I , CBr_4 , CCl_3Br , CHCl_2Br , CCl_4 , C_2Cl_6 , $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{Br}$, $\text{C}_2\text{H}_5\text{I}$,



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U.S. Cl. X.R.

96—90, 45.2