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IMAGEWISE PHOTOCHROMIC RESPONSIVE ELEMENT AND PROCESS

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U.S. Cl. 96—90 3 Claims

ABSTRACT OF THE DISCLOSURE

Imagewise photochromic response having a decay time of 2–30 minutes in the dark is obtained using certain spiropyrans activated by aromatic ketones.

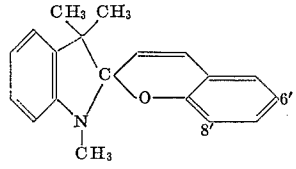
This invention relates to a process for photographic printing and to articles and compositions suitable therefor. This invention further relates to methods of eliciting photochromic response from normally photoinsensitive spiropyrans and to sheet materials having photochromic potential.

It has heretofore been known that certain nitro-substituted spiropyrans were photochromic and such compounds are set forth in detail, for example, in U.S. Patent No. 3,100,778. Such compounds are available by syntheses employing substituted intermediates, e.g. aldehydes, some of which are not very readily obtained or may be relatively expensive.

This invention seeks to provide photochromic compositions employing photoinsensitive unsubstituted or at least chromophorically unsubstituted spiropyrans. As used herein the expression chromophorically unsubstituted refers particularly to the absence of nitro-groups or other powerful electron-withdrawing groups. Such substances are also described as subphotochromic and are further characterized by being reversibly transformable into more intensely colored forms by the addition of energy. In the present invention the addition of energy is effected from an essentially uncolored excited molecule in the triplet state.

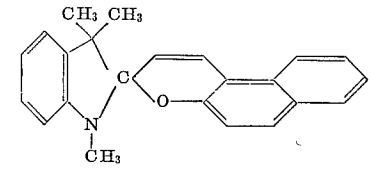
Some illustrative examples of the spiropyrans useful in this invention, with the names and abbreviations hereinafter sometimes employed for convenience, are:

I



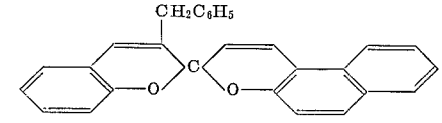
1,3,3-trimethylindolinobenzospiropyran, or, alternatively, 1,3,3-trimethylbenzoindolinopyranospirane. Abbreviated: BIPS. Numbers show the positions of possible substituents which may be halogen or methoxy.

II



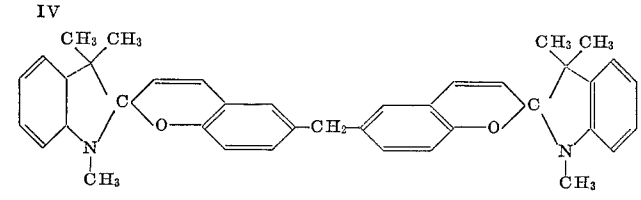
1,3,3 - trimethylindolinonaphthospiropyran, or, alternatively, 1,3,3-trimethylnaphthoindolinopyranospirane. Abbreviated: NIPS.

III



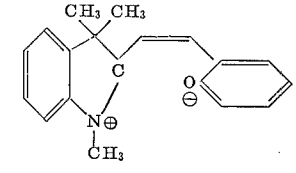
3 - benzyl benzo - β - naphthospiropyran. Abbreviated: BBNS.

IV



6',6' - methylene bis(1,3,3 - trimethylindolenobenzospiropyran).

Chromophorically unsubstituted spiropyrans of the class illustrated above are generally nearly colorless compounds in which the pyran ring is intact either as crystalline solids or as solutions in most solvents. They are not readily converted to the merocyanine form in which the pyran ring is opened by light of wavelengths near the visible range. Thus, the conversion of IPS, or one of its resonance structures, to



in which form it is intensely purple, appears not to occur using light in the near ultraviolet although Bercovici and Fisher, Journal of the American Chemical Society, vol. 86, page 5687 (1965), have recently shown that reaction occurs in certain solvents at about —100° C. when irradiated by light of 365 mμ wavelength in the presence of benzophenone as a sensitizer. At lower temperatures, as the system became rigid, the reaction became very slow.

It has now been found that certain systems which are substantially rigid are usefully photochromic at substantially ambient temperatures and that the rigidity of the systems apparently retards the thermal reversal of the reaction in the absence of actinic radiation. These systems are obtained from compositions comprising spiropyran, triplet forming sensitizer and polymeric film-forming vehicle in suitable solvent blended together and formed into

desired sheet or solid form with substantial removal of solvent. The process is carried out in the substantial absence of actinic radiation.

These compositions of the invention are conveniently considered as photochromic lacquers but are actually employed not only for applying coatings to form laminates, but may be cast as films and formed as self-sustaining films or sheets. It appears that any polymeric vehicle and solvent combination can be used which is unreactive and compatible with the other components of the composition. It is preferred, however, to employ polymeric vehicles and solvents which have no more than weak light absorption with extinction coefficients of less than about 100 in the region around 3500 to 4000 A. inasmuch as such absorptions may interfere with photochromic response. Thus, a solution of polyvinylbutyral in 1,2-dichloroethane is a generally suitable vehicle and solvent combination. Other polymers which may be employed using suitable solvents include polymethyl methacrylate and other acrylates and methacrylates, cellulose acetate, vinyl acetal polymers, polyvinyl acetate in homopolymers and in copolymers with vinyl chloride.

The term triplet-forming sensitizers includes that class of aromatic ketones which tend to be activated to the triplet state by near ultraviolet light. Such ketones normally have excitation energies of from about 50 to about 75 kilocalories per mole (see, for example, Hammond et al., J. Am. Chem. Soc. vol. 86, page 3217 et sq. (1964). Benzophenone, naphthophenone, benzyl and acetophenone are among common examples of such ketones.

Broadly speaking the triplet-forming sensitizers are selected to have characteristics of

(1) Solubility of at least 50–100 percent that of the photochrome in solid polymeric binder;
(2) A lowest excited singlet level below that of the photochrome;
(3) A lowest triplet level above that of the photochrome;
(4) Poor fluorescence and
(5) Favoring intersystem crossing.

For rapid photochromic response it is usually necessary to employ triplet-forming sensitizers in amounts of at least half the amount of spiropyrans by weight and upward. Commonly about twice the weight is adequate to provide adequate response to a flash from a 40 w.-sec. xenon lamp of only a few milliseconds duration.

The most remarkable features of the compositions herein described are the fact that the response, i.e. color change, is obtained at temperatures around normal ambient temperatures, about 10° to 40° C. and that response is obtained only after the polymeric vehicles are substantially free from solvent. In such a vehicle, response is obtained in a substantially rigid or quasi-rigid solution in which a diffusion controlled reaction is not expected. In producing phototropic coated articles of the invention, the fluid composition is spread out as a coating and then solvent is removed to give a photochromically responsive coating. For certain purposes, such as production of light responsive light screens for display windows, such a coating may be applied to clear plastic or even to glass. In this case, the entire coated area is exposed to light and uniform coloring takes place. For other purposes advantage from the invention is secured by incorporation of the ingredients in or over a photosensitive coating of quite low sensitivity which requires development as, for example, a lithographic plate. Imagewise exposure then produces a visible image which serves to provide a temporary image for proofing and also indicates that the item has been exposed thereby avoiding reexposing. Such an effect is also of considerable advantage in printing enlargements or other exposures where burning in parts or dodging is employed as proofing occurs concomitantly with exposure so that a balance of exposure is more readily achieved.

The following examples will show compositions suitable for practicing the invention.

EXAMPLE 1

A stock solution is prepared by dissolving polyvinylbutyral (M.W. about 50,000) in 1,2-dichloroethane to give a 10 percent weight per weight solution. To a 94.5 g. portion of this solution are added 0.5 g. each of benzophenone (as sensitizer) and 1,3,3-trimethylbenzo-indolinopyranospirane (abbreviated, as noted above, BIPS) and the mixture stirred until complete solution has occurred. The solution is then coated on a highly calendered paper to a thickness of about 0.1 mm. and the solvent evaporated.

All of these operations are advantageously carried out under somewhat subdued light or at least light essentially devoid of radiation below about 3700 A. Naturally if the coating solution also contains photosensitive materials, e.g. silver halides, which may be sensitive over the visible range, further precautions will be necessary.

A portion of the coated paper is cut and used for printing a normal photographic negative using a xenon flashlamp which emits a burst of light at 40 w.-sec. for about 0.001 second. A sharp reddish blue image is produced which gradually fades during about 2 minutes in the dark at normal temperatures. Exposure can be repeated many times before total photochromic response is lost. Exposure under like conditions of a simalar sheet which contains no benzophenone gives no response.

Similar sheets having 10 percent (0.05 g.) of benzophenone of added given substantially no photochromic response. When about 0.25 g. of benzophenone is employed, e.g. 50 percent, a weaker image is obtained than with 0.5 g. Also, when higher amounts are employed the depth of color attained from a given exposure is enhanced, in general, up to about 300 percent, i.e. 1.5 g. of benzophenone in the above composition.

EXAMPLE 2

Solutions of 0.25 g. of BIPS and 0.5 g. of naphthophenone are prepared using the polyvinylbutyral stock solution of Example 1 and additional, 1,2-dichloroethane:

Solution	Stock solution (g.)	Dichloroethane (g.)	Viscosity of solution (centipoises)
A	42.5		850
B	34.0	8.5	345
C	25.5	17.0	ca. 100

These solutions, without evaporation of solvent, are exposed between quartz plates 0.1 mm. apart to the flash of light used in Example 1. Only solution A gives a very weak and fugitive color which disappears almost instantly.

Another solution is prepared using 10 percent by weight of polyvinyl formal of M.W. about 34,000 in 1,2-dichloroethane as a base solution and dissolving 0.5 g. of BIPS and 1.0 g. of naphthophenone in 85 g. of the solution to give a very thick solution having a viscosity of about 2000 centipoises. A 0.1 mm. film of the unevaporated solution is exposed to light as above and gives no detectible image. The solution is coated to a thickness of 0.1 mm. on a paper backing to give a photochromic imaging medium as in Example 1 and the solvent evaporated. The resultant, essentially solvent-free film is exposed to ultraviolet light through a negative as in Example 1 and a sharp blue image is obtained. The image persists for about 5 minutes in the dark.

EXAMPLE 3

A number of solutions of different binders are used in preparing photochromic imaging media by coating on paper which, after drying are exposed as in Example 2 for about 0.001 second.

(a) An 11.6 percent solution of the copolymer of 88 percent vinyl chloride and 12 percent vinyl acetate in dichloroethane is used as the vehicle by dissolving 0.5 g.

of BIPS and 0.1 g. of naphthophenone in 85 g. of the solution. Image persistence is about 2 minutes.

(b) The preparation is repeated employing 85 g. of a 10 percent solution of cellulose acetate in methyl ethyl ketone, 0.5 g. of BIPS and 1.0 g. of 4,4'-dimethyl benzophenone as sensitizer. Image persistence is about 20 minutes, the image is dark blue.

(c) Part (b) above is repeated using 42.5 g. of a 20 percent solution of polyvinyl acetate in methyl ethyl ketone for the same amounts of BIPS and of the same sensitizer. Image persistence is about 10 minutes.

(d) A 25 percent solution of polymethyl methacrylate in methyl ethyl ketone is employed as above, dissolving 0.5 g. of BIPS and 1.0 g. of 4,4'-dimethoxybenzophenone in 34 g. of the solution and coating paper as above. Image persistence after exposure as above is 14 minutes.

(e) The procedure of part (d) is repeated except that benzophenone is employed as sensitizer and the binder is a 25 percent solution of polystyrene in toluene. Sensitization is appreciably less pronounced. The medium blue image fades after about 3 minutes.

EXAMPLES 4–16

A series of photochromic imaging sheets are prepared using various sensitizers in the proportion of 1.0 g. sensitizer, 0.5 g. BIPS in 85 g. of 10 percent solution of polyvinylbutyral in dichloroethane. The compounds, where available the excitation energies and the image persistence observed are tabulated herebelow.

Example No.	Sensitizer	Excitation energy (Kcal./mole)	Image persistence (min.)
4	1,3,5-triacetylbenzene	74.0	4
5	Thioxanthone	65.2	----------
6	2,4-dimethylbenzophenone.	----------	12
7	4-phenyl benzophenone	60.6	ca.25
8	Benzophenone	68.0	10
9	4-chlorobenzophenone	----------	7
10	4,4'-dimethoxybenzophenone.	----------	18
11	4,4'-bis(dimethylamino) benzophenone.	61.0	30
12	1-indianone	----------	4
13	9-xanthenone	74.5	17
14	2-acenaphthone	59.0	20
15	9-fluorenone	52.5	3½
16	Duroquinone	51.0	1

EXAMPLES 17–21

A series of photochromic imaging coated papers are made as above using a solution of 85 g. of the above 10 percent polyvinyl butyral solution, 0.5 g. 3-benzyl benzo-β-naphthospiropyran (BBNS) and either 0.5 or 1.0 g. of sensitizers as shown in the following table.

Example	Sensitizer	Image persistence (min.)
17	0.5 g. benzophenone	20
18	0.5 g. thioxanthone	30
19	1.0 g. 4, 4'-dimethoxybenzophenone	ca. 20
20	1.0 g. 4-benzoylbisphenyl	30
21	1.0 g. naphthophenone	30

EXAMPLE 22

Another series of imaging papers is made using chromogenically unsubstituted spiropyrans, i.e. BIPS having single chlorine or bromine substituents in the 6' position or a methoxy substituent in the 8' position and using β-acetonaphthone, β-benzonaphthone or benzophenone as sensitizer at 200 percent by weight of the spirane. In each case good blue images are obtained which fade over about 10 to 20 minutes.

EXAMPLE 23

To 67 g. of a coating composition suitable for lithographic plates as described in U.S. Patent 3,136,637 are added 0.5 g. BIPS and 1.0 g. β-naphthophenone dissolved in 181.5 g. of 1,2-dichloroethane. The solution is coated to a thickness of below 0.001 inch and dried in the dark. Exposure to ultraviolet light through a negative gives a photochoromic proofing image which fades after a few minutes. Development of the plate proceeds normally and printing also is unaffected by the photochromic residues present. Similar results are obtained using other materials and sensitizers as described in the above examples.

EXAMPLE 24

A melamine-sulfonamide-formaldehyde resin as described in US. Patent 2,809,954 is employed as vehicle by dissolving 104 grams in 120 grams of methyl ethyl ketone. To 20 g. of the solution are added 0.5 g. of BIPS and 1.0 g. β-naphthophenone and the rather thin solution is coated on paper as above to about 0.002 inch thickness and dried in the dark to a light yellow coating. Exposure to a flash through a negative as before gives a blue-black image.

A somewhat more viscous coating solution is prepared by concentrating 160 g. of the above solution of polymer to 123 grams and then using 15 grams of the resulting solution in which to dissolve 0.5 gram of 6'-bromo-BIPS and 1.0 gram of naphthophenone. This solution is coated similarly on paper and dried. The resultant paper provides an excellent blue image when exposed as above.

What is claimed is:

1. A composition adapted to the deposition of a substantially solid flexible phototropic coating on a solid substrate comprising, in combination,

(A) a solution of polymeric film-forming binder vehicle in solvent therefor,

(B) at least one aromatic ketone excitable to the triplet state in the range over which phototropic response is desired and then becoming an energy donor, and

(C) at least one subphotochromic compound of the class of

1,3,3-trimethylindolinobenzospiroxyran,
1,3,3-trimethylindolinonaphthospiropyran,
3-benzyl benzo-β-naphthospiropyran or
6',6'-methylene bis(1,3,3,-trimethylindolenobenzospiropyran,

transformable by the addition of energy to a more highly colored form.

2. A photochromic imaging medium comprising the combination of a self-supporting backing and the essentially solvent free residue of a composition according to claim **1.**

3. The process for photographic imaging comprising the step of exposing a substantially solid polymeric binder comprising a subphotochromic compound and sensitizer therefor in combination according to claim **2** to actinic radiation in predetermined areas.

References Cited

UNITED STATES PATENTS

3,212,898 10/1965 Cerreta.
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C. & E. News, June 3, 1963, p. 53.

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U.S. Cl. X.R.

350—160; 252—300

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,486,899 Dated December 30, 1969

Inventor(s) Harvey A. Brown

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

Column 2, line 40, "IPS" should read --BIPS--. Column 3, line 29, "benzyl" should read --benzil--. Column 5, Example No. 5, under heading Excitation... "65.2" should read --65.5--; Example No. 12, under heading Sensitizer "1-indianone" should read --1-indanone--.

SIGNED AND
SEALED
JUN 9 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents