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3,100,703

PHOTOGRAPHIC PROCESS UTILIZING
CYANINE DYE BASES

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This invention relates to a photographic process capable of producing colored photographic prints. The process is suitable for producing prints of a specific single color as well as full-color photographic prints involving suitable utilization of the primary colors of the visible spectrum. A further aspect of the invention is the availability of a photosystem suitable for the production of photoresists, lithographic printing surfaces, and the like.

In copending applications filed by Eugene Wainer including the following:

Serial No. 787,112, filed January 16, 1959, and issued July 3, 1962, as U.S. Patent 3,042,515

Serial No. 841,459, filed September 22, 1959

Serial No. 841,460, filed September 22, 1959, and issued July 3, 1962, as U.S. Patent 3,042,516

Serial No. 842,569, filed September 28, 1959, and issued July 3, 1962 as U.S. Patent 3,042,517

Serial No. 1,161, filed January 8, 1960, and issued July 3, 1962, as U.S. Patent 3,042,518

Serial No. 1,162, filed January 8, 1960, and issued July 3, 1962, as U.S. Patent 3,042,519

Serial No. 22,703, filed April 18, 1960, and issued October 2, 1962, as U.S. Patent 3,056,673, and

Serial No. 23,130, filed April 19, 1960, and issued July 24, 1962, as U.S. Patent 3,046,125

a variety of photosystems are described, utilizing in the main combinations of various aromatic amines, organic compounds containing halogens, and plastic bases suitably disposed on an applicable substrate. In said copending applications, exposure to light alone or, variously, exposure to light followed by heat treatment is sufficient to produce colored print-out image at high speeds from an originally substantially colorless product. The assumption was made that the mechanism of operation of the photochemical reaction in these photosystems involved the formation of free radicals, based on the photolytic dissociation of the organic halogen compound as the result of light absorption by such organic halogen compounds. As a consequence, the spectral sensitivity of such previously described reactions was assumed to be dependent upon the spectral range in which this organic halogen compound would adsorb light and break up into free radicals.

In our co-pending application Serial No. 42,233 (filed July 12, 1960), issued June 25, 1963, as United States Patent 3,095,303, we described the use of styryl dye bases and higher vinylene homologs thereof in combination with certain classes of organic halogen compounds to provide a photosensitive composition which was sensitive to visible light.

We have now found that cyanine dye bases may likewise be used in combination with similar organic halogen compounds to provide a photosensitive composition sensitive to visible light. Furthermore, many of the cyanine dye bases have the advantage of imparting higher photographic speed to the photosensitive mixture, particularly in the red end of the spectrum. The greater variety of structures available in the cyanine dye base series enables selection of compounds with high sensitivity in particular narrow areas of the visible spectrum, which is of great importance in color photographic applications.

Specifically, we have found that a family of weakly

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colored dyes or dye progenitors, belonging to the class of cyanine dye bases, are capable of producing intense colors of high brilliance with narrow spectral ranges of absorption when utilized as a photosystem in combination with suitable organic halogen-containing compounds. The variety of the colored cyanine-base type compounds is sufficiently broad to blanket the visible range with respect to their light-absorption qualities and also with respect to the nature of the color which can be produced as the result of exposure to light when utilized in combination with suitable organic halogen compounds. More important, however, as distinguished from the photosystems of the aforementioned Wainer applications, is the fact that through use of such dye bases a full range of sensitivity to the visible is available. In view of the broad variety of dye bases available from the class indicated, it is thus possible in the present photosystem to expose a blue-sensitive variety to blue light to yield an intense yellow color, a green-sensitive variety to green light to produce a magenta color, a red-sensitive variety to red light to produce a cyan color, etc. The color of the developed image is thus complementary to the color of the exposing light, which is a necessary characteristic of a color negative material. The sharp cutting absorption, both of the progenitor and the color form produced as the result of exposure to light, is such that increments of absorption throughout the visible may be produced as desired for specialized effects.

While we do not wish to be bound to any specific theory as to the reason for the ability to blanket the visible with respect to sensitivity and development of color, it appears that, either as a result of exposure to light or possibly simply as the result of mixture of the organic halogen-containing compound and the weakly colored dye, a complex is formed which requires less energy to raise it to an excited state to permit the desired photolytic reaction to take place than when such complexes do not form.

It has been pointed out that the dye progenitor is weakly colored and, as a result of exposure to light in the presence of the organic halogen compound, a brilliant, intense, sharp cutting color is obtained. Equally important as the foregoing is our finding that, as a result of exposure to light with or without subsequent development by heat, a sharp difference in solubility in certain solvents exists between unexposed and exposed areas. This finding is of exceptional importance in order to eliminate any residual color which may exist from the progenitor itself and which might mask the desired print-out effects. More important than the elimination of such color-masking effects is the fact that such differences in solubility may be utilized for fixing and stabilization of the printed image. Equally important is our finding that, as a result of such solvent extraction, hydrophilic-hydrophobic differentiation is available, depending on whether or not the areas have been exposed to light. Thus, it appears that the developed-out dye image is ionic in character, exhibits hydrophilic properties, and tends to be insoluble in non-polar solvents; whereas the unexposed dye progenitor, even in the presence of the organic halogen-containing compound, is a covalent non-ionic compound, soluble in a variety of organic solvents, and tends to be hydrophobic in character. Such hydrophobic properties may be enhanced by placing the photosystem in a hydrophobic base. As a consequence, the system can be utilized as a foundation of photoetch purposes and as a means for producing a lithographic plate.

Solvents which may be utilized for the above described fixing and developing include ethers, esters, chlorinated solvents, benzene, toluene, and the like. A differentiation is obtained even with water-compatible solvents such as acetone.

In general terms, therefore, our novel photosensitive system is utilized in a variety of ways. If it is desired to produce a single color of permanent nature as a result of a print-out reaction in the visible, a weakly colored cyanine dye base is chosen having absorption characteristics compatible with the source of light available in the visible. By virtue of its inherent color, the choice is simplified. This is combined with a suitable organic halogen-containing compound and placed on a suitable substrate. After exposure to light, a print-out image of intense brilliance is obtained, the unexposed portions remaining the original color. The development of color may be enhanced by a brief heating for between 1 and 10 seconds at approximately 85–100° C. and preferably about 100° C. prior to solvent fixing. The developed print is then treated with a solvent, such as ether or benzene, which removes the undecomposed dye base, leaving only the developed image fixed to the substrate.

By utilizing multipacks, with an appropriate selection of color formers and exposure to the full spectral range of visible light, full-color prints may be obtained. Thus when utilizing multipacks, exposure of the film to a colored subject produces a negative image in colors complementary to the exposing light. After removal of the unexposed light-sensitive material by solvent extraction, a contact print through the negative on a second sheet of the same sensitive film results in a positive image in the same colors as the original exposure. Removal of unexposed light-sensitive material by solvent extraction of the positive print gives a stable product.

Similarly, our color-sensitive material may be used to make positive prints from commercially available color-negative materials, either by contact printing or by projection printing with an enlarger.

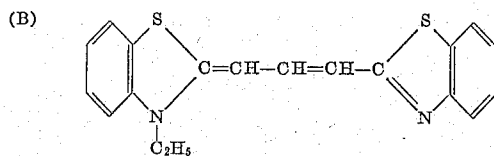
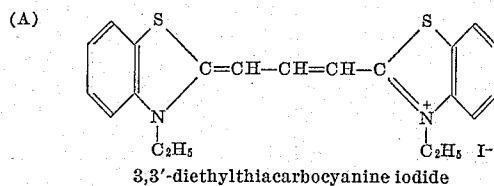
Full color prints may also be obtained by printing registered dot patterns of the combination of cyanine base and suitable organic halogen compounds on a white or transparent backing. By utilizing known printing techniques of high resolution, the various color progenitors may be placed sufficiently close to each other so that, as a result of exposure and fixing, a full color rendition is obtained. Conversely, color separation negatives may be obtained by standard techniques utilizing simultaneous exposures in one-shot three-color cameras available commercially.

The invention may be utilized as a foundation for a lithographic plate by minor modifications of the foregoing procedure.

The process may be modified by placing the photosensitive system on a hydrophilic substrate, such as paper, and then washing out the developed dye image with water so as to expose the paper backing in these areas. In this case, the unexposed, undecomposed system is hydrophobic and the exposed portions are hydrophilic, even though no developed dye color remains in the hydrophilic areas. Washing out the developed image with water in this way does not remove either the unexposed cyanine dye base or the unreacted organic halogen compound or the complex which may have formed by combination of the two. It is therefore possible, after drying the washed sheet, to re-expose with a blanket exposure to light and cause development of the remaining light-sensitive material, giving a positive image which requires no fixing. Our new process is thus applicable to direct positive photocopy, capable of copying colored as well as black-and-white materials.

Thus, in general, the photosensitive systems of this invention comprise a light-sensitive coating composed of a mixture of a cyanine dye base with a halogen-containing source of photolytically producible free radicals, either coated on a substrate or suitably dispersed in a solution of a binder such as nitrocellulose, polystyrene, ethyl cellulose, polyvinyl chloride, Saran, or the like, and subsequently coated on a substrate either as an adherent coating or as a non-adhering or strippable self-sustaining film.

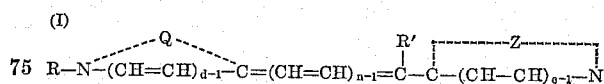
The cyanine dye bases useful for the purposes of our invention are of several types, including those used commercially as "supersensitizers" in conventional silver halide photography. Although not themselves strong sensitizers, such bases impart increased sensitizing action to cyanine dyes when such combinations are employed in silver halide emulsions. In general cyanine dye bases are known corresponding to all the different classes of cyanine dyes, including symmetrical and unsymmetrical monomethine cyanines, carbocyanines, dicarbocyanines, tricarbocyanines, hemicyanines, pyrrolocyanines and azacyanines. The cyanine dye bases may be regarded as de-quaternized cyanine dyes, as illustrated below for diethylthiacarbocyanin iodide (A) and the base (B) derived from it.



Alternatively, cyanine dye bases are derived from heterocyclic bases by a wide variety of reactions well-known to those skilled in the art. Typical heterocyclic bases useful in such reactions are the following:

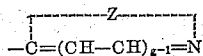
2-methylbenzothiazole
2-methylbenzoxazole
2-methylbenzimidazole
2-methylthiazoline
Quinaldine
Lepidine
1-methylisoquinoline
2-methyl- α -naphthothiazole
2-methyl- β -naphthothiazole
Alpha-picoline
Gamma-picoline
3-methylisoquinoline
2,4-dimethylthiazole
2-methyl-4-phenylthiazole
2-methylthiazole
2,3,3-trimethylindolenine
2,4-dimethylselenazole
2-methylbenzoselenazole
2,4-dimethyloxazole
2-methyl- α -naphthoxazole
2-methyl- β -naphthoxazole
2-methyl-4,5,6,7-tetrahydrobenzothiazole
2-methyl-4,5,6,7-tetrahydrobenzoxazole
2-methyl-5,6,7,8-tetrahydro-4-cycloheptathiazole
2-methyl-5,6-dihydro-4-cyclopentathiazole
2-methyl-6,7-dihydro-4-H-pyrano(4,3D)thiazole
2-methyl-6,7-dihydro-4-H-thiopyrano(4,3D)thiazole
2-methyl-5,6-dihydro-4-H-pyrano(3,2D)thiazole
2-cyanomethylquinoline
2-cyanomethylbenzothiazole
4-cyanomethylquinoline
2-cyanomethylbenzimidazole
2-cyanomethylpyridine
4-cyanomethylpyridine

Cyanine bases useful in our novel photo process are characterized by the following general formulas:



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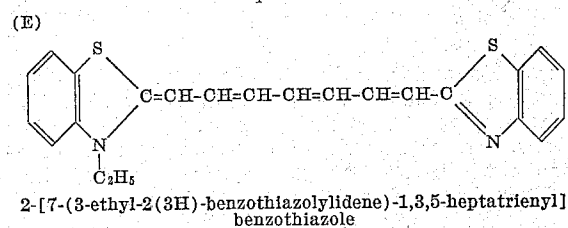
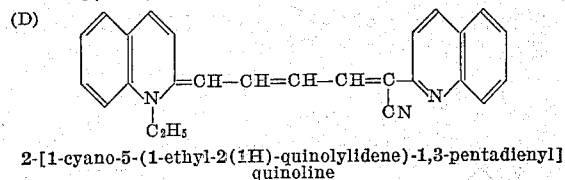
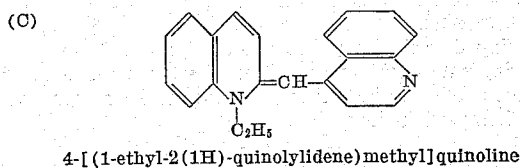
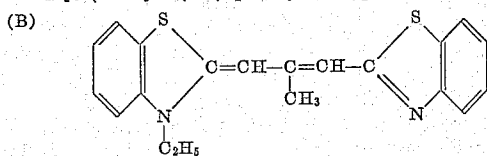
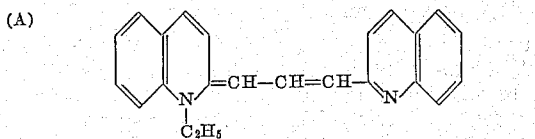
wherein d and e each represents a positive integer of from 1 to 2; n represents a positive integer of from 1 to 4; R represents an organic radical selected from the group consisting of alkyl, aralkyl and aryl groups; R' represents a member selected from the group consisting of hydrogen, $-\text{CN}$ and a radical characterized by the general formula,



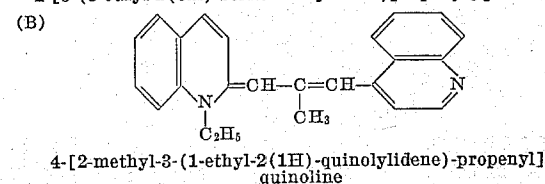
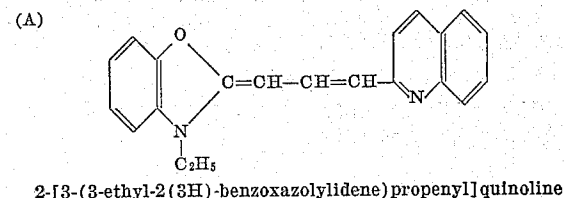
g is a positive integer of from 1 to 2 and Q , Z , and Z' each represents the non-metallic atoms (C, S, Se, O and N) necessary to complete a heterocyclic organic nucleus containing from 5 to 6 atoms in the ring.

Cyanine dye bases characterized by the above general formula may be symmetrical or unsymmetrical, of varying chain lengths; and they may have substituents on the rings or on the chain. Examples of several types are depicted below.

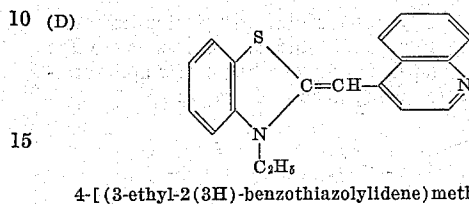
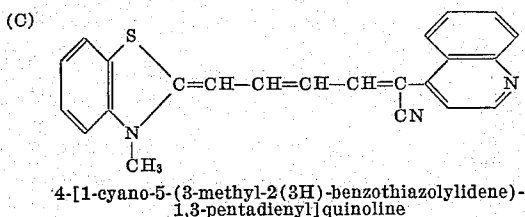
(1) Symmetrical compounds:



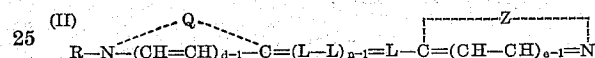
(2) Unsymmetrical bases:



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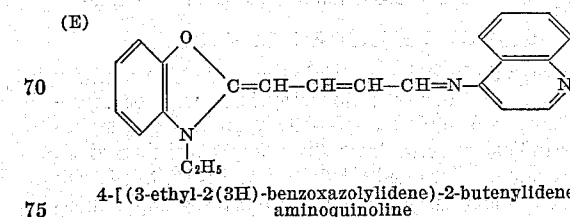
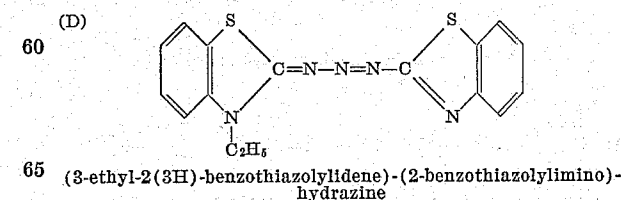
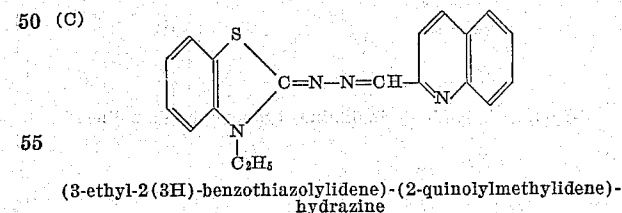
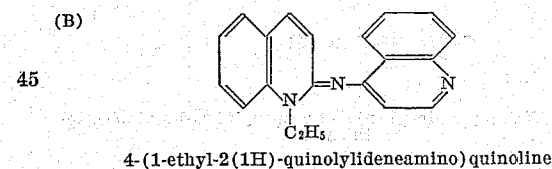
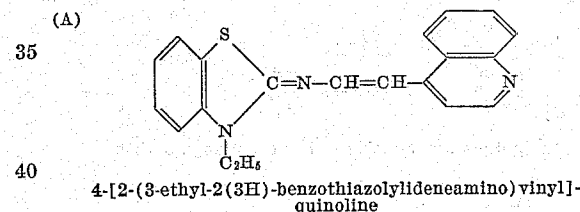


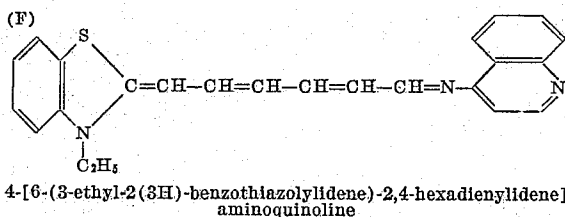
Azacyanine bases useful in our photoprocess may be regarded as related to the cyanine dye bases by replacement by nitrogen of one or more methine groups in the chain joining the two heterocyclic nuclei. They may be characterized by the following general formula:



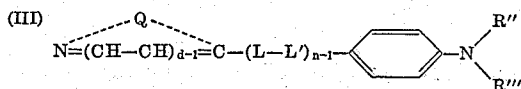
wherein d , e , n , R , Q and Z each has the same meaning as in general Formula I above, and each L represents a member selected from the group consisting of CH and N and may be the same or different, at least one L being a nitrogen atom.

Typical azacyanine bases are listed below:





A further class of bases useful in our photoprocess are those containing nitrogen in the chain, related to the styryl dye bases and their vinylenes homologs, and corresponding to the following general formula:

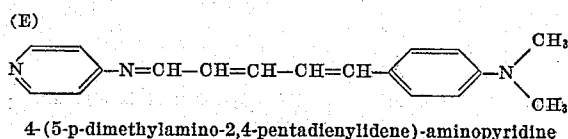
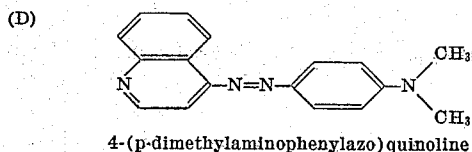
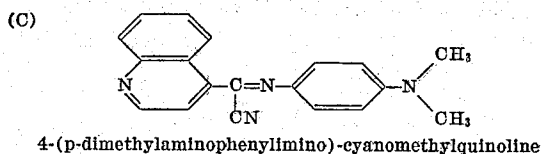
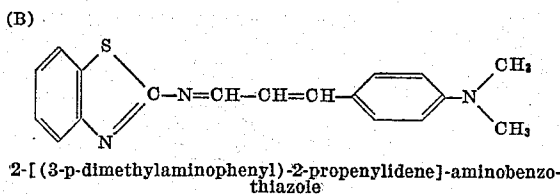
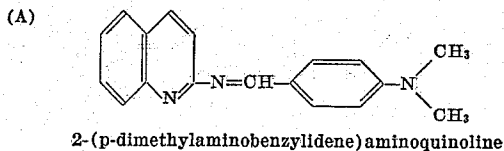


wherein R'' and R''' represent alkyl or benzyl and may be the same or different from one another, d represents either 1 or 2, n represents a positive integer from 1 to 4, L and L' each represents a member selected from the group consisting of $-\text{CH}=\text{}$,



and $-\text{N}=\text{}$ and may be the same or different, at least one L or L' being a nitrogen atom, and Q represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the ring.

Bases typical of this class include the following:



ORGANIC HALOGEN COMPOUND

The organic halogen-containing compounds useful for the purposes of our invention may in general be represented by the formula, $\text{R}-\text{C}-\text{X}_3$, wherein R is a monovalent radical selected from the group consisting of H , Cl , Br , alkyl, substituted alkyl, aryl and substituted aryl; and each X is a halogen selected from the group consist-

ing of Cl , Br and I . Organic compounds we have found useful include:

Carbon tetrabromide	Hexachloroethane
Carbon tetrachloride	Hexabromoethane
Chloroform	Benzotrichloride
Bromoform	Benzothibromide
Pentabromoethane	p-Nitrobenzotribromide

It is preferred that the combination of cyanine dye base and organic halogen-containing compound be dispersed in a film-forming binder such as any of those disclosed in the aforementioned Wainer applications.

Suitable film-forming binder solutions include the following:

- 15 Ethyl cellulose in methyl alcohol
- Nitrocellulose in methyl alcohol or acetone
- Polystyrene in benzene
- Polyvinyl chloride in tetrahydrofuran
- Polyvinylidene copolymer in methyl ethyl ketone
- 20 Cellulose acetate in acetone
- Polyvinyl acetate in toluene plus acetone

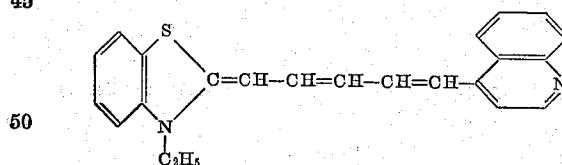
In addition, conventional plasticizers may be incorporated into the above solutions or, if desired, hydrocarbons may be added as a diluent in the composition. Suitable hydrocarbon diluents, which appear to play no part in the photochemical reaction, include paraffin- and isoparaffin-hydrocarbons, having the general formula, $\text{C}_n\text{H}_{2n+2}$, wherein n ranges from about 10 up to 70. When added to the system, it is preferred that they be added in solution.

In the compositions of the present invention it is preferred to provide about 10 to 100 parts by weight of the organic halogen-containing compound for each part by weight of cyanine dye base, dispersed or dissolved in about 200 parts by weight of a 10% solution of a film-forming plastic.

Having described our invention in general terms, the following examples are indicative of specific methods of practice and are to be construed as illustrative rather than as limitative of the invention.

Example 1

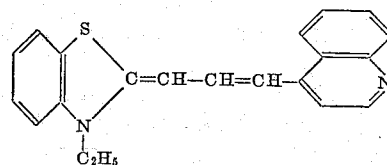
Fifty milligrams of 4-[5-(3-ethyl-2(3H)-benzothiazolylidene)-1,3-pentadienyl]quinoline



were added to 16 cc. of a 1% solution of ethyl cellulose in toluene containing 2.8 g. of carbon tetrabromide. The mixture was coated on clear transparent cellulose acetate sheets. The coating was salmon color. One-second exposure to a sunlamp through a negative gave an excellent print-out image of good density. The image was blue in color. Fixing was accomplished by extracting the unreacted starting material with a brief wash in a solvent system consisting of three parts of ethyl acetate in seventeen parts toluene (3:17).

Example 2

Fifty milligrams of 4-[3-(3-ethyl-2(3H)-benzothiazolylidene)-propenyl]quinoline

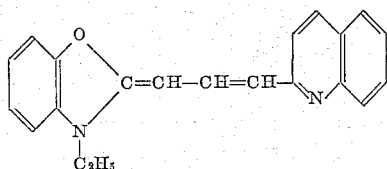


and 2.8 grams of carbon tetrabromide were dissolved in 10 cc. of acetone and 6 cc. ethyl acetate, then coated on

clear transparent cellulose acetate film. Two-seconds exposure through a negative to a sunlamp or a photoflood lamp gave an excellent print-out image. The image color was blue. Fixing was achieved with the technique described in Example 1. When this mixture was coated on white opaque cellulose acetate and exposed on a Bausch and Lomb 250-millimeter grating monochromator, the time required to give a reflection density of 1.0 was recorded. This mix showed 1.0 density in the time range of twenty to ninety seconds over the spectral range of 3900 A. and 6300 A. Peak sensitivity was noted at 4700 A., requiring only twenty seconds to given density 1.0.

Example 3

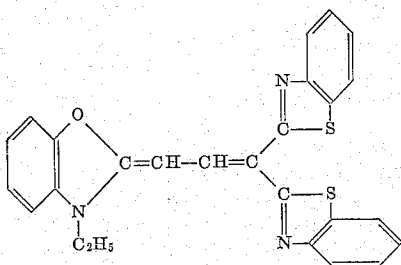
Twenty-five milligrams of 2-[3-(3-ethyl-2(3H)-benzoxazolydene)propenyl]quinoline



were dissolved in 16 cc. of a 1% solution of ethyl cellulose in toluene and containing 1.4 g. of carbon tetrabromide. The mixture was coated on white opaque polyvinyl chloride sheets. The color of the coating was pink. A two-second exposure through a negative to a sunlamp gave excellent print-out images. When a microfilm negative was projected onto the coating, using a standard 35-millimeter slide projector with a 500-watt lamp and a distance sufficient to give a ten-diameter projection, an excellent print-out rendition of the negative was observed with a thirty-second exposure. Fixing was accomplished in the manner described in Example 1.

Example 4

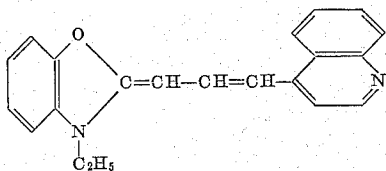
Fifty milligrams of (3-ethyl-2(3H)-benzoxazolydene)-ethylidene-di-2-benzothiazolymethane



were dissolved in a solution of 8 cc. tetrahydrofuran and 8 cc. acetone with 2.8 g. carbon tetrabromide. This mixture was coated on clear transparent cellulose acetate sheets and exposed through a negative to the ultraviolet irradiation of a General Electric sunlamp. Excellent print-out images were observed with five-second exposures. The color of the image was red. Fixing was achieved in the manner described in Example 1.

Example 5

Twelve and one-half milligrams of 4-[(3-ethyl-2(3H)-benzoxazolydene)propenyl]quinoline

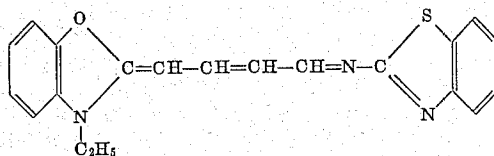


were dissolved in 8 cc. acetone containing 1.4 g. carbon tetrabromide, then coated on clear transparent cellulose acetate sheets. When exposed through a negative to a sunlamp for two seconds, these coatings gave direct print-out images of good density. The color of the image was

violet. Fixing was performed in the manner described in Example 1.

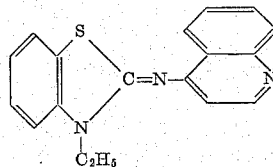
Example 6

Fifty milligrams of 2-[4-(3-ethyl-2(3H)-benzoxazolydene)-2-butenylidene]-aminobenzothiazole



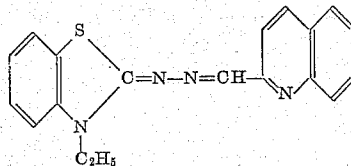
were dissolved in 16 cc. of a 1% solution of ethylcellulose in toluene, containing 3.7 grams of pentabromoethane and 1 cc. of methanol. The yellow mixture was coated on a polyvinyl chloride sheet. A fifteen-second exposure through a negative to the light from a photoflood lamp gave an excellent print-out image. The image color was brown. Fixing was accomplished by extracting the unreacted starting materials with a toluene wash.

In a similar fashion, photosensitive coatings may be prepared, utilizing the following azacyanine dye bases:



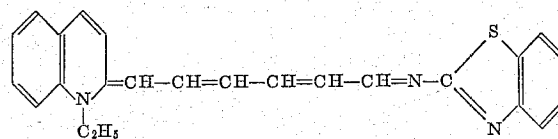
4-(3-ethyl-2(3H)-benzothiazolylidene)-aminoquinoline

The color of the image formed by exposure to light is yellow.



(3-ethyl-2(3H)-benzothiazolylidene)-(2-quinolylmethylidene)-hydrazine

The color of the image formed by exposure to light is reddish orange.



2-[6-(1-ethyl-2(1H)-quinolylidene)-2,4-hexadienylidene]-aminobenzothiazole

The color of the image formed by exposure to light is reddish orange.

Example 7

To 5 cc. of a 1% solution of the cyanine dye base, 2-[(3-ethyl-2(3H)-benzoxazolydene)-propenyl]-quinoline, in acetone was added 0.5 gram of carbon tetrabromide. This mixture was coated on a multilith master and exposed under a negative to two General Electric 275-watt sunlamps for one minute. An excellent image printed out. After swabbing the print with water, the master was mounted in the duplicating machine and the machine run in the usual manner. The water-swabbed master picked up ink on the image area and transferred it to the receiving sheet with little or no ink in the background.

Example 8

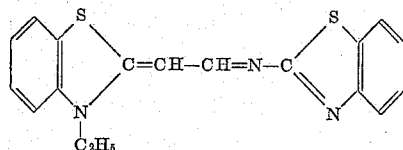
A solution of 50 mg. of the cyanine dye base, 2-[(3-ethyl-2(3H)-benzoxazolydene)-propenyl]-quinoline, 2.8 g. of CBr_4 and 100 mg. of eicosane in 15 ml. of acetone was coated on a casein-surfaced paper sheet. This was exposed under a positive transparency to a pho-

to flood lamp, giving a negative photocopy. The sheet was swabbed with a weakly acid buffer solution which washed away the negative image, leaving the weakly colored cyanine dye base unchanged in the unexposed area. Reexposure to the photoflood lamp resulted in darkening of the previously unexposed area, giving a positive copy of the original transparency.

While not necessary for the purposes of our invention, the permanence and brilliance of the color images produced may be enhanced by the formation of lakes through treatment with metal salt solutions such as salts of copper, chromium, cobalt, phosphotungstic acid, phosphomolybdic acid, aluminum, and the like.

Example 9

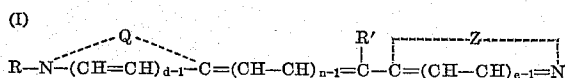
Fifty milligrams of 2-[(3-ethyl-2(3H)-benzothiazolyldene)-ethylidene]-aminobenzothiazole



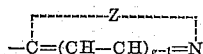
were dissolved in 16 cc. of a 1% solution of ethyl cellulose in toluene, containing 2.8 grams of carbon tetrabromide and 1 cc. of methanol. The light-yellow mixture was coated on a polyvinyl chloride sheet. A twenty-second exposure through a negative to the ultraviolet of a sunlamp, or a thirty-second exposure to a photoflood lamp, gave excellent print-out images. The image color was brown. Fixing was achieved by extracting the unreacted starting materials with a toluene wash.

Having now described our invention in accordance with the patent statutes, we claim:

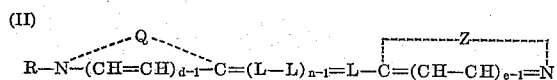
1. A non-silver photosensitive composition which prints out a visible image directly and solely as a result of exposure to suitable radiation, said composition consisting essentially of: a photolytically active organic halogen containing compound selected from the group consisting of alkyl and aralkyl compounds in which at least three halogen atoms are attached to a single carbon atom, said halogens being selected from the group consisting of Cl, Br, and I; and a cyanine dye base selected from the group represented by general Formulas I, II, and III below,



wherein d and e each represents a positive integer of from 1 to 2; n represents a positive integer of from 1 to 4; R represents an organic radical selected from the group consisting of alkyl, aralkyl and aryl groups; R' represents a member selected from the group consisting of hydrogen, $-CN$ and a radical characterized by the general formula,

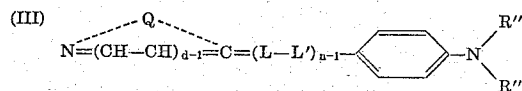


and g is a positive integer from 1 to 2, Q , Z and Z' each represents the nonmetallic atoms selected from the group consisting of C, S, Se, O and N necessary to complete a heterocyclic organic nucleus containing from 5 to 6 atoms in the ring;



wherein d , e , n , R , R' , Q and Z each has the same meaning as in general Formula I above, and each L represents a member selected from the group consisting of CH and

N and may be the same or different, at least one L being a nitrogen atom;



wherein R'' and R''' represent alkyl or benzyl and may be the same or different from one another, d represents either 1 or 2, n represents a positive integer from 1 to 4, L and L' each represents a member selected from the group consisting of $-CH=$,



and $-N=$ and at least one of L and L' being a nitrogen atom, and Q represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the ring said halogen containing compound being present in an amount sufficient to sensitize said dye base.

2. The composition of claim 1 dispersed in a film-forming plastic.

3. The composition of claim 2 as a self-supporting film.

4. An article consisting of the composition of claim 2 coated on a solid substrate.

5. The composition of claim 1 wherein the organic halogen-containing compound CBR_4 .

6. The composition of claim 1 wherein the proportion of the organic halogen-containing compound relative to the cyanine dye base is between about 10 and 100 parts by weight of organic halogen-containing compound.

7. The composition of claim 1 wherein the cyanine dye base is 4-[5-(3-ethyl-2(3H)-benzothiazolyldene)-1,3-pentadienyl]quinoline.

8. A multilayer pack for producing colored photographic prints which comprises a plurality of layers each of which comprises a composition according to claim 1, each of said layer compositions being sensitive to light of a wave-length different from the wave-length to which any other of said compositions is sensitive; said layers being on a solid supporting surface.

9. A process for producing colored photographic prints which comprises preparing at least one composition according to claim 1; coating a solid supporting surface therewith, exposing the resulting article to a colored subject, thereby producing a negative image in color complementary to said colored subject.

10. The process of claim 9 wherein the image is intensified by heating for between 1 and 10 seconds after exposure.

11. The process of claim 9 wherein the developed print is treated with a solvent to wash away the undecomposed dye base.

12. A process for producing a positive image where a negative produced by the process of claim 9 is printed onto another sheet of the same material.

13. The process of claim 9 wherein the permanence and brilliance of the color image produced is enhanced by treating the image with a metal salt solution to form a lake.

14. The process of claim 9 wherein the substrate is paper and after the colored image is produced, washing the developed image with water, drying the washed sheet, re-exposing the same with a blanket exposure, thereby producing a positive image of the subject.

15. A process for producing a litho master, comprising preparing the composition of claim 1; coating a casein-filled paper therewith; exposing the composition to light through a suitable negative, thereby producing a positive image in color; swabbing the exposed sheet with water to render the background ink-repellent, the image area then being ink-receptive.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

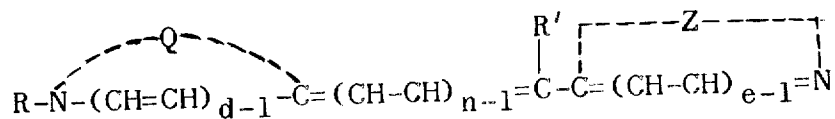
Patent No. 3,100,703

August 13, 1963

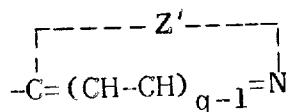
Robert H. Sprague et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

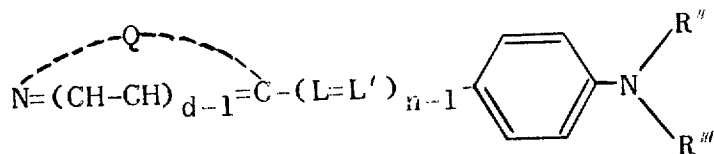
Column 4, line 14, for "diethylthiacarbocyanin" read -- diethylthiacarbocyanine --; lines 74 and 75, the formula should appear as shown below instead of as in the patent:



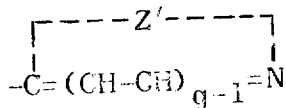
column 5, lines 8 and 9, the formula should appear as shown below instead of as in the patent:



column 7, lines 15 to 18, the formula should appear as shown below instead of as in the patent:

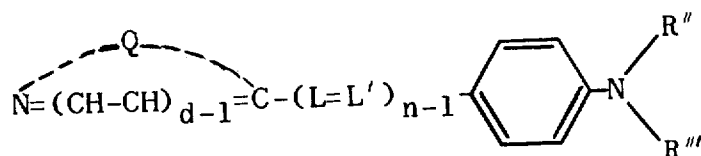


column 11, line 43, for "aralykyl" read -- aralkyl --; lines 60 and 61, the formula should appear as shown below instead of as in the patent:



3,100,703

same column 11, line 73, strike out "R'"; column 12, lines 3 to 6, the formula should appear as shown below instead of as in the patent:



same column 12, line 19, after "ring" insert a comma.

Signed and sealed this 12th day of May 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents