

# United States Patent Office

3,397,981

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3,397,981

# PHOTOGRAPHIC SENSITIZING DYES OF THE MEROCYANINE AND STYRYL TYPES IN SIL- VER HALIDE PHOTOGRAPHIC EMULSIONS

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No Drawing. Continuation-in-part of application Ser. No. 226,756, Sept. 27, 1962. This application Mar. 7, 1966, Ser. No. 532,100

**7 Claims. (Cl. 96—102)**

## ABSTRACT OF THE DISCLOSURE

Merocyanine and styryl dyes derived from 1,2-alkylene benzimidazoles and 1,2-alkylene naphthimidazoles are valuable spectral sensitizers for hydrophilic colloid silver halide emulsions used in coating light-sensitive layers and photographic elements.

This application is a continuing application of Lincoln and Brooker, U.S. Ser. No. 226,756, filed Sept. 27, 1962, now abandoned.

This invention relates to photographic sensitizing dyes, and more particularly, to merocyanine type and styryl dyes derived from 1,2-alkylene imidazole bases and their syntheses.

Certain merocyanine and certain styryl dyes useful in increasing the sensitivity of photographic silver halide emulsions have been known. New classes of these dyes have been desired.

One object of our invention is to provide novel merocyanine and styryl dyes having a bridged structure that are valuable for use in photography.

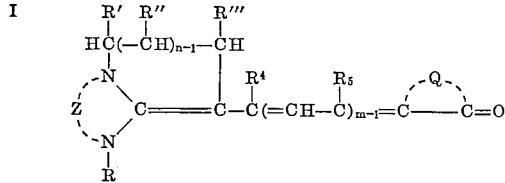
Another object is to provide merocyanine and styryl dyes which extend the sensitivity of photographic silver halide emulsions into longer wavelength regions of the spectrum.

Another object is to provide a method for making our bridged merocyanine and bridged styryl dyes.

Still another object of our invention is to provide photographic silver halide emulsions sensitized with our dyes.

Still further objects will become evident from the following specification and claims.

According to our invention, we provide new merocyanine type dyes including those represented by the formula:



wherein Z represents the nonmetallic atoms necessary to complete a heterocyclic ring, such as those of the benzimidazole series, e.g.,

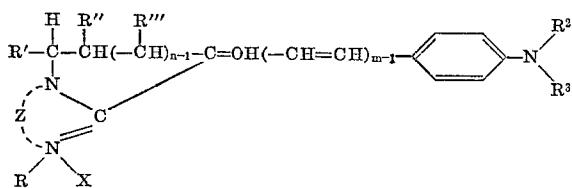
benzimidazole,  
4-chlorobenzimidazole,  
5-chlorobenzimidazole,  
6-chlorobenzimidazole,  
7-chlorobenzimidazole,  
4-methylbenzimidazole,  
5-methylbenzimidazole,  
6-methylbenzimidazole,  
5-bromobenzimidazole,  
6-bromobenzimidazole,  
4-phenylbenzimidazole,  
5-phenylbenzimidazole,  
4-methoxybenzimidazole

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5-methoxybenzimidazole,  
 6-methoxybenzimidazole,  
 5-iodobenzimidazole,  
 6-idobenzimidazole,  
 5 4-ethoxybenzimidazole,  
 5-ethoxybenzimidazole,  
 tetrahydrobenzimidazole,  
 5,6-dimethoxybenzimidazole,  
 5-hydroxybenzimidazole,  
 10 6-hydroxybenzimidazole,  
 etc.,  
 those of the naphthimidazole series, e.g.,  
 naphth[2,3-d]imidazole,  
 15 4-chloronaphth[2,3-d]imidazole,  
 5-chloronaphth[2,3-d]imidazole,  
 6-bromonaphth[2,3-d]imidazole,  
 7-iodonaphth[2,3-d]imidazole,  
 8-chloronaphth[2,3-d]imidazole,  
 20 5-methylnaphth[2,3-d]imidazole,  
 6-methoxynaphth[2,3-d]imidazole,  
 6-methylnaphth[2,3-d]imidazole,  
 7-methoxynaphth[2,3-d]imidazole,  
 7-ethylnaphth[2,3-d]imidazole,  
 25 etc., e.g.,  
 naphth[2,1-d]imidazole,  
 5-chloronaphth[1,2-d]imidazole,  
 6-bromonaphth[1,2-d]imidazole,  
 6-iodonaphth[1,2-d]imidazole,  
 30 7-methylnaphth[1,2-d]imidazole,  
 6-methoxynaphth[1,2-d]imidazole,  
 5-ethoxynaphth[1,2-d]imidazole,  
 etc., and  
 naphth[1,2-d]imidazole,  
 35 4-chloronaphth[2,1-d]imidazole,  
 5-chloronaphth[2,1-d]imidazole,  
 6-iodonaphth[2,1-d]imidazole,  
 7-bromonaphth[2,1-d]imidazole,  
 4-methylnaphth[2,1-d]imidazole,  
 40 5-methoxynaphth[2,1-d]imidazole,  
 6-ethylnaphth[2,1-d]imidazole,  
 5-hydroxynaphth[2,1-d]imidazole, etc., etc.;

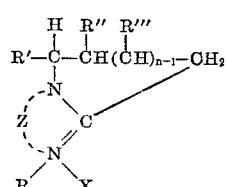
R represents an alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-amyl, n-octyl,  $\beta$ -hydroxyethyl,  $\beta$ -chloroethyl,  $\beta$ -acetoxy,  $\beta$ -sulfoethyl, sulfo-propyl, sulfobutyl, carboxymethyl, carboxyethyl, carboxy-propyl, carboxybutyl, etc.; n is the integer 1 or 2; m is the integer 1 or 2; and Q represents the nonmetallic atoms necessary to complete an acidic ketomethylene heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, including heterocyclic rings such as those of the rhodanine series (e.g., rhodanine, 3-methylrhodanine, 3 - ethylrhodanine, 3-phenylrhodanine, 3- $\alpha$ -naphthylrhodanine, etc.), those of the pyrazolone series (e.g., 3-methyl - 1 - phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 1-(2-benzothiazolyl)-3-methyl - 5 - pyrazolone, etc.), those of the isoxazolone series (e.g., 3-phenyl-5(4H)isoxazolone, 3 - methyl-5(4H)isoxazolone, etc.), those of the oxindole series (e.g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), those of the 2,4,6-triketohexahydro-pyrimidine series (e.g., barbituric acid series) and the 4,6 - diketo-2-thiohexahydro-pyrimidine series (e.g., 2-thiobarbituric acid series), as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-n-propyl, 1-n-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-di-n-propyl, 1,3-diisopropyl, 1,3 - dicyclohexyl, 1,3-di( $\beta$ -methoxyethyl), etc.), or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.) or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives, those of the 2(3H)imidazo[1,2-a]pyridone series

those of the 5,7 - dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine series (e.g., 5,7 - dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2 - a]pyrimidine, etc.), those of the 2-thio-2,4(3H,5H) - oxazoledione series, (e.g., 3-ethyl-2-thio-2,4-oxazolidinedione, etc.), those of the thianaphthenone series (e.g., 3(2H)-thianaphthenone, etc.), those of the 2 - thio-2,5-thiazolidinedione series (i.e., the 2-thio-2,5-(3H,4H)thiazoledione series) (e.g., 3 - ethyl-2-thio-2,5-thiazolidinedione, etc.), those of the 2,4-thiazolidinedione series (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3 - phenyl-2,4-thiazolidinedione, etc.), those of the thiazolidinone series (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-1-4-thiazolidinone, 3- $\alpha$ -naphthyl-4-thiazolidinone, etc.), those of the 4-thiazolinone series (e.g., 2-ethylmercapto-4-thiazolinone, 2-alkylphenylamino-4-thiazolinones, 2-diphenylamino-4-thiazolinone, etc.), those of the 2-amino-2,4-oxazolinone (i.e., pseudohydantoin) series, those of the 2,4-imidazolinedione (hydantoin) series (e.g., 2,4-imidazolinedione, 3-ethyl-2,4-imidazolinedione, 3-phenyl-2,4 - imidazolinedione, 3 -  $\alpha$ -naphthyl-2,4-imidazolinedione, 1,3 - diethyl - 2,4-imidazolinedione, 1-ethyl-3- $\alpha$ -naphthyl - 2,4 - imidazolinedione, 1,3-diphenyl-2,4-imidazolinedione, etc.), those of the 2-thio-2,4-imidazolinedione (i.e., 2 - thiohydantoin) series (e.g., 2-thio-2,4-imidazolinedione, 3 - ethyl-2-thio-2,4-imidazolinedione, 3-phenyl - 2-thio - 2,4-imidazolinedione, 3- $\alpha$ -naphthyl-2-thio - 2,4 - imidazolinedione, 1,3-diethyl-2-thio-2,4-imidazolinedione, 1 - ethyl - 3- $\alpha$ -naphthyl-2-thio-2,4-imidazolinedione, 1,3-diphenyl-2-thio-2,4-imidazolinedione, etc.), those of 5-imidazolinone series (e.g., 2-n-propylmercapto-5-imidazolinone, etc.), etc., as well as heterocyclic nuclei containing a sulfone group, such as those described in U.S. Patent 2,748,114, (e.g., 4 - thiazolidone - 1,1 - dioxide, 3(2H)-thianaphthenone-1,1-dioxide, etc.) (especially a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, 3 of said atoms being carbon atoms, 1 of said atoms being a nitrogen atom, and 1 of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom; R', R'', and R''' each represents the hydrogen atom, a lower alkyl group, such as methyl, ethyl, propyl, butyl, etc., or an aryl group, such as phenyl; R<sup>4</sup> and R<sup>5</sup> each represent the hydrogen atom, an alkyl group, such as methyl, ethyl, etc., and an aryl group, such as phenyl, such that when m is 2, R<sup>4</sup> is hydrogen; and new styryl dyes including those represented by the formula:

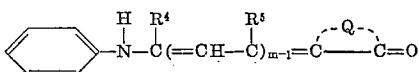


wherein Z, R, R', R'', R''', n and m are as previously defined; X represents an acid radical (e.g., Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>SO<sub>4</sub><sup>-</sup>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>, SCN<sup>-</sup>, etc.); R<sup>2</sup> and R<sup>3</sup> each represent a hydrogen atom, an alkyl group, e.g., methyl, ethyl, propyl, butyl, etc., or aryl, e.g. phenyl.

According to the process of our invention, we prepare the merocyanine dyes of Formula I above by condensing a cycloammonium quaternary salt represented by the formula:

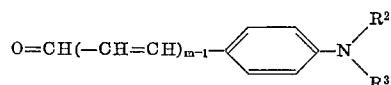


wherein Z, R, R', R'', R''', X and n are as defined previously, with a compound having the formula:



wherein R<sup>4</sup>, R<sup>5</sup>, Q and m are as defined previously. The condensation can advantageously be carried out in the presence of a basic condensing agent, e.g., the organic tertiary amines, such as triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, etc., N-methylpiperidine, N - ethylpiperidine, N,N-dimethylaniline, N,N-diethylaniline, etc. The condensations can advantageously be effected in the presence of an inert solvent, e.g., ethanol, n-propanol, isopropanol, 1,4 - dioxane, pyridine, quinoline, etc. Heating accelerates the condensations, and temperatures varying from room temperature to the reflux temperature of the solvent in the reaction mixture are used.

Our styryl dyes are made to advantage by the reactions of our invention in which the cyclammonium quaternary salt having the Formula III is condensed with an aldehyde having the formula:



wherein R<sup>2</sup>, R<sup>3</sup> and m are as defined previously. This condensation is advantageously effected in the presence of a basic condensing agent, such as piperidine, and in the presence of an inert solvent, e.g., ethanol, propanol, 1,4-dioxane, pyridine, quinoline, etc. Heating accelerates the reaction which is conveniently carried out between room temperature and the reflux temperature of the solvent in the reaction mixture.

The intermediates represented by Formula III are prepared advantageously by the reaction of a 1,2-diaminobenzene, a 1,2 - diaminonaphthalene or a 2,3-diaminonaphthalene compound with a lactone such as  $\gamma$ -butyrolactone, (e.g.  $\gamma$ -butyrolactone,  $\beta$ -methyl- $\gamma$ -butyrolactone,  $\beta$  - ethyl -  $\gamma$ -butyrolactone,  $\beta$ -propyl- $\gamma$ -butyrolactone,  $\beta$ -butyl -  $\gamma$ -butyrolactone,  $\beta$ -phenyl- $\gamma$ -butyrolactone,  $\beta$ , $\gamma$ -dimethyl -  $\gamma$ -butyrolactone,  $\gamma$ -methyl- $\gamma$ -butyrolactone,  $\gamma$ -ethyl -  $\gamma$ -butyrolactone,  $\gamma$ -propyl- $\gamma$ -butyrolactone,  $\beta$ -phenyl- $\gamma$ -methyl- $\gamma$ -butyrolactone, etc.) or a  $\delta$ -valerolactone (e.g.,  $\delta$  - valerolactone,  $\beta$ -methyl- $\delta$ -valerolactone,  $\beta$  - ethyl -  $\delta$  - valerolactone,  $\beta$  - propyl- $\delta$ -valerolactone,  $\gamma$  - methyl -  $\delta$ -valerolactone,  $\gamma$ -ethyl- $\delta$ -valerolactone,  $\delta$ -methyl- $\delta$ -valerolactone,  $\delta$ -ethyl- $\delta$ -valerolactone,  $\delta$ -propyl- $\delta$ -valerolactone,  $\beta$  - phenyl- $\delta$ -valerolactone,  $\gamma$ -phenyl- $\delta$ -valerolactone,  $\beta$ , $\gamma$  - dimethyl- $\delta$ -valerolactone,  $\beta$ , $\gamma$ , $\delta$ -trimethyl- $\delta$ -valerolactone, etc.). The diaminobenzene or diaminonaphthalene compound used is provided with the appropriate substituents so they will be present on the base formed. Alternatively these substituents can be substituted on the base after its formation. The cyclization reaction can be effected by heating the diaminobenzene or the diaminonaphthalene and lactone at atmospheric pressure or at an elevated pressure in an autoclave. In the presence of suitable solvents, such as diphenyl ether, or chlorobenzene the reaction can be effected at lower temperatures. The base is then converted to the quaternary salt by heating with the appropriate alkylating agent.

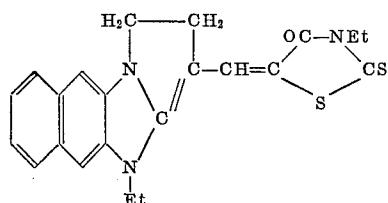
In a preferred reaction, the intermediate of Formula III can be prepared directly without first forming the base. In this reaction the 1,2-diaminobenzene, 1,2-diaminonaphthalene, or 2,3-diaminonaphthalene has an alkyl group on one of the amino groups. The alkyl group may be methyl, ethyl, propyl, butyl, etc. One of these (benzene or naphthalene) derivatives is then condensed with the appropriate lactone by heating in the presence of an acid, such as phosphoryl chloride, a mixture of hydrobromic acid and acetic acid, etc. in a suitable solvent, such as dimethylacetamide. The chloride salt of the quaternary ammonium compound formed in the presence

of phosphoryl chloride can be converted to the salts having other anions by conventional means.

The following representative examples will illustrate more fully the manner whereby we practice our invention.

## DYE 1

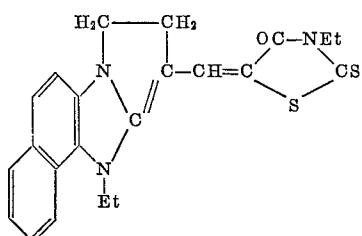
3-ethyl-5-[(4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]naphth[2,3-d]imidazolyl)-methylene]rhodanine



3 - ethyl - 1,2 - trimethylenenaphth[2,3-d]imidazolium iodide (1 mol., 1.82 g.) and 5-acetanilidomethylene-3-ethyl rhodanine (1 mol., 1.63 g.) were mixed in dry pyridine (20 ml.) and heated to reflux temperature, triethylamine (2 mols., 1.4 ml.) added and the mixture refluxed for thirty minutes. The mixture was then chilled, crystalline dye filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine the yield of pure dye was 0.15 g. (11%) M.P. 308-309° C.

## DYE 2

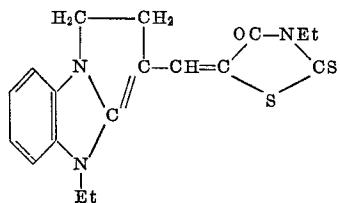
3-ethyl-5-[4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]naphth[1,2-d]imidazolyl)methylene]rhodanine



1 - ethyl - 2,3 - trimethylenenaphth[1,2 - d]imidazolium-p-toluenesulfonate (1 mol., 2.04 g.), 5-acetanilidomethylene-3-ethylrhodanine (1 mol., 1.63 g.) and triethylamine (2 mols., 1.4 ml.) were dissolved in dry pyridine (20 ml.) and heated under reflux for ten minutes. The reaction mixture was then chilled, crystalline dye filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine the yield of pure dye was 0.1 g. (5%) M.P. 299°-300° C. dec.

## DYE 3

3-ethyl-5-[(4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]benzimidazolyl)methylene]rhodanine



3 - ethyl - 1,2 - trimethylenenaphthimidazolium - p - toluenesulfonate (1 mol., 3.58 g.), 5-acetanilidomethylene-3-ethylrhodanine (1 mol., 3.56 g.) and triethylamine (2 mols., 2.8 ml.) were dissolved in dry pyridine (30 ml.) and heated under reflux for ten minutes. The reaction mixture was then chilled, crystalline dye filtered off,

washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol the yield of pure dye was 1 g. (25%) M.P. 277°-278° C. dec.

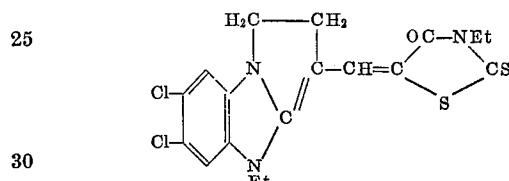
## DYE 4

3-ethyl-5-[(5-ethyl-4(5H)piperidino[1,2-a]naphth[2,3-d]imidazolyl)methylene]rhodanine

3 - ethyl - 1,2 - tetramethylenenaphth[2,3 - d]imidazolium-p-toluenesulfonate (1 mol., 2.1 g.), 5-acetanilidomethylene-3-ethyl rhodanine (1 mol., 1.6 g.) and triethylamine were dissolved in dry pyridine (20 ml.) and heated under reflux for thirty minutes. The reaction mixture was then chilled and crude dye precipitated from solution by pouring into water with stirring. The solid dye was filtered off, washed with methyl alcohol and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.7 g. (33%) M.P. 259°-260° C. dec.

## DYE 5

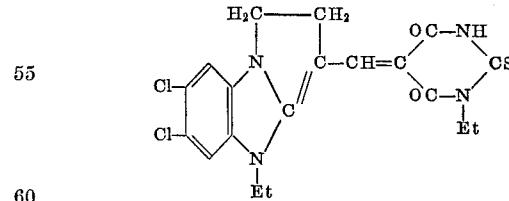
5-[(6,7-dichloro-4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]benzimidazol-3-yl)methylene]-3-ethylrhodanine



5,6 - dichloro-3-ethyl - 1,2 - trimethylenenaphthimidazolium iodide (1 mol., 1.9 g.) and 5-acetanilidomethylene-3-ethylrhodanine (1 mol., 1.5 g.) were mixed in dry pyridine (25 ml.) and heated to reflux temperature, triethylamine (2 mols., 1.4 ml.) added and the entire mixture refluxed for fifteen minutes. The mixture was then chilled and the dye obtained crystalline by adding an excess of methyl alcohol with stirring. The dye was then filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol the yield of pure dye was 0.4 g. (20%), M.P. 311-312° C. dec.

## DYE 6

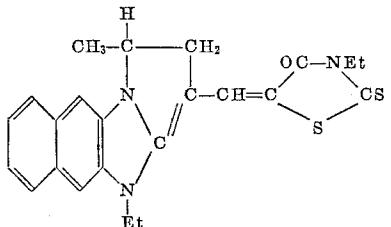
5 - [6,7 - dichloro - 4 - ethyl - 1,2 - dihydro - 4H - pyrrolo[1,2 - a]benzimidazol - 3 - yl)methylene] - 1 - ethyl-2-thiobarbituric acid



5,6 - dichloro-3-ethyl-1,2-trimethylenenaphthimidazolium iodide (1 mol., 1.9 g.) and 5-anilinomethylene-1-ethyl-2-thiobarbituric acid (1 mol., 1.37 g.) which had been heated to a melt with acetic anhydride (4 mols., 1.88 ml.), were mixed in dry pyridine (35 ml.) and heated to reflux temperature, triethylamine (2 mols., 1.4 ml.) added and the entire mixture refluxed for fifteen minutes. The mixture was then chilled and the dye obtained crystalline by adding an excess of methyl alcohol with stirring, crystalline dye filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol the yield of pure dye was 0.4 g. (20%), M.P. above 320° C.

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DYE 7

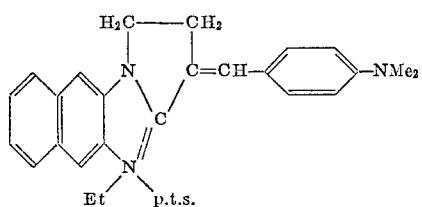
3 - ethyl - 5 - [(4-ethyl-1-methyl-2,1-dihydro-4H-naphtho[2,3-d]pyrrolo[1,2-a]imidazol-3-yl)methylene]rhodanine



4-ethyl - 1 - methyl-2,3-dihydro-1H-naphtho[2,3-d]pyrrolo[1,2-a]imidazolium iodide (1 mol., 189 g.) and 5-acetanilidomethylene-3-ethylrhodanine (1 mol., 1.63 g.) were mixed in dry pyridine (25 ml.) and heated to reflux temperature, triethylamine (2 mols., 1.4 ml.) added and the entire mixture refluxed for fifteen minutes. The mixture was then chilled and the dye obtained solid by adding an excess of water with stirring. The dye was then filtered off, washed with methyl alcohol and dried. After two recrystallizations from pyridine and methyl alcohol the yield of pure dye was 0.3 g. (11%), M.P. 295-296° C. dec.

## DYE 8

3 - p - dimethylaminobenzylidene - 4 - ethyl-2,3-dihydro-1H - pyrrolo[1,2 - a]naphth[2,3-d]imidazolium-p-toluenesulfonate

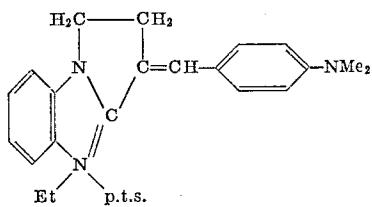


3 - ethyl - 1,2 - trimethylenebenzimidazolium-p-toluenesulfonate (1 mol., 2.04 g.) and p-dimethylaminobenzaldehyde (1 mol. plus 100% excess, 1.49 g.) were mixed in absolute ethyl alcohol (15 ml.), piperidine (1 drop) added and the mixture refluxed for two hours.

The mixture was then chilled, crystalline dye filtered off, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.55 g. (20%) M.P. 298°-299° C. dec.

## DYE 9

3 - p - dimethylaminobenzylidene-4-ethyl-2,3-dihydro-1H-pyrrolo[1,2-a]benzimidazolium-p-toluenesulfonate



3 - ethyl - 1,2 - trimethylenebenzimidazolium-p-toluenesulfonate (1 mol., 3.58 g.) and p-dimethylaminobenzaldehyde (1 mol. plus 100% excess, 2.98 g.) were mixed in absolute ethyl alcohol (30 ml.), piperidine (3 drops) added and the mixture heated under reflux for 2 hours.

The mixture was then chilled, crystalline dye filtered off, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.7 g. (15%) M.P. 250°-251° C. dec.

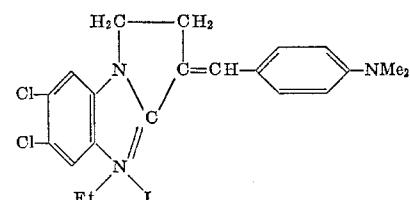
## 8

## DYE 10

6,7-dichloro-3-p-dimethylaminobenzylidene-4-ethyl-2,3-dihydro-1H-pyrrolo[1,2-a]benzimidazolium iodide

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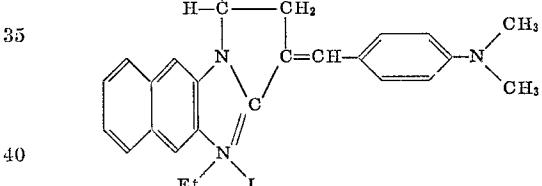
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## DYE 11

3 - p - dimethylaminobenzylidene - 4 - ethyl-1-methyl-2,3-dihydro - 1H - naphtho[2,3 - d]pyrrolo[1,2 - a]imidazolium iodide



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4-ethyl-1-methyl-2,3-dihydro - 1H - naphtho[2,3-d]pyrrolo[1,2-a]imidazolium iodide (1 mol., 1.89 g.) and p-dimethylaminobenzaldehyde (1 mol. plus 100% excess, 1.49 g.) were mixed in absolute ethyl alcohol (50 ml.), piperidine (5 drops) added and the entire mixture refluxed for thirty minutes. The mixture was then chilled, crystalline dye filtered off, washed with acetone and dried. After two recrystallizations from methyl alcohol the yield of pure dye was 0.9 g. (36%), M.P. 320-321° C. dec.

Other merocyanine type dyes of our invention represented by Formula I are made by methods similar to those illustrated by Dyes 1 through 7. For example dyes such as the following:

3-ethyl-5-[(4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]naphth[2,3-d]imidazolyl)allylidene]rhodanine  
3-ethyl-5-[(4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]naphth[2,3-d]imidazolyl)allylidene]rhodanine  
3-ethyl-5-[(4-ethyl-1,2-dihydro-4H-pyrrolo[1,2-a]benzimidazolyl)allylidene]rhodanine  
3-ethyl-5-[(5-ethyl-4(SH)piperidino[1,2-a]naphth[2,3-d]imidazolyl)allylidene]rhodanine

Similarly other merocyanine dyes in which the rhodanine and barbituric acid nuclei are replaced by other keto-methylene heterocyclic nuclei are made according to our invention.

Other styryl dyes represented by Formula II are made according to our invention by methods similar to those illustrated by Dyes 8 through 11.

The preparation of the cyclammonium quaternary salts represented by Formula III is illustrated by the following typical examples.

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## 3-ethyl-1,2-trimethylenenaphth[1,2-d]imidazolium-p-toluene sulfonate

This intermediate was prepared as follows: 1,2-diaminonaphthalene (1 mol., 31.6 g.) and  $\gamma$ -butyrolactone (1 mol., 17.2 g.) were mixed and heated at 270°-290° C. for seven hours at which time water (7 ml.) had been collected. The remaining mixture which was a glassy mass was distilled under reduced pressure (B.P. 145°-165° C. at 1.5 mm.). The product was distilled over as a yellow mass and was obtained solid by stirring with an excess of ether. At this point the solid was filtered off, stirred with acetone, filtered off again, washed with a small amount of acetone and dried. The yield of yellow solid 1,2-trimethylenenaphth[1,2-d]imidazole was 15 g. (36%) M.P. 121-122° C.

One mol., 10.4 g. of 1,2-trimethylenenaphth[1,2-d]imidazole and ethyl-p-toluenesulfonate (1 mol. plus 10% excess) were mixed and heated at 115° C. for thirty-six hours. The mixture was then cooled and the glassy mass obtained as a pale pink solid by refluxing with an excess of acetone. The product was then filtered off, washed with acetone and dried. The yield of crude pink solid was 20 g. (98%) M.P. 181-182° C. dec.

## 3-ethyl-1,2-tetramethylenenaphth[2,3-d]imidazolium-p-toluenesulfonate

1,2-tetramethylenenaphth[2,3-d]imidazole (1 mol., 9 g.) made by reacting 2,3-diaminonaphthalene with  $\delta$ -valerolactone as described by Mosby, Journal of Organic Chemistry, vol. 24, page 419, March 1959, and ethyl-p-toluenesulfonate (1 mol. plus 10% excess 11 g.) were mixed and heated at 120° for three hours. The product as a hard cake was then cooled, ground under acetone, filtered off, washed with acetone and dried. The yield of light tan solid was 16 g. (94%) M.P. 201°-202° C. dec.

## 3-ethyl-1,2-trimethylenebenzimidazolium-p-toluene sulfonate

1,2-trimethylenebenzimidazole (1 mol., 15.8 g.) made by reacting 2-aminoaniline with  $\gamma$ -butyrolactone as described by Reppe et al., Annalen der Chemie, Band 595-596, page 209, 1955, and ethyl-p-toluenesulfonate (1 mol., 20 g.) were mixed and heated on a steam bath for thirty-six hours. The salt formed as a hard white cake which was ground under acetone, filtered off, washed with acetone and dried. After drying the yield of salt was 33 g. (92%) M.P. 133-134° C.

## 3-ethyl-1,2-trimethylenenaphth[2,3-d]imidazolium-p-toluenesulfonate

1,2-trimethylenenaphth[2,3-d]imidazole (1 mol., 12 g.) made by heating 2,3-diaminonaphthalene with  $\gamma$ -butyrolactone, and ethyl-p-toluenesulfonate (1 mol. plus 10% excess, 12.7 g.) were mixed and heated on a steam bath for twenty-four hours. The product as a viscous mass was then cooled, washed with ether, the ether decanted and the salt obtained solid by stirring with an excess of acetone and dried. After two recrystallizations from ethyl alcohol the yield of pure salt was 11 g. (44%) M.P. 172-173° C.

## Anhydro-3-(3-sulfobutyl)1,2-trimethylenenaphth[2,3-d]imidazolium hydroxide

1,2-trimethylenenaphth[2,3-d]imidazole (1 mol., 20.8 g.) and 2,4-butene sulfone (1 mol., 13.6 g.) were mixed, heated at 130° C. for one hour, then heated at 110° C. for thirty-six hours and this product as a tan cake was ground under acetone. The salt was then filtered off, washed with acetone and dried. The yield of crude product was 32.5 g. (96%) M.P. above 310° C.

## 5,6-dichloro-3-ethyl-1,2-trimethylenebenzimidazolium iodide

4,5-dichloro-N-ethyl-2-aminoaniline (1 mol., 41 g.) and  $\gamma$ -butyrolactone (1 mol., 17.2 g.) were mixed, phos-

phoryl chloride (1 mol., 18.3 ml.) added and much heat was evolved. After several minutes, the evolution of heat subsided and the purple viscous mixture heated at reflux temperatures for fifteen minutes. At this point, the dark brown mixture was cooled, dissolved in refluxing methyl alcohol (450 ml.) and the salt converted to the iodide by adding solid sodium iodide (2 mols., 9.2 g.) to the dark methyl alcohol solution with stirring. The iodide salt precipitated from solution as a gray solid. After chilling the mixture the gray solid was filtered off, washed with methyl alcohol and dried. The yield of product was 33 g. (43%) M.P. 282-283° C. dec.

## 1-methyl-2,3-dihydro-1H-naphtho[2,3-d]pyrrolo[1,2-a]imidazole

2,3-diaminonaphthalene (1 mol., 31.6 g.) and  $\gamma$ -methylbutyrolactone were mixed in chlorobenzene (20 ml.) and the mixture heated under reflux distilling off the chlorobenzene along with water as it was formed. When all of the chlorobenzene was distilled off (20 ml.) more of chlorobenzene was added and the mixture again heated under reflux distilling off the chlorobenzene with more water. After (6.4 ml.) of water had been collected the remaining chlorobenzene was removed and the residual mixture distilled under reduced pressure (B.P. 180° C. at 2 mm.). The yield of product as a yellow oil was 8 g. (18%).

## 4-ethyl-1-methyl-2,3-dihydro-1H-naphtho[2,3-d]pyrrolo[1,2-a]imidazolium iodide

1-methyl-2,3-dihydro-1H-naphtho[2,3-d]pyrrolo[1,2-a]imidazole (1 mol., 8 g.) and iodoethane (1 mol. plus 200% excess, 16.8 g.) were mixed and heated on a steam bath in the dark for twenty hours. The mixture was then cooled, stirred with an excess of ether, ether decanted and the product obtained as a white solid by stirring with an excess of acetone. The solid was then filtered off, washed with acetone and dried. The yield of white solid was 11 g. (81%) M.P. 276-277° C. dec.

Any of our intermediates can be solubilized with other groups, such as carboxyalkyl, acetoxyalkyl, etc., by reacting the base of the intermediate with the appropriate reactant. For example, a carboxymethyl group can be added by reacting the base of the intermediate with  $\alpha$ -bromoethylacetate, or a carboxyethyl group can be added by reacting the base with  $\beta$ -bromopropionic acid. An acetoxyethyl group can be added by reacting the base with  $\beta$ -bromoethanol followed by acetic anhydride.

Our dyes are useful in spectrally sensitizing photographic silver halide including silver halide emulsions when incorporated therein. The dyes are especially useful for extending the spectral sensitivity of the customarily employed silver chloride, silver chlorobromide, silver bromide, silver bromoiodide and silver chlorobromiodide developing out emulsions using a hydrophilic colloid carrier such as gelatin, its water-soluble derivatives, polyvinyl alcohol, its water-soluble derivatives and copolymers, water-soluble vinyl polymers such as polyacrylamide, imidized polyacrylamide, etc., and other water-soluble film-forming materials that form water-permeable coatings, such as colloidal albumin, water-soluble cellulose derivatives like ethanol amine cellulose acetate, etc. To prepare emulsions sensitized with one or more of our new dyes, it is only necessary to disperse the dye or dyes in the emulsions. The methods of incorporating dyes in emulsions are simple and well known to those skilled in the art. In practice, it is convenient to add the dyes to the emulsion in the form of a solution in a suitable solvent. Methanol, ethanol, propanol, etc., acetone and pyridine are used to advantage. The dyes are advantageously incorporated in the finished, washed emulsions and should be uniformly distributed throughout the emulsions.

The concentration of the dyes in the emulsions can vary

widely and will depend upon the type of emulsion and the effect desired. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art, upon making the ordinary tests and observations customarily used in the art of emulsion making.

To prepare a hydrophilic colloid-silver halide emulsion sensitized with one or more of our new dyes, the following procedure is satisfactory. A quantity of dye is dissolved in a suitable solvent such as an alcohol, acetone, pyridine, etc. and a volume of this solution, which may be diluted with water, containing the dye, is slowly added to about 1000 cc. of gelatino-silver halide emulsion, with stirring. Stirring is continued until the dye is uniformly dispersed in the emulsion.

The above statements are only illustrative, as it will be apparent that the dyes can be incorporated in photographic emulsions by any of the other methods customarily employed in the art, e.g., by bathing a plate or film upon which an emulsion is coated in a solution of the dye in an appropriate solvent. However, bathing methods are ordinarily not to be preferred. Emulsions sensitized with the dyes can be coated on suitable supports, such as glass, cellulose derivative film, resin film or paper in the usual manner.

Photographic silver halide emulsions, such as those listed above, containing the sensitizing dyes of my invention can also contain such addenda as chemical sensitizers (e.g., sulfur sensitizers, such as allyl thiocarbamide, thiurea, allylisothiocyanate, cystine, etc.), various gold compounds, such as potassium chloroaurate, auric trichloride, etc. (see U.S. Patents 2,540,085; 2,597,856; and 2,597,915, for example), various palladium compounds (such as palladium chloride (U.S. 2,540,086), potassium chloropalladate (U.S. 2,598,079), etc.), or mixtures of such sensitizers), antifogants (e.g., benzotriazole, nitrobenzimidazole, 5-nitroindazole, etc. (see Mees, "The Theory of the Photographic Process," Macmillan Pub., p. 460), or mixtures thereof), hardeners (e.g., formaldehyde (U.S. 1,763,533), chrome alum (U.S. 1,763,533), glyoxal (Ger. 538,713), dibromacrolein (Br. 406,750), etc.), color couplers (e.g., such as those described in U.S. Patent 2,423,730, Spence and Carroll U.S. application 771,380, filed Aug. 29, 1947, now U.S. Patent 2,640,776, issued June 2, 1953, etc.), or mixtures of such addenda. Dispersing agents for color couplers, such as substantially water-insoluble, high boiling crystalloid materials, such as those set forth in U.S. Patents 2,322,027 and 2,304,940, can also be employed in the above-described emulsions.

The following example will serve to further illustrate how our dyes are used to sensitize photographic emulsions.

#### EXAMPLE 1

A sensitizing amount of each of the dyes from the preceding examples was added to separate portions of a gelatino-silver halide emulsion. Each of these emulsions were coated on pieces of cellulose ester supports and dried. Spectrographic exposures were made on each coating and these were processed in a photographic developer having the composition:

	G.
p-Methylaminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate·H <sub>2</sub> O	52.5
Potassium bromide	5.0
Water to make 1 liter.	

fixed in a conventional sodium thiosulfate fixing bath, washed and dried. The following table summarizes the wavelength of light to which the maximum sensitivity was produced and the longest wavelength light to which each emulsion was sensitized.

TABLE 1

Dye Number	Silver halide in Emulsion	Sensitivity Maximum, m $\mu$	Dye Sensitizes to light of m $\mu$
1	Silver bromoiodide	570	620
2	do	550	610
3	do	550	610
4	do	585	625
5	Silver chlorobromide	580	480-625
6	Silver bromoiodide	575	620
7	do	505	540
8	do	580	640
9	do	535	555
10	do	480	530
11	do	( <sup>1</sup> )	660
12	do	530	590

<sup>1</sup> Not definite.

Similarly it can be shown that other dyes of our invention can be used to advantage to sensitize silver halide emulsions.

The immediate 1,2-alkylenebenzimidazole and 1,2-alkylenenaphthimidazole nuclei are not equivalent to the related 1,2-alkylenebenzoxazoles, 1,2-alkylenenaphthoxazoles, 1,2-alkylenebenzothiazoles, and 1,2-alkylenenaphthothiazoles of copending Lincoln and Heseltine, U.S. Ser. No. 226,757, filed Sept. 27, 1962. The following example will serve to illustrate the said nonequivalence.

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#### EXAMPLE 2

A gelatino-silver bromoiodide emulsion was divided into five portions and each of the said portions was treated with a sensitizing amount of one of the carbocyanine dyes identified as Dyes A, B, C, D and E. A separate coating was made for each of the five sensitized emulsions on separate pieces of a photographic film support. When dried, these emulsion coatings were each exposed to a wedge spectograph and given photographic processing using a hydroquinone type of developer, washed, fixed in a conventional sodium thiosulfate fixing bath, washed and dried. The wavelength of light producing the maximum sensitization was determined from the processed wedge spectogram for each emulsion coating.

The light absorption  $\lambda_{\text{max.}}$  in methanol was determined for each of the Dyes A through E.

The following table lists the light absorption  $\lambda_{\text{max.}}$  in methanol, the sensitization maximum and the difference between light wavelengths producing sensitization max and  $\lambda_{\text{max.}}$

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Dye	Light Absorption $\lambda_{\text{max.}}$ in Methanol (m $\mu$ )	Sensitization maximum (m $\mu$ )	Difference between Light Wavelengths producing Sensitization max and $\lambda_{\text{max.}}$ (m $\mu$ )
A	520	600	80
B	525	550	25
C	510	560	42
D	520	550	30
E	555	590	35

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The following describes the Dyes A through E by their structural formulae.

Dye	Structural formula
A	
B	

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Dye	Structural formula
C	
D	
E	

Dye A containing the 1,2-trimethylenenaphthimidazole nucleus of the immediate application demonstrates aggregation as evidenced by the  $80 \text{ m}_{\mu}$  difference between the light wavelength producing sensitization maximum and the absorption  $\lambda_{\text{max.}}$  Dyes B, C, D, and E, which do not have a 1,2-alkylenenaphthimidazole or 1,2-alkylenebenzimidazole nucleus of the application, do not aggregate as evidenced by a difference in the wavelength producing sensitization maximum and absorption  $\lambda_{\text{max.}}$  that is, from about 47—about 69% lower than the difference for Dye A. It is readily apparent from these comparative data that the immediate 1,2-trimethylenenaphthimidazole nucleus is not equivalent to either the nuclei of Lincoln and Heseltine, U.S. Ser. No. 226,757, that is, 1,2-trimethylenbenzothiazole, and 1,2-tetramethylenenaphthoxazole, or the prior art benzoxazole nucleus.

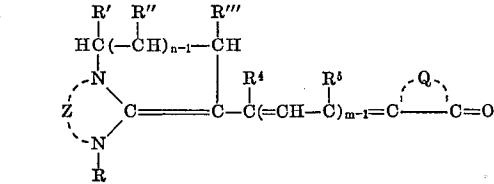
The dyes A through E were prepared by condensing the appropriate intermediates dissolved in organic solvent by heating in the presence of a basic condensing agent such as triethylamine. Dye A was prepared by condensing 3-ethyl-1,2-tetramethylenenaphth[2,3-d]imidazolium p-toluenesulfonate described previously herein, with 2- $\beta$ -acetanilidovinyl-3-ethylbenzothiazolium iodide. Dye B was prepared by condensing 2,3-trimethylenenaphthimidazolium bromide made as described in copending Lincoln and Heseltine, U.S. Ser. No. 226,757, filed Sept. 27, 1962 with 2- $\beta$ -acetanilidovinyl-3-ethylbenzoxazolium iodide. Dye C was prepared by heating a solution of 2,3-tetramethylenenaphth[2,3-d]oxazolium iodide, prepared as described in U.S. Ser. No. 226,757, and ethyl ortho formate. Dye D is well known in the art. Dye E was prepared by the method described for Dye B but substituting 2- $\beta$ -acetanilidovinyl-3-ethylbenzothiazolium iodide in place of 2- $\beta$ -acetanilido-3-ethylbenzoxazolium iodide.

The merocyanine and styryl dyes of our invention derived from 1,2-alkylene benzimidazoles and 1,2-alkylenenaphthimidazoles are valuable sensitizers for use in hydrophilic colloid silver halide emulsions used in photography. These dyes extend the sensitivity of photographic silver halide emulsions containing them into longer wavelengths.

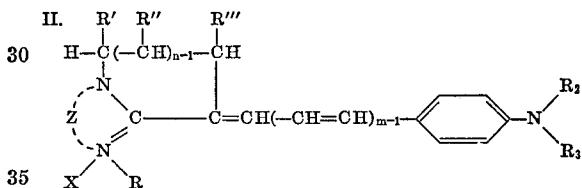
The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A light-sensitive layer containing silver halide and a sensitizing dye selected from dyes having the formula:

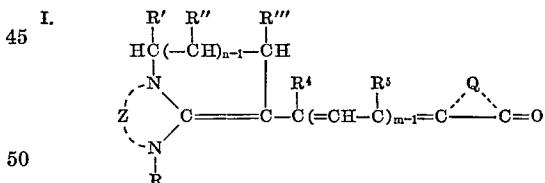


wherein Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the class consisting of a benzimidazole nucleus, and a naphthimidazole nucleus; n represents an integer of from 1 to 2; m represents an integer from 1 to 2; R represents an alkyl group having from 1 to 8 carbon atoms; R', R'', and R''' each represents a member selected from the class consisting of the hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and a phenyl group; R<sup>4</sup> and R<sup>5</sup> each represents a member selected from the class consisting of the hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, and a phenyl group, such that when m is 2, R<sup>4</sup> is hydrogen; and Q represents the nonmetallic atoms necessary to complete an acidic ketomethylene heterocyclic nucleus containing from 5 to 6 atoms in the nucleus; and the dyes having the formula:



wherein Z, R, n and m are as defined; X represents an acid radical; R<sub>2</sub> and R<sub>3</sub> each represents a member selected from the class consisting of the hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and a phenyl group; and R', R'' and R''' are as defined previously.

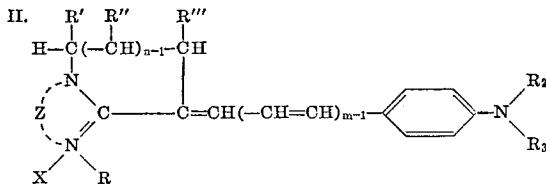
2. A light-sensitive layer of claim 1 containing a sensitizing dye selected from dyes having the formula:



wherein Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the class consisting of a benzimidazole nucleus, and a naphthimidazole nucleus; n represents an integer of from 1 to 2; m represents an integer from 1 to 2; R represents an alkyl group having from 1 to 8 carbon atoms; R', R'', and R''' each represents a member selected from the class consisting of the hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and a phenyl group; R<sup>4</sup> and R<sup>5</sup> each represents a member selected from the class consisting of the hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, and a phenyl group, such that when m is 2, R<sup>4</sup> is hydrogen; and Q represents the nonmetallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the nucleus selected from the class consisting of a rhodanine nucleus, a pyrazolone nucleus, an isoxazolone nucleus, an oxindole nucleus, a 2,4,6-triketohexahydropyrimidine nucleus, a 4,6-diketo-2-thioxohexahydropyrimidine nucleus, a 2(3H)-imidazo[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine nucleus, a 2-thio-2,4-(3H,5H)oxazolidinedione nucleus, a thianaphthphenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a 4-thiazolinone nucleus, a 2-

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imino - 2,4 - oxazolinone nucleus, a 2,4-imidazolinedione nucleus, a 2-thio-2,4-imidazolinedione nucleus, and a 5-imidazolinone nucleus; and the dyes having the formula:



wherein Z, R, n and m are as defined; X represents an acid radical; R<sub>2</sub> and R<sub>3</sub> each represents a member selected from the class consisting of the hydrogen atom, an alkyl group having from 1 to 4 carbon atoms and a phenyl group; and R', R'' and R''' are as defined previously.

3. A light-sensitive layer of claim 1 containing 3-ethyl-5-[(4-ethyl-1,2-dihydro - 4H - pyrrolo[1,2-a]naphth[2,3-d]imidazolyl)methylene]rhodanine.

4. A light-sensitive layer of claim 1 containing 3-ethyl-

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5-[(5 - ethyl - 4(5H) - piperidino[1,2-a]naphth[2,3-d]imidazolyl)methylene]rhodanine.

5. A light-sensitive layer of claim 1 containing 3-ethyl-5-[(4-ethyl-1-methyl - 1,2 - dihydro - 4H - naphtho[2,3-d]pyrrolo[1,2-a]imidazol-3-yl)methylene]rhodanine.

6. A light-sensitive layer of claim 1 containing 3-p-dimethylaminobenzylidene - 4 - ethyl-2,3-dihydro-1H-pyrrolo[1,2-a]naphth[2,3-d]imidazolium-p-toluenesulfonate.

7. A light-sensitive layer of claim 1 containing 3-p-dimethylaminobenzylidene-4-ethyl - 1 - methyl-2,3-dihydro-1H-naphtho[2,3-d]pyrrolo[1,2-a]imidazolium iodide.

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