United States Patent

Brooker et al.

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[54] **SILVER HALIDE EMULSIONS CONTAINING A DYE DERIVED FROM 4,6-DIARYL SUBSTITUTED PICOLINIUM SALTS AS DESENSITIZER**

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[52] U.S. Cl. **96/101,** 96/102, 260/240, 260/240.5

[51] Int. Cl. **G03c 1/36,** G03c 1/08

[58] Field of Search 96/101, 102; 260/240, 240.5

[56] **References Cited**

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[57] **ABSTRACT**

Photographic silver halide emulsions containing cyanine, styryl and merocyanine dyes derived from 4,6-diaryl substituted picolinium salts, which either sensitize or desensitize silver halide emulsions and photographic elements containing said emulsions are described. 3'-Ethyl-1,4,6-triphenyl-2-pyridothiacyanine iodide, 2-(3-nitrostyryl)-1,4,6-triphenylpyridinium iodide and 3-ethyl-5-{[1,4,6-tri(-methoxy-phenyl)-2(1H)-pyridylidene]-ethylidene} rhodanine are illustrative of the dye compounds employed.

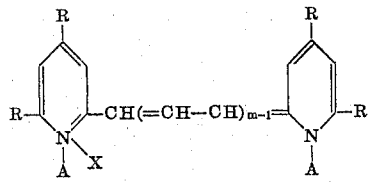
19 Claims, No Drawings

SILVER HALIDE EMULSIONS CONTAINING A DYE DERIVED FROM 4,6-DIARYL SUBSTITUTED PICOLINIUM SALTS AS DESENSITIZER

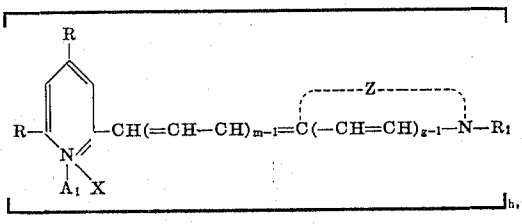
This invention relates to photographic silver halide emulsions containing cyanine, styryl and merocyanine dyes derived from 4,6-diaryl substituted picolinium salts, which either sensitize or desensitize silver halide emulsions and to photographic elements containing said emulsions.

The dyes present in the photographic silver halide emulsions and photographic elements of our invention include those having the following general formulas:

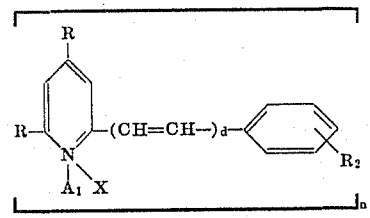
I.



II.

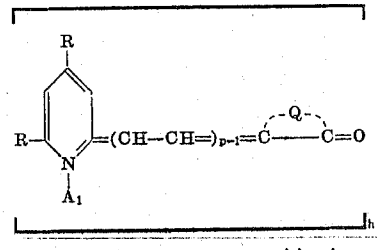


III.

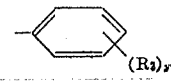


and

IV.



wherein *d*, *g* and *n* each represents a positive integer of from one to two, *m* represents a positive integer of from one to four, *p* represents a positive integer of from one to three, R represents a phenyl nucleus (including substituted phenyl) such as phenyl, an alkylphenyl preferably containing from one to four carbon atoms in the alkyl portion such as p-methylphenyl, p-ethylphenyl, p-propylphenyl, p-isopropylphenyl, p-butylphenyl, m-methylphenyl, m-ethylphenyl, etc., an alkoxyphenyl preferably containing from one to five carbon atoms in the alkoxy portion such as p-methoxyphenyl, p-ethoxyphenyl, p-propoxyphenyl, p-isopropoxyphenyl, p-butoxyphenyl, p-pentyloxyphenyl, m-methoxyphenyl, m-ethoxyphenyl, m-propoxyphenyl, m-butoxyphenyl, m-pentyloxyphenyl, 2,5-dimethoxyphenyl, 2,5-diethoxyphenyl, 2,5-dipentyloxyphenyl, etc., a halogen substituted phenyl such as p-chlorophenyl, p-bromophenyl, p-fluorophenyl, m-chlorophenyl, 3,4-dichlorophenyl, etc., a nitrophenyl such as p-nitrophenyl, o-nitrophenyl, etc., and the like, R_1 represents an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, sec.-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dododecyl, etc., especially an alkyl group having one to four carbon atoms, allyl, a sulfoalkyl group such as β-sulfoethyl, γ-sulfopropyl, γ-sulfobutyl or ω-sulfobutyl, for example, a hydroxyalkyl group such as β-hydroxyethyl, γ-hydroxypropyl or ω-hydroxybutyl, for example, an alkoxyalkyl group such as β-methoxyethyl, β-ethoxyethyl, β-propoxyethyl, γ-methoxypropyl or γ-ethoxypropyl, for example, a carboxyalkyl group such as carboxymethyl, β-carboxyethyl, γ-carboxypropyl or ω-carboxybutyl, for example, an alkanoyloxyalkyl group such as β-acetoxyethyl, β-propionyloxyethyl, γ-acetoxypropyl, ω-acetoxybutyl or ω-butyryloxybutyl, for example, an alkoxycarbonylalkyl group such as methoxycarbonylmethyl, β-methoxycarbonylethyl, β-ethoxycarbonylethyl, γ-ethoxycarbonylpropyl or ω-ethoxycarbonylbutyl, for example, an aralkyl group such as benzyl or phenethyl, for example, or an aryl group (including substituted aryl) such as phenyl, tolyl, chlorophenyl, sulfophenyl or carboxyphenyl, for example, R_2 represents a dialkylamino group, preferably in the 4-position on the phenyl nucleus and containing from two to about 10 carbon atoms, such as dimethylamino, diethylamino, methylethylamino, dipropylamino, diisopropylamino or dibutylamino, for example, or a nitro group preferably in the 3-position on the phenyl nucleus, X represents an acid anion, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, methyl sulfate, ethyl sulfate, perchlorate, benzenesulfonate, p-toluenesulfonate, etc., A represents a monovalent group such as a hydroxyalkyl group preferably containing from two to four carbon atoms, e.g., β-hydroxyethyl, γ-hydroxypropyl, ω-hydroxybutyl, etc., a dialkylamino group preferably containing from two to about 10 carbon atoms, e.g., dimethylamino, diethylamino, methylethylamino, dipropylamino, diisopropylamino, dibutylamino, etc., a dialkylaminoalkyl group wherein each of said alkyl and dialkyl groups preferably contain from two to about 10 carbon atoms, e.g., dimethylaminoethyl, dimethylaminopropyl, diethylaminoethyl, diethylaminopropyl, dimethylaminodecyl, methylethylaminoethyl, etc., and the group



wherein *y* represents a positive integer of from one to two and R_3 represents a hydrogen atom or a substituent, preferably in the 4-position on the phenyl nucleus, such as an alkyl group preferably containing from one to four carbon atoms, e.g., methyl, ethyl, propyl, butyl, etc., an alkoxy group preferably containing from one to four carbon atoms, e.g., methoxy, ethoxy, propoxy, butoxy, etc., a halogen atom, e.g., chlorine, bromine, etc., a dialkylamino group preferably containing from two to about 10 carbon atoms, e.g., dimethylamino, diethylamino, methylethylamino, dipropylamino, diisopropylamino, dibutylamino, etc., a nitro group, a phenylazo group, an alkylthio group preferably containing from one to four carbon atoms, e.g., methylthio, ethylthio, propylthio, isopropylthio, butylthio, etc., or a heterocyclic nucleus, e.g., 2-methyl-5 (or 6) -benzothiazolyl, 2-methyl-5 (or 6)-benzoxazolyl, 2-methyl-5 (or 6) -benzimidazolyl, etc., A_1 represents a member selected from A when *n* is 1, and a divalent alkylene group preferably containing from two to 10 carbon atoms, e.g., ethylene, propylene, 1,3-propylene, 1,4-butylene, 1,6-hexamethylene, etc., when *n* is 2, Z represents the nonmetallic atoms required to complete a 5 to 6-membered heterocyclic nucleus, such as those selected from the class consisting of a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 5-phenylthiazole 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc., a benzothiazole nucleus, (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.), a naphthothiazole nucleus, (e.g.,

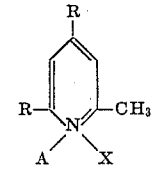
α-naphthothiazole, β-naphthothiazole, 5-methoxy, β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 8-methoxy-α-naphthothiazole, 7-methoxy-α-naphthothiazole, etc.), a thionaphtheno-7', 6', 4,5-thiazole nucleus (e.g., 4'-methoxythianaphtheno-7', 6', 4,5-thiazole, etc.), an oxazole nucleus (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), a benzoxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 5-chlorobenzoxazole, 6-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.) a naphthoxazole nucleus (e.g., α-naphthoxazole, β-naphthoxazole, etc.), a selenazole nucleus (e.g., 4-methylselenazole, 4-phenylselenazole, etc.), a benzoselenazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc), a naphthoselenazole nucleus (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.), a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, etc.), a 2-pyridine nucleus (e.g., 2-pyridine, 5-methyl-2-pyridine, etc.), a 4-pyridine nucleus (e.g., 4-pyridine, 3-methyl-4-pyridine, etc.), a 2-quinoline nucleus 2-quinoline, 3-methyl-2-quinoline, 5-ethyl-2-quinoline, 6-chloro-2-quinoline, 8-chloro-2-quinoline, 6-methoxy-2-quinoline, 8-ethoxy-2-quinoline, 8-hydroxy-2-quinoline, etc.), a 4-quinoline nucleus (e.g., 4-quinoline, 6-methoxy-4-quinoline, 7-methyl-4-quinoline, 8-chloro-4-quinoline, etc.), a 1-isoquinoline nucleus (e.g., 1-isoquiniline, 3,4-dihydro-1-isoquinoline, etc.), a 3-isoquinoline nucleus (e.g., 3-isoquinoline, etc.), a 3,3-dialkylindolenine nucleus (e.g., 3,3-dimethylindolenine, 5- or 6-nitro-3,3-dimethyl-, or 5- or 6-cyano-3,3-dimethylindolenines, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), an imidazole nucleus (e.g., imidazole, 1-alkylimidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, etc.), a benzimidazole nucleus (e.g., benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, etc.), a napthimidazole nucleus (e.g., 1-alkyl-α-naphthimidazole, 1-aryl-β-naphthimidazole, 1-alkyl-5-methoxy-α-naphthimidazole, etc.), etc., and Q represents the nonmetallic atoms required to complete a 5 to 6-membered heterocyclic nucleus selected from those including a 2-pyrazolin-5-one nucleus (e.g., 3-methyl-1-phenyl-2-pyrazolin-5-one, 1-phenyl-2-pyrazoline-5-one, 1-(2-benzothiazolyl)-3-methyl-2-pyrazolin-5-one, etc.), an isoxazolone nucleus (e.g., 3-phenyl-5(4H)-isoxazolone, 3-methyl-5-(4H)-isoxazolone, etc.), an oxindole nucleus (e.g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), a 2,4,6-triketohexahydropyrimidine nucleus (e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-propyl, 1-heptyl, etc.), or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-dipropyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β-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, 1-p-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives), a rhodanine nucleus (i.e., a 2-thio-2,4-thiazolindinedione nucleus), such as rhodanine, 3-alkyl-rhodanines (e.g., 3-ethylrhodanine, 3-allylrhodanine, etc.), 3-carboxyalkylrhodanines (e.g., 3-(2-carboxyethyl)rhodanine, 3-(4-carboxybutyl)rhodanine, etc.), 3-sulfoalkylrhodanines (e.g., 3-(2-sulfoethyl)rhodanine, 3-(3-sulfopropyl)rhodanine, 3-(4-sulfobutyl)rhodanine, etc.), or 3-arylrhodanines (e.g., 3-phenyl-rhodanine, etc.), etc., a 2(3H)-imidazo-[1,2-α]pyridone nucleus, a 5,7-dioxo-6,7-dihydro-5-thiazolo-[3,2-α]pyrimidine nucleus (e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-α]pyrimidine, etc.), a 2-thio-2,4-oxazolidinedione nucleus (i.e., a 2-thio-2,4(3H,5H)oxazoledione nucleus) (e.g., 3-ethyl-2-thio-2, 4-oxazolidinedione, 3-(2-sulfoethyl)-2-thio-2,4-oxazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-oxazolidinedione, 3-(3-carboxypropyl)-2-thio-2,4 -oxazolidinedione, etc.), a thianaphthenone nucleus (e.g., 3-(2H)-thianaphthenone, etc.), a 2-thio-2,5-thiazolidinedione nucleus (i.e., a 2-thio-2,5(3H,4H)-thiazoledione nucleus) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.), a 2,4-thiazolidinedione nucleus (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl-2,4,-thiazolidinedione, 3-α-naphthyl-2,4-thiazolidinedione, etc.), a thiazolidinone nucleus (e.g., 4-thiazolidinone, 3-ethyl-4-thiazolidinone, 3-phenyl-4-thiazolidinone, 3-α-naphthyl-4-thiazolidinone, etc.), a 2-thiazolin-4-one nucleus (e.g., 2-ethylmercapto-2-thiazolin-4-one, 2-alkylphenylamino-2-thiazolin-4-one, 2-diphenylamino-2-thiazolin-4-one, etc.), a 2-imino-4-oxazolidinone (i.e., pseudohydantoin) nucleus, a 2,4-imidazolidinedione (hydantoin) nucleus (e.g., 2,4-imidazolidinedione, 3-ethyl-2,4-imidazolidinedione, 3-phenyl-2,4-imidazolidinedione, 3-α-naphthyl-2,4-imidazolidinedione, 1,3-diethyl-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2, 4-imidazolidinedione, 1-ethyl-3-α-naphthyl-2,4-imidazolidinedione, 1,3-diphenyl-2,4-imidazolidinedione, etc.), a 2-thio-2, 4-imidazolidinedione (i.e., 2-thiohydantoin) nucleus (e.g., 2-thio-2,4-imidazolidinedione, 3-ethyl-2-thio-2,4,-imidazolidinedione, 3-(4-sulfobutyl)-2-thio-2,4-imidazolidinedione, 3-(2-carboxyethyl)-2-thio-2,4-imidazolidinedione, 3-phenyl-2-thio-2,4-imidazolidinedione, 3-α-naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diethyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-phenyl-2-thio-2,4-imidazolidinedione, 1-ethyl-3-α-naphthyl-2-thio-2,4-imidazolidinedione, 1,3-diphenyl-2-thio-2,4-imidazolidinedione, etc.), a 2-imidazolin-5-one nucleus (e.g., 2-propylmercapto-2-imidazolin-5-one, etc.), etc. (especially a heterocyclic nucleus containing five atoms in the heterocyclic ring, three of said atoms being carbon atoms, one of said atoms being a nitrogen atom, and one of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom).

The above-defined dye compounds include both sensitizers and desensitizers for light-sensitive photographic silver-halide emulsions. Those that are sensitizers contain no desensitizing groups and are the preferred species, whereas those that are desensitizers always contain at least one strongly negative group such as a nitro or phenylazo substituent on a phenyl nucleus. All of the above compounds are crystalline and soluble in water and alcohol.

It is an object of the invention to provide photographic silver halide emulsions containing one or more of the dye compounds, described hereinbefore, and more especially containing those species of dyes which function as sensitizers. Another object is to provide photographic elements containing the new photographic emulsions of the invention. Other objects will become apparent hereinafter from a consideration of the description and appended claims.

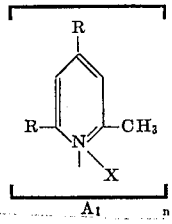
We prepare the dye compounds defined by formulas I, II, III and IV from the picolinium salt intermediates represented by the formulas:

V.



and

VI.

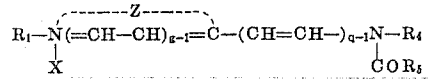


wherein n, R, X, A and A_1 are as previously defined. In general, the dyes are produced by heating a mixture of a quaternary salt of above formulas V or VI with the appropriate intermediate. The reaction mixtures are heated to advantage in any suitable solvents used in dye synthesis including solvents such as ethanol, propanol, dioxane, pyridine, quinoline, and the like, at temperatures up to the reflux temperature of the mixture. Advantageously, the reaction is carried out in the presence of a basic condensing agent such as a tertiary amine, e.g., trimethylamine, triethylamine, tri-n-propylamine, tri-n-butyl- amine, N-methylpiperidine, N-ethylpiperidine, N,N-dimethylaniline, N,N-diethylaniline, etc.

The symmetrical cyanine dyes of formula I are prepared to advantage by heating a mixture of a compound of formula V with diethoxymethyl acetate (forms carbocyanine), trimethoxypropene (forms dicarbocyanine), 1-anilino-5-phenylimino-1,3-pentadiene hydrochloride (forms tricarbocyanine), etc., preferably in a solvent and in the presence of a tertiary amine such as mentioned above.

The unsymmetrical cyanine dyes of formula II when n is are prepared advantageously by heating a mixture of a compound of formula V with a compound of the formula:

VII.

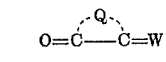


wherein G, R_1, X and Z are as previously defined, g represents a positive integer of from one to two R_4 represents an aryl group of from 6–7 carbon atoms, e.g., phenyl, p-tolyl, etc., and R_5 represents an alkyl group of from 1–12 carbon atoms. This is preferably carried out in a suitable solvent and in the presence of a basic condensing agent. The unsymmetrical cyanine dyes of formula II wherein n is 2 are prepared in generally similar manner from a mixture of a compound of formula VI with formula VII.

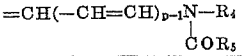
The styryl dyes of formula III are prepared to advantage by heating a mixture of a compound of formula V or formula VI with the appropriate N,N-disubstituted p-aminobenzaldehyde, N,N-disubstituted p-aminocinnamaldehyde, m-nitrobenzaldehyde, etc., preferably in a suitable solvent and in the presence of a basic condensing agent.

The merocyanine dyes of formula IV are made to advantage by heating a mixture of a compound of formula V or formula VI with a compound of the formula:

VIII.



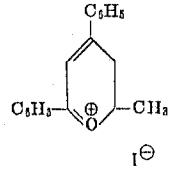
wherein Q is as defined previously and W represents the group



wherein p, R_4, and R_5 are as previously defined.

The preparation of the new photographic silver halide emulsions of our invention and the dyes incorporated in said emulsions is described hereinafter.

EXAMPLE 1—2-METHYL-4,6-DIPHENYLPYRYLIUM IODIDE



Sulfuric acid (30 ml.) was slowly added to acetic anhydride (100 ml.) and the mixture was heated at 70° C. for 2 hours. Acetophenone (30 ml.) and an additional portion of acetic anhydride (15 ml.) were then added and the mixture heated at 50° C. for 24 hours. To the cooled mixture ethanol (200 ml.) was added and the mixture was chilled for 3 hours. The product was collected on the filter and washed with ether.

The sulfoacetate was suspended in water (1,000 ml.) and converted to the iodide by stirring with sodium iodide (20 g.) at 60° C. for 1 hour. The product was collected on the filter and washed with water and then ethanol. The crude yield was 22 g. (53 percent). After one recrystallization from ethanol it melted at 220°–222° C. with decomposition.

The following pyrylium salts were also prepared by the method of above example 1 (characteristics in table 1).

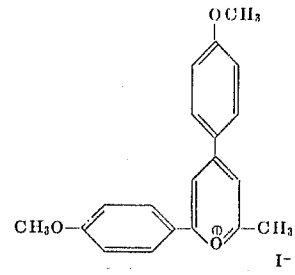
A 4,6-Di-(4-chlorophenyl)-2-methylpyrylium iodide

B 4,6-Di-(3,4-dichlorophenyl)-2-methylpyrylium iodide

TABLE 1

	Yield	Melting Point ° C.	Solvent of recrystallization
A	64%	235–236	ethanol
B	90%	194–195	ethanol

EXAMPLE 2—4,6-DI(4-METHOXYPHENYL)-2-METHYLPYRYLIUM IODIDE



To a mixture of acetic anhydride (50 ml.) and boron-trifluoride ethyl ether (50 ml.), 4-methoxyacetophenone (27 ml.) was added and the mixture heated at 50° C. for 16 hours. The cooled mixture was diluted with ether (200 ml.) and chilled for 2 hours. The product was collected on the filter and washed with ether. The crude yield was 35.6 g. (72 percent).

The fluoborate was suspended in water (1,000 ml.) and converted to the iodide by stirring with sodium iodide (20 g.) at 60° for 1 hour. The product was collected on a filter and washed with water and then alcohol. The crude yield was 33.2 g. Recrystallized from ethanol it melted at 244°–246° C. with decomposition.

The following pyrylium salts were also prepared by the method of above example 2 (characteristics in table 2).

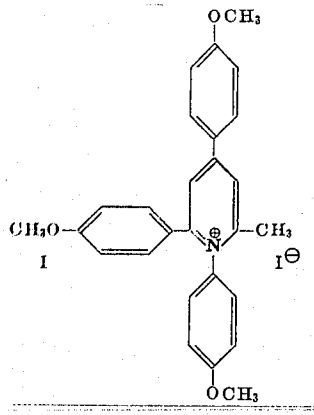
A 4,6-Di-(2,5-dimethoxyphenyl)-2-methylpyrylium fluoborate

B 2-Methyl-4,6-di-2-thienylpyrylium fluoborate

TABLE 2

	Yield	Melting Point ° C.
A	37%	189–190
B	95%	214–215

EXAMPLE 3—1,4,6-TRI(4-METHOXYPHENYL)-2-PICOLINIUM IODIDE



To a stirred suspension of 4,6-di(4-methoxyphenyl)-2-methylpyrylium iodide (10 g.) in benzene (200 ml.) 4-anisidine (5 g.) was added. The mixture was heated under reflux with a water takeoff for 3 hours. To the cooled mixture ether (400 ml.) was added and the product was collected on the filter and washed with ether. The crude yield was 11.4 g. (92 percent). Recrystallized from ethanol it melted at 223-4° C.

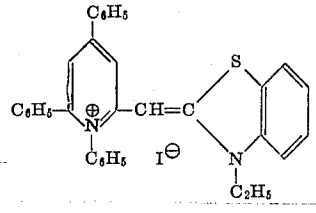
The following picolinium salts were also prepared by the method of above example 3 (characteristics in table 3).

A 1-(2-Hydroxyethyl)-4,6-diphenyl-2-picolinium iodide
B 1-(2-Diethylaminoethyl)-4,6-diphenyl-2-picolinium iodide
C 1-(3-Dimethylaminopropyl)-4,6-diphenyl-2-picolinium iodide
D 1-(Dimethylamino-4,6-diphenyl-2-picolinium iodide
E 1,4,6-Triphenyl-2-picolinium iodide
F 1-(4-Chlorophenyl)-4,6-diphenyl-2-picolinium iodide
G 1-(4-Methylthiophenyl)-4,6-diphenyl-2-picolinium iodide
H 1-(4-Diethylaminophenyl)-4,6-diphenyl-2-picolinium iodide
I 1-(4-Nitrophenyl)-4,6-diphenyl-2-picolinium iodide
J 1,1-Ethylene-bis-(4,6-diphenyl-2-picolinium iodide)
K 1-(3,4-Dichlorophenyl)-4,6-diphenyl-2-picolinium iodide
L 4,6-Di-(4-chlorophenyl)-1-(4-diethylaminophenyl)-2-picolinium iodide
M 4,6-Di-(3,4-dichlorophenyl)-1-(3-dimethylaminopropyl)-2-picolinium iodide

Table 3

	Crude Yield	Melting Point	Recrystallization Solvent
°c.			
A	96%	146–147	186–
B	63%	186–189	Ethanol
C	76%	184–186	Ethanol
D	45%	—	—
E	98%	243–245	Ethanol
F	99%	270–272	Ethanol
G	89%	169–172	Ethanol
H	61%	—	—
I	95%	211–212	Ethanol
J	99%	161–163	Ethanol
K	89%	233–234	Ethanol
L	56%	238–239	Ethanol
M	30%	187–188	Ethanol

EXAMPLE 4—3'-ETHYL-1,4,6-TRIPHENYL-2-PYRIDOTHIACYANINE IODIDE



To a solution of 1,4,6-triphenyl-2-picolinium iodide (1.12 g.) in pyridine (10 ml.) and acetic anhydride (2 ml.) 3-ethyl-2-ethylthiobenzothiazole ethylsulfate (0.92 g.) was added followed by triethylamine (3 ml.). The mixture was heated under reflux for 5 minutes and the dye thrown out with water (300 ml.), collected on the filter and washed with water. After two recrystallizations from ethanol, the yield of dye was 0.85 g. (51 percent). The orange crystals melted at 281°–283° C.

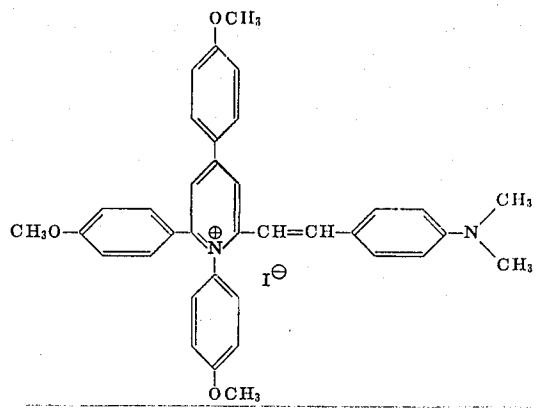
The following cyanines were also prepared by the method of above example 4 (characteristics in table 4).

A 1-(4-Chlorophenyl)-3'-ethyl-4,6-diphenyl-2-pyridothiacyanine iodide
B 3-Ethyl-1-(2-hydroxyethyl)-4,6-diphenyl-2-pyridothiacyanine iodide
C 1-(4-Diethylaminophenyl)-3'-ethyl-4,6-diphenyl-2-pyridothiacyanine iodide
D 1-(3-Diethylaminopropyl)-3'-ethyl-4,6-diphenyl-2-pyridothiacyanine iodide
E 4,6-Di-(3,4-dichlorophenyl)-3'-ethyl-1-(4-phenylazophenyl)-2-pyridothiacyanine iodide
F 1,1-Ethylenebis-(3'-ethyl-4,6-diphenyl-2-pyridothiacyanine iodide)
G 3'-Ethyl-1-(4-nitrophenyl)-4,6-diphenyl-2-pyridothiacyanine iodide

Table 4

	Yield	Melting Point °C.	Recrystallization Solvent
A	62%	263–264	Ethanol
B	31%	221–222	Ethanol
C	22%	292–293	Ethanol
D	14%	217–218	Ethanol
E	9%	>300	Ethanol
F	4%	252–253	Ethanol
G	15%	286–287	Ethanol

EXAMPLE 5—2-(4-DIMETHYLAMINOSTYRYL)-1,4,6-TRT-(4-METHOXYPHENYL)-PYRIDINIUM IODIDE



To a mixture of 1,4,6-tri-(4-methoxyphenyl)-2-picolinium iodide (1.35 g.) and 4-dimethylaminobenzaldehyde (0.41 g.) in ethanol (10 ml.) piperidine (3 ml.) was added and the mixture heated under reflux for 1 hour. The dye was thrown out with water (300 ml.), collected on the filter and washed. After two recrystallizations from ethanol the yield of dye was 0.80 g. (48 percent). The red crystals melted at 209°–211° C.

The following 4-dimethylaminostyrylpyridinium salts were prepared by the method of example 5 (characteristics in table 5).

A 2-(4-Dimethylaminostyryl)-1-(2-hydroxyethyl)-4,6-diphenyl-pyridinium iodide

B 4,6-Di-(4-chlorophenyl)-1-(3-dimethylaminopropyl)-2-(4-dimethylaminostyryl)pyridinium iodide

C 1-(4-Chlorophenyl)-2-(4-dimethylaminostyryl)-4,6-diphenyl-pyridinium iodide

D 4,6-Di-(3,4-dichlorophenyl)-1-(4-diethylaminophenyl)-2-(4-dimethylaminostyryl)pyridinium iodide

E 4,6-Di-(4-chlorophenyl)-2-(4-dimethylaminostyryl)-1-(2—HYDROXYETHYL)pyridinium iodide

F 1,1-Hexamethylene-bis-[2-(4-dimethylaminostyryl)-4,6-diphenyl pyridinium iodide]

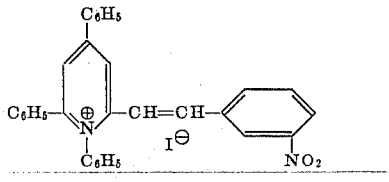
G 2-(4-Dimethylaminostyryl)-1-(2-methyl-6-benzothiazolyl)-4,6-diphenylpyridinium iodide

H 2-(4-Dimethylaminostyryl)-1-(4-nitrophenyl)-4,6-diphenyl pyridinium iodide

Table 5

	Yield	Melting Point	Recrystallization Solvent
A	20%	217–219	Ethanol
B	35%	194–196	Ethanol
C	41%	287–189	Ethanol
D	22%	>300	Ethanol
E	13%	231–232	Ethanol
F	15%	191–192	Ethanol
G	13%	>300	Ethanol
H	8%	>300	Ethanol

EXAMPLE 6—2-(3-NITROSTYRYL)-1,4,6-TRIPHENYLPYRIDINIUM IODIDE



To a mixture of 1,4,6-triphenyl-2-picolinium iodide (1.12 g.) and 3-nitrobenzaldehyde (0.38 g.) in ethanol (10 ml.) piperidine (5 drops) was added and the mixture was heated under reflux for 1 hour when it was chilled for 8 hours and the dye collected on the filter. After two recrystallizations from ethanol the yield was 0.35 g. (24 percent). The pale yellow crystals did not melt below 300° C.

The following nitrostyryl dyes were also prepared by the method of above example 6 (characteristics in table 6).

A 1-(2,4-Dichlorophenyl)-2-(3-nitrostyryl)-4,6-diphenyl pyridinium iodide

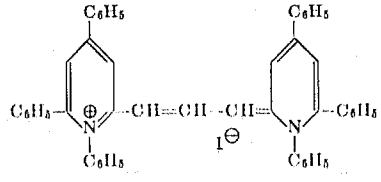
B 2-(4-Nitrostyryl)-4,6-diphenyl-1-(4-phenylazophenyl)-pyridinium iodide

C 4,6-Di-(3,4-dichlorophenyl)-2-(3-nitrostyryl)-1-(4-phenylazophenyl)pyridinium iodide

Table 6

	Yield	Melting Point °C.	Recrystallization Solvent
A	26%	140–141	Ethanol
B	16%	298–299	Ethanol
C	26%	261–262	Ethanol

EXAMPLE 7—1,1',4,4',6,6'-HEXAPHENYL-2,2'-PYRIDOCARBOCYANINE IODIDE



To a mixture of 1,4,6-triphenyl-2-picolinium iodide (2.24 g.) and diethoxymethylacetate (3ml.) in dimethylacetamide (10 mls.) diazbicyclooctane (3 g.) was added and the mixture was heated at 120°–130° for one-half hour. The dye was thrown out with water, collected on the filter and washed. After two recrystallizations from ethanol, the yield of the dye was 0.58 g. (30 percent). The dark brown crystals melted at 283°–284° C.

The following symmetrical carbocyanines were prepared by the method of example 7 (characteristics in table 7).

A 1,1'-Di-(4-chlorophenyl)-4,4',6,6'-tetraphenyl-2,2'-pyridocarbocyanine iodide

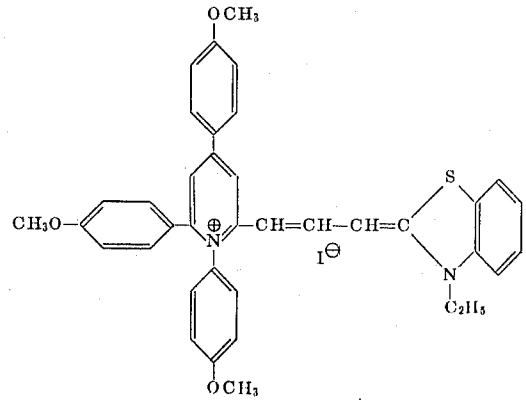
B 1,1'-Di(4-diethylaminophenyl)-4,4',6,6'-tetraphenyl-2,2'-pyridocarbocyanine iodide

C 4,4',6,6'3,4-dichlorophenyl-1,1'-di-(4-phenyl-azophenyl)-2,2'-pyridocarbocyanine iodide

Table 7

	Yield	Melting Point °C.	Recrystallization Solvent
A	11%	273–275	Ethanol
B	13%	>300	Ethanol
C	7%	22–223	Ethanol

EXAMPLE 8—3'-ETHYL-1,4,6-TRI(4-METHOXYPHENYL)-2-PYRIDO-THIACARBOCYANINE IODIDE



To a mixture of 1,4,6-tri-(4-methoxyphenyl)-2-picolinium iodide, and acetic anhydride (2 ml.) in pyridine (10 ml.) 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide (1.13 g.) was added followed by triethylamine (3 ml.). The mixture was heated under reflux for 5 minutes. The dye was thrown out with water, collected on the filter and washed. After two recrystallizations the yield of the dye was 0.86 g. (45 percent). The crystals melted at 259°–260° C.

The following thiacarbocyanines were also prepared by the method of above example 8 (characteristics in table 8).

A 3'-Ethyl-1-(2-hydroxyethyl)-4,6-diphenyl-2-pyridothiacarbocyanine iodide

B 1-(4-Diethylaminophenyl)-3'-ethyl-4,6-diphenyl-2-pyridothiacarbocyanine iodide

C 1-(2-Diethylaminoethyl)-3'-ethyl-4,6-diphenyl-2-pyridothiacarbocyanine iodide

D 1-Dimethylamino-3'-ethyl-4,6-diphenyl-2-pyridothiacarbocyanine iodide

E 1,1-Ethylene-bis-(3'-ethyl-4,6-diphenyl-2-pyridothiacarbocyanine iodide)

F 4,6-Di(3,4-dichlorophenyl)-3'-ethyl-1-(4phenylazophenyl)-2-pyridothiacarbocyanine iodide

Table 8

	Yield	Melting Point °C.	Recrystallization Solvent
A	30%	225–226	Ethanol
B	50%	265–266	Ethanol
C	51%	187–188	Ethanol
D	8%	174–175	Ethanol
D	25%	252–254	Ethanol
F	10%	274–275	Ethanol

The following oxacarbocyanines were also prepared following the method above of example 8 from the corresponding picolinium salts and 2-β-acetanilidovinyl-3-ethylbenzoxazole iodide (1.09 g.) (characteristics in table 9).

A–1 3-Ethyl-1′,4′,6′-tri-(4-methoxyphenyl)-oxa-2′-pyridocarbocyanine iodide

B–1 1′-Dimethylamino-3-ethyl-4′,6′-diphenyl-oxa-2′-pyridocarbocyanine iodide

C–1 1′-(4-Diethylaminophenyl)-3-ethyl-4′,6′-diphenyl-oxa-2′-pyridocarbocyanine iodide

D–1 1′-(3-Dimethylaminopropyl)-3-ethyl-4′,6′-diphenyl-oxa-2′-pyridocarbocyanine iodide

Table 9

	Yield	Melting Point °C.	Recrystallization Solvent
A–1	21%	269–270	Ethanol
B–1	3%	188–189	Methanol/ethyl acetate
C–1	35%	249–250	Ethanol
D–1	34%	168–170	Ethanol

The following benzothiacarbocyanines were also prepared following the method of above example 8 from the corresponding picolinium salts and 2-β-anilinovinyl-1-ethyl-β-naphthothiazolium-p-toluenesulfonate (characteristics in table 10).

A–2 1-(2-Diethylaminoethyl)-3′-ethyl-4,6-diphenyl-4′,5′-benzo-2-pyridothiacarbocyanine iodide

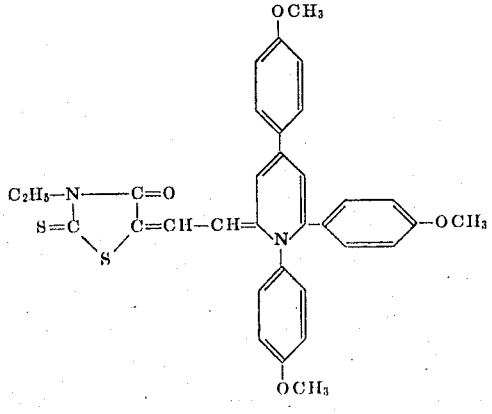
B–2 1-(4-Diethylaminophenyl)-3′-ethyl-4,6-diphenyl-4′,5′-benzo-2-pyridocarbocyanine iodide

C–2 3′-Ethyl-1,4,6-tri-(4-methoxyphenyl)-4′,5′-benzo-2-pyridothiacarbocyanine iodide

Table 10

	Yield	Melting Point °C.	Recrystallization Solvent
A–2	63%	172–174	Methanol
B–2	32%	220–222	Methanol
C–2	41%	245–246	Ethanol

EXAMPLE 9—3-ETHYL-5-{[1,4,6-TRI(4-METHOXYPHENOL)-2(1H)-PYRIDYLIDENE]-ETHYLIDENE}RHODANINE



To a mixture of 1,4,6-tri-(4-methoxyphenyl)-2-picolinium iodide (1.35 g.) 5-acetanilidomethylene-3-ethylrhodanine (0.77 g.) in pyridine (10 ml.), acetic anhydride (3 ml.) and triethylamine (4 ml.) were added and the mixture was refluxed for one-half hours. The dye was thrown out with water and collected on the filter. After two recrystallizations from ethanol, the yield of the dye was 0.20 g. (14 percent). The dark crystals melted at 196°–197° C.

The following merocarbocyanines were also prepared following the method of example 9 (characteristics in table 11).

A 5-{]1-(2-Diethylaminoethyl)-4,6-diphenyl-2(1H)-pyridyli-dene]ethylidene}-3-ethylrhodanine

B 5-{[4,6-Di-(3,4-dichlorophenyl)-1-(4-phenylazophenyl)-2(1H)-pyridylidene]ethylidene}-3-ethylrhodanine

C 3-Ethyl-5-{[1-(4-nitrophenyl)-4,6-diphenyl-2(1H)-pyridyl-idene]-ethylidene}rhodanine

D N,N-Ethylene-bis-(3-ethyl-5-[(4,6-diphenyl-2(1H)-pyridyl-idene)ethylidene]rhodanine

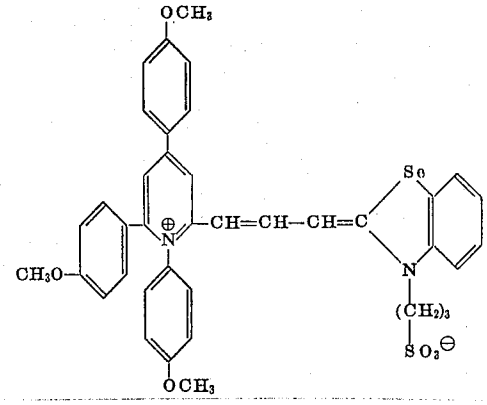
Table 11

	Yield	Melting Point °C.	Recrystallization Solvent
A	24% 24%	133–134	Methanol
B	22%	277–278	Dimethylacetamide
C	15%	208–210	Methanol
D	24%	159–160	Dimethylacetamine

In place of the 5-acetanilidomethylene-3-ethylrhodanine in the above example there may be substituted any other corresponding quaternary salts defined herein by symbol Q to give the corresponding merocyanine dye compounds having similar photographic utility.

EXAMPLE 10

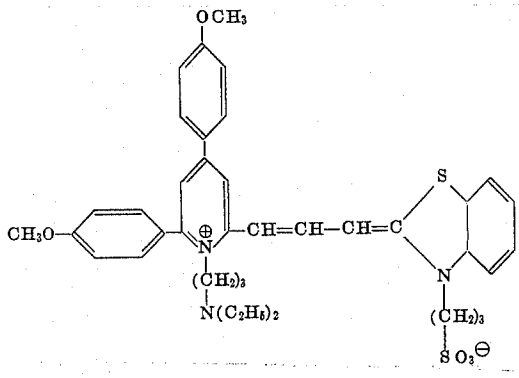
Anhydro-1,4,6-tris-(4-methoxyphenyl)-3′-(3-sulfopropyl)-2-pyridoselenacarbocyanine hydroxide



A mixture of 1,4,6-tris(4-methoxyphenyl)-2-picolinium iodide (1.8 g.), anhydro-2-β-acetanilidovinyl-3-(3′-sulfopropyl) benzoselenazolium hydroxide (1.4 g.), acetic anhydride (5 ml.) and triethylamine (8 ml.) in pyridine (10 ml.) was heated under reflux for 5 minutes, allowed to cool and poured over ether (400 ml.) The dye was collected on the filter, washed and recrystallized twice from ethanol. Yield, 36 percent; m.p., 237.9° C.

EXAMPLE 11

Anhydro-1-(3-diethylaminopropyl)-4,6-bis(4-methoxyphenyl)-3′-(3-sulfopropyl)-2-pyridothiacarbocyanine hydroxide



A mixture of 1-(3-diethylaminopropyl)-4,6-bis(4-methoxyphenyl)-2-picolinium iodide (2.7 g.), anhydro-2-β-acetanilidovinyl-3-(3sulfopropyl)-benzothiazolium hydroxide (2.1 g.), acetic anhydride (3 ml.) and triethylamine (5 ml.) in pyridine (15 ml.) was heated under reflux for 10 minutes, allowed to cool and poured over ether (400 ml.). The dye was collected by filtration, washed and recrystallized twice from ethanol. Yield, 6 percent; m.p. 220°–230° C.

EXAMPLE 12

This example illustrates the increase in sensitivity produced in photographic silver halide emulsions by a number of the preferred dyes used in preparing the emulsions of the invention.

The dyes were tested in a silver bromoiodide emulsion containing 0.77 mole percent iodide of the type described by Trivelli and Smith, *Phot. Journal*, 79, 330 (1939). The dyes, dissolved in suitable solvents, were added to separate portions of the emulsions at the concentrations indicated. The emulsions were then coated at a coverage of 432 mg. silver/ft.^{2} on a cellulose acetate film support. A sample of each coating was exposed on an Eastman IB Sensitometer and to a wedge spectrograph, processed for 3 minutes in a developer of the following composition:

DEVELOPER

N-methyl-p-aminophenol sulfate	2.0 g.
Sodium sulfite (anhydrous)	90.0 g.
Hydroquinone	8.0 g.
Sodium carbonate (monohydrate)	52.5 g.
Potassium bromide	5.0 g.
Water to make	1.0 l.

and then fixed, washed and dried. The sensitizing values obtained are shown in the following table 12.

TABLE 12.—PHOTOGRAPHIC SENSITIZING DATA

Dye of Ex. No.	Dye concentration (g.) mol. silver	Emulsion type	Sensitizing range (mu)	Sensitizing max. (mu)
4	0.04	Bromoiodide	to 570	530
4A	0.08	do	to 570	530
4B	0.07	do	to 570	525
4C	0.08	do	to 578	530
4D	0.08	do	to 560	525
4F	0.08	do	to 560	525
5	0.10	do	to 640	575
5A	0.07	do	to 630	575
5B	0.09	do	to 640	580
5C	0.08	do	to 630	580
5D	0.10	do	to 650	580
5E	0.07	do	to 660	575
5F	0.04	do	to 640	580
5G	0.08	do	to 650	575
7	0.17	do	550–720	670
7A	0.18	do	550–720	675
7B	0.20	do	580–710	675
8	0.00	do	to 710	620
8A	0.07	do	to 700	620
8B	0.05	do	to 710	620
8C	0.07	do	to 650	600
8D	0.04	do	to 670	625
8E	0.10	do	to 680	630
8A-1	0.08	do	to 670	585
8B-1	0.04	do	to 660	585
8C-1	0.05	do	to 660	590
8D-1	0.04	do	to 660	585
8A-2	0.03	do	to 710	650
8B-2	0.04	do	to 720	650
8C-2	0.09	do	to 720	650
9	0.09	do	to 700	630
9A	0.07	do	to 690	630
9D	0.07	do	to 690	630
10	.08	do	to 710	600
11	.08	do	to 700	600

For certain applications in modern color photography, sensitizing maxima in the 595 mμ to 615 mμ range are required. The dyes of examples 8C, 10 and 11 have a sensitizing maxima within the range just mentioned.

In the preparation of the photographic emulsions of the invention, the dyes are advantageously incorporated in the washed, finished silver halide emulsion and should, of course, be uniformly distributed throughout the emulsion. The methods of incorporating dyes in emulsions are relatively simple and well known to those skilled in the art of emulsion making. For example, it is convenient to add the dyes from solutions in appropriate solvents, in which case the solvent selected should be completely free from any deleterious effect on the ultimate light-sensitive materials. Methanol, isopropanol, pyridine, etc., alone or in admixtures, have proven satisfactory as solvents for the majority of the dyes. The type of silver halide emulsions that can be sensitized with the dyes include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides, for example, emulsions comprising natural materials such as gelatin, albumin, agar-agar, gum arabic, alginic acid, etc., and hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, and the like.

The concentration of the dyes in the emulsion can vary widely, i.e., from about 5 to 100 mg. per liter of flowable emulsion. The specific concentration will vary according to the type of light-sensitive material in the emulsion and according to the effects desired. The suitable and most economical concentration for any given emulsion will be apparent to those skilled in the art upon making the tests and observations customarily used in the art of emulsion making.

To prepare a gelatino-silver halide emulsion with one of my new dyes, the following procedure is satisfactory: A quantity of the dye is dissolved in a suitable solvent and a volume of this solution containing from 5 to 100 mg. of dye is slowly added to about 1,000 cc. of a gelatino-silver halide emulsion. With most of the dyes, 10 to 20 mg. of dye per liter of emulsion suffice to produce the maximum sensitizing or desensitizing effect with the ordinary gelatino-silver halides including silver chloride, bromide, bromoiodide, chlorobromide, chlorobromoiodide, etc., emulsions. With fine-grain emulsions, which include most of the ordinary employed gelatino-silver chloride emulsions and the like, somewhat larger concentrations of dye may be necessary to secure optimum sensitizing or desensitizing effect. While the preceding has dealt with emulsions comprising gelatin, it will be understood that these remarks apply generally to any emulsions wherein part or all of the gelatin is substituted by another suitable hydrophilic colloid such as mentioned above. One or more dyes can be in the emulsion.

The above statements are only illustrative and are not to be understood as limiting our invention in any sense, as it will be apparent that the dyes can be incorporated by other methods in many of the photographic silver halide emulsions customarily employed in the art. For instance, the dyes can be incorporated by bathing a plate or film upon which an emulsion has been coated, in the solution of the dye in an appropriate solvent. Bathing methods, however, are not to be preferred ordinarily.

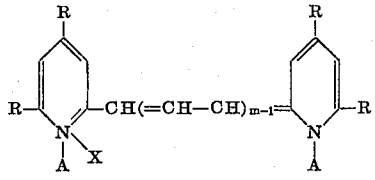
Photographic silver halide emulsions such as those listed

above, containing the dyes described herein can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers, (e.g., allyl thiocarbamide, thiourea, allylisothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see U.S. Pat. to W. D. Baldsiefen No. 2,540,085, granted Feb. 6, 1951; R. E. Damschroder No. 2,597,856, granted May 27, 1952, and H. C. Yutzy et al. No. 2,597,915, granted May 27, 1952), various palladium compounds, such as palladium chloride (W. D. Baldsiefen U.S. Pat. No. 2,540,086, granted Feb. 6, 1951), potassium chloropalladate (R. E. Stauffer et al. U.S. Pat. No. 2,598,079, granted May 27, 1952), etc., or mixture of such sensitizers; antifoggants, such as ammonium chloroplatinate (A. P. H. Trivelli et al. U.S. Pat. No. 2,566,245, granted Aug. 28, 1951), ammonium chloroplatinite (A. P. H. Trivelli et al. U.S. Pat No. 2,566,263, granted Aug. 28, 1951), benzotriazole, nitrobenzimidazole, 5-nitroindazole, benzidine, mercaptans, etc., (see Mees, "The Theory of the Photographic Process," MacMillan Pub., 1942, page 460), or mixtures thereof; hardeners, such as formaldehyde (A. Miller U.S. Pat. No. 1,763,533, granted June 10, 1930), chrome alum (U.S. Pat. No. 1,763,533), glyoxal (J. Brunken U.S. Pat No. 1,870,354, granted Aug. 9, 1932), dibromacrolein (O. Block et al. British Pat. No. 406,750, accepted Mar. 8, 1934), etc.; color couplers, such as those described in I. F. Salminen et al., U.S. Pat. No. 2,423,730 granted July 7, 1947, Spence and Carroll U.S. Pat. No. 2,640,776, issued June 2, 1953, etc.; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in U.S. Patents to E. E. Jelley et al. No. 2,322,027, granted June 15, 1943, and L. D. Mannes et al. No. 2,304,940, granted Dec. 15, 1942, can also be employed in the photographic emulsions of our invention.

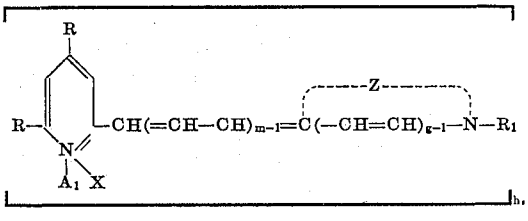
We claim:

1. A photographic silver halide emulsion containing a methine dye selected from those represented by the following formulas:

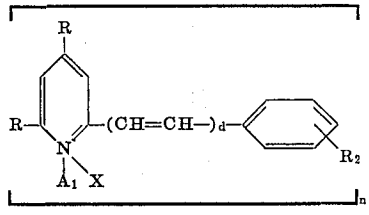
I.



II.

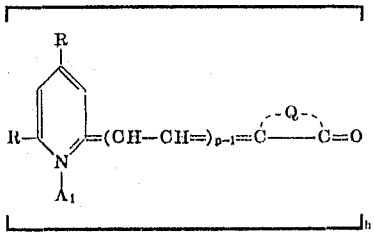


III.

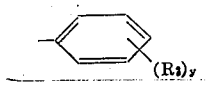


and

IV.



wherein R represents a member selected from the group consisting of phenyl, alkylphenyl, alkoxyphenyl, halogen substituted phenyl and nitrophenyl, R_1 represents a member selected from the group consisting of an alkyl group, allyl, a sulfoalkyl group, a hydroxyalkyl group, an alkoxyalkyl group, a carboxyalkyl group, an alkanoyloxyalkyl group, an alkoxycarbonylalkyl group, an aralkyl group or an aryl group, R_2 represents a member selected from the group consisting of a dialkylamino group and a nitro group, X represents an acid anion, A represents a member selected from the group consisting of a hydroxyalkyl group, a dialkylamino group, a dialkylaminoalkyl group and the group



wherein *y* represents a positive integer of from 1 to 2 and R_3 represents a member selected from the group consisting of a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom, a dialkylamino group, a nitro group, a phenylazo group, an alkylthio group, a 2-methyl-5(or 6)-benzothiazolyl group, a 2-methyl-5(or 6)-benzoxazolyl group and a 2-methyl-5(or 6)-benzimidazolyl group, A_1 represents a member selected from A when *n* is 1, and a divalent alkylene group when *n* is 2, Z represents the nonmetallic atoms required to complete a heterocyclic nucleus selected from the group consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thionaphtheno-7', 6', 4, 5-thiazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a thiazoline nucleus, a 2-pyridine nucleus, a 4-pyridine nucleus, a 2-quinoline nucleus, a 4-quinoline nucleus, a 1-isoquinoline nucleus, a 3-isoquinoline nucleus, a 3,3 -dialkylindolenine nucleus, an imidazole nucleus, a benzimidazole nucleus, and a naphthimidazole nucleus, and Q represents the nonmetallic atoms required to complete a heterocyclic nucleus selected from the group consisting of a 2-pyrazolin-5-one nucleus, an isoxazolone nucleus, an oxindole nucleus, a 2,4,6-triketohexahydropyrimidine nucleus, a rhodanine nucleus, a 2(3H)-imidazo[1,2-a]pyridone nucleus, a 5,7-dioxo-6,7-dihydro5-thiazolo[3,2-a] pyrimidine nucleus, a 2-thio-2,4-oxazolidinedione nucleus, a thianaphthenone nucleus, a 2-thio-2,5-thiazolidinedione nucleus, a 2,4-thiazolidinedione nucleus, a thiazolidinone nucleus, a 2-thiazolin-4-one nucleus, a 2-imino-4-oxazolidinone nucleus, a 2,4-imidazolidinedione nucleus, a 2-thio-2,4-imidazolidinedione nucleus and a 2-imidazolin-5-one nucleus.

2. A photographic silver halide emulsion in accordance with claim 1 wherein the methine dye has the formula numbered I.

3. A photographic silver halide emulsion in accordance with claim 1 wherein the methine dye has the formula numbered II.

4. A photographic silver halide emulsion in accordance with claim 1 wherein the methine dye has the formula numbered III.

5. A photographic silver halide emulsion in accordance with claim 1 wherein the methine dye has the formula numbered IV.

6. A photographic silver halide emulsion in accordance with claim 1 containing the dye 3'-ethyl-1,4,6-triphenyl-2-pyridothiacarbocyanine iodide.

7. A photographic silver halide emulsion in accordance with claim 1 containing the dye 2-(4-dimethylaminostyryl)-1,4,6-tri-(4-methoxyphenyl)pyridinium iodide.

8. A photographic silver halide emulsion in accordance with claim 1 containing the dye 2-(3-nitrostyryl)-1,4,6-triphenylpyridinium iodide.

9. A photographic silver halide emulsion in accordance with claim 1 containing the dye 1,1',4,4'6,6'-hexaphenyl-2,2'-pyridocarbocyanine iodide.

10. A photographic silver halide emulsion in accordance with claim 1 containing the dye 3'-ethyl-1,4,6-tri(4-methoxyphenyl)-2-pyridothiacarbocyanine iodide.

11. A photographic silver halide emulsion in accordance

with claim 1 containing the dye 1,1-ethylene-bis-(3'-ethyl-4,6-diphenyl-2-pyridothiacarbocyanine iodide).

12. A photographic silver halide emulsion in accordance with claim 1 containing the dye 1-(4-diethylaminophenyl)-3'-ethyl-4,6-diphenyl-4',5'-benzo-2-pyridocarbocyanine iodide.

13. A photographic silver halide emulsion in accordance with claim 1 containing the dye 3-ethyl-5-{[1,4,6-tri-(4-methoxyphenyl)-2(1H)-pyridylidene]-ethylidine}rhodanine.

14. A photographic silver halide emulsion in accordance with claim 1 containing the dye 1,1-hexamethylene-bis-[2-(4-dimethylaminostyryl)-4,6-diphenylpyridinium iodide].

15. A photographic element comprising a support having coated thereon at least one layer containing a photographic silver halide emulsion of claim 1.

16. A photographic element comprising a support having coated thereon at least one layer containing a photographic silver halide emulsion of claim 2.

17. A photographic element comprising a support having coated thereon at least one layer containing a photographic silver halide emulsion of claim 3.

18. A photographic element comprising a support having coated thereon at least one layer containing a photographic silver halide emulsion of claim 4.

19. A photographic element comprising a support having coated thereon at least one layer containing a photographic silver halide emulsion of claim 5.

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