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SILVER HALIDE EMULSIONS CONTAINING SUPERSENSITIZING
CYANINE DYE COMBINATIONS
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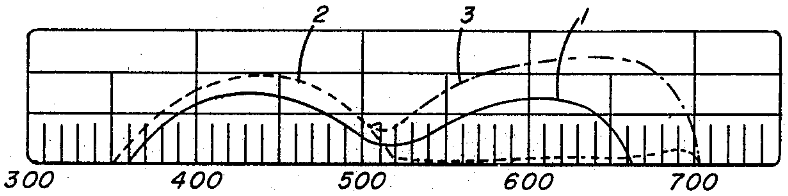

1. DYE II – 3, 3'-DIETHYL–1, 1'–DIPHENYL–1H–IMIDAZOLO [4,5-b] QUINOCARBOCYANINE IODIDE
2. DYE D–5–[DI (1–ETHYL–2 (1H)–NAPHTHO [1,2-d] THIAZOLYLIDENE) ISOPROPYLIDENE] –2,2–DIMETHYL–1,3–DIOXANE–4,6–DIONE
3. DYE II + DYE D

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SILVER HALIDE EMULSIONS CONTAINING SUPERSENSITIZING CYANINE DYE COMBINATIONS

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U.S. Cl. 96—104 38 Claims

ABSTRACT OF THE DISCLOSURE

Silver halide emulsions have been supersensitized with combinations of certain imidazolo[4,5-b]quinoline carbocyanine and holopolar carbocyanine dyes.

This invention relates to new supersensitizing combinations for photographic silver halide emulsions comprising (1) certain imidazolo[4,5-b]quinoline carbocyanine and (2) holopolar carbocyanine dyes, and more particularly to novel photographic silver halide emulsions sensitized with these supersensitizing combinations and to photographic elements prepared therewith.

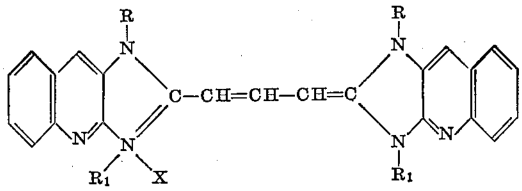
It is well known in the art of making photographic emulsions that certain dyes of the cyanine class extend the sensitivity of photographic emulsions of the gelatino-silver halide kind, when the dyes are incorporated in the emulsions. It is well known that certain cyanine dyes in combination alter the sensitivity of photographic silver halide emulsions even more advantageously for certain applications than do the individual dyes in such emulsions. However, there is still needed in the art for new supersensitizing combinations comprising cyanine dyes.

I have now found a new and advantageous supersensitizing combination for sensitizing photographic silver halide emulsions comprising certain imidazolo[4,5-b]quinoline carbocyanine and holopolar carbocyanine dyes. The new dye combinations are compatible with the emulsions giving clear layers with excellent keeping stability and causing relatively little, if any, fogging in both fresh and incubated condition.

It is, therefore, an object of the invention to provide new supersensitizing combinations of certain cyanine dyes for sensitizing photographic emulsions. Another object is to provide novel photographic silver halide emulsions containing such supersensitizing combinations and photographic elements prepared therewith. Other objects will become apparent from a consideration of the general description and examples, and the appended claims.

The imidazolo[4,5-b]quinoline carbocyanine dyes useful in practicing my invention include those dyes represented by the following general formula:

(I)

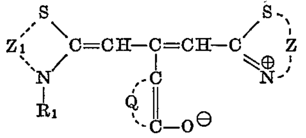


wherein R represents an alkyl group, preferably a lower alkyl containing from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl, dodecyl, etc.,

or an aryl group, e.g., phenyl, tolyl, xylyl, etc., R_1 represents an alkl group, preferably a lower alkyl containing from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl, dodecyl, etc., or a sulfoalkyl group, e.g., β-sulfoethyl, γ-sulfopropyl, ω-sulfobutyl, etc., and X represents an acid anion, e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, p-toluenesulfonate, methyl sulfate, ethyl sulfate, etc.

The holopolar carbocyanine dyes useful in practicing my invention include those dyes represented by the following general formula:

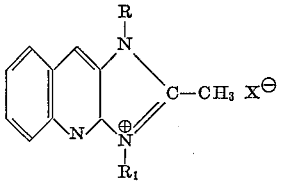
(II)



wherein R_1 is as previously defined, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus such as a barbituric acid nuleus, a 5(4H)-isoxazolone nucleus, a 2,4-chromandione nucleus, a 4,6-(1H, 5H)-pyrimidinedione nucleus, a 1,3-dioxane-4,6-dione nucleus, of a 3H-naphthol[2,1-b]pyran-1,3-(2H)-dione nucleus, and Z_1 and Z_2 each represents the non-metallic atoms necessary to complete the heterocyclic nucleus such as a naphthol[1,2-d]thiazole nucleus, a naphtho[2,1-d]thiazole nucleus, or a 4,5-dihydronaphtho[1,2-d]-thiazole nucleus.

The cyanine dyes of Formula I above of the invention are conveniently prepared by heating a mixture of a compound of the formula:

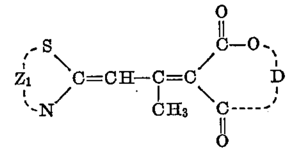
(III)



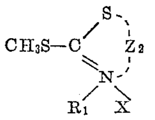
wherein R, R_1 and X are as previously defined, with diethoxymethyl acetate, preferably in a suitable inert solvent and in the presence of a basic condensing agent. For further details, reference can be had to copending application of Jenkins and Brooker, Ser. No. 286,450, filed June 10, 1963, now U.S. Patent 3,326,688 wherein the preparation of dye compounds of Formula I are described.

The holopolar carbocyanine dyes of the invention defined by Formula II above can be prepared by various methods. For example, the dyes containing the barbituric acid nucleus or the 5(4H)-isoxazolone nucleus (such as Dyes A, E, F and G herein) are well known and can be prepared in accordance with methods described in Brooker et al., U.S. Reissue Patent No. 24,292, dated Mar. 19, 1957. The dyes containing the 2,4-chromandione nucleus, or the 3H-naphtho[2,1-b]pyran-1,3(2H)-dione nucleus, are prepared by reacting approximately equimolar proportions of an intermediate compound of the formula:

IV



with a compound of the formula:



wherein R_1, X, Z_1 and Z_2 are as previously defined, and D represents the non-metallic atoms necessary to complete a 2,4-chromandione nucleus or a 3H-naphtho[2,1-b]pyran-1,3(2H)-dione nucleus. To illustrate, 3-[di-(1-ethyl - 2(1H)naphtho[1,2-d]thiazolylidene)isopropylidene]-2,4-chromandione (Dye B herein was prepared as follows:

3-[(1-ethylnaphtho[1,2-d]thiazolin - 2-ylidene - 2-isopropylidene]-2,4-chromandione (4.13 g., 0.01 moles), 1-ethyl - 2-methylthionaphtho[1,2-d]thiazolium p-toluenesulfonate (4.31 g., 0.01 mole), acetic anhydride (20 ml.) and triethylamine (5 ml.) were mixed together and heated with stirring at refluxing temperature for 25 min. and then chilled. The solid dye which formed was removed by filtration and dried. The yield of crude dye was 2.80 g. (45%).

The dye was purified by dissolving it in warm cresol, filtering the solution and diluting the filtrate with 3 volumes of methanol to bring about recrystallization. The yield of dye after two such purifications was 1.00 g. (16%), M.P. 327–328 degrees dec.

The intermediate compound of Formula IV in the above reaction, 3-[(1-ethylnaphtho[1,2-d]-thiazolin - 2-ylidene) - 2-isopropylidene]2,4-chromandione, was prepared in the following manner:

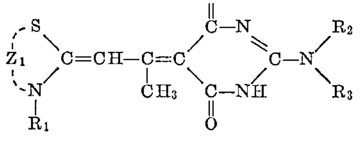
1-ethyl - 2-methylnaphtho[1,2-d]thiazolium p-toluenesulfonate (4.0 g., 0.01 mole), 4-hydroxycoumarin (1.62 g., 0.01 mole), pyridine (20 ml.) and triethylorthoacetate (10 ml.) were mixed together and heated at refluxing temperatures for one hour. After chilling, the reaction mixture was filtered to remove the solid dye that had precipitated. The dye was washed with a little methanol and dried. The yield of crude dye was 3.0 g. (73%).

The dye was purified by dissolving it in boiling pyridine, filtering the solution, diluting it with two volumes of methanol to recrystallize the dye and chilling it. The yield after two such recrystallizations was 0.9 g. (22%), M.P. 237–238 degrees C. dec.

It will be apparent from the foregoing that any other of the dye compounds coming under Formula II containing the 2,4-chromandione nucleus or the 3H-naphtho[2,1-b]pyran-1,3-(2H)-dione nucleus can be prepared in generally similar manner by appropriate selection of intermediates defined by above Formulas IV and V. For example, the dye 2-{bis[(3-ethyl-2-benzothiazolinylidene)methyl]methylene} - 3H-naphtho[2,1-b]pyran-1,3-(2H)-dione can be prepared in above manner by reacting 2-[(3-ethyl - 2-benzothiazolinylidene) - 1-methylethylidene]-3H-naphtho-[2,1-b]pyran - 1,3(2H)-dione with 3-ethyl-2-ethylthiobenzothiazolium ethosulfate. Reference can be had for further details to copending application of Holtzclaw et al., Ser. No. 603,786, filed Dec. 22, 1966, now U.S. Patent 3,440,053, wherein such holopolar carbocyanine dyes are described and claimed.

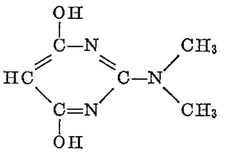
For the preparation of holopolar carbocyanine dyes of Formula II above containing the 4,6-pyrimidinedione nucleus, a compound of the formula:

VI



wherein R_1 and Z_1 are as previously defined, and R_2 and R_3 each represents a lower alkyl group (e.g., methyl, ethyl, etc.) is reacted with a compound of Formula V above following the procedure described above for the preparation of the dyes containing the 2,4-chromandione nucleus. Thus, for example, 2-dimethylamino - 5-[di(1-ethyl - 2(1H)-naphtho[1,2 - d]thiazolydiene)-isopropylidene] - 4,6(1H, 5H) - pyrimidinedione M.P. 222-224 degrees C. (Dye C herein) was prepared from 2-dimethyl - 5 - [1 - ethyl - 2(1H)-naphthol[1,2-d]thiazolylidine)isopropylidene] - 4,6(1H, 5H)-pyrimidinedione and 1-ethyl - 2-methylthionaphtho - [1,2-d]thiazolium p-toluenesulfonate.

The intermediate of Formula VI in the above reaction was prepared in similar manner to that described above for the preparation of the dyes containing the 2,4-chromandione nucleus, i.e., by reacting 1-ethyl - 2-methylnaphtho[1,2-d]thiazolium p-toluenesulfonate with 2-dimethylamino-4,6-pyrimidinediol of the formula:



The above diol was prepared in the following manner:

1,1-dimethylguanidine sulfate (182 g., 1 mol) was added to a solution of sodium methoxides in methanol (15 g. sodium in 300 ml. methanol). After heating under reflux for thirty minutes, diethyl malonate (106 g., 1 mol) was added and the mixture refluxed for sixteen hours. After cooling, the mixture was diluted with 450 ml. of water and acidified with acetic acid. The solid was collected by filtration and dried. Yield of product 63.2 g. (61%), M.P.>310 degrees C.

By appropriate selection of intermediates defined by Formulas V and VI, it will be apparent that any other of the dye compounds of Formula II containing the 4,6-pyrimidinedione nucleus can be readily prepared by the foregoing procedures.

To prepare the holopolar carbocyanine dyes of Formula II above containing the 1,3-dioxane-4,6-dione nucleus, such as Dye D herein, a convenient method comprises reacting a 1-alkyl-2-alkylmercaptonaphtho[1,2 - d]thiazolium quaternary salt was a 5-(1-alkylnaphtho[1,2-d]thiazolin-2-ylidene)isopropylidene - 2,2 - dialkyl-1,3-dioxane-4,6-dione, in pyridine, in the presence of a nitrogen base such as triethylamine. Further details of their preparation can be had by reference to copending application of Donald W. Heseltine, Ser. No. 463,024, filed June 10, 1965, now U.S. Patent 3,440,052 wherein such holopolar carbocyanine dyes are described and claimed.

Included among the dyes of Formula II above are the following typical dye compounds.

Dye No.:	Compound
I	3,3' - dimethyl - 1,1' - diphenyl - 1H - imidazolo[4,5 - b]-quinocarbocyanine iodide.
II	3,3' - diethyl - 1,1' - diphenyl - 1H - imidazolo[4,5 - b]-quinocarbocyanine iodide.
III	Anhydro - 1,1' - diphenyl - 3,3' - di(4 - sulfobuytl) - 1H - imidazolo[4,5 - b] quinocarbocyanine hydroxide monosodium salt.
IV	1,1',3,3'-tetraethyl - 1H - imidazolo[4,5-b]quinocarbocyanine iodide.

Included among the dyes of Formula II above are the following typical dye compounds.

Dye No.:	Compound
A	5 - [di(1 - ethyl - 2(1H) - β - naphthothiazolylidene)isopropylidene] - 1,3 - di(β - methoxyethyl)barbituric acid.
B	3 - [di(1 - ethyl - 2(1H) - naphtho[1,2 - d]thiazolylidene)isopropylidene]-2,4 - chromandione.
C	2 - dimethylamino - 5 - [di(1 - ethyl - 2 (1H) - naphtho[1,2-d]thiazolylidene) isopropylidene] - 4,6 - (1H,5H) - pyrimidinedione.
D	5 - [di(1 - ethyl - 2(1H) - naphtho[1,2 - d]thiazolylidene)isopropylidene]-2,2 - dimethyl - 1,3 - diozane - 4,6 - dione.
E	1,3 - diethyl - 5 - [(1 - ethyl - 4,5 - dihydro - 2(1H) - naphtho[1,2 - d]thiazolylidene) (1 - methyl - 2(1H) - naphtho[1,2 - d]thiazoyidene)isopropylidene]barbituric acid.
F	1,3 - diethyl - 5 - [(1 - ethyl - 4,5 - dihydro - 2(1H) - naphtho[1,2 - d] thiazolylidene) (3 - ethyl - 2(3H) - naphtho[2,1 - d]thiazolylidene)isopropylidene]barbituric acid.
G	4-[di(1-ethyl-2(1H) - β - naphthothiazolylidene)isopropylidene]3 - phenyl-5(4H)-isoxazolone.

According to my invention I incorporate one or more of the dyes represented by Formula I above with one or more of the holopolar carbocyanine dyes represented by Formula II above. My invention is particularly directed to the ordinarily employed gelatino-silver-halide developing-out emulsions. However, my supersensitizing combinations can be employed in silver halide emulsions in which the carrier or vehicle is a hydrophilic colloid other than gelatin, such as, for example, albumin, agaragar, gum arabic, alginic acid, etc., or a hydrophilic resin such as polyvinyl alcohol, polyvinyl pyrrolidone, a cellulose ether, a partially hydrolyzed cellulose acetate, etc., which has no deleterious effect upon the light-sensitive silver halide. The dyes of Formula I and Formula II can be employed in the combinations of the invention in various concentrations depending upon the particular emulsion, concentration of the silver halide, particular results desired, etc. The optimum concentration of an individual sensitizing dye can be determined in a manner well known to those skilled in the art by measuring the sensitivity of a series of test portions of the same emulsion, each portion containing a different concentration of the sensitizing dye. The optimum concentration of my supersensitizing combinations can, of course, be readily determined in the same manner, by measuring the sensitivity of a series of test portions of the same emulsion, each portion containing different concentrations of the individual dyes in the combination. In determining the optimum concentration for the supersensitizing combination, it is advantageous to employ, at first, concentrations of the individual dyes less than their optimum concentrations. The concentrations of the individual dyes can then be increased until the optimum concentration of the supersensitizing combination is determined.

The methods of incorporating sensitizing dyes in silver halide emulsions are well known to those skilled in the art and these known techniques are employed in dispersing the dyes of our invention in the emulsions. These sensitizing dyes can be directly dispersed in the emulsions, or they can first be dissolved in some convenient solvent, such as pyridine, methyl alcohol, acetone, etc. (or mixtures of such solvents), or diluted with water in some instances, and added to the emulsions in the form of these solutions. If desired, the dyes can be separately dissolved in a given solvent and added separately to the emulsion, or they can be dissolved in the same or different solvent and these solutions mixed together before addition is made to the silver halide emulsions. The dyes of the invention can be dispersed in the finished emulsions and should be uniformly distributed throughout the emulsions before the emulsions are coated on a suitable support, such as paper, glass, cellulose ester film, polyvinyl resin film (e.g., polystyrene film, polyvinyl chloride film, etc.), polyester film, etc. The following procedure has been found quite satisfactory: Stock solutions of the dyes of Formulas I and II above are prepared by separately dissolving these dyes in appropriate solvents as described above. Then, to the flowable silver halide emulsion, the desired amount of stock solution of one of the dyes is slowly added while stirring the emulsion. Stirring is continued until the dye is thoroughly incorporated in the emulsion. Then, the desired amount of stock solution of the other dye is slowly added to the emulsion while stirring. Stirring is continued until the second dye is thoroughly incorporated in the emulsion. The supersensitized emulsions can then be coated on a suitable support and the coating allowed to dry. In some instances, it may be desirable to heat the supersensitized emulsion for a few minutes before coating onto the suitable support. The details of such coating techniques are well known to those skilled in the art. The foregoing procedure and proportions are to be regarded only as illustrative. Clearly, my invention is directed to any silver halide emulsion containing a combination of the aforesaid dyes whereby a supersensitizing effect is obtained.

My invention is primarily directed to the ordinary employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloroiodide, -chlorobromiodide, -bromide and -bromiodide developing-out emulsions. Emulsions which form the latent image mostly inside the silver halide grains, such as the emulsions set forth in Knott et al. U.S. Patent 2,456,956, dated Dec. 21, 1948, can also be employed in practicing my invention.

The following examples will serve to illustrate further the manner of practicing my invention. To different portions of the same batch of melted photographic gelatino-silver bromoiodide emulsion, containing 0.77 mole percent iodide, of the type described by Trivelli and Smith, Phot. Journal, 79, 330 (1939) were added a solution of each of the dye sensitizers I to IV and A to G, and combinations of I+A, II+A to G, III+A and IV+A, as indicated in the following Table 1. In each case, after being digested at 50 degrees C. for 10 minutes, the emulsion was coated at a coverage of 432 mg. of silver per square foot onto a cellulose acetate film support. A sample of each coating was given identical exposure on an Eastman Sensitometer (Type IB) through a No. 16 Wratten Filter, which transmits substantially no light of wavelength shorter than about 520 mμ, for ⅕ second to a tungsten light source and processed for 3 minutes in a developer having the following composition:

DEVELOPER

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

and then fixed in a conventional sodium thiosulfate fixing bath, washed and dried. Densitometric measurements were then made of the developed images of each coating. The relative speed values were calculated based on an arbitrary relative speed of 100 for the coatings sensitized with 0.08 g. of Dyes I, III, and IV per mole of silver halide, and the gamma values determined. These values along with the fog values are shown in Table 1 below.

TABLE 1

	Dye and Concentration (g./mol. of Silver Halide)	Wratten No. 16 Filter		
		Relative speed	Gamma	Fog
Example No.:				
1	I(0.08)	100	2.08	0.09
2	I(0.08) plus A(0.02)	399	2.24	0.08
3	II(0.08)	263	2.40	0.08
4	II(0.08) plus A(0.02)	795	2.10	0.08
5	II(0.08) plus B(0.02)	851	2.35	0.08
6	II(0.08) plus C(0.02)	617	2.36	0.08
7	II(0.08) plus D(0.02)	933	2.16	0.08
8	II(0.08) plus E(0.02)	575	2.20	0.08
9	II(0.08) plus F(0.02)	589	2.46	0.08
10	II(0.08) plus G(0.02)	562	2.40	0.08
11	A(0.02)	(1)	(1)	0.06
12	B(0.02)	4.6	2.64	0.06
13	C(0.02)	71	2.68	0.06
14	D(0.02)	46	2.06	0.06
15	E(0.02)	(1)	(1)	0.06
16	F(0.02)	295	3.30	0.06
17	G(0.02)	257	2.86	0.06
18	III(0.08)	100	2.86	0.07
19	III(0.08)plus A(0.02)	417	2.94	0.07
20	IV(0.08)	100	1.99	0.08
21	IV(0.08) plus A(0.02)	380	1.90	0.08

[1] Sl. image.

The above table shows that the various supersensitizing dye combinations in every case gave substantially higher relative speeds, with no increase in fog, as compared with the individual dye components. For example, the combination of Dye II and Dye D (Example 7) shows a relative speed of 933, whereas these two dyes individually show relative speeds of but 263 (Example 3) and 46 (Example 14), respectively. In this instance, the relative speed obtained with the combination was greater by a factor of about 3 times the sum of the relative speeds of the individual dyes, thus indicating that the dye combinations of the invention provide unexpected and highly desirable supersensitizing results.

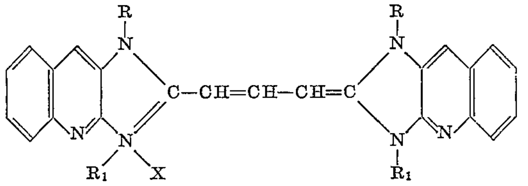
In the accompanying drawing, curve **1** represents the sensitivity of an ordinary gelatino-silver bromoiodide emulsion sensitized with just 3,3′-diethyl-1,1′-diphenyl-1H-imidazolo[4,5-b]quinocarbocyanine iodide (Dye II), curve **2** represents the sensitivity of the same emulsion sensitized with just 5-[di(1-ethyl-2(1H)-naphtho[1,2-d]thiazolylidene)isopropylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (Dye D), while curve **3** represents the sensitivity of the same emulsion sensitized with both 3,3′-diethyl-1,1′-diphenyl-1H-imidazolo[4,5-b]quinocarbocyanine iodide and 5-[di(1-ethyl-2(1H)-naphtho[1,2-d]thiazolylidene)isopropylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (Dye II+Dye D). Sensitometric measurements for emulsions sensitized in the manner shown in the drawing are given in Table 1.

Photographic silver halide emulsions, such as those listed above, containing the supersensitizing combinations of my invention 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 Baldsiefen U.S. Patent 2,540,085, issued Feb. 6, 1951; Bamschroder U.S. Patent 2,597,856, issued May 27, 1952; and Yutzy et al., U.S. Patent 2,597,915, issued May 27, 1952), various palladium compounds, such as palladium chloride (Baldsiefen U.S. Patent 2,540,086, issued Feb. 6, 1951), potassium chloropalladate (Stauffer et al., U.S. Patent 2,598,079, issued May 27, 1952), etc., or mixtures of such sensitizers; antifoggants, such as ammonium chloroplatinate (Trivelli et al., U.S. Patent 2,566,245, issued Aug. 28, 1951), ammonium chloroplatinite (Trivelli et al., U.S. Patent 2,566,263, issued Aug. 28, 1951), benzotriazole, nitrobenzimidazole, 5-nitro-indazole, benzidine, mercaptans, etc. (see Mees: "The Theory of the Photographic Process," MacMillan Pub., 1942, page 460), or mixtures thereof; hardeners, such as formaldehyde (Miller U.S. Patent 1,763,533, issued June 10, 1930), chrome alum (1,763,533), glyoxal (Brunken U.S. Patent 1,870,354, issued Aug. 9, 1932), dibromacrolein (Block et al., British Patent 406,750, accepted Mar. 8, 1934), etc.; color couplers, such as those described in Salminen et al., U.S. Patent 2,423,730, issued July 7, 1947; Spence and Carroll, U.S. Patent 2,640,776, issued June 2, 1953, etc.; or mixtures of such addenda. Dispersing agents for color couplers, such as those set forth in Jelley et al., U.S. Patent 2,322,027, issued June 15, 1943, and Mannes et al., U.S. Patent 2,304,940, issued Dec. 15, 1942, can also be employed in the above-described emulsions.

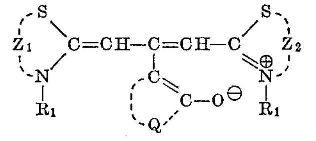
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A photographic silver halide emulsion containing a supersensitizing combination of (1) a dye having the general formula:



and (2) a holopolar dye having the general formula:



wherein R represents a member selected from the group consisting of an alkyl group and an aryl group, R_1 represents a member selected from the group consisting of an alkyl group and a sulfoalkyl group, X represents an acid anion, Q represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a barbituric acid nucleus, a 5(4H)-isoxazolone nucleus, a 2,4-chromandione nucleus, a 4,6-(1H, 5H)-pyrimidinedione nucleus, a 1,3-dioxane-4,6-dione nucleus and a 3H-naphtho[2,1-b]pyran-1,3(2H)-dione nucleus, and Z_1 and Z_2 each represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a naphtho[1,2-d]thiazole nucleus, a naphtho[2,1-d]thiazole nucleus and a 4,5-dihydronaphtho[1,2-d]thiazole nucleus.

2. A photographic silver halide emulsion in accordance with claim **1** wherein said dyes (1) and (2) are symmetrical.

3. A photographic silver halide emulsion in accordance with claim **1** wherein said emulsion is a silver bromoiodide emulsion.

4. A photographic silver halide emulsion of claim **1** wherein said Q represents a barbituric acid nucleus.

5. A photographic silver halide emulsion of claim **1** wherein Q represents a 5(4H)-isoxazolone nucleus.

6. A photographic silver halide emulsion of claim **1** wherein said Q represents a 2,4-chromandione nucleus.

7. A photographic silver halide emulsion of claim **1** wherein Q represents a 4,6(1H, 5H)-pyrimidinedione nucleus.

8. A photographic silver halide emulsion of claim **1** wherein Q represents a 1,3-dioxane-4,6-dione nucleus.

9. A photographic silver halide emulsion of claim **1** wherein Q represents a 3H-naphtho[2,1-b]pyran-1,3(2H)-dione nucleus.

10. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′-dimethyl-1,1′-diphenyl-

1H-imidazolo[4,5-b]quinocarbocyanine iodide and 5-[di-(1 - ethyl - 2(1H) - β - naphthothiazolylidene)isopropylidene]-1,3-di(β-methoxyethyl)barbituric acid.

11. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′-diethyl-1,1′-diphenyl-1H-imidazolo[4,5-b]quinocarbocyanine iodide and 5-[di-(1 - ethyl - 2(1H) - β - naphthothiazolylidene)isopropylidene]-1,3-di(β-methoxyethyl)barbituric acid.

12. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′-diethyl-1,1′-diphenyl-1H-imidazolo[4,5-b]quinocarbocyanine iodide and 3-[di-(1-ethyl-2(1H)-naphtho[1,2-d]thiazolylidene)isopropylidene]-2,4-chromandione.

13. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′ - diethyl - 1,1′ - diphenyl-1H - imidazolo[4,5 - b]quinocarbocyanine iodide and 2-dimethylamino - 5 - [di(1 - ethyl - 2(1H) - naphtho[1,2-d]thiazolylidene)isopropylidene] - 4,6(1H, 5H) - pyrimidinedione.

14. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′-diethyl-1,1′-diphenyl-1H-imidazolo[4,5 - b]quinocarbocyanine iodide and 5 - [di-(1 - ethyl - 2(1H) - naphtho[1,2 - d]thiazolylidene)isopropylidene] - 2,2 - dimethyl - 1,3 - dioxane - 4,6 - dione.

15. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′ - diethyl - 1,1′ - diphenyl-1H - imidazolo[4,5 - b]quinocarbocyanine iodide and 1,3 - diethyl - 5 - [(1 - ethyl - 4,5 - dihydro - 2(1H)-naphtho[1,2 - d]thiazolylidene)(1 - methyl - 2(1H)-naphtho[1,2 - d]thiazolylidene)isopropylidene]barbituric acid.

16. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′ - diethyl - 1,1′ - diphenyl-1H - imidazolo[4,5 - b]quinocarbocyanine iodide and 1,3 - diethyl - 5 - [(1 - ethyl - 4,5 - dihydro - 2(1H)-naphtho[1,2 - d]thiazolylidene)(3 - ethyl - 2(3H) - naphtho[2,1 - d]thiazolylidene)isopropylidene]barbituric acid.

17. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 3,3′ - diethyl - 1,1′ - diphenyl-1H - imidazolo[4,5 - b]quinocarbocyanine iodide and 4-[di(1 - ethyl - 2(1H) - β - naphthothiazolylidene)isopropylidene]-3-phenyl-5(4H)isoxazolone.

18. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes anhydro - 1,1′ - diphenyl - 3,3′-di(4 - sulfobutyl) - 1H - imidazolo[4,5 - b]quinocarbocyanine hydroxide, monosodium salt and 5-[di(1-ethyl-2(1H) - β - naphthothiazolylidene)isopropylidene]-1,3-di(β-methoxyethyl)barbituric acid.

19. A photographic silver halide emulsion in accordance with claim **1** wherein said supersensitizing combination comprises the dyes 1,1′,3,3′ - tetraethyl - 1H - imidazolo[4,5 - b]quinocarbocyanine iodide and 5 - [di(1-ethyl - 2(1H) - β - naphthothiazolylidine)isopropylidene]-1,3-di(β-methoxyethyl)barbituric acid.

20. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **1**.

21. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **2**.

22. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **3**.

23. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **4**.

24. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **5**.

25. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **6**.

26. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **7**.

27. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **8**.

28. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **9**.

29. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **10**.

30. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **11**.

31. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **12**.

32. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **13**.

33. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **14**.

34. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **15**.

35. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **16**.

36. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **17**.

37. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **18**.

38. A photographic element comprising a support coated with at least one layer containing a photographic silver halide emulsion of claim **19**.

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