July 19, 1960 J. E. JONES **2,945,763**

GREEN SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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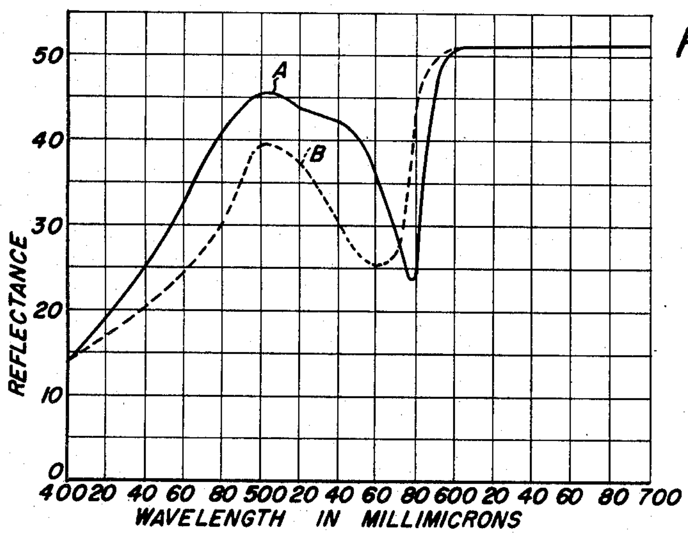

Fig. 1

A = ANHYDRO-5,5',6,6'-TETRACHLORO-1,1'-DIETHYL-3,3'-DI(3-SULFOBUTYL)BENZIMIDAZOLOCARBOCYANINE HYDROXIDE

B = A PLUS 3-ETHYL-2-(2-PHENYLIMINOPROPYLIDENE)-β-NAPHTHOTHIAZOLINE

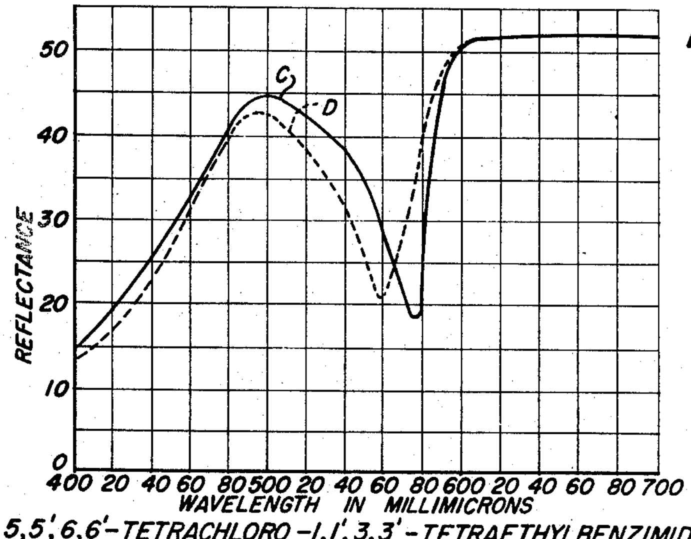

Fig. 2

C = 5,5',6,6'-TETRACHLORO-1,1',3,3'-TETRAETHYLBENZIMIDAZOLOCARBOCYANINE IODIDE

D = C PLUS 1-METHYL-2-BENZOYLMETHYLENE-β-NAPHTHOTHIAZOLINE

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GREEN SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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11 Claims. (Cl. 96—104)

This invention relates to photography, and more particularly, to a method for altering the sensitivity of green-sensitized photographic silver halide emulsions.

It has long been known that benzimidazolocarbocyanine dyes are useful in sensitizing photographic silver halide emulsions to the green region of the spectrum, i.e., that portion of the spectrum lying between about 500 and 600 mμ. These dyes have been of particular interest as green-sensitizers, and in particular, in the emulsions intended for use in color photography, since they are generally characterized by very sharp absorption. Dyes of this type have been previously described in the technical and patent literature. See, for example, Ogata "Proceedings of the Imperial Academy" (Tokyo), vol. 9 (1933), page 602. Among the most useful of the benzimidazolocarbocyanine dyes are those containing one or more chlorine atoms substituted on the benzene ring of the benzimidazole nucleus.

However, many of these benzimidazolocarbocyanine dyes suffer from the disadvantage that their maximum absorptions are so deep that there is considerable difficulty in color reproduction, especially the reproduction of orange colors whose reflectance is changing rapidly with wavelengths in the region of the maximum absorptions of these dyes, which is about 575 mμ.

I have now found a novel means of hypsochromically shifting the absorptions of these useful dyes, and in many instances, in providing supersensitizing effects with these dyes at the same time.

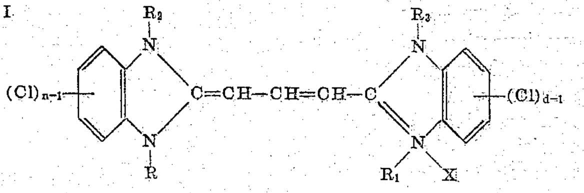
It is, therefore, an object of my invention to provide an improved means of sensitizing photographic silver halide emulsions to the green region of the spectrum. Another object is to produce photographic silver halide emulsions having improved green sensitivity. Still another object is to provide photographic silver halide emulsions which have been supersensitized by a combination of the above-mentioned sensitizing dyes with certain heterocyclic compounds as hereinafter defined.

Other objects will become apparent from a consideration of the following description and examples.

My invention is diagrammatically represented by the accompanying drawings which are explained in detail below.

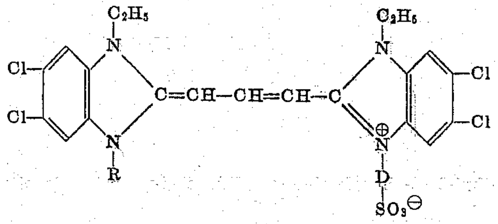
According to my invention, I accomplish the above objects by combining a benzimidazolocarbocyanine dye with a heterocyclic base containing an extracyclic ketone group or imino group. As indicated above, the benzimidazolocarbocyanine sensitizing dyes used in my invention have been previously described in the prior art. These sensitizing dyes include those represented by the following general formula:

I.



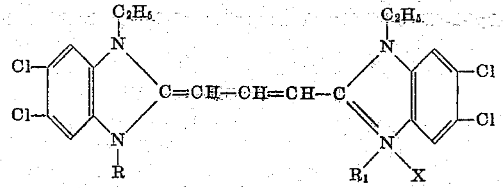
wherein R and R_1 each represents and alkyl group, such as methyl, ethyl, β-hydroxyethyl, n-propyl, n-butyl, β-carboxyethyl, γ-carboxypropyl, δ(or 4)-carboxylbutyl, β-sulfoethyl, γ-sulfopropyl, γ-sulfobutyl, δ-sulfobutyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms), R_2 and R_3 each represents an alkyl group, such as methyl, ethyl, n-propyl, n-butyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms) or an aryl group, such as phenyl, o-, m- or p-tolyl, etc. (e.g., a mononuclear aromatic group of the benzene series), d and n each represents a positive integer of from 1 to 3 and X represents an acid radical, such as chloride, bromide, iodide, benzenesulfonate, p-toluenesulfonate, methylsulfate, ethylsulfate, perchlorate, etc. As indicated above, the dyes, such as those illustrated by Formula I above, which are particularly useful in color photography, comprise those dyes containing one or more chlorine atoms substituted on the benzene ring of the benzimidazole nucleus. Where either R or R_1 of Formula I represents acid-substituted alkyl groups, such as a sulfoalkyl group, the dyes are generally regarded as anhydro dyes, and a particularly useful group of such dyes can be represented by the following general formula:

Ia



wherein R has the values given above, and D represents an alkylene group, such as ethylene, trimethylene, tetramethylene, γ-methyltrimethylene, etc. Another group of dyes embraced by Formula I which are particularly useful in my invention can be represented by the following general formula:

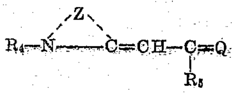
Ib



wherein R and R_1 each have the values given above (especially alkyl groups of the formula C_mH_{2m+1}, wherein *m* represents a positive integer of from 1 to 4) and X has the values given above.

The heterocyclic bases which can advantageously be employed in combination with the benzimidazolocarbocyanine dyes of my invention can be represented by the following general formula:

II

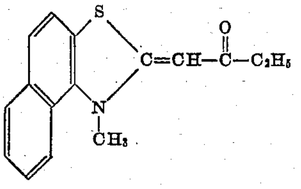


wherein R_4 represents an alkyl group, such as methyl, ethyl, n-propyl, n-butyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms), R_5 represents an alkyl group, such as methyl, ethyl, etc. (e.g., an alkyl group containing from 1 to 2 carbon atoms), or an aryl group, such as phenyl, o-, m- or p-tolyl (e.g., a mononuclear aromatic group of the benzene series), Q represents an oxygen atom or an arylimino group, such as phenylimino, tolylimino, chlorophenylimino, etc. (e.g., a mononuclear arylimino group), and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the naphthothiazoline series or the naphthoselenazoline series. The carbocyclic rings of the nuclei defined by Z above can contain inert substituents, such as alkyl groups (e.g., methyl, ethyl, etc.), alkoxy groups (e.g., methoxyl, ethoxyl, etc.), etc.

The benzimidazolocarbocyanine dyes of my invention, containing a sulfoalkyl group on at least one of the nitrogen atoms, can be prepared according to the methods described in copending applications, Serial No. 680,003, filed August 23, 1957, in the names of J. E. Jones and J. Spence, now patent No. 2,912,329, granted November 10, 1959, and Serial No. 698,324, filed November 25, 1957, in the names of L. G. S. Brooker and G. H. Keyes, now U.S. Patent 2,917,516, granted December 15, 1959. Certain of the benzimidazolocarbocyanine dyes useful in practicing my invention are also described in Van Lare U.S. Patent 2,739,149, issued March 20, 1956.

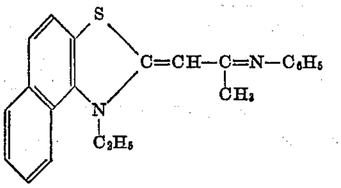
Typical of the compounds embraced by Formula II are the following:

(1)



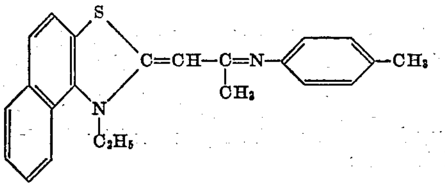
1-methyl-2-propionylmethylene-β-naphthothiazoline

(2)



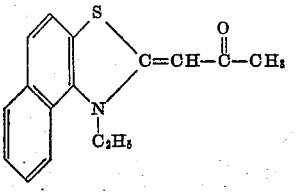
1-ethyl-2-(2-phenyliminopropylidene)-β-naphthothiazoline

(3)



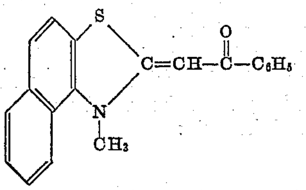
1-ethyl-2-[2-(p-tolylimino)propylidene]-β-naphthothiazoline

(4)



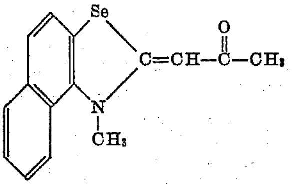
2-acetonylidene-1-ethyl-β-naphthothiazoline

(5)



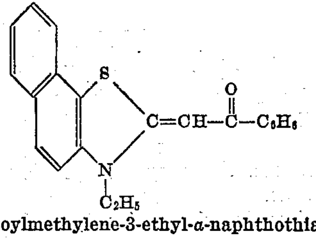
1-methyl-2-benzoylmethylene-β-naphthothiazoline

(6)



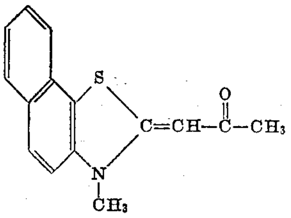
2-acetonylidene-1-methyl-β-naphthoselenazoline

(7)



2-benzoylmethylene-3-ethyl-α-naphthothiazoline

(8)



2-acetonylidene-3-methyl-α-naphthothiazoline

The heterocyclic bases of my invention represented by Formula II above have also been described in the prior art. The compounds of Formula II, wherein Q represents an oxygen atom, can be prepared according to the method described in Brooker et al. U.S. Patent 2,112,139, issued March 22, 1938. The compounds of Formula II, wherein Q represents an arylimino group, can be prepared as described in Brooker et al. U.S. Patent 2,298,732, issued October 13, 1942.

Many of the compounds represented by Formula II above are colorless and have an absorption maximum lying outside of the visible region of the spectrum. It was, therefore, unexpected to find that these compounds could be combined with the benzimidazolocarbocyanine sensitizing dyes of my invention to produce a hypsochromic shift in the absorption of the sensitizing dye, and at the same time in certain cases, to produce a supersensitizing effect. By a supersensitizing effect, I mean that photographic silver halide emulsions can be sensitized by a combination of the compounds of Formula II and the benzimidazolocarbocyanine dye to obtain a speed value which cannot be obtained with either ingredient alone. This effect has been compared previously to synergism, which is sometimes encountered in other branches of chemistry. I have further found that the degree of hypsochromic shift in the absorption of the benzimidazolocarbocyanine dyes can be controlled to some extent by the amount of the compound of Formula II which is added. Of course, addition of increased quantities of the compound of Formula II will produce an increased shift in absorption up to a point which varies from dye to dye and addition of further quantities of the compounds of Formula II beyond that point does not produce a corresponding shift in the absorption characteristics. The optimum amount of the compound of Formula II employed in my invention can vary, depending upon the effect desired. The most advantageous amounts of the sensitizing dye and the compound of Formula II can be determined by running a series of test emulsions wherein various quantities of either ingredient are employed. In general, the amount of sensitizing dye used can vary rather widely and I have found that from about 5 to about 200 mg. per mole of silver halide are quite adequate. The amount of compound of Formula II can likewise be varied, as described above, and I have found that from about 10 to about 200 mg. per mole of silver halide of the compounds of Formula II are quite adequate. The ratio of the amount of sensitizing dye to the compound of Formula II can likewise be varied, and I have found that, in general, this ratio can vary from about 1:5 to about 5:1 (by weight). The benzimidazolocarbocyanine dyes and compounds of Formula II can be incorporated into the emulsions of my invention according to known methods. For instance, these compounds can be first dissolved in an inert solvent, such as methanol, ethanol, pyridine, acetone, etc., or mixtures of these solvents, and added to the emulsion in the form of these solutions. If desired, a common solution containing both ingredients can be prepared and stock amounts of this solution then added to the photographic emulsions. After adding the benzimidazolocarbocyanine dye and the compound of Formula II, with stirring to insure uniform distribution thereof, the emulsions can then be digested for a short period of time prior to coating on a suitable support, such as glass, cellulose derivative film, metal, paper, polyvinyl acetal film, etc. After coating to a suitable thickness, the film can then be allowed to dry.

My invention is primarily directed to the ordinarily employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloroiodide, -chlorobromiodide, -bromide and -bromiodide developing-out emulsions. While the results in the following table were obtained using gelatino-silver-bromiodide emulsions, excellent results have also been obtained using gelatino-silver-chlorobromide emulsions. Emulsions which form the latent image mostly inside the silver halide grains, such as the emulsions set forth in E. B. Knott et al. U.S. Patent 2,456,956, dated December 21, 1948, can also be employed in practicing my invention.

Photographic silver halide emulsions, such as those listed above, containing the sensitizing 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 U.S. Patents W. D. Baldsiefen 2,540,085, granted February 6, 1951; R. E. Damschroder 2,597,856, granted May 27, 1952, and H. C. Yutzy et al. 2,597,915, granted May 27, 1952), various palladium compounds, such as palladium chloride (W. D. Baldsiefen U.S. 2,540,086, granted February 6, 1951), potassium chloropalladate (R. E. Stauffer et al. U.S. 2,598,079, granted May 27, 1952), etc., or mixtures of such sensitizers; antifoggants, such as ammonium chloroplatinate (A. P. H. Trivelli et al. U.S. 2,566,245, granted August 28, 1951), ammonium chloroplatinite (A. P. H. Trivelli et al. U.S. 2,566,263, granted August 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. 1,763,533, granted June 10, 1930), chrome alum (1,763,533), glyoxal (J. Brunken U.S. 1,870,354, granted August 9, 1932), dibromacrolein (O. Block et al. Br. 406,750, accepted March 8, 1934), etc.; color couplers, such as those described in I. F. Salminen et al. U.S. Patent 2,423,730, granted 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 U.S. patents E. E. Jelley et al. 2,322,027, granted June 15, 1943, and L. D. Mannes et al. 2,304,940, granted December 15, 1942, can also be employed in the above-described emulsions.

The following examples will serve to illustrate the manner of practicing my invention. To different portions of the same batch of photographic gelatino-silver-bromiodide emulsion were added (1) a benzimidazolocarbocyanine dye of the type illustrated in Formula I or *Ia* or *Ib* and (2) a combination of a benzimidazolocarbocyanine dye and a heterocyclic base of the type illustrated in Formula II. Before coating, the emulsions containing the addenda were digested for a short time in a tank maintained at 50–52° C. The different portions of emulsion were then coated on conventional supports and exposed in the usual manner in an Eastman Type *Ib* Sensitometer through a Wratten No. 12 filter, i.e., a filter which transmits only light having a wavelength greater than 495 mμ, and in a spectrograph. The exposed coatings were then developed for 3 minutes (except in Examples 4–7, development was for 4 minutes) in a developer having the following composition:

	Grams
N-methyl-p-aminophenolsulfate	2.0
Hydroquinone	8.0
Sodium sulfite (anhydrous)	90.0
Sodium carbonate (monohydrate)	52.5
Potassium bromide	5.0

Water to make one liter.

No data showing the sensitometric properties of the compounds of Formula II alone are given, since it has been found that these derivatives have little or no sensitizing action of their own on the emulsions used. Different emulsions were used in some of the examples, although the emulsions in each individual example were obtained from the same batch. In Table A, the coatings of Examples 1–3 were obtained from the same batch of unsensitized emulsion, the coatings of Examples 4–7 were obtained from the same batch of unsensitized emulsion and the coatings of Examples 8–10 were obtained from the same batch of unsensitized emulsion. The emulsions used in Examples 4–7 had a speed somewhat higher than that of the emulsions used in Examples 1–3. The minus blue relative speeds (i.e., the speed of the unsensitized emulsion being set at 100 for purposes of comparison), gamma, fog and absorption maximum (λ maximum) for each of the coatings are given in the following table:

TABLE A

Example	Addenda (g./mol. AgX)	Minus Blue Exposure			
		Rel. Speed	Gamma	Fog	λ Max.
1	(*a*) 5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide (.080)	100	2.0	0.06	573
	(*b*) dye (*a*) (.080) plus compound 1 (.035)	103	2.3	.06	568
2	(*c*) dye (*a*) (.080) plus compound 2 (.035)	110	2.1	.06	565
3	(*d*) dye (*a*) (.080) plus compound 3 (.035)	120	2.0	.06	563
4	(*e*) dye (*a*) (.090)	100	0.95	.11	575
	(*f*) dye (*a*) (.090) plus compound 4 (.120)	130	0.90	.10	572
5	(*g*) dye (*a*) (.090) plus compound 5 (.120)	78	0.97	.08	560
6	(*h*) anhydro-5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide (.090)	90	1.02	.06	578
	(*i*) dye (*h*) (.090) plus compound 4 (.120)	110	1.06	.06	570
7	(*j*) dye (*h*) (.090) plus compound 2 (.120)	90	1.68	.13	556
8	(*k*) dye (*a*) (.05)	100	2.6	.07	576
	(*l*) dye (*a*) (.05) plus compound 6 (.065)	275	2.6	.07	572
9	(*m*) dye (*a*) (.05) plus compound 8 (.065)	250	2.5	.07	572
10	(*n*) dye (*a*) (.05) plus compound 7 (.065)	250	2.7	.08	572

In Table A above, the sensitizing dyes used contained chlorine substituents on the benzene ring of the benzimidazole nucleus. However, it is not essential that these dyes have chlorine substituents in every instance, although it has been found that the chlorine-substituted dyes are quite outstanding in their properties. Beneficial effects have also been obtained wherein the benzimidazolocarbocyanine dyes of my invention contained no substituents, or contained substituents other than chlorine, such as bromine, acetyl, ethylcarbamyl, methyl, ethyl, etc., attached to the benzene ring of the benzimidazole nuclei. I have also found that the beneficial effects of my invention can be obtained using unsymmetrical benzimidazole dyes, i.e., dyes wherein one of the benzimidazole nuclei has been replaced by a different basic nucleus, such as benzoxazole, benzothiazole, etc. In general, my invention has been found to be most useful wherein the sensitizing dye is a symmetrical benzimidazolocarbocyanine dye, i.e., dyes wherein the benzimidazole nuclei are identical insofar as substituents on the nitrogen atoms and on the benzene ring are concerned. In the following table, the results were obtained in exactly the manner described above with respect to the coatings of Table A. The emulsion used was a conventional gelatino-silver-bromiodide emulsion and the coatings were prepared as described for Table A. Exposure and development were identical to that of Table A, the time of development being about 4 minutes for each of the exposed coatings. The speed, gamma and fog, together with absorption maximum for each of the coatings are given in the following table:

TABLE B

Example	Addenda (g./mol. AgX)	Minus Blue Exposure			
		Rel. Speed	Gamma	Fog	λ Max.
11	(*o*) 5,5′-dichloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide (.08)	100	1.7	.08	575
	(*p*) dye (*o*) compound 2 (.065)	135	2.5	.09	565
12	(*q*) 1,1′-di-n-butyl-5,5′,6,6′-tetrachloro-3,3′-diethylbenzimidazolocarbocyanine iodide (.08)	166	2.8	.08	580
	(*r*) dye (*q*) (.08) plus compound 2 (.065)	186	2.8	.08	580
13	(*s*) 5,5′,6,6′-tetrachloro-3,3′-diethyl-1,1′-diphenylbenzimidazolocarbocyanine iodide (.08)	148	2.8	.08	585
	(*t*) dye (*s*) (.08) plus compound 2 (.065)	145	2.9	.08	570
14	(*u*) anhydro-1,1′-di(β-carboxyethyl)-5,5′,6.6′-tetrachloro-3,3′-diethylbenzimidazolocarbocyanine hydroxide (.08)	166	2.9	.07	580
	(*v*) dye (*u*) (.08) plus compound 3 (.065)	178	3.1	.07	575
15	(*w*) 1,1′-di(4-carboxybutyl)-5,5′,6,6′-tetrachloro-3,3′-diethylbenzimidazolocarbocyanine iodide (.08)	98	2.8	.06	580
	(*x*) dye (*w*) (.08) plus compound 3 (.065)	165	2.8	.07	575
16	(*y*) anhydro-1,1′-dicarboxyethyl-6,6′-dichloro-3,3′-diethylbenzimidazolocarbocyanine hydroxide (.08)	20	.6	.07	575
	(*z*) dye (*y*) (.08) plus compound 4 (.065)	107	2.2	.07	570
17	(*a′*) 5,5′,6,6′-tetrabromo-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide (0.08)	155	2.5	.07	580
	(*b′*) dye (*a′*) (.08) plus compound 3 (.065)	186	2.6	.08	570
18	(*c′*) 1,1′-(β-dicarboxyethyl)-4,5,4′,5′-tetrachloro-3,3′-diethylbenzimidazolocarbocyanine iodide (.08)	25	3.1	.07	590
	(*d′*) dye (*c′*) (.08) plus compound 1 (.065)	125	3.1	.07	580
19	(*e′*) anhydro-4,4′,5,5′-tetrachloro-3,3′-diethyl-1,1′-di(4-sulfobutyl)benzimidazolocarbocyanine hydroxide (.08)	36	3.3	.08	545
	(*f′*) dye (*e′*) (.08) plus compound 1 (.065)	57	3.1	.07	540
20	(*g′*) 1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide (.08)	11	.3	.08	530, 560
	(*h′*) dye (*g′*) (.08) plus compound 2 (.065)	30	2.2	.20	525, 560
21	(*i′*) dye (*g′*) (.08) plus compound 3 (.065)	25	2.4	.11	525

My invention can be further described with reference to the accompanying drawings which are diagrammatic reproductions of the reflectance curves for several of the coatings of the examples in Table A.

In Fig. 1, curve A represents the reflectance (percent) for a processed ordinary gelatino-silver-bromiodide emulsion containing anhydro-5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide, while curve B represents the reflectance (percent) of the sensitized emulsion illustrated by curve A, but to which 3-ethyl-2-(2-phenylimino-propylidene)-β-naphthothiazoline had been added. The sensitometric properties of these coatings are illustrated in Examples 6 and 7 above.

In Fig. 2, curve C represents the reflectance (percent) of a processed ordinary gelatino-silver-bromiodide emulsion containing 5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide, while curve D represents the reflectance (percent) of the emulsion represented by curve C, to which 1-methyl-2-benzoylmethylene-β-naphthothiazoline had been added. The sensitometric properties of these coatings are shown in Examples 4 and 5 above.

It can be seen by reference to Fig. 1 that a shift in absorption from 578 mμ to about 556 mμ occurs upon addition of a compound of Formula II, while in Fig. 2, a shift of from 575 mμ to 550 mμ occurs when using a compound of Formula II.

It has also been found that various hemicyanine dyes, such as 2-(2-anilino-1-butenyl)-α-naphthothiazole ethiodide can be employed in combination with the benzimidazolocarbocyanine dyes of my invention, so that useful supersensitizing effects can be obtained. For example, combining the afore-mentioned hemicyanine dye with Dye (*a*) of Table A, produced a 275% increase in speed, although there was a shift in absorption of only from 576 to 572 mμ.

As indicated above, many of the benzimidazolocarbocyanine dyes of my invention can be prepared according to methods previously described in the prior art. The following examples will serve to illustrate the preparation of several dyes useful in practicing my invention, as well as intermediates necessary for the preparation of these dyes. It will be seen by reference to these examples that my invention contemplates benzimidazolocarbocyanine dyes containing two chlorine atoms on a single benzene ring of the benzimidazole nucleus, regardless of their position on the ring. It is to be understood that my invention also contemplates benzimidazolocarbocyanine dyes containing no substituents on the benzene ring of the benzimidazole nucleus.

Example A.—1,1′-di(β-carboxyethyl)-4,4′,5,5′-tetrachloro-3,3′-diethylbenzimidazolocarbocyanine iodide

β-Iodopropionic acid (2 g., 2 mols.) and 6,7-dichloro-1-ethyl-2-methylbenzimidazole (4.5 g., 2 mols.+100% excess) were heated together on a steam bath for four hours. A solution of sodium ethoxide (0.58 g. of sodium and 50 ml. of absolute ethyl alcohol) was added to the quaternary salt, the mixture was refluxed for ten minutes and cooled. Then chloral (0.74 g., 1 mol.) was added and the resulting mixture was refluxed for one hour. The reaction mixture was chilled and the solid filtered off and then it was suspended in 60 ml. of water containing 2 g. of sodium iodide. After chilling for two hours, the crude dye was filtered off. The dye was suspended in 60% methyl alcohol and the suspension was heated to boiling and then cooled. After filtering, the dye was suspended in 60 ml. of methyl alcohol, cooled and filtered. The dye was obtained as brownish crystals in a 6% yield, M.P. 205–206° C. with decomposition.

Example B.—1,1′-di(4-carboxybutyl)-5,5′,6,6′-tetrachloro-3,3′-diethylbenzimidazolocarbocyanine iodide

4-bromovaleric acid (1.8 g., 2 mols.) and 5,6-dichloro-1-ethyl-2-methylbenzimidazole (4.6 g., 2 mols.+100% excess) were heated together on a steam bath for four hours. A solution of sodium ethoxide (0.58 g. of sodium in 50 ml. of absolute ethyl alcohol) was added to the quarternary salt, the mixture was refluxed for ten minutes and cooled. Then chloral (0.74 g., 1 mol.) was added and the resulting mixture was refluxed for one hour. The reaction mixture was chilled and the solid filtered off and then it was suspended in 60 ml. of water containing 2 g. of sodium iodide. After standing for two hours, the crude dye was filtered off. The dye was dissolved in 400 ml. of 70% methyl alcohol and one ml. of triethylamine, the solution was filtered and the filtrate made acid with glacial acetic acid. The pure dye was obtained as brownish-orange crystals in a 5% yield, M.P. 256–257° C. with decomposition.

Example C.—Anhydro-4,4′,5,5′-tetrachloro-3,3′-diethyl-1,1′-di(4-sulfobutyl)benzimidazolocarbocyanine hydroxide

Anhydro-4,5-dichloro-3-ethyl-2-methyl-1-(4-sulfobutyl)-benzimidazolium hydroxide (3.65 g., 2 mols.) and chloral (0.74 g., 1 mol.) were added to a solution of sodium ethoxide (0.58 g. of sodium in 60 ml. of absolute ethyl alcohol), and the reaction mixture was refluxed for one hour. The mixture was chilled, the solid was filtered off and the residue was suspended in 60 ml. of water containing 5 g. of sodium iodide. After chilling, the crude dye was filtered off. The dye was suspended in 100 ml. of hot methyl alcohol, the suspension was cooled and filtered. The dye was obtained as reddish crystals in a 25% yield, M.P. 294–295° C. with decomposition.

Example D.—Anhydro-4,5-dichloro-3-ethyl-2-methyl-1-(4-sulfobutyl)-benzimidazolium hydroxide

6,7-Dichloro-1-ethyl-2-methylbenzimidazole (23.2 g.) and 1,4-butane sultone (13.6 g.) were heated together at 170° C. The temperature increased to 210° C. and solid separated. The mixture was heated at 150° C. for one hour. The solid was crushed and washed with acetone. The yield of cream crystals was 32 g.

Example E.—6,7-dichloro-1-ethyl-2-methylbenzimidazole

To a suspension of 252 g. (1 mol.) of crude 5,6-dichloro-N-ethyl-2-nitroaniline in 2400 ml. of water and 20 ml. of concentrated hydrochloric acid at 70° C. was added 246 g. (3 mol.+33% excess) of iron powder in small portions and with vigorous stirring. The reaction mixture was stirred for an additional four hours at 75–85° C. A filter-aid was added and the suspended solid filtered off. The solid and liquid fractions were extracted separately with chloroform. The chloroform extracts were combined and the solvent removed on a steam bath. To the cooled residue was added, with shaking, 200 ml. of acetic anhydride. The acetic acid and excess acetic anhydride were distilled off slowly until the internal temperature finally reached 200° C. The residue was extracted with 3% hydrochloric acid and the extract was made alkaline with sodium hydroxide. The base was extracted with ether. The ether solution was dried over solid potassium hydroxide. After filtering, the filtrate was concentrated and the residue was fractionated. The base was obtained as a colorless oil in a 40% yield, B.P. 162–167° C./1 mm.

Example F.—5,6-dichloro-N-ethyl-2-nitroaniline

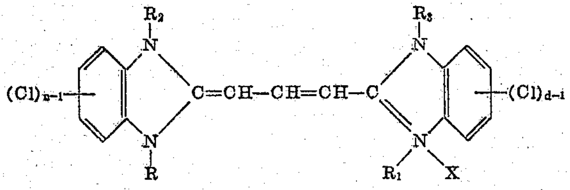
To 430 ml. of a 70% solution of ethylamine in water was added 229 g. (1 mol.) of 2,3,4-trichloronitrobenzene in small portions with stirring. Most of the solid dissolved and the solution became warm. It was cooled in an ice-water bath and then allowed to stand at room temperature overnight. The reaction mixture was diluted with 2 l. of water, filtered, and the solid washed with water and air dried for 24 hours. The crude damp produce was used without further purification. A 2 g. sample was recrystallized from ethyl alcohol and 1.8 g. of bright orange needles were obtained, M.P. 50–53° C.

Unsymmetrical benzimidazolocarbocyanine dyes useful in my invention can be prepared as described in Gevaert Belgian Patent 532,735, granted November 13, 1954.

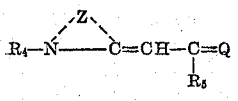
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion containing (1) a sensitizing dye selected from those represented by the following general formula:



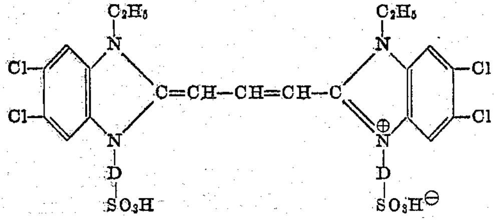
wherein R and R_1 each represents an alkyl group, R_2 and R_3 each represents a member selected from the group consisting of an alkyl group and an aryl group, *d* and *n* each represents a positive integer of from 1 to 3, and X represents an acid radical, and (2) a compound selected from those represented by the following general formula:



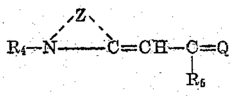
$$R_4-\overbrace{N-\!-\!-C}^{Z}=CH-\underset{R_5}{C}=Q$$

wherein R_4 represents an alkyl group, R_5 represents a member selected from the group consisting of an alkyl group and an aryl group, Q represents a member selected from the group consisting of an oxygen atom and an arylimino group, and Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the naphthothiazoline series and those of the naphthoselenazoline series.

2. A photographic silver halide emulsion containing (1) a symmetrical sensitizing dye selected from those represented by the following general formula:



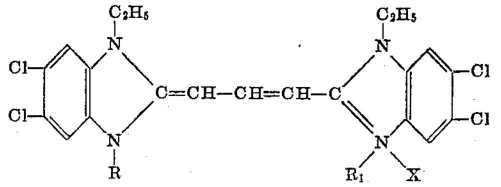
wherein D represents an alkylene group, and (2) a compound selected from those represented by the following general formula:



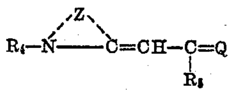
$$R_4-\overbrace{N-\!-\!-C}^{Z}=CH-\underset{R_5}{C}=Q$$

wherein R_4 represents an alkyl group, R_5 represents a member selected from the group consisting of an alkyl group and an aryl group, Q represents a member selected from the group consisting of an oxygen atom and an arylimino group, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the naphthothiazoline series and those of the naphthoselenazoline series.

3. A photographic silver halide emulsion containing (1) a symmetrical sensitizing dye selected from those represented by the following general formula:

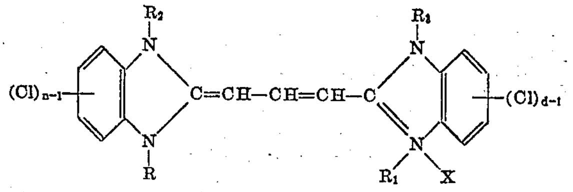


wherein R and R_1 each represents an alkyl group and X represents an acid radical, and (2) a compound selected from those represented by the following general formula:

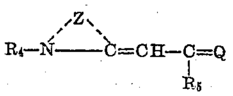


wherein R_4 represents an alkyl group, R_5 represents a member selected from the group consisting of an alkyl group and an aryl group, Q represents a member selected from the group consisting of an oxygen atom and an arylimino group, and Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the naphthothiazoline series and those of the naphthoselenazoline series.

4. A phoptographic silver bromiodide emulsion containing (1) a sensitizing dye selected from those represented by the following general formula:

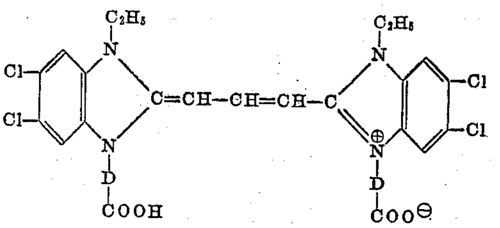


wherein R and R_1 each represents an alkyl group, R_2 and R_3 each represents a member selected from the group consisting of an alkyl group and an aryl group, *d* and *n* each represents a positive integer of from 1 to 3, and X represents an acid radical, and (2) a compound selected from those represented by the following general formula:

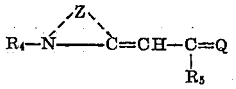


wherein R_4 represents an alkyl group, R_5 represents a member selected from the group consisting of an alkyl group and an aryl group, Q represents a member selected from the group consisting of an oxygen atom and an arylimino group, and Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the naphthothiazoline series and those of the naphthoselenazoline series.

5. A photographic silver halide emulsion containing (1) a symmetrical sensitizing dye selected from those represented by the following general formula:

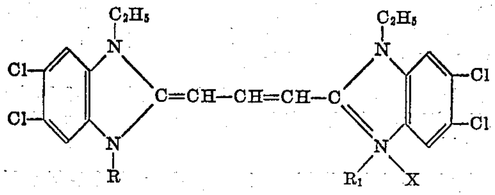


wherein D represents an alkylene group, and (2) a compound selected from those represented by the following general formula:

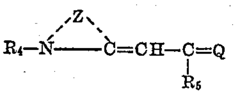


wherein R_4 represents an alkyl group, R_5 represents a member selected from the group consisting of an alkyl group and an aryl group, Q represents a member selected from the group consisting of an oxygen atom and an arylimino group, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the naphthothiazoline series and those of the naphthoselenazoline series.

6. A photographic silver bromiodide emulsion containing (1) a symmetrical sensitizing dye selected from those represented by the following general formula:



wherein R and R_1 each represents an alkyl group and X represents an acid radical, and (2) a compound selected from those represented by the following general formula:



wherein R_4 represents an alkyl group, R_5 represents a member selected from the group consisting of an alkyl group and an aryl group, Q represents a member selected from the group consisting of an oxygen atom and an arylimino group, and Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of those of the naphthothiazoline series and those of the naphthoselenazoline series.

7. A photographic gelatino-silver-halide developing-out emulsion containing anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide and 2-acetonylidene-1-ethyl-β-naphthothiazoline.

8. A photographic gelatino-silver-halide developing-out emulsion containing anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide and 1-methyl-2-benzoylmethylene-β-naphthothiazoline.

9. A photographic gelatino-silver-halide developing-out emulsion containing 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide and 1-methyl-2-propionylmethylene-β-naphthothiazoline.

10. A photographic gelatino-silver-halide developing-out emulsion containing 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide and 3-ethyl-2-(2-phenyliminopropylidene)-β-naphthothiazoline.

11. A photographic gelatino-silver-halide developing-out emulsion containing 5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide and 2-acetonylidene-1-methyl-β-naphthoselenazoline.

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