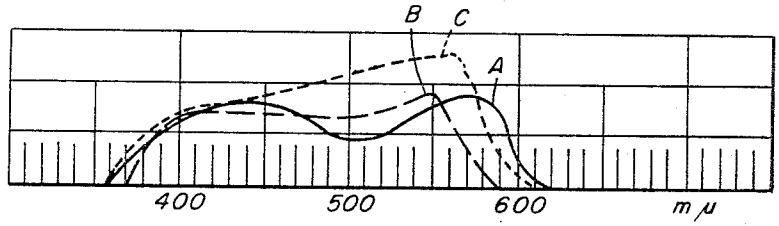
Jan. 16, 1968 J. E. JONES ET AL 3,364,031

SUPERSENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

Filed June 24, 1963

Fig. 1

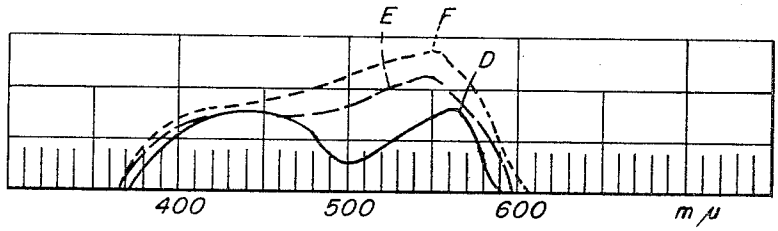


A = Dye I, Anhydro - 5, 5', 6, 6' - Tetrachloro - 1, 1' - Diethyl - 3, 3' - Di(3 - Sulfobutyl) Benzimidazolocarbocyanine Hydroxide

B = Dye IX, 1 - Carboxyethyl - 5, 6 - Dichloro - 3 - Ethyl - 1', 3', 3' - Trimethylbenzimidazoloindocarbocyanine Iodide

C = Dye I Plus Dye IX

Fig. 2



D = Dye II, 5, 5' - Dichloro - 1, 1', 3, 3' - Tetraethylbenzimidazolo - carbocyanine Iodide

E = Dye VI, Anhydro - 5, 6 - Dichloro - 1 - Ethyl - 1', 3', 3' - Trimethyl - 3 - (4 - Sulfobutyl) Benzimidazoloindocarbocyanine Hydroxide

F = Dye II Plus Dye VI

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SUPERSENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

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12 Claims. (Cl. 96—104)

This invention relates to photographic silver halide emulsions containing certain benzimidazolocarbocyanine dyes, and as supersensitizers therefore, certain benzimidazoloindocarbocyanine dyes.

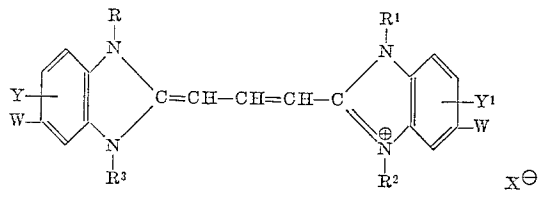
It is known in the art of making photographic emulsions that certain dyes of the cyanine class alter the sensitivity of photographic emulsions of the gelatino-silver-halide kind, when the dyes are incorporated in the emulsions. It is also known that the sensitization produced by a given dye varies somewhat with the type of emulsion in which the dye is incorporated. Furthermore, the sensitization of a given emulsion by a given dye may be altered by varying the conditions in the emulsion. For example, the sensitization may be increased by increasing the silver ion concentration or decreasing the hydrogen ion concentration (i.e., increasing the alkalinity), or both. Thus, sensitization can be increased by bathing plates, coated with a spectrally sensitized emulsion, in water or in aqueous solutions of ammonia. Such a process of altering the sensitivity of a sensitized emulsion by increasing the silver ion concentration and/or by decreasing the hydrogen ion concentration is commonly called "hypersensitization." Hypersensitized emulsions have generally poor keeping qualities.

We have now found a means of altering the sensitivity in emulsions containing certain benzimidazolcarbocyanine dyes. Since the conditions in the emulsion, i.e., the hydrogen ion and/or the silver ion concentration undergo little or no change in our method, we shall designate our method as a kind of supersensitization.

It is therefore an object of our invention to provide photographic silver halide emulsions containing certain benzimidaozolocarbocyanine dyes and, as supersensitizers therefor certain benzimidazoloindocarbocyanine dyes. Another object is to provide such supersensitized emulsions which are characterized by having single sensitivty maxima at wavelengths intermediate between those of the emulsions sensitized with the dyes individually. Another object is to provide a process for preparing these sensitized silver halide emulsions. Other objects will become evident from a consideration of the following specification and claims.

The benzimidazolocarbocyanine dyes useful in practicing our invention can advantageously be represented by the following formula:

I.

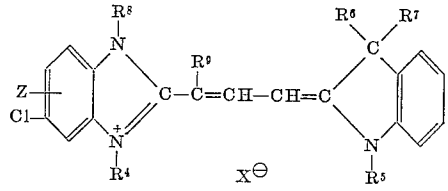


wherein R, R^1, R^2 and R^3 each represents the same or a different group selected from the class consisting of an alkyl group, e.g., methyl, ethyl, propyl, butyl, allyl(vinylmethyl), etc., a sulfoalky group, e.g., sufomethyl, β-sulfoethyl, 3-sulfopropyl, 3-sulfobutyl, 2-sulfobutyl, 4-sulfobutyl, etc., and a carboxyalkyl group, e.g., carboxymethyl, β-carboxyethyl, 2-carboxypropyl, 3-carboxybutyl, 4-carboxybutyl, etc.; W represents the acetyl group, the chlorine atom or the bromine atom; Y and Y^1 each represents

an atom selected from the class consisting of hydrogen, chlorine and bormine; and $X^\ominus$ represents an acid anion, e.g., chloride, bromide, iodide, perchlorate, sulfate, methyl sulfate, ethyl sulfate, p-toluenesulfonate, benzenesulfonate, thiocyanate, etc.

The benzimidazoloindocarbocyanine dyes useful in practicing our invention can advantageously be represented by the formula:

II



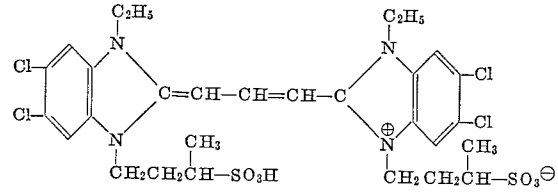
wherein R^4 and R^5 each represents the same or a different group selected from the class consisting of an alkyl group (e.g., methyl, ethyl, propyl, butyl, allyl(vinylmethyl), etc.), a sulfoalkyl group (e.g., sulfomethyl, sulfoethyl, 3-sulfobutyl, 4-sulfobutyl, etc.), and a carboxyalkyl group (e.g., carboxymethyl, β-carboxyethyl, 3-carboxypropyl, 4-carboxylbutyl, etc.); a phenyl group (e.g., phenyl, 4-methylphenyl, etc.), R^6 and R^7 each represents the same or a different alkyl group (e.g., methyl, ethyl, propyl, butyl, allyl, etc.); R^8 represents a group selected from the class represented by R^4 and an alkylene group (e.g., methylene, ethylene, etc.); R^9 represents a member selected from the class consisting of the hydrogen atom and the methylene group, such that when R^8 is an alkylene group, R^9 is the methylene group, and R^8 and R^9 together form an alkylene bridge; Z represents an atom selected from the class consisting of hydrogen, chlorine, and bromine; and $X^\ominus$ is as defined previously.

According to our invention, we incorporate one or more of the benzimidazolocarbocyanine dyes of Formula I with one or more the benzimidazoloindocarbocyanines of Formula II in a photographic silver halide emulsion. Our invention is particularly directed to the ordinarily employed gelatino-silver halide emulsions in which the silver halide may be silver chloride, silver bromide, silver chloroiodide, silver chlorobromoiodide, etc. However, our supersensitizing combinations can be employed to advantage in silver halide emulsions in which the carrier or vehicle used is a gelatin substitute, e.g., a resinous material such as polyvinyl alcohol, albumin, etc., or a hydrophilic cellulosic material which has no deleterious effect on the light-sensitive silver halide.

The concentration of the dyes used in our emulsions can be varied considerably depending upon the particular dyes used, the emulsion and the particular results desired. The optimum concentrations can be determined by methods well known in the art, in which the sensitivity is determined for a series of test portions of the emulsion desired, each portion containing a different concentration of the dyes.

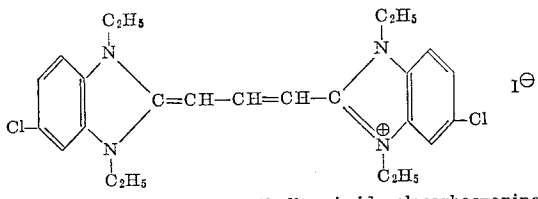
Included among the benzimidazolocarbocyanine dyes of Formula I used to advantage according to our invention are the following typical examples.

I



Anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide

II



5,5'-dichloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide

III

5,5',6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide

IV

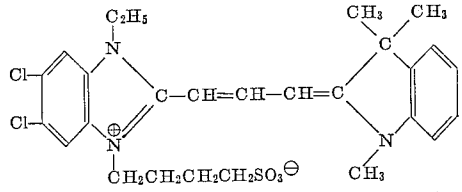
5,5'-diacetyl-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide

V

Anhydro-1,1'-di(β-carboxyethyl)-5,5',6,6'-tetrachloro-3,3'-diethylbenzimidazolocarbocyanine hydroxide

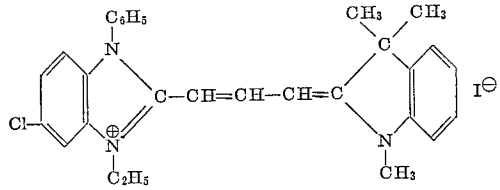
Included among the benzimidazoloindocarbocyanine dyes of Formula II used to advantage according to our invention are the following typical examples.

VI



Anhydro-5,6-dichloro-1-ethyl-1',3',3'-trimethyl-3-(4-sulfobutyl)benzimidazoloindocarbocyanine hydroxide

VII



5-chloro-3-ethyl-1',3',3'-trimethyl-1-phenylbenzimidazoloindocarbocyanine iodide

VIII

5,6-dichloro-1-ethyl-1',3',3'-trimethyl-3-phenylbenzimidazoloindocarbocyanine iodide

IX

1-carboxyethyl-5,6-dichloro-3-ethyl-1',3',3'-trimethylbenzimidazoloindocarbocyanine iodide

X

4,5-dichloro-1,3-diethyl-1',3',3'-trimethylbenzimidazoloindocarbocyanine perchlorate

Also included among the dyes useful according to our invention are the following additional examples. Dyes XI and XII further illustrate the dyes of Formula I and Dye XIII illustrates a bridged dye of Formula II.

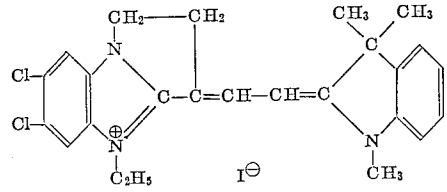
XI

Anhydro-4,4',5,5'-tetrachloro-3,3'-diethyl-1,1'-disulfobutylbenzimidazolocarbocyanine hydroxide

XII

5,5'-dibromo-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide

XIII



5,6-dichloro-3-ethyl-1,8-ethylene-1',3',3'-trimethylbenzimidazoloindocarbocyanine iodide

Photographic silver halide emulsions, such as those described, containing the supersensitizing combinations of our 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; Damschroder 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-nitroindazole, 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 June 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.

Our invention is still further illustrated by the following examples which show the supersensitizing effects of our dye combinations and also the single mixed aggregate sensititvity maxima that are at a wavelength between those produced by the individual dyes. The single mixed aggregate is of special importance in color materials where the benzimidazolo-carbocyanine dyes alone tend to sensitize too deeply to be useful in the green region of the spectrum.

Example 1

A silver bromoiodide emulsion was made of the type described by Trivelli and Smith, Phot. Journal, Vol. 79, 330 (1939). The melted emulsion was divided into separate portions to which were added a solution of the sensitizer or combination of sensitizers indicated in Table 1. After being digested at 50° C. for 10 minutes, each of the portions of the sensitized emulsions was coated on a separate support and dried. A portion of each of the dried coatings was exposed on an Eastman Sensitometer (Type 1B) for 1 second to light of sunlight quality modulated with a Wratten #15 filter and processed for 3 minutes in a developer having the composition:

p-Methylaminophenol sulfate	g	2.0
Sodium sulfite, desiccated	g	90.0
Hydroquinone	g	8.0
Sodium carbonate, monohydrate	g	52.5
Potassium bromide	g	5.0
Water to make	liter	1.0

fixed in a conventional sodium thiosulfate fixing bath, washed and dried. Densitometric measurements were made of the developed images on each coating. The relative speed values were calculated based on an arbitrary relative speed of 100 for the coating sensitized with 0.2 gram of Dye I per mole of silver, and the gammas (i.e., a value representing the slopes of the straight line portion of the curves relating developed image density to the amount of exposure used to produce the latent image resulting in the developed image) were determined.

The reflectance spectra of another portion of the coatings for each dye or dye combination was plotted for light in the visual region with a General Electric Recording Spectrophotometer. The single absorption maxima obtained from these curves are listed in Table 1 along with the relative speeds, gammas and fog values.

TABLE 1

Dye and Concentration (g./mole of silver)	Absorption Maximum (mμ)	Relative Speed	Gamma	Fog
I (0.10)		73	2.50	.09
I (.2)	579	100	2.16	.10
I (.1)+VI (.15)	567	135	2.26	.09
I (.1)+VII (.074)	571	115	2.27	.09
I (.1)+VIII (.15)	571	112	2.20	.09
I (.1)+IX (.15)	568	148	2.24	.10
I (.1)+X (.15)	566	141	2.20	.11
VI (.074)		47	3.18	.07
VI (.15)	555	69	2.62	.08
VII (.074)	549	37	3.48	.07
VII (.15)		42	3.20	.08
VIII (.074)		45	3.68	.08
VIII (.15)	560	48	2.70	.08
IX (.074)		35.5	3.22	.06
IX (.15)	552	62	3.06	.06
X (.074)		18	3.22	.07
X (.15)	490, 516	24	3.28	.08

This example shows that relative speeds as high as 148 were obtained from 0.1 g. Dye I+0.15 g. Dye IX per mole of silver while 0.1 g. of Dye I and 0.15 g. of Dye IX per mole of silver gave relative speeds of 73 and 62, respectively, when used separately.

Example 2

Coatings were made as in Example 1 excepting that Sensitizers II, VI and the combination of these were used. The coatings were treated as in Example 1 to determine the absorption maximum, relative speed, gamma and fog values which are recorded in the following table. The relative speeds were calculated based on an arbitrary relative speed of 100 for the coating sensitized with 0.2 g. of Dye II per mole of silver.

TABLE 2

Dye and Concentration (g./mole of silver)	Absorption Maximum (mμ)	Relative Speed	Gamma	Fog
II (.1)		76	1.41	.06
II (.2)	566	100	1.84	.05
II (.1)+VI (.15)	556	182	2.44	.08
VI (.074)		115	3.10	.06
VI (.15)	555	123	2.60	.06

This example shows that relative speeds as high as 182 were obtained from 0.1 g. of Dye II+0.15 g. of Dye VI per mole of silver while 0.1 g. of Dye II and 0.15 g. of Dye VI per mole of silver gave relative speeds of 76 and 123, respectively, when used separately.

Example 3

Coatings were made as in Example 1 excepting that Sensitizers I, XII, XIII, I+XIII and XII+XIII were used. The coatings were treated as in Example 1 to determine the absorption maximum, relative speed, gamma and fog values excepting that the sensitometric exposures were made using Wratten Filters #16+#61 instead of Wratten #15 Filter. The relative speed values were calculated based on an arbitrary relative speed of 100 for the coating sensitized with 0.16 g. of Dye XIII per mole of silver.

TABLE 3

Dye and Concentration (g./mole of silver)	Absorption Maximum (mμ)	Relative Speed	Gamma	Fog
XIII (0.16)	547	100	1.21	.05
XII (0.16)	567	95	1.38	.05
XIII (0.08)+XII (0.08)	557	151	0.96	.04
I (0.16)	577	107	1.48	.04
XIII (0.08)+I (0.08)	566	138	1.35	.06

Example 4

Coatings were made as in Example 1 excepting that Sensitizers XI, X and XI+X were used. The coatings were treated as in Example 1 to determine the relative speed, gamma and fog values excepting that the sensitometric exposures were made using Wratten Filter #16 instead of Wratten #15 Filter. The relative speed values were calculated based on an arbitrary relative speed of 100 for the coating sensitized with 0.165 g. of Dye XI per mole of silver. The data are listed in Table 4.

TABLE 4

Dye and Concentration (g./mole of silver)	Relative Speed	Gamma	Fog
XI (0.165)	100	1.60	0.05
X (0.165)	135	1.27	0.05
XI (0.082)+(0.082)	513	1.27	0.05

Example 5

Coatings were made as in Example 1 excepting that Sensitizers III, IV, V, VI, III+VI, IV+VI and V+VI were used. The coatings were treated as in Example 1 to determine the absorption maximum, relative speed, gamma and fog values excepting that the sensitometric exposures were made during a Wratten #61 Filter instead of Wratten #15 Filter. The relative speed values were calculated based on an arbitrary relative speed of 100 for the coating sensitized with 0.2 g. of Dye III per mole of silver. The data obtained are summarized in the following table.

TABLE 5

Dye and Concentration (g./mole of silver)	Absorption Maximum (mμ)	Relative Speed	Gamma	Fog
III (.1)		73	2.12	.06
III (.2)	577	100	2.20	.06
III (.1)+VI (.15)	563	145	2.10	.06
IV (.1)		53	2.00	.06
IV (.2)	578	73	2.18	.07
IV (.1)+VI (.15)	565	135	2.48	.06
V (.1)		73	2.40	.06
V (.2)	576	91	2.32	.06
V (.1)+VI (.15)	569	138	2.26	.06
VI (.074)		83	2.86	.06
VI (.15)	555	91	2.42	.06

This example shows that relative speeds as high as 145 were obtained from 0.1 g. of Dye III+0.15 g. of Dye VI per mole of silver while 0.1 g. of Dye III and 0.15 g. of Dye VI per mole of silver gave relative speeds of 73 and 91, respectively, when used separately.

The invention is still further illustrated by a description of the preparation of typical dyes used or by references describing them.

Dyes I and XI are described in a general formula of Jones and Spence U.S. Patent 2,912,329, issued Nov. 10, 1959.

Dyes II and III are described as Examples 1 and 2, respectively, of Van Lare U.S. Patent 2,739,149, issued Mar. 20, 1956.

Dye IV is described as Example 1 of Brooker et al. U.S. Patent 2,778,823, issued Jan. 22, 1957.

Dye V is prepared by the method described for Example B in Jones U.S. Patent No. 2,945,763, issued July 19, 1960, excepting that an equivalent amount of β-iodopropionic acid was used in place of 4-bromovaleric acid. The Dye V made in this way when isolated appeared to be lacking HI.

Dye VI is prepared as follows. A mixture of 1.8 g. (1 mol.) of anhydro-5,6-dichloro-1-ethyl-2-methyl-3-(4-sulfobutyl)benzimidazolium hydroxide and 2.23 g. (1 mol.) of 2-β-acetanilidovinyl - 1,3,3 - trimethyl-3H-indolinium iodide in 20 ml. of absolute ethyl alcohol containing 1.01 g. of triethylamine was heated at the refluxing temperature for 2 hours. The cool mixture was treated

with diethyl ether, the supernatant liquid was decanted, and the residue was washed with diethyl ether. Then the remaining residue was dissolved in acetone, a little water was added and the dye became crystalline after the addition of sodium iodide. The yield of dye was 0.9 g. (32%) crude and 0.45 g. (16%) after two recrystallizations from 50% aqueous methanol.

The anhydro - 5,6-dichloro-1-ethyl-2-methyl-3-(4-sulfobutyl)benzimidazolium hydroxide was prepared by heating a mixture of 23.2 g. of 5,6-dichloro-1-ethyl-2-methylbenzimidazole and 13.6 g. of 1,4-butane sultone at 125° until the vigorous initial reaction was over and then at 160° for 30 minutes. After cooling, the resulting mass became crystalline when it was treated with hot acetone. After chilling the suspension, the solid was collected on a filter and washed with acetone. The yield of desired product was 24.5 g.

Dyes VII and VIII are described as Examples 13 and 14, respectively, in Wilmanns et al. U.S. 2,289,300, issued July 7, 1942.

Dyes IX and X are prepared by the method described by Wilmanns et al. for Example 14. For example, to make Dye IX 1-(β-carboxyethyl)-5,6-dichloro-3-ethyl-2-methylbenzimidazolium iodide (made by methods well known in the art) is used, and to make Dye X 4,5-dichloro-1,3-diethyl-2-methylbenzimidazolium iodide is used in place of 1-ethyl-2-methyl-3-phenyl-5,6-dichlorobenzimidazolium ethyl sulfate. The iodide salt of Dye X is then readily converted by methods well known in the art to the perchlorate salt.

Dye XII is described in Brooker et al. U.S. Patent 2,778,823, issued Jan. 22, 1957, as Example 3.

Dye XIII was prepared as follows, 5,6-dichloro-3-ethyl-1,2-trimethylenebenzimidazolium iodide (1 mole, 1.9 g.), 2-β-acetanilidovinyl - 1,3,3 - trimethyl-3H-indolium iodide and triethylamine (2 mols, 1.4 ml.) were dissolved in dry pyridine (20 ml.) and heated under reflux for 15 minutes. The reaction mixture was chilled and the solid products filtered from the filtrate. The filtrate was stirred with an excess of ether, causing the dye to crystallize from the solution. The precipitated dye was filtered off, dried and recrystallized twice from methanol to give a yield of 0.2 g., M.P. 285–286° C. dec.

Our invention is still further illustrated with the accompanying drawings, FIGS. 1 and 2, which show spectrophometric curves obtained for a photographic element coated with a silver bromoiodide emulsion sensitized with specific sensitizing dyes or supersensitizing combinations thereof.

FIG. 1 contains spectrophotometric curves A, B and C for emulsions described in Example 1. Curve A was obtained from the emulsion containing for each mole of silver (in the silver halide) 0.1 g. of Dye I, anhydro-5,5',6,6'-tetrachloro-1,1' - diethyl - 3,3'-di(3-sulfobutyl)benzimidazolocarbocyanine hydroxide. Curve B was obtained from the emulsion containing for each mole of silver 0.15 g. of Dye IX, 1-carboxyethyl-5,6-dichloro-3-ethyl-1',3',3' - trimethylbenzimidazoloindocarbocyanine iodide. Curve C was obtained from the emulsion containing for each mole of silver 0.1 g. of Dye I plus 0.15 g. of Dye IX.

FIG. 2 contains spectrophotometric curves D, E and F for emulsions described in Example 2. Curve D was obtained from the emulsion containing for each mole of silver, 0.1 g. of Dye II, 5,5'-dichloro-1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide. Curve E was obtained from the emulsion containing for each mole of silver, 0.15 g. of Dye VI, anhydro-5,6-dichloro-1-ethyl-1',3',3'-trimethyl - 3 - (4-sulfobutyl)benzimidazoloindocarbocyanine hydroxide. Curve F was obtained from the emulsion containing for each mole of silver 0.1 g. of Dye II plus 0.15 g. of Dye VI.

Curve C, FIG. 1, illustrates the single mixed aggregate sensitivity maximum for one of our supersensitizing combinations. The sensitivity maxima for curves A and B fall on either side of the mixed aggregate.

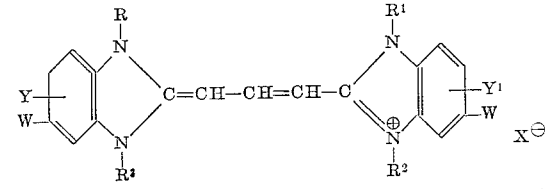
Curve F, FIG. 2, demonstrates the same effect relative to curves D and E.

Photographic silver halide elements coated with emulsions containing our supersensitizing combinations of certain benzimidazolocarboncyanine dyes and certain benzimidazoloindocarbocyanine dyes are valuable. Our elements are characterized by having substantially higher relative speeds than the elements containing emulsions sensitized with the individual dyes. Another valuable characteristic obtained with emulsions containing our supersensitizing combinations is the single mixed aggregate sensitivity maxima that are at a wavelength between those produced by the individual dyes. This is of special importance in color materials where the benzimidazolocarbocyanine dyes alone tend to sensitize too deeply to be useful in the green region of the spectrum. Because of the single mixed aggregate sensitivity maxima our supersensitizing combinations are valuable for use in color materials, including use in the green region of the spectrum.

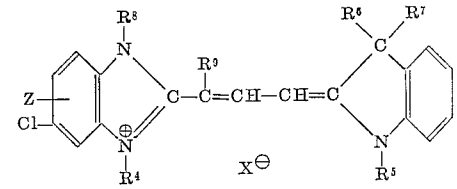
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic silver halide emulsion containing a supersensitizing combination of (1) at least one benzimidazolocarbocyanine dye having the formula:



wherein R, R^1, R^2 and R^3 each represents a member selected from the class consisting of an alkyl group, a sulfoalkyl group and a carboxyalkyl group; W represents a member selected from the class consisting of the acetyl group, the chlorine atom and the bromine atom; Y and Y^1 each represents an atom selected from the class consisting of hydrogen, chlorine and bromine; and $X^{\ominus}$ represents an acid anion, and (2) at least one benzimidazoloindocarbocyanine dye having the formula:



wherein R^4 and R^5 each represents a group selected from the class consisting of an alkyl group, a sulfoalkyl group, a carboxyalkyl group, and a phenyl group; R^6 and R^7 each represents an alkyl group; R^8 represents a group selected from the class consisting of an alkyl group, a carboxyalkyl group, a phenyl group and an alkylene group; R^9 represents a member selected from the class consisting of the hydrogen atom and the methylene group, such that when R^8 is an alkylene group, R^9 is the methylene group and R^8 and R^9 together form an alkylene bridge having from 2 to 3 carbon atoms; Z represents an atom selected from the class consisting of hydrogen, chlorine and bromine; and $X^{\ominus}$ is as described previously.

2. A photographic silver halide emulsion of claim 1 containing a supersensitizing combination of a benzimidazolocarbocyanine dye and a benzimidazoloindocarbocyanine dye in which the said benzimidazoloindocarbocyanine

dye is anhydro - 5,6 - dichloro - 1 - ethyl - 1',3',3' - trimethyl - 3 - (4 - sulfobutyl)benzimidazoloindocarbocyanine hydroxide.

3. A photographic silver halide emulsion of claim 1 containing a supersensitizing combination of a benzimidazolocarbocyanine dye and a benzimidazoloindocarbocyanine dye in which the said benzimidazoloindocarbocyanine dye is 1 - carboxyethyl - 5,6 - dichloro - 3 - ethyl-1',3',3' - trimethylbenzimidazoloindocarbocyanine iodide.

4. A photographic silver halide emulsion of claim 1 containing a supersensitizing combination of a benzimidazolocarbocyanine dye and a benzimidazoloindocarbocyanine dye in which the said benzimidazoloindocarbocyanine dye is 4,5 - dichloro - 1,3 - diethyl - 1',3',3' - trimethylbenzimidazoloindocarbocyanine perchlorate.

5. A photographic silver halide emulsion of claim 1 containing a supersensitizing combination of a benzimidazolocarbocyanine dye and a benzimidazoloindocarbocyanine dye in which the said benzimidazoloindocarbocyanine dye is 5 - chloro - 3 - ethyl - 1',3',3' - trimethyl - 1-phenylbenzimidazoloindocarbocyanine iodide.

6. A photographic silver halide emulsion of claim 1 containing a supersensitizing combination of a benzimidazolocarbocyanine dye and a benzimidazoloindocarbocyanine dye in which the said benzimidazoloindocarbocyanine dye is 5,6 - dichloro - 1 - ethyl - 1',3',3' - trimethyl-3-phenylbenzimidazoloindocarbocyanine iodide.

7. A photographic silver halide emulsion containing a supersensitizing combination of anhydro-5,5',6,6'-tetrachloro - 1,1' - diethyl - 3,3' - di(3 - sulfobutyl)benzimidazolocarbocyanine hydroxide with 1 - carboxyethyl - 5,6-dichloro - 3 - ethyl - 1',3',3' - trimethylbenzimidazoloindocarbocyanine iodide.

8. A photographic silver halide emulsion containing a supersensitizing combination of 5,5' -dichloro - 1,1',3,3'-tetraethylbenzimidazolocarbocyanine iodide with anhydro - 5,6 - dichloro - 1 - ethyl - 1',3',3' - trimethyl - 3 - (4-sulfobutyl)benzimidazoloindocarbocyanine hydroxide.

9. A photographic silver halide emulsion containing a supersensitizing combination of 5,5',6,6' - tetrachloro-1,1',3,3' - tetraethylbenzimidazolocarbocyanine iodide with anhydro - 5,6 - dichloro - 1 - ethyl - 1',3',3' - trimethyl - 3 - (4 - sulfobutyl)benzimidazoloindocarbocyanine hydroxide.

10. A photographic silver halide emulsion containing a supersensitizing combination of anhydro - 5,5',6,6' - tetrachloro - 1,1' - diethyl - 3,3' - di(3 - sulfobutyl)benzimidazolocarbocyanine hydroxide with 4,5 - dichloro - 1,3 - diethyl - 1',3',3' - trimethylbenzimidazoloindocarbocyanine perchlorate.

11. A photographic silver halide emulsion containing a supersensitizing combination of anhydro - 4,4',5,5' - tetrachloro - 3,3' - diethyl - 1,1' - disulfobutylbenzimidazolocarbocyanine hydroxide with 4,5 - dichloro - 1,3 - diethyl-1',3',3' - trimethylbenzimidazoloindocarbocyanine perchlorate.

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

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