United States Patent Office

2,912,329
Patented Nov. 10, 1959

2,912,329

GREEN SENSITIZATION FOR PHOTOGRAPHIC EMULSIONS CONTAINING COUPLER DISPERSIONS

Jean E. Jones and John Spence, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Application August 23, 1957
Serial No. 680,003

5 Claims. (Cl. 96—100)

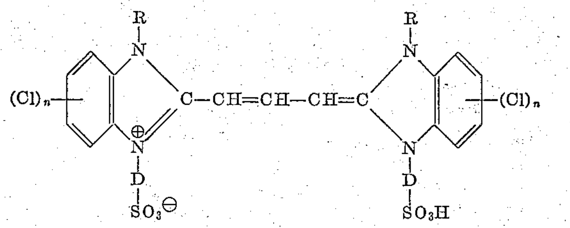
This invention relates to spectrally (optically) sensitized photographic silver halide emulsions containing color couplers, i.e., color-forming compounds which couple with the oxidation products of a color developer, such as a phenylenediamine developer, to provide a colored image.

It is known that certain sensitizing dyes are particularly useful in combination with photographic silver halide emulsions containing color couplers in that no interference takes place between the color couplers and the sensitizing dyes, insofar as displacement of the sensitizing dye fom the silver halide grains by the color coupler is concerned. See, for example, Spence and Carroll U.S. Patent 2,640,776. However, not all sensitizing dyes which can be employed in combination with color couplers are useful in color photography, inasmuch as a number of such dyes give rise to or contribute to the formation of undesirable fog.

Accordingly, it is an object of our invention to provide improved green sensitization for photographic emulsions containing color couplers for the magenta image. Another object is to provide green sensitization without undesirable fog for color emulsions containing color couplers. Still another object is to provide a method for making an improved green sensitized photographic emulsion. Other objects will become apparent from a consideration of the following examples and description.

The above objects are accomplished by sensitizing photographic silver halide emulsions containing a color coupler with a spectral sensitizing dye selected from those represented by the following general formula:

I.



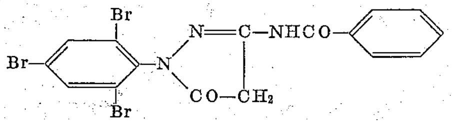
wherein R represents a lower alkyl group, such as methyl, ethyl, etc. (e.g., an alkyl group containing from 1 to 2 carbon atoms), *n* representse a positive integer of from 1 to 2 and D represents an alkylene group, such as ethylene, trimethylene, tetramethylene, ω-methyltrimethylene, etc. We have found that the dyes represented by Formula I above wherein the acid substituents on the nitrogen atoms of the chlorinated benzimidazole nucleus are 4-sulfobutyl or 3-sulfobutyl, are especially useful for the purposes of our invention.

The spectral sensitizing dyes of Formula I are quite unique in that they contain both an anion and cation (i.e., a zwitterion). Such dyes are usually named anhydro dyes, as though water had been split from the hydrogen of a sulfo group and a hypothetical hydroxyl group attached to one of the heterocyclic nitrogen atoms. These dyes have the conventional resonance system of carbocyanine dyes; it is to be understood that the particular resonance structure shown in Formula I is merely illustrative, and that the negative charge of the sulfonic acid group can be on either sulfo group (or both, depending on ionization of second sulfo group). A zwitterion results in either case. Such matters are well understood by those skilled in the art.

The spectral sensitizing dyes of Formula I have their maximum absorption in the green region of the spectrum and they exhibit excellent blue-green separation. Accordingly, these dyes are used in combination with coupler dispersions for the magenta or purple image. Couplers for the magenta image which have been found particularly useful in our invention comprise the well-known class of color-forming compounds known as pyrazolone couplers. The structure of the couplers is not as critical, however, as the nature of the particular sensitizing dyes employed, insofar as we have been able to determine. This is mentioned in somewhat greater detail below.

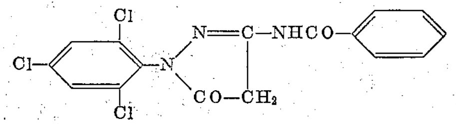
The following compounds illustrate the class of magenta couplers which are useful in practicing our invention:

(1)



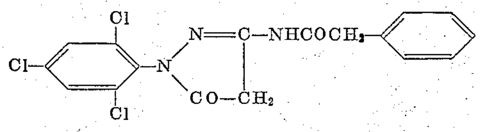
1-(2′,4′,6′-tribromophenyl)-3-benzamido-5-pyrazolone

(2)



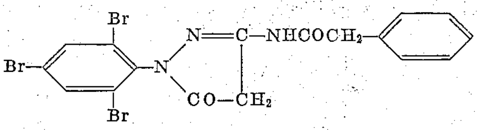
1-(2′,4′,6′-trichlorophenyl)-3-benzamido-5-pyrazolone

(3)



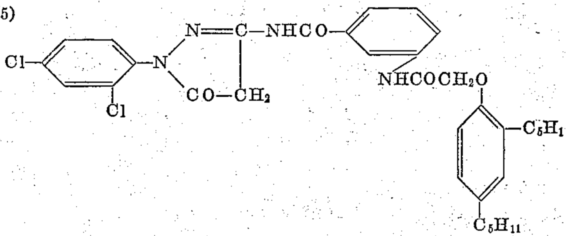
1-(2′,4′,6′-trichlorophenyl)-3-phenylacetamido-5-pyrazolone

(4)



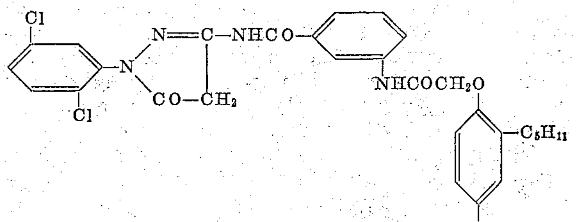
1-(2′,4′,6′-tribromophenyl)-3-phenylacetamido-5-pyrazolone

(5)



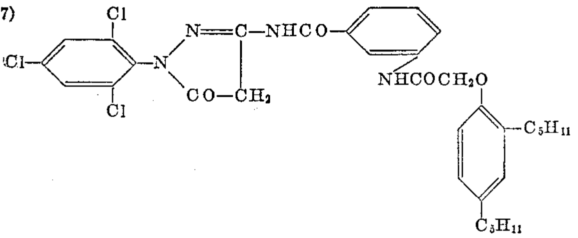
1-(2′,4′-dichlorophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacetamido)-benzamido]-5-pyrazolone

(6)



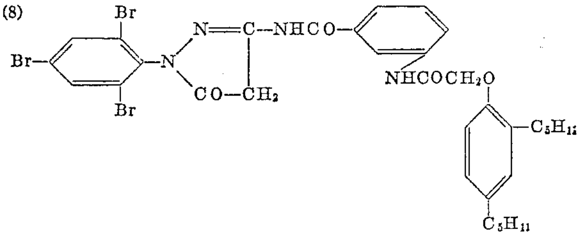
1-(2′,5′-dichlorophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacetamido)-benzamido]-5-pyrazolone

(7)



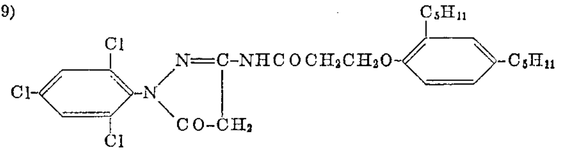
1-(2',4',6'-trichlorophenyl) - 3 - [3'' - (2''',4'''-di-tert. amylphenoxyacetamido)-benzamido]-5-pyrazolone

(8)



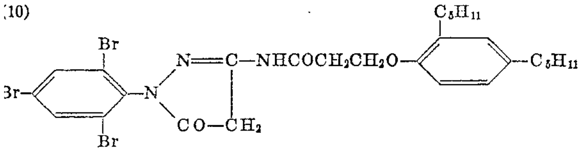
1-(2',4',6'-tribromophenyl) - 3 - [3'' - (2''',4'''-di-tert. amylphenoxyacetamido)-benzamido]-5-pyrazolone

(9)



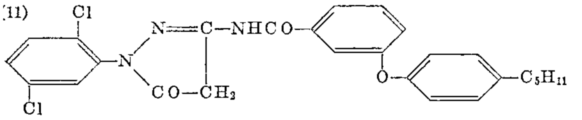
1 - (2',4',6' - trichlorophenyl) - 3 - [β - 2''',4'''-di-tert. amylphenoxy)-propionamido]-5-pyrazolone

(10)



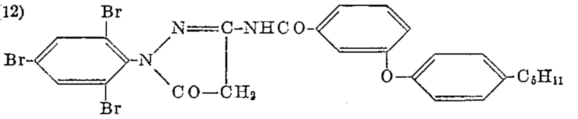
1 - (2',4',6' - tribromophenyl) - 3 - [β - 2''',4'''-di-tert. amylphenoxy)-propionamido]-5-pyrazolone

(11)



1-(2',5'-dichloro)-3-[3''-(4'''-tert. amylphenoxy)-benzamido]-5-pyrazolone

(12)



1-(2',4',6'-tribromophenyl)-3-[3''-(4'''-tert. amylphenoxy)-benzamido]-5-pyrazolone

In the preparation of photographic elements for color photography employing the new green-sensitive emulsions of our invention, any of the customary procedures can be used. It is known, for example, that blue-, green- and red-sensitive photographic silver halide emulsions are employed in subtractive color photography and the green-ensitive emulsions of our invention can be employed in combination with blue- and red-sensitive emulsions in any desired manner. Thus, the separate emulsions can be coated on a support as separate layers, e.g., a support of cellulose acetate film, resin film, paper, etc., can be coated with a layer of a red-sensitive emulsion containng a color coupler, and upon this, a layer of a greenensitive emulsion of our invention containing a color ormer or coupler can be coated. Upon the green-sensiive layer, a yellow filter layer can be coated, and upon he filter layer, a layer of a blue-sensitive emulsion conaining a color former which produces a yellow image an be coated. Typical multi-emulsion photographic lements involving color couplers or color formers in he emulsion, to which our invention is applicable, are described in U.S. Patents 1,055,155, dated March 4, 1913; 2,304,940, dated December 15, 1942 and 2,322,027, dated June 15, 1943.

Our invention is also applicable to color photographic emulsion material wherein the emulsions are mixed instead of disposed in separate layers. Moreover, our invention is also applicable for producing single emulsions containing color-formers for making component color pictures. In addition to the sensitizing dyes and color-formers, the emulsions employed in our invention can also contain the usual additions to emulsions, e.g., stabilizers, etc.

Our invention is especially useful where the emulsions contain, in addition to a color-former, a dispersing agent for the color-former, e.g., the water-insoluble but water-permeable materials set forth in U.S. Patents 2,304,940 and 2,322,027, such as water-insoluble but water-permeable cellulose esters, e.g., water-insoluble, but water-permeable cellulose acetate, cellulose acetate-phthalate, cellulose nitrate, etc., water-insoluble, but water-permeable cellulose ethers, water-insoluble but water-permeable natural and synthetic resins, high-boiling, substantially water-insoluble crystalloidal materials, such as N-n-amylphthalimide, tetrahydrofurfuryl benzoate, triphenyl phosphate, n-butyl sulfone, ethyl-N,N-di-n-butylcarbamate, ethyl-N-phenylcarbamate, tetrahydrofurfuryl succinate, ethyl benzyl malonate, methyl phthalate, n-butyl phthalate, n-amyl phthalate, β-methoxyethyl phthalate, β-ethoxyethyl phthalate, β-butoxyethyl phthalate, butyl p-methoxybenzoate, n-hexyl benzoate, benzophenone, p-sec-amylbenzophenone, tricresyl phosphate, diphenyl mono-p-tert. butyl phenyl phosphate, monophenyl di-o-chlorophenyl phosphate, tri-o-phenylphenyl phosphate, p-toluenesulfonyl methyl-o-toluidine, p-toluenesulfonyl dimethylamide, p,p'-di-amylbenzenesulfonamide, p-toluenesulfonyl di-n-butyl amide, N,N'-diethyl-N,N'-diphenyl urea, N,N-di-n-butyl urea, etc.

Our invention is especially useful with emulsions in which the color-former is dispersed in one or more of the aforesaid substantially water-insoluble, high-boiling crystalloidal materials. These crystalloidal materials are organic and have boiling points above about 175° C. These crystalloidal materials have a high solvent action for the color-formers and for the dyes formed therefrom and are permeable to photographic processing solutions. These crystalloidal materials have been referred to as "oil formers" because they have the property of producing an oily or liquid solution when mixed with the coupler, even though the coupler is a solid. The crystalloidal materials are generally liquid at ordinary temperatures or low melting solids (below 100° C.). The most useful compounds contain one or more polar groups such as halogen, hydroxyl, carboxylic acid, amide, ketone, etc.

The above-mentioned color couplers provide a magenta image upon development with color developers, such as N,N-dimethyl - p - phenylenediamine, N,N - diethyl - p - phenylenediamine, N - carbamidomethyl - N-methyl - p - phenylenediamine, N^4 - carbamidomethyl-N^4 - tetrahydrofurfuryl - 2 - methyl - p - phenylenediamine, N^4 - ethyl - N^4 - carboxymethyl - 2 - methyl-p - phenylenediamine, N^4 - carbamidomethyl - N^4 - ethyl-2 - methyl - p - phenylenediamine, N^4 - ethyl - N^4 - tetrahydrofurfuryl - 2 - methyl - p - phenylenediamine, N^4-ethyl - N^4 tetrahydrofurfuryl - 2 - methyl - p - aminophenol, 3 - acetylamino - 4 - aminodimethylaniline, N-ethyl - N - β - methanesulfonamidoethyl - 4 - aminoaniline, N - ethyl - N - β methanesulfonamido - ethyl-3 - methyl - 4 - aminoaniline, the sodium salt of N-methyl - N - β - sulfo - ethyl - p - phenylenediamine etc.

In Table A, the unique effect obtained with one of the dyes of Formula I above is illustrated. The table also illustrates the effect provided by a similar dye containing only ethyl groups attached to the nitrogen atoms of the chlorinated benzimidazole nuclei. The results were obtained as follows:

To a melted negative-speed gelatino-silver-bromiodide emulsion was added a spectral sensitizing dye (0.132 g./mol. AgX) as identified in the table in methanol solution. A coupler dispersion containing 1-(2′,4′,6′-trichlorophenyl)-3-[3″-(2‴,4‴-di - tert. amylphenoxyacetamido)-benzamido]-5-pyrazolone (0.142 g./mol. AgX) in dibutylphthalate was then added. A spreading agent, such as saponin, and hardener, such as formaldehyde, were then added. The emulsions were then divided into several batches and each batch coated on a cellulose acetate support, chilled, set and dried. After exposure in an Eastman Type I*b* Sensitometer through a Wratten Filter No. 61 (i.e., a filter which transmits visible radiation only between 480 and 560 mμ., with a maximum between 520 and 530 mμ.), the film strips were processed through the Kodak Color Negative Process for the times indicated. This process is described in detail in an article by W. T. Hanson and W. I. Kisner in "Soc. Mot. Pic. TV Eng.," vol. 61, No. 6. pages 667–701, December 1953. The relative speed for each of the batches, as compared to a control at a density of 0.3 above fog, was almost identical (allowing for slightly different curve shapes). However, a marked difference in fog density was apparent, these figures being given in the following table:

TABLE A

Coating No.	Dye	Fog			
		8′	12′	16′	20′
1	I	0.28	0.53	0.92	1.23
2	II	.07	.11	.22	.39

I=5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidazolo-carbocyanine iodide.
II=anhydro-5,5′6,6′-tetrachloro-1,1′-diethyl-3,3′-di(4-sulfobutyl)benzimidazolocarbocyanine hydroxide.

The above data clearly shows the marked difference in fog unexpectedly provided by the sulfobutyl dye. It is quite significant that dyes, which are structurally related to dyes I and II in that they contain only one sulfoalkyl group, do not provide the unique advantages illustrated for dye II of Table A. These related dyes, such as anhydro - 5,6 - dichloro-1-ethyl - 1′,3,3′ - trimethyl - 3 - sulfobutylbenzimidazoloindocarbocyanine hydroxide, show a fog level in combination with color couplers which is almost identical with dye I of Table A thus making these dyes much less useful for the purposes of the present invention.

In a manner similar to that illustrated in Table A, other dyes embraced by general Formula I above, such as anhydro - 5,5′, 6,6′ - tetrachloro - 1,1′ - diethyl - 3,3′-di(3 - sulfobutyl)benzimidazoloindocarbocyanine hydroxide, can be used in combination with color couplers, such as those identifiied as couplers 1–12 above.

In preparing emulsions in accordance with our invention, the sensitizing dyes can be added to the emulsions in accordance with customary procedures, i.e., by adding a solution of the dye in an appropriate solvent to the emulsions, such as illustrated in preparing the coatings of Table A above. Solvents other than the methyl alcohol illustrated above can also be used; such solvents include pyridine, acetone, etc., or mixtures of such solvents. The amount of sensitizing dye employed can be varied, depending upon the characteristics of the particular emulsion employed, results desired, etc. In general, from about 5 to 100 mg. of dye per liter of emulsion is sufficient to obtain maximum sensitization.

In most cases, it is convenient to add the sensitizing dyes to the emulsions before the coupler dispersion is added.

The color-formers (couplers) are incorporated in the emulsions in the customary manner, e.g., by adding a dispersion of the coupler in a water-insoluble but water-permeable material to the emulsion, or by adding a dispersion of the alkali metal salt of the coupler in water. When employing dispersions of couplers in the aforesaid crystalloidal materials, the coupler (colo former) which has been mixed with the high-boiling organic crystalloidal material to produce an oil-like mixture can be dispersed in water or gelatin solution or in any aqueous binder of colloidal character which i miscible with the silver halide emulsion. The dispersion can be effected with the aid of a homogenizer, colloid mill or the like, and the dispersions can be stabilized by the addition of emulsifying agents such as those of the well-known higher fatty alcohol sulfate type. The dispersion may also be formed by dispersing a solution of coupler and crystalloidal material in a solvent of low boiling point such as butyl acetate with water or gelatin solution and subsequently removing the low-boiling solvent by evaporation. Here also an emulsifying agen can be used. It is important that the mixture of coupler and crystalloidal material be a liquid at ordinary temperatures, so that liquid particles are formed when the mixture of coupler and crystalloidal material is emulsified in water and mixed with the emulsion, the particles retaining the coupler in solution, yet being readily penetrated by the photographic developing solution and other processing baths. The nature and proportions of the coupler and the crystalloidal material should be chosen so that the particles are liquid under the conditions of coating and processing the emulsion. With the aforesaid crystalloidal materials, there is little or no tendency to crystallization even when the coupler is present in a proportion amounting to 50% or more of the high-boiling crystalloidal material. The crystalloidal materials should also be substantially colorless and stable toward light, heat and moisture, in addition to being inert to the various processing baths which may be encountered such as developers, oxidized developers, silver remova baths and fixing baths. They should have a sufficiently low refractive index so that solutions of the couplers in them have approximately the same refractive index as gelatin, thereby minimizing the opacity or light scattering of the coating. Most couplers themselves have high refractive indices and for this reason it is desirable that the oil formers have low refractive indices. The crystalloidal materials should be easily dispersible in the emulsions and should be chemically inert toward the couplers and dyes formed therefrom.

Our invention is directed primarily to the ordinarily employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chlorobromiodide, -iodochloride, -bromide and -bromiodide developing-out emulsions. These ordinarily employed silver halide developing-out emulsions are emulsions which form "surface" latent image (see British Patent 581,772, accepted October 24, 1946). However, silver halide emulsions which form latent image mostly inside the silver halide grains (see British Patent 581,772 supra) can also be employed in practicing our invention.

The dyes of general Formula I above can be prepared according to methods previously described in the prior art, such as illustrated in Van Lare U.S. Patent 2,739,149, issued March 20, 1956. The preparation of one of the dyes useful in our invention is illustrated in the following examples:

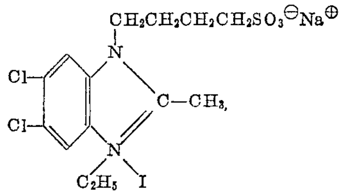
Example 1.—4-iodobutane sulfonic acid, sodium salt

$$ICH_2CH_2CH_2CH_2SO_3Na$$

To a solution of 5 gm. (1 mol.) of sodium iodide in 115 ml. of methyl alcohol was added 13.6 g. (1 mol.) of 1,4-butanesulfone and the reaction mixture refluxed for 1½ hours. The reaction mixture was concentrated to a small volume and the mixture chilled. The solid was filtered off and washed with methyl alcohol. A yield of 71 g., 62% of colorless solid was obtained. The filtrates and washings were combined and concentrated to 50 ml. and diluted with 200 ml. of acetone. After chilling, the solid was filtered off and washed with acetone. A second crop of 23 g. 20% of slightly yellowish solid was obtained. On evaporating the filtrates and washings to dryness, a residue of 19 g. 16% of quite yellow solid was obtained.

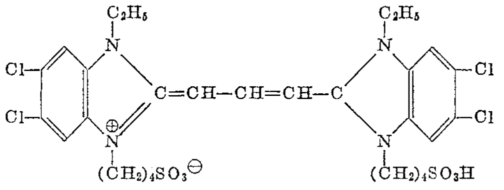
This is an adaptation of the method of Helberger et al., Ann., 565, 27 (1949), used in preparing the potassium salt.

Example 2.—5,6-dichloro-1-ethyl-2-methyl-3-(4-sulfobutyl)benzimidazolium iodide, sodium salt



An intimate mixture of 22.9 g. (1 mol.) of 5,6-dichloro-1-ethyl-2-methylbenzimidazole and 28.6 g. (1 mol.) of 4-iodobutane-sulfonic acid, sodium salt was heated at 170–180° C. for 2 hours. The hard glassy solid became crystalline after boiling with acetone for four hours. The large pieces were ground in a mortar and total solid refluxed an additional 2 hours with fresh acetone. The solid was filtered off and washed with acetone. A yield of 48 g. 93% of yellowish powder was obtained.

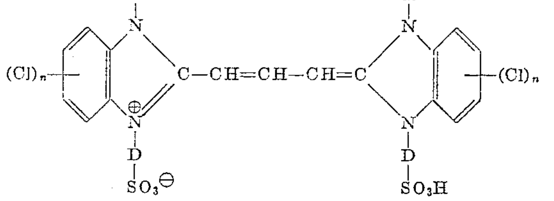
Example 3.—Anhydro-5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′ - di(4 - sulfobutyl) - benzimidazolocarbocyanine hydroxide



To a solution of 5.8 g. (5 mols.) of sodium in 500 ml. of ethyl alcohol was added 51.5 g. (2 mols.) of 5,6-dichloro - 1 - ethyl - 2 - methyl - 3 - (4 - sulfobutyl)benzimidazolium iodide, sodium salt and then 9.65 g. (1 mol.) of chloral alcoholate. The reaction mixture was refluxed for 1 hour and, after cooling, the solid filtered off. The solid was then suspended in 400 ml. of water and 10 gm. of sodium iodide. The solid was filtered off and again suspended in 400 ml. of water and 10 gm. of sodium iodide. After filtering, the solid was suspended in 200 ml. of methyl alcohol and 5 gm. of sodium iodide. After a second washing with methyl alcohol and sodium iodide, the dye was obtained as a red solid in a 30% yield, M.P. 289–290° C. dec.

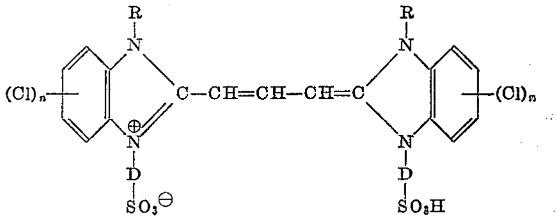
What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A green-sensitive photographic silver halide emulsion for color photography containing a color-former for the magenta image capable of reacting with the oxidation products of a phenylenediamine developer to form an azomethine dye, and a spectral sensitizing dye selected from those represented by the following general formula:



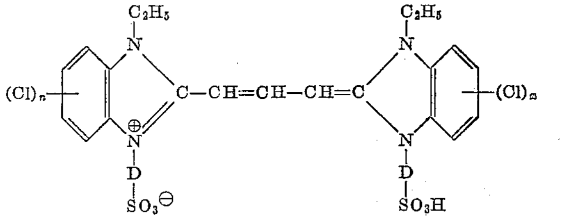
wherein R represents an alkyl group containing from 1 to 2 carbon atoms, *n* represents a positive integer of from 1 to 2 and D represents an alkylene group containing from 2 to 4 carbon atoms.

2. A green-sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely-divided liquid particles of a mixture of a pyrazolone color-former for the magenta image capable of forming an azomethine dye with the oxidation products of a phenylenediamine developer, and a spectral sensitizing dye selected from those represented by the following general formula:



wherein R represents an alkyl group containing from 1 to 2 carbon atoms, *n* represents a positive integer of from 1 to 2, and D represents an alkylene group containing from 2 to 4 carbon atoms.

3. A green-sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely-divided liquid particles of a mixture of a 5-pyrazolone color-former for the magenta image capable of forming an azomethine dye with the oxidation products of a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said green-sensitive emulsion being sensitized to the green with at least one spectral sensitizing dye selected from the group consisting of those dyes represented by the following general formula:



wherein *n* represents a positive integer of from 1 to 2 and D represents an alkylene group containing from 2 to 4 carbon atoms.

4. A green-sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely-divided liquid particles of a mixture of a 5-pyrazolone color-former for the magenta image capable of forming an azomethine dye with the oxidation products of a phenylenediamine developer, and a substantially water-insoluble, low molecular weight, organic, crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for the color-former and for the dye formed therefrom, and being permeable to photographic processing solutions, the nature and proportions of the color-former and crystalloidal material being so chosen that particles are liquid under conditions of coating and processing the emulsion, said green-sensitive emulsion being sensitized to the green with anhydro-5,5′,6,6′-tetrachloro-1,1′-diethyl - 3,3′ - di(4 - sulfobutyl)benzimidazolocarbocyanine hydroxide.

5. A green-sensitive gelatino-silver-halide emulsion for color photography containing dispersed therein finely-divided liquid particles of a mixture of 1-(2′,4′,6′-tetrachlorophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacet-

amido)-benzamido]-5-pyrazolone and a substantially water-insoluble, low molecular weight, organic crystalloidal material having a boiling point above about 175° C., said crystalloidal material having a high solvent action for said pyrazolone compound and for the dye formed therefrom by coupling with the oxidation products of a phenylenediamine color developer, and being permeable to photographic processing solutions, the nature and proportions of the pyrazolone compound and crystalloidal material being so chosen that particles thereof are liquid under conditions of coating and processing the emulsion, said green-sensitive emulsion being sensitized to the gree with anhydro-5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(sulfobutyl)benzimidazolocarbocyanine hydroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,503,776	Sprague	Apr. 11, 195
2,688,545	Carroll et al.	Sept. 7, 195
2,701,198	Carroll et al.	Feb. 1, 195
2,739,149	Van Lare	Mar. 20, 195