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## COLOR PHOTOGRAPHIC LIGHT-SENSITIVE MATERIALS FOR COLOR PRINTS SHOWING EXCELLENT COLOR REPRODUCTION

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**Int. Cl. G03c** *1/14, 1/16, 1/18*
**U.S. Cl. 96—68** **13 Claims**

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## ABSTRACT OF THE DISCLOSURE

A multiple layer type color photographic silver halide light-sensitive material for color prints having at least a blue-sensitive photographic emulsion layer in which the spectral sensitivity of the blue-sensitive silver halide emulsion layer is limited to the region of about 440 to about 460 nm., in which at least one dye having its absorption maximum at a wavelength region shorter than about 440 nm. and/or in a region of about 460 to about 520 nm. is incorporated in the blue-sensitive photographic emulsion layer of the light-sensitive material and/or in a layer coated on the blue-sensitive photographic emulsion layer.

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## BACKGROUND OF THE INVENTION

### Field of the invention

This invention relates to a multi-layer color photographic material, more particularly it relates to a multilayer color photographic film having an improved spectral sensitivity distribution of the blue-sensitive emulsion layer thereof. That is to say, the invention relates particularly to a color photographic film or a color paper suitable for making color prints from a transparent positive or a color negative having insufficient masking.

### Description of the prior art

Many methods have been known for making color photographs, but the method most employed at present is a subtractive color process based on the three primary color theory.

Dyes composing the color photographic image in the subtractive color process usually comprise a yellow dye having an absorption maximum at 420–460 nm., a magenta dye having an absorption maximum at 520–570 nm., and a cyan dye having an absorption maximum at 640–700 nm. However, the shape of the spectral absorption curve of each of the dyes used in practice is broad with respect to the wavelength, and each of the dyes has an undesirable absorption at a region other than the necessary absorption region. This undesirable absorption by the dye is one of the factors which induces a reduction in the color reproduction property of color photographic images. Further, when such a color photographic image is used for making color prints, the color reproduction property is further reduced.

In order to minimize the deteriorating influence of the undesirable absorption in making color prints in such a case, one technique wherein a light-sensitive material containing a masking mechanism therein is employed in the ordinary negative to positive process. However, in the case of making color prints from a transparent positive, such a masking technique (incorporated mask) cannot be employed and it is necessary to use complicated procedures such as an additional masking film and an additional masking step.

Therefore, if a color print is made using a transparent positive or a color photographic image formed with insufficient masking, color mixing will occur to reduce the color saturation.

In a green-sensitive emulsion layer and a red-sensitive emulsion layer of a general color photographic material for color prints, the spectrally sensitive region of each of the emulsion layers is sharply separated by the use of a proper sensitizing dye and thereby the desirable maximum wave-length region of the spectral sensitivity is determined.

However, in a blue-sensitive emulsion layer of an ordinary color photographic material having silver halide emulsion layers, the absorption region intrinsic to the silver halide in the emulsion is utilized and thus the spectrally sensitive region of the blue-sensitive layer is broad, a factor greatly different from the green-sensitive layer and the red-sensitive layer which are each spectrally sensitized with a dye. In short, the reduction in the color reproduction property of the blue-sensitive layer caused by the undesirable absorption of the dye described above has heretofore been considered unavoidable.

## SUMMARY OF THE INVENTION

One object of this invention is to provide a multi-layer type color photographic light-sensitive material illustrating lowered "color mixing" which also has a color reproduction almost the same as the original.

A further object of this invention is to provide a multilayer type photographic silver halide light-sensitive material for prints wherein the spectrally sensitive maximum wavelength of the blue-sensitive emulsion layer is a wavelength region which includes less undesirable side absorptions of the cyan dye and magenta dye and which is almost the same as the absorption maximum of a yellow dye, that is to say, in the region of substantially from 440 nm. to 460 nm.

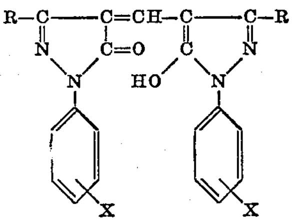
Another object of this invention is to provide a process of producing such a multi-layer type color photographic light-sensitive material.

These objects of the invention are attained by incorporating at least one dye having an absorption maximum in the wavelength region shorter than 440 nm. and/or a dye having an absorption maximum at 460–520 nm. in the blue sensitive photographic emulsion layer and/or in at least one of the layers, which may be a silver halide emulsion layer, of a multi-layer type silver halide color photographic light-sensitive material for color prints, which is coated over the blue sensitive photographic emulsion layer, whereby the spectrally sensitive wavelength region of the blue-sensitive layer is substantially limited to 440–460 nm. region.

## DETAILED DESCRIPTION OF THE INVENTION

As the dyes used in this invention, dyes represented by the following General Formulae I, II, and III are effectively used, either alone or as a combination thereof. The compounds represented by General Formulae I and III are novel dyes.

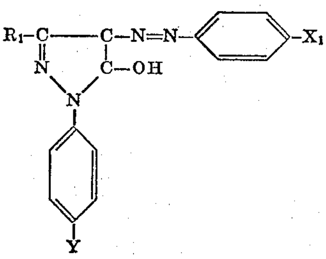
General Formula I:



wherein R represents an amino group, a hydroxyl group, or —OR′ (where R′ is a methyl group or an ethyl group) and X represents $—COO^{-}M^{+}$ or $—SO_3^{-}M^{+}$ ($M^{+}$ is a cation such as a hydrogen ion, an alkali metal ion such as a sodium ion or a potassium ion, or an ammonium ion, preferably $M^+$ is a potassium ion).

Any combination of groups R and X may be used. By changing R, the position (wavelength) of the absorption maximum may shift, but it is in the range of from about 360 nm. to about 430 nm.

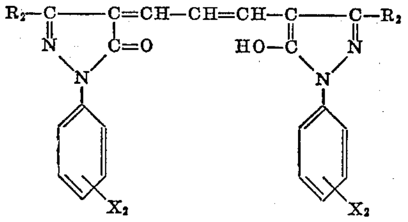
General Formula II:



wherein $R_1$ represents a methyl group, $-COOC_2H_5$, or $-COO^-M_1^+$; $X_1$ and Y each represents a hydrogen atom or $-SO_3^-M_1^+$, and $M_1^+$ is a cation like $M^+$ and is preferably a sodium ion or a potassium ion.

Any combination of the groups of $R_1$, $X_1$ and Y can be used and the absorption maximum wave length is in the region of from about 390 nm. to 440 nm.

General Formula III:



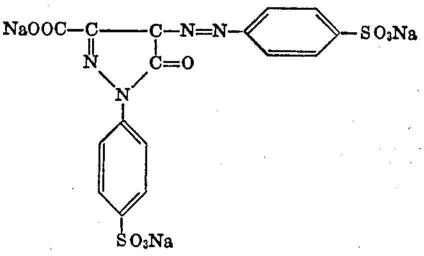
wherein $R_2$ and $X_2$ are the same as R and X.

Any combination of the groups of $R_2$ and $X_2$ can be used and the absorption maximum is at about 500 nm.

The amount of the dyes of the General Formula I, II, and III is not critical and generally a range of these dyes in an amount of from about $3\times10^{-4}$ to about $3\times10^{-1}$ mole/mole silver halide based on the silver halide present in the blue-sensitive silver halide emulsion layer can be used.

Practical examples of the dyes used in this invention and the syntheses thereof are illustrated below.

Dye 1:



### SYNTHESIS 1

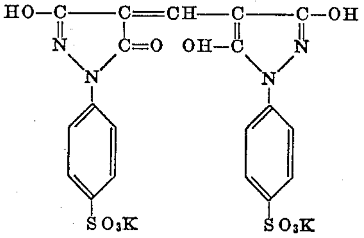
A mixture of 17.3 g. (1/10 mole) of sulfanilic acid, 7.3 g. of sodium nitrite, 44 cc. of a 10% aqueous sodium hydroxide solution, and 50 cc. of water was prepared and was designated solution A. Ice was added to an aqueous hydrochloric acid solution of 32 cc. of concentrated hydrochloric acid and 70 cc. of water and, under stirring, the mixture under the condition that the temperature of the mixture was not over 10° C., solution A prepared above was added dropwise to the mixture.

After the addition was completed, the mixture was further stirred for 30 minutes at temperatures of lower than 10° C. to obtain an aqueous solution of a diazo compound.

Thereafter, 28.4 g. of 3-carboxy-1-(p-sulfophenyl)-5-pyrazolone was dissolved in a mixture of 100 cc. of 10% aqueous sodium hydroxide solution and 100 cc. of water and, under stirring, the aqueous diazo compound solution prepared above was added dropwise to the solution thus prepared, whereby a coupling reaction occurred to form a dye. 1000 cc. of aqueous saturated sodium chloride solution was added to the solution of the dye to cause salting out. The dye was recovered by filtration and then subjected to salting out again to obtain 25 g. of the desired product.

The aqueous solution of the dye has its desired absorption maximum at 430 nm.

Dye 2:



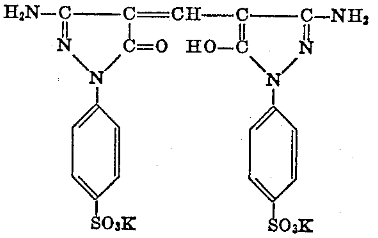
### SYNTHESIS 2

13 g. of 1-(p-sulfophenyl)-3-oxy-5-pyrazolone was dissolved in 200 cc. of methanol and 10 cc. of triethylamine with stirring, and after adding 5 g. of diphenylformamidine to the solution the mixture was heated for 3 hours on a water bath under refluxing.

On the other hand, 7 g. of anhydrous potassium acetate was dissolved in 100 cc. of methanol with heating and the solution was added to the solution prepared above, whereby the potassium salt of the desired dye was precipitated. The system was cooled to room temperature, recovered by filtration under suction, washed with methanol and dried to give 9 g. of the desired product.

The aqueous solution of the dye had its absorption maximum at 384 nm.

Dye 3:

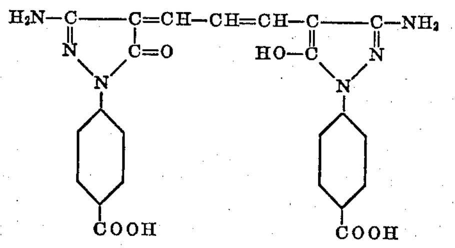


### SYNTHESIS 3

Dye 3 was produced from 3-amino-1-(p-sulfophenyl)-5-pyrazolone and diphenylformamidine following the procedure of Synthesis 2.

The aqueous solution of the dye had its absorption maximum at 396 nm.

Dye 4:

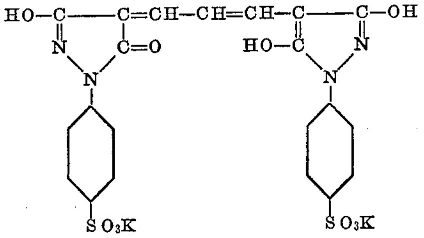


### SYNTHESIS 4

11 g. of 3-amino-1-(p-carboxy)-5-pyrazolone was dissolved in a mixture of 200 cc. of methanol and 15 cc. of triethylamine and after adding 6.4 g. of malondialdehyde-dianil hydrochloride to the solution, the mixture was heated for 3 hours on a water bath with refluxing. 3.1 g. of potassium hydroxide was dissolved in 100 cc. of methanol with heating, and after filtering the resulting solu-

tion to remove undissolved matter, the methanol solution was added to the mixture prepared above, whereby the potassium salt of the desired product was precipitated. The reaction product liquid was cooled to room temperature and the crystals thus precipitated were collected by filtration under suction, washed well with methanol, and dried to give 10.5 g. of the desired dye. The aqueous solution of the dye had its absorption maximum at 499 nm.

Dye 5:



## SYNTHESIS 5

Dye 5 was obtained from pyrazolone and malondialdehydedianil following the procedure of Synthesis 4. The aqueous solution of the dye had its absorption maximum at 492 nm.

Dyes other than the above can be produced by methods similar to those of Syntheses 1, 2 and 4.

By the present invention, color reproduction is markedly improved, in particular the mixing of yellow dye into a cyan dye and a magenta dye when a cyan dye and a magenta dye of an original are printed, i.e., the occurrence of undesirable coloring in the blue-sensitive emulsion layer, is greatly reduced.

The color photographic light-sensitive materials of this invention have never been known, and even if it would be anticipated that the color reproduction might be improved if the region of sensitivity distribution was narrowed, a method of accurately controlling the spectrally sensitive region as in the present invention has never been known.

The incorporation of the dye referred to above in a color photographic material for prints means that a blue-sensitive emulsion layer, a green-sensitive emulsion layer, and a red-sensitive emulsion layer are insensitive to light of the wavelength region cut by the dye, and thus the dye of this invention may be incorporated in the blue-sensitive silver halide photographic emulsion layer and/or in any emulsion layer of the light-sensitive material coated on the blue-sensitive silver halide photographic emulsion layer. It is particularly preferable to incorporate the dye of this invention in the blue-sensitive emulsion layer or in a protective gelatin layer coated on the blue-sensitive emulsion layer.

The dyes previously described may be added to the emulsion layer alone, but better results can be obtained when a combination of suitable dyes is added as shown in examples of this invention.

The incorporation of such a dye or dyes is accompanied by, as a matter of course, a reduction in sensitivity of the blue-sensitive emulsion layer and in this case it is required to use a silver halide emulsion having a higher sensitivity, as compared with the case of using no such dye. Accordingly, it is natural that the yellow dye image in the blue-sensitive layer becomes coarser, but because the granularity of the yellow dye image is not as important as the grain shape of the magenta dye, the minor influence thereof may be ignored.

By the addition of the dye light scattering is also reduced, and in particular the reproduction of the fine details of the image is improved. This is quite desirable in printing materials.

Practical embodiments and the merits of our invention are explained further in detail by the following examples. The dyes used in this invention are not limited to the dyes shown in the examples, but any dyes satisfying the conditions previously indicated can be used in this invention.

## Example 1

A red-sensitive emulsion was prepared in the following manner. 300 g. of a 5.2 wt. percent aqueous gelatin solution was added to 700 g. of a negative photographic emulsion consisting of 77 g. of silver iodo-bromide grains containing 3 mole percent iodide ions and having a mean grain size of 0.35 micron, 49 g. of gelatin and 574 g. of water and then the mixture was maintained at 35.0° C. to yield a sol.

120 ml. of a methanol solution of a 0.05% of anhydro - 9 - ethyl - 3,3' - (2 - hydroxy - 1-sulfopropyl)-naphthothiacarbocyanine hydroxide and then 40 ml. of a 0.5% aqueous solution of 5-methyl-7-hydroxy-1,3,4-triazaindrizine were added to the sol. One gram of a cyan coupler, N-n-dodecyl-1-hydroxy-2-naphthoic acid amide, was dissolved in a mixture of 1 ml. of dibutyl phthalate and 2 ml. of ethyl acetate by heating and the solution was dispersed by emulsification in 10 g. of a 10 wt. percent aqueous gelatin solution in the presence of 1.2 ml. of a 5% aqueous solution of sodium dodecylsulfate. The coupler dispersion thus prepared was added to the mixture prepared above so that the content of the coupler was 0.2 mole per mole of silver halide.

Furthermore, 10 ml. of a 2% aqueous solution of 1-hydroxy-3,5- dichloro-S-triazine sodium salt and 2 ml. of a 4% aqueous solution of saponin were added to the mixture.

The silver halide emulsion for the red-sensitive emulsion layer thus prepared was coated on a cellulose triacetate support (so that the dry thickness of the layer was 4.0$\mu$) having an antihalation layer, and then a thin gelatin layer was coated on the red-sensitive emulsion layer.

A green-sensitive emulsion was prepared in the following manner. 300 g. of a 5.2 wt. percent aqueous gelatin solution was added to 700 g. of a negative photographic emulsion consisting of 77 g. of silver iodo-bromide grains containing 3 mol percent iodide ions and having a means grain size of 0.43 micron, 49 g. of gelatin and 574 g. of water, and the mixture was maintained at 35.0° C. to yield a sol.

110 ml. of a 0.1% methanol solution of anhydro-3,3'-disulfopropyl-9-ethyl-5,5'-diphenyl - oxacarbocyanine hydroxide and then 40 ml. of a 0.5% aqueous solution of 5-methyl-7-hydroxy-1,3,4-triazaindrizine were added to the sol. 1.5 of a magenta coupler, 1-(2,4,6-trichlorophenyl)-3-dodecylamido-5-pyrazolone was dissolved in a mixture of 1.5 ml. of tricresyl phosphate and 2 ml. of ethyl acetate under heating, and the solution was dispersed, by emulsification in 10 g. of a 10 wt. percent gelatin solution in the presence of 1.2 ml. of a 5% aqueous solution of sodium dodecylsulfate. The coupler dispersion thus prepared was added to the silver halide-containing mixture prepared above so that the content of the coupler was 0.23 mole per mole of silver halide. Moreover, the same hardening agent and surface active agent as in the case of preparing the red-sensitive emulsion layer were added to the photographic emulsion for green-sensitive emulsion layer.

The photographic emulsion for the green-sensitive emulsion layer thus prepared was coated on the thin gelatin layer on the red-sensitive emulsion layer formed above so that the dry thickness of the layer was 4.5 microns. Onto the green-sensitive emulsion layer a yellow colloidal silver gelatin layer containing colloidal silver of a 0.03 micron mean grain size was uniformly coated to a dry thickness of 1.0 micron.

Then, the following two kinds of emulsion for the blue-sensitive emulsion layer were prepared, and each of them was coated onto samples of the colloidal silver-containing gelatin layer on the green-sensitive emulsion layer. These light-sensitive films were named Specimen 1 and Specimen 2, respectively.

Specimen 1.—150 g. of a 5.2% aqueous gelatin solution was added to 850 g. of the same silver halide emulsion (the mean grain size of the silver halide was 0.43

micron) used in preparing the green-sensitive emulsion layer, and the mixture was maintained at 35° C. to yield a sol. The following materials were added successively to the sol.

40 ml. of a 0.5% aqueous solution of 5-methyl-7-hydroxy-1,3,4-triazaindrizine was added to the sol; 1.5 g. of a yellow coupler, 4-dodecylbenzoyl-2-methoxy-acetanilide was dissolved in a mixture of 2.0 ml. of dibutyl phthalate and 1.5 ml. of ethyl acetate under heating and the solution obtained was dispersed by emulsification in 10 g. of a 10 wt. percent aqueous gelatin solution in the presence of 1.2 ml. of 5% aqueous solution of sodium dodecylsulfate. The coupler dispersion obtained was added to the silver halide emulsion mixture prepared above so that the content of the coupler was 0.22 mole per mole of silver halide. Moreover, the same hardening agent and surface active agent as used in producing the green sensitive emulsion layer were added to the blue-sensitive photographic emulsion.

The blue-sensitive emulsion thus prepared was coated onto the yellow colloidal silver-gelatin layer formed on the green-sensitive emulsion layer (as indicated above) to a dry thickness of 5 microns, and then a thin gelatin layer was coated onto the blue-sensitive layer as a protective layer to give Specimen 1.

Specimen 2.—150 g. of 5.2 wt. percent aqueous gelatin solution was added to 850 g. of a negative photographic emulsion consisting of 93 g. of silver halide grains containing 3 mole percent iodide ions and having a mean grain size of 0.6 micron, 60 g. of gelatin, and 697 g. of water, and the mixture was maintained at 35° C. to yield a sol. Then, 100 ml. of a 5% aqueous solution of 4,4-bis[3-amino - 1 - (p-sulfo-phenyl)-pyrazole-5-on]-monomethineoxonol dipotassium salt (absorption maximum wave length 396 nm.) was added to the sol prepared above. The stabilizer, yellow coupler emulsion, hardening agent, and surface active agent added were the same as in preparing Specimen 1 to produce the blue-sensitive emulsion for Specimen 2. The blue-sensitive emulsion thus prepared was coated onto the yellow colloidal silver-gelatin layer on the green-sensitive emulsion layer formed above to a dry thickness of 5 microns, and then a thin gelatin layer was coated uniformly onto the blue-sensitive layer as a protective layer to yield Specimen 2.

By subjecting each of the two specimens, Specimen 1 and Specimen 2 to a reversal processing by an ordinary developing solution, a positive color image was obtained in each case. The compositions of the developing solution were as follows:

Black and white developing solution

| | | |
|---|---|---|
| Water | ml | 800 |
| N-methyl-p-aminophenol | g | 4.5 |
| Hydroquinone | g | 5.5 |
| Anhydrous sodium sulfite | g | 50 |
| Sodium carbonate (mono-hydrate) | g | 30.5 |
| Potassium bromide | g | 1.5 |
| 0.1% aqueous potassium iodide solution | ml | 10 |
| Potassium thiocyanide (10% aqueous soln.) | ml | 20 |

Water added to make the total volume 1 liter.

Color developing liquid

| | | |
|---|---|---|
| Water | ml | 800 |
| Benzyl alcohol | ml | 5.0 |
| Anhydrous sodium sulfite | g | 5.0 |
| Tri-sodium phosphate ($12 \cdot H_2O$) | g | 40 |
| Sodium hydroxide | g | 1.5 |
| Potassium bromide | g | 0.5 |
| Ethylene diamine | ml | 5.0 |
| Citrazinic acid | g | 1.5 |
| p - amino - N - ethyl - N - β - methanesulfonamidoethyl-m-toluidine sulfate | g | 10.5 |

Water added to make the total volume 1 liter,

The reversal processing for the specimens was conducted in the following manner.

The specimen was developed by the black and white developing solution having the above composition for 10 minutes at 24° C., then washed with water, and the whole area of the specimen was exposed uniformly to intense white light. Then, the specimen was developed by the color developing solution having the above-mentioned composition for 15 minutes at 24° C., washed with water, bleached, fixed, and washed with water.

In addition to these specimens, a light-sensitive film having only a red-sensitive emulsion layer containing the cyan coupler as described hereinbefore in Example 1 was prepared, exposed to a tungsten lamp of a color temperature of 2854° K. through a conventional optical wedge, and subjected to the above-mentioned reversal processing using the developing solution indicated above, whereby a cyan colored strip was obtained.

Each of Specimen 1 and Specimen 2 was exposed to a tungsten lamp of a color temperature of 2854° K. using the cyan-colored strip obtained above instead of the optical wedge to obtain a print image.

The color mixing of the print was evaluated by comparing the gradient ratio of the R density and the G density $\gamma_G/\gamma_R$ and also the gradient ratio of the R density and the B density $\gamma_B/\gamma_R$ of the specimens with those of the cyan colored strip which is designated the original. The results are shown in Table 1.

TABLE 1

| | Original | Specimen 1 | Specimen 2 |
|---|---|---|---|
| $\gamma_G/G_R$ | 0.19 | 0.23 | 0.22 |
| $\gamma_B/G_R$ | 0.11 | 0.26 | 0.20 |

## Example 2

The specimen identified as Specimen 1 in Example 1 was prepared as Specimen 1 of this example.

Specimen 3 was prepared by coating a blue-sensitive emulsion prepared as below onto the yellow colloidal layer on the same green-sensitive emulsion layer as in Specimen 1, i.e., both specimens were identical except for the blue-sensitive emulsion.

That is to say, 150 g. of a 5.2 wt. percent aqueous gelatin solution was added to 850 g. of a negative photographic emulsion consisting of 93 g. of silver iodo-bromide grains containing 3 mole percent iodide ions and having a mean grain size of 0.8 micron, 60 g. of gelatin, and 697 g. of water, and the mixture was maintained at 35° C. to yield a sol.

100 ml. of a 5% aqueous solution of 4,4-bis[3-amino-1 - (p - sulfophenyl) - pyrazole - 5 - on]-monomethineoxonole dipotassium salt and 30 ml. of a 10% aqueous solution of 4 - (p - sulfophenylazo) - 3 - carboxy-1-(p-sulfophenyl)pyrazole - 5 - on trisodium salt (absorption maximum wavelength: 430 mm.) were added to the sol and further the same stabilizer, yellow coupler emulsion, hardening agent, and surface active agent as used in forming Specimen 1 were added thereto to give the emulsion for the blue-sensitive layer. This blue-sensitive emulsion was coated onto the yellow colloidal silver-gelatin layer on the green-sensitive emulsion layer which was further formed on the red-sensitive emulsion layer of the same structure as in Specimen 1 to a dry thickness of 5 microns. A thin gelatin layer was uniformly coated onto the blue-sensitive layer as a protective layer to give Specimen 3.

Onto each of the specimens, Specimen 1 and Specimen 3, the cyan-colored strip prepared as in Example 1 or a magenta-colored strip prepared by the same procedure as in Example 1 as in the case of preparing the cyan-colored strip was printed, and the specimens were subjected to the same developing procedures as in Example 1. The results are shown in Table 2 and Table 3.

TABLE 2

(Original was cycan colored strip

| | Original | Specimen 1 | Specimen 2 |
|---|---|---|---|
| $\gamma_G/\gamma_R$ | 0.19 | 0.23 | 0.22 |
| $\gamma_B/\gamma_R$ | 0.11 | 0.26 | 0.17 |

TABLE 3

(Original was magenta-colored one)

| | $\gamma_B/\gamma_G$ |
|---|---|
| Original | 0.30 |
| Specimen 1 | 0.45 |
| Specimen 3 | 0.37 |

## EXAMPLE 3

Specimen 1 in this example was the same as Specimen 1 in Example 3. Specimen 4 was prepared by coating the photographic emulsion for the blue-sensitive emulsion layer prepared as below onto the green-sensitive emulsion layer having the same composition as Specimen 1.

That is to say, 150 g. of a 5.2 wt. percent aqueous gelatin solution was added to 850 g. of a negative photographic emulsion consisting of 93 g. of silver iodo-bromide grains containing 3 mole percent iodide ions, 60 g. of gelatin, and 697 g. of water, and the mixture was maintained at 35° C. to yield a sol.

100 ml. of a 5% aqueous solution of 4,4-bis[3-amino-1-(p-sulfophenyl)pyrazole - 5 - on]-monomethineoxonole dipotassium salt, 30 ml. of a 10% aqueous solution of 4-(p - sulfophenylazo) - 3 - carboxy - 1 - (p - sulfophenyl)-pyrazole - 5 - on trisodium salt, and then 30 ml. of 5% aqueous solution of 4,4 - bis[3 - oxy - 1 - (p - sulfophenyl)pyrazole - 5 - one] - trimethineoxonol dipotassium salt (absorption maximum wavelength: 492 nm.) were added to the sol, and the same stabilizer yellow coupler emulsion, hardening agent, and surface active agent as in Specimen 1 were further added to the above mixture. The blue-sensitive emulsion thus prepared was coated onto the colloidal silver-gelatin layer on the green-sensitive emulsion layer further formed on the red-sensitive emulsion layer the same as in Specimen 1 to a dry thickness of 5 microns to give Specimen 4.

Onto each of Specimen 1 and Specimen 4 the cyan-colored strip prepared as in Example 2 (or the magenta-colored strip prepared as in Example 2) was printed, and each of them was subjected to the same developing procedures as in Example 2. The results are shown in Table 4 and Table 5.

TABLE 4

| | Original | Specimen 1 | Specimen 2 |
|---|---|---|---|
| $\gamma_G/\gamma_R$ | 0.19 | 0.23 | 0.22 |
| $\gamma_B/\gamma_R$ | 0.11 | 0.26 | 0.17 |

TABLE 5

(Original was magenta-colored specimen)

| | $\gamma_B/\gamma_G$ |
|---|---|
| Original | 0.30 |
| Specimen 1 | 0.45 |
| Specimen 4 | 0.33 |

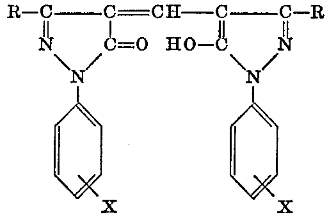
As is clear from Examples 1–3 and the results shown in Tables 1–5, the ratios $\gamma_B/\gamma_R$ and $\gamma_B/\gamma_G$ of the light-sensitive materials of this invention are far nearer the values of the originals as compared with the light-sensitive materials containing no dyes of this invention. In other words, by limiting the maximum distribution of the spectral sensitivity of the blue-sensitive emulsion layer to substantially 440–460 nm. by incorporating the dye of this invention, yellow dye mixing in the case of printing an image composed of a cyan dye and a magenta dye as an original can be remarkably reduced and a color print having color tones substantially the same as that of the original can be obtained.

While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

What we claim is:

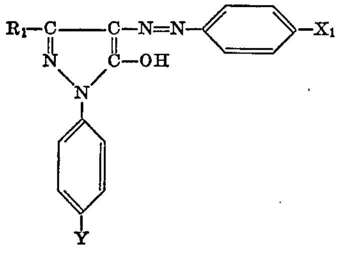
**1.** A multiple layer type color photographic silver halide light-sensitive material for color prints having at least a blue-sensitive photographic emulsion layer in which the spectral sensitivity of the blue-sensitive silver halide emulsion layer is limited to the region of about 440 to about 460 nm. wherein at least one dye having its absorption maximum at a wave length region shorter than about 440 nm. and/or in a region of about 460 to about 520 nm. is incorporated in said blue-sensitive photographic layer and/or in at least one layer coated on said blue-sensitive photographic emulsion layer of the light-sensitive material.

**2.** The material of claim **1** wherein the dye is of the formula:



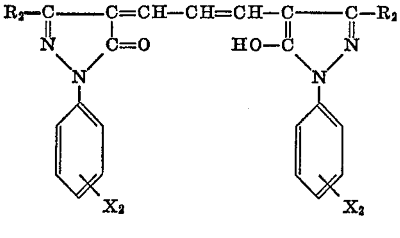
wherein R represents an amino group, a hydroxyl group, or —OR′, wherein R′ is a methyl group or an ethyl group and X represents $—COO^-M^+$ or $—SO_3^-M^+$, wherein $M^+$ is a cation.

**3.** The material of claim **1** wherein the dye is of the formula:



wherein $R_1$ represents a methyl group, $—COOC_2H_5$, or $—COO^-M_1^+$; $X_1$ and Y each represents a hydrogen atom or $—SO_3^-M^+$, wherein $M^+$ and $M_1^+$ each is a cation.

**4.** The material of claim **1** wherein the dye is of the formula:



wherein $R_2$ represents an amino group, a hydroxyl group, or —OR′, wherein R′ is a methyl group or an ethyl group and $X_2$ represents $—COO^-M^+$ or $—SO_3^-M^+$, wherein $M^+$ is a cation.

**5.** The material of claim **2** wherein said dye is present in said element at a level of from about $3\times10^{-4}$ to $3\times10^{-1}$ mole/mole of silver halide in said blue-sensitive photographic emulsion layer.

**6.** The material of claim **3** wherein said dye is present in said element at a level of from about $3\times10^{-4}$ to $3\times10^{-1}$ mole/mole of silver halide in said blue-sensitive photographic emulsion layer.

**7.** The material of claim **4** wherein said dye is present in said element at a level of from about $3\times10^{-4}$ to $3\times10^{-1}$ mole/mole of silver halide in said blue-sensitive photographic emulsion layer.

**8.** The material of claim **2** wherein $M^+$ is selected from the group consisting of a hydrogen ion, an alkali metal ion and an ammonium ion.

**9.** The material of claim **8** wherein $M^+$ is a potassium ion.

**10.** The material of claim **3** wherein $M_1^+$ is a sodium ion or a potassium ion.

**11.** The material of claim **4** wherein $M^+$ is selected from the group consisting of a hydrogen ion, an alkali metal ion and an ammonium ion.

**12.** The material of claim **11** wherein $M^+$ is a potassium ion.

**13.** The material of claim **1** wherein said dye is incorporated in said blue-sensitive photographic emulsion layer and/or a gelatin protective layer coated on said blue-sensitive photographic emulsion layer.

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