United States Patent Office

3,476,564

Patented Nov. 4, 1969

3,476,564

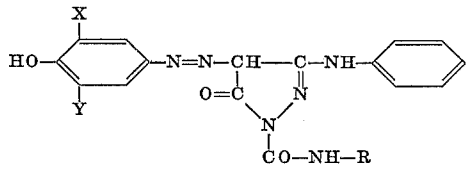
SILVER HALIDE EMULSION CONTAINING AN AZO-PYRAZOLONE COUPLER

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No Drawing. Filed May 3, 1966, Ser. No. 547,189
Int. Cl. G03c 1/04
U.S. Cl. 96—100 6 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive silver halide emulsion is shown which contains at least one colored azo coupler of the formula



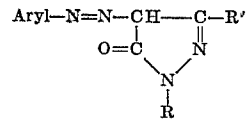
wherein Y is hydrogen, halogen or carboxyl, X is halogen or carboxyl, and R is an aryl radical having at least one water-solubilizing group and at least one group imparting non-diffusivity to the coupler.

This invention relates to novel compounds and their use as color couplers in color photography.

It is known that colored images produced in multilayer film constructions by chromogenic development often results in unsatisfactory color rendition due to secondary absorptions by the image-forming indophenol or azomethine dyes. Correction is normally accomplished by the use of colored masks which are produced during the chromogenic development, such masks being provided by using colored coupler materials. For example, whereas colorless couplers of the alpha-naphthol type provide a blue image on a colorless background, colored couplers of the 4-phenylazo-1-naphthol type provide blue images on an orange or magenta background. Likewise, whereas colorless couplers of the pyrazolone type produce magenta images on a colorless background, colored couplers of the 4-phenylazo-pyrazolone type produce magenta images on a yellow background. Further information on the mechanism of such reactions and on masking technology can be obtained from Vittum, Sawdey, Herdle and School, J.A.C.S. 72, p. 1533 (1950); Vittum and Brown, J.A.C.S. 68, p. 2235 (1946); Evans, Hanson Jr. and Brewer, "Principles of Color Photography," p. 565 and fol.

One of the problems encountered with the use of colored couplers is a decreased reactivity in the coupling reaction as compared with corresponding colorless coupler. As a result, sensitivity is decreased, often to the point of rendering the colored coupler essentially useless. The low reactivity of such colored couplers appears to be an

intrinsic characteristic of the colored azo coupler compounds, perhaps due to either the structure of the original colorless coupler or the structure of the diazotized molecule used to obtain the azo dye or to the entire structure of the moieties joined by the azo radical. This lower reactivity is observed most frequently in colored couplers of the 4-arylazo-pyrazolone class which correspond to the formula

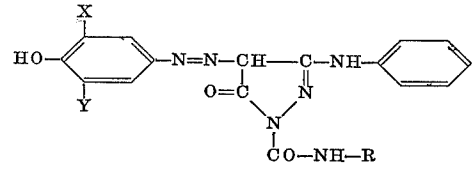


In U.S. Patent No. 2,983,608 colored pyrazolone coupler compounds are described which, because of certain substitution on the pyrazoline ring, are stated to be sufficiently reactive to provide compensation for unwanted blue absorption of the magenta dye produced upon color development. However, considerable improvement in reactivity of colored couplers without lowering the molar extinction coefficient has been desired.

It is therefore an object of this invention to provide new colored couplers having relatively high coupling reactivity.

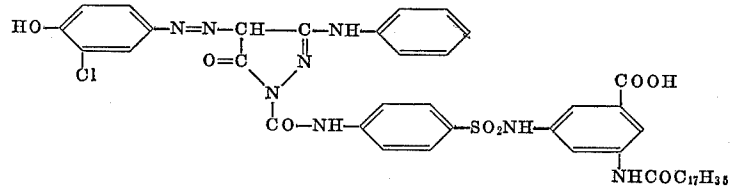
Other objects and advantages will be apparent from the following description.

In accordance with this invention it has been found that colored couplers having the aforementioned advantages are represented by the structural formula



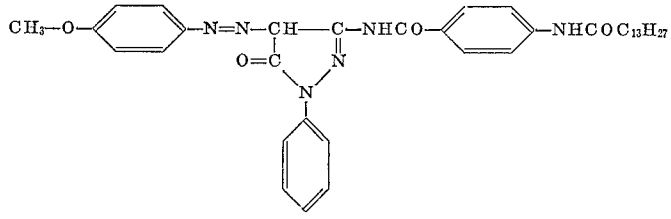
wherein Y is hydrogen, halogen (e.g. chlorine, bromine), or carboxyl, X is halogen or carboxyl, and R is hydrogen, alkyl (e.g. C_1–C_{20} alkyl) or aryl (including substituted aryl, e.g. substituted phenyl). Preferably R is an aryl radical having a water solubilizing group (e.g. carboxylic acid or salt thereof, sulfonic acid or salt thereof, sulfamidic group, etc.) and a group imparting non-diffusibility and substantivity (e.g. long chain or C_{10}–C_{20} alkyl carboxamido groups, etc.). Such couplers are particularly characterized by their high degree of reactivity in the chromogenic development reaction. Of particular value are those couplers in which R comprises p-phenylsulfonamidophenyl.

The high molar extinction coefficient of this class of yellow dyes can be illustrated by comparing one of the preferred dyestuffs of this invention with well known colored couplers. The colored coupler



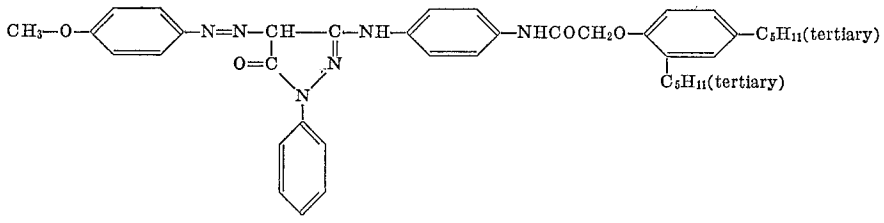
exhibits a molar extinction coefficient in butyl acetate of 2.38×10^4 whereas the coupler

(I)



and coupler

(II)



(III)

have a corresponding molar extinction coefficient in butyl acetate of 1.89×10^4 and 2.31×10^4, respectively. The Coupler II is of the well known 3-acylamino-pyrazolone type, and the Coupler III is of the 1-phenyl-3-anilino-pyrazolone type. Pyrazolone compounds of the type exemplified by II and III have been considered in U.S. Patent No. 2,983,608, including their molar extinction coefficients. Comparison of these molar extinction coefficients indicates that the colored couplers of the present invention also display a high value for the molar extinction coefficient and accordingly can be used in relatively small quantities in the photographic emulsion. Moreover, it is alternatively possible to use the colored couplers of this invention in thinner layers, thereby permitting greater definition and improved resoltuion of the photographic material.

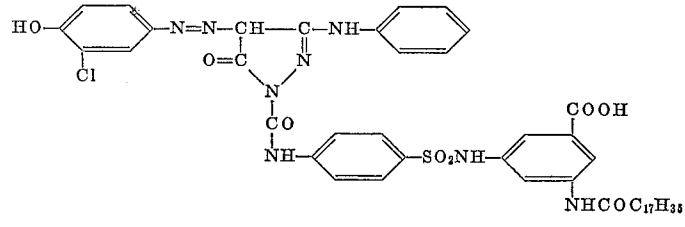
The colored couplers of this invention are particularly suitable for use in negative-type color photographic materials capable of yielding, by printing on paper or color positive film, faithful reproduction of the original image with good saturation and improved sharpness. These color couplers may be employed as the only coupler material in a photosensitive layer, or they may be used in admixture with colorless couplers to further control the masking effect.

By exposing to a light image a sample of a silver halide photographic material comprising an emulsion layer which is sensitized to green light and which contains a color coupler of this invention, a magenta colored negative image of the original subject can be produced by conventional chromogenic development with a N,N-diethyl-p-phenylenediamine developer. The characteristics of the resulting magenta dye are essentially the same as described in Italian Patent No. 632,532, since the same dye is formed. Superimposed on the magenta colored negative image is a yellow colored positive image of the original subject, representing the "masking image" which, upon printing from the negative using suitable filters, compensates for the undesirable light absorption of the magenta dye.

The following examples illustrate the preparation of the colored couplers of this invention, it being understood that they are presented for purposes of illustration and not of limitation.

EXAMPLE 1

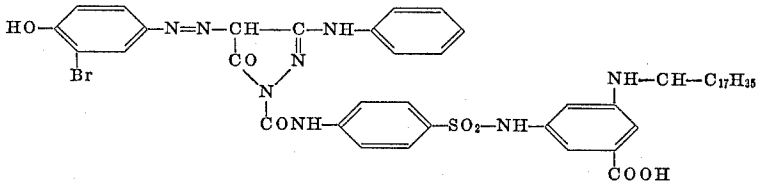
77.5 grams of 1-p-(3'-carboxy-5'-stearoyl aminophenylsulfamyl)-phenylcarbamyl-3-anilino-5 pyrazolone were dissolved in 900 ml. of water and 25 ml. of 36° Baumé caustic soda. This solution was neutralized using thiazole yellow as indicator and 40 grams of sodium carbonate. To this solution, stirred and cooled to 0° C., was added over a period of one-half hour an aqueous solution of the diazonium salt from 14.3 grams of 2-chloro-4-aminophenol. Stirring was continued until the reaction was complete, and the mixture was acidified with hydrochloric acid, using Congo red as indicator. The product was then recovered by filtration, was washed to neutrality with cold water, and was then crystallized from acetic acid. The colored product had the formula:



N (calculated) 12.05%. N (found) 11.39%. Absorption peak in dimethylformamide 410 millimicrons.

EXAMPLE 2

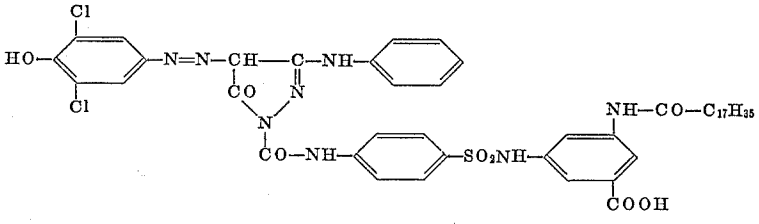
Following the procedure of Example 1, with the substitution of a solution of the diazonium salt obtained from 19 grams of 2-bromo-4-aminophenol for the diazonium salt of 2-chloro-4-aminophenol, the following colored coupler was obtained:



N (calculated) 11.51%. N (found) 11.39%. Absorption peak in dimethylformamide 410 millimicrons.

EXAMPLE 3

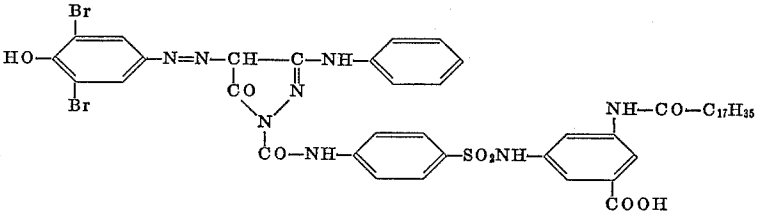
Following the procedure of Example 1, with the substitution of a solution of the diazonium salt obtained from 22.4 grams of 2,6-dichloro-4-aminophenol for the diazonium salt of 2-chloro-4-aminophenol, the following colored coupler was obtained:



N (calculated) 11.66%. N (found) 11.0%. Absorption peak in dimethylformamide 410 millimicrons.

EXAMPLE 4

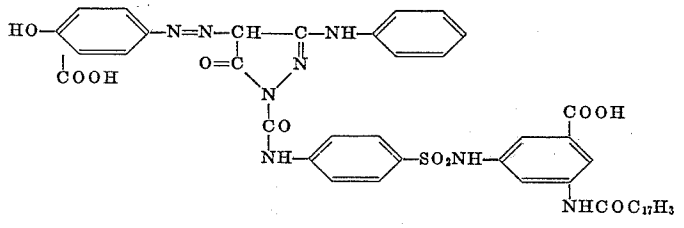
Following the procedure of Example 1, with the substitution of a solution of the diazonium salt obtained from 26.6 grams of 2,6-dibromo-4-aminophenol for the diazonium salt of 2-chloro-4-aminophenol, the following colored coupler was obtained:



N (calculated) 10.56%. N (found) 10.31%. Absorption peak in dimethylformamide 410 millimicrons.

EXAMPLE 5

Following the procedure of Example 1, with the substitution of a solution of the diazonium salt obtained from 15.3 grams of 5-aminosalicylic acid for the diazonium salt of 2-chloro-4-aminophenol, the following colored coupler was obtained:

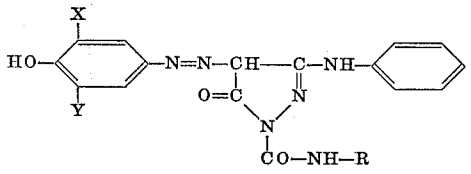


N (calculated) 11.95%. N (found) 11.00%. Absorption peak in methanol 430 millimicrons.

Various other embodiments of the present invention and additional uses therefore will be apparent to those skilled in the art without departing from the scope or spirit of this disclosure.

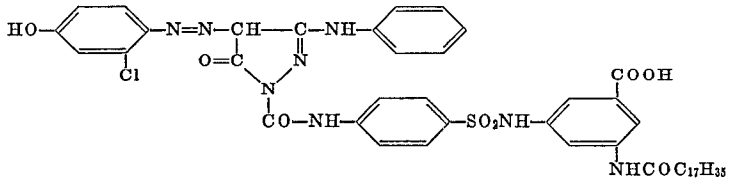
What is claimed is:

1. A photosensitive silver halide emulsion layer containing a colored azo coupler having the formula

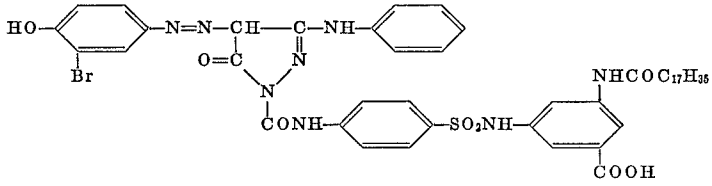


wherein Y is hydrogen, halogen or carboxyl, X is halogen or carboxyl, and R is a p-phenylsulfonamidophenyl radical having at least one water-solubilizing group and at least one group imparting non-diffusivity to the coupler.

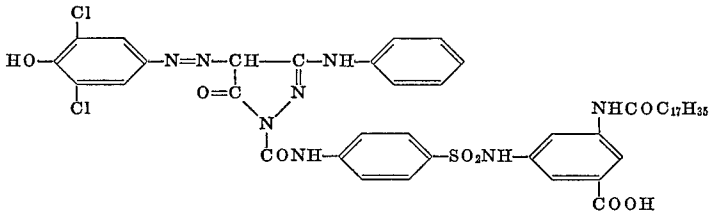
2. The emulsion of claim 1 wherein said colored azo coupler has the formula



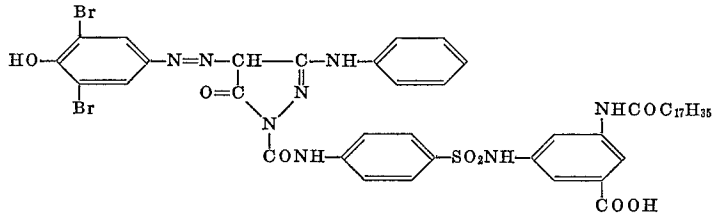
3. The emulsion of claim 1 wherein said colored azo coupler has the formula



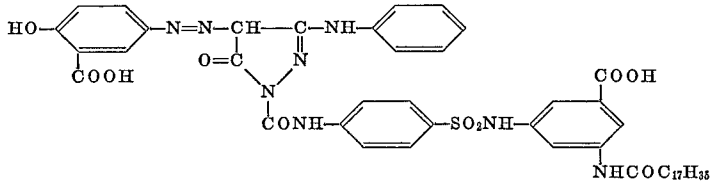
4. The emulsion of claim 1 wherein said colored azo coupler has the formula



5. The emulsion of claim 1 wherein said colored azo coupler has the formula



6. The emulsion of claim 1 wherein said colored azo coupler has the formula



References Cited

UNITED STATES PATENTS

2,455,170	11/1948	Glass et al.	96—9
3,227,551	1/1966	Barr et al.	96—100

FOREIGN PATENTS

632,532	1/1962	Italy.

J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—9

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,476,564 Dated November 4, 1969

Inventor(s) Brunello Mariani, Alberto Guzzi and Eugenio Tisselli

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading, second inventor's name should be --Guzzi--, instead of "Guizzi";

Column 1, line 47, "School" should be --Scholl--;

Column 2, line 18, "pyrazoline" should be --pyrazolone--;

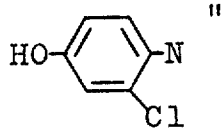
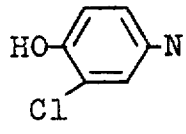
Column 2, bottom, the diagram should be labelled --(I)--;

Column 3, diagram, "(I)" should be --(II)--;

Column 3, diagram, "(II)" should be --(III)--;

Column 3, diagram, "(III)" should be deleted.

Column 7, Claim 2, first ring in structure,

"  " should be --  --.

Signed and sealed this 25th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents