

1

2,725,291

AZO DYE COUPLERS HAVING TWO COUPLING NUCLEI

Bruce Graham, Rochester, N. Y., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application May 1, 1952,

Serial No. 285,544

6 Claims. (Cl. 95-6)

This invention relates to color photography and particularly to coupler compounds for use in photographic processes.

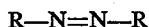
Color-forming compounds which react with the development product of aromatic amino developing agents to form colored images upon photographic development are well known. Generally, these color-forming compounds or couplers are colorless or substantially colorless. This lack of color is usually desirable where the coupler is to be incorporated in the emulsion layer and the unused coupler remains after formation of the colored image. When the coupler is used in the developing solution, it may be colored without detriment to the final image, and some colored couplers are known, such as paraphenylazo acetoacetanilide which was disclosed in Mannes and Godowsky Patent 2,108,602.

Colored couplers containing a chromophore system which is broken up during the coupling reaction with the result that the original color of the coupler is destroyed and a new color formed at those points where development occurs, are described in Glass, Vittum and Weissberger U. S. Patents 2,453,661, 2,455,169, 2,455,170 and 2,521,908. These compounds have an arylazo group on the 4-position of the coupler which splits off during the coupling reaction producing one molecule of azomethine dye (with pyrazolones) or indoaniline dye (with phenols or naphthols).

A difficulty accompanying the use of colored couplers of this type is that their tinctorial strength is so high that it is necessary to dilute them with uncolored couplers in order to gain a satisfactory ratio between the tinctorial strength of the colored coupler and the developed dye.

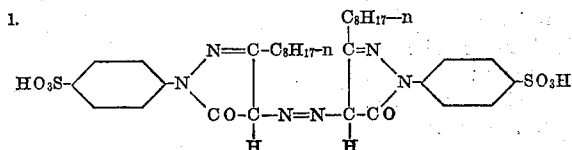
It is therefore an object of the present invention to provide a method for increasing the amount of coupled dye formed from a colored coupler in a silver halide emulsion. A further object is to provide a masking method for color photography in which the proper ratio of tinctorial strength of the uncoupled and coupled dyes is obtained. A still further object is to provide a photographic film containing novel colored couplers. Other objects will appear from the following description of my invention.

These objects are accomplished by using as colored couplers compounds having the structure

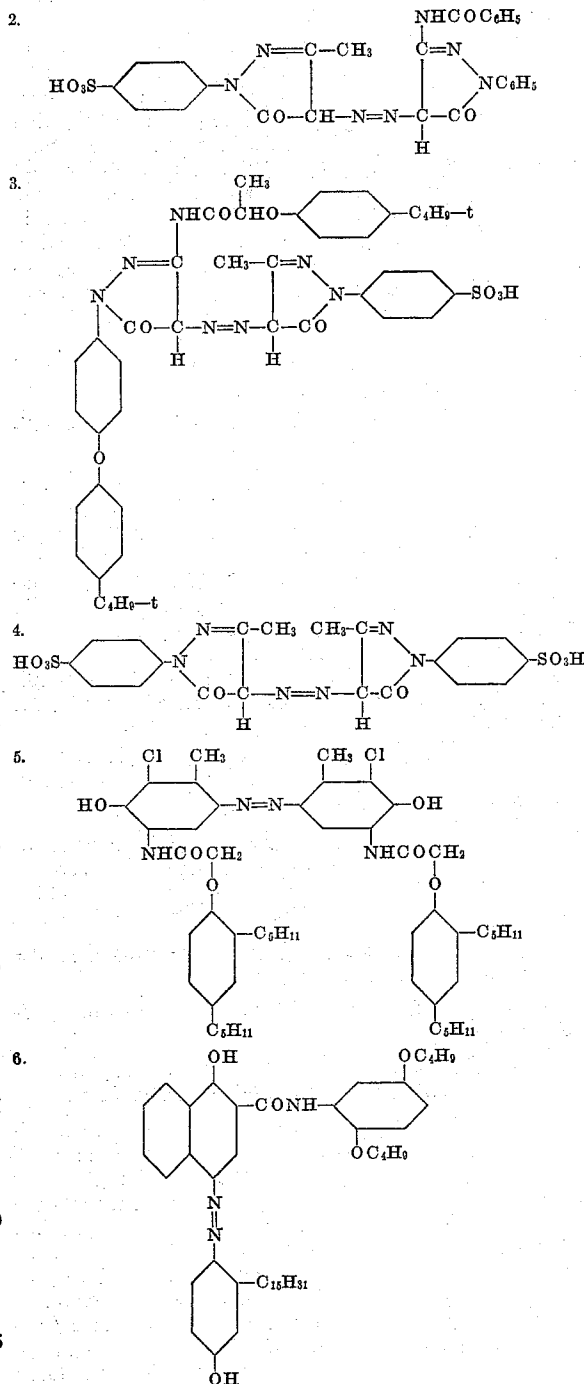


where R represents a 4-pyrazolone, 4-phenol or 4-naphthol nucleus which may be the same or different and which may contain different substituent groups such as alkyl, halogen, carboxylic acid, sulfonic acid, sulfonamide, alkylamine, acylamine or alkoxy. When R is a phenol, the phenolic ring should contain a substituent group of at least four carbon atoms.

The following compounds may be used according to my invention:



2



The compounds of my invention are prepared as follows:

Example 1.—4-azobis[1-(p-sulfophenyl)-3-n-octyl-5-pyrazolone]

1-p-sulfophenyl-3-n-octyl-5-pyrazolone (a). Ethyl pelargonoylacetate (13.8 parts) was dissolved in 600 parts of alcohol. This was added to a hot solution of 11.4 parts of p-sulfophenylhydrazine in 600 parts of 1% acetic acid. This mixture was refluxed two hours, concentrated to one-half its volume, and cooled. The resulting white solid was collected and washed with cold water, 14 parts (a), M. P. 265-275°. Analysis: Calculated for $C_{17}H_{24}N_2O_4S$: C, 57.9; H, 6.9; N, 7.9; S, 9.1. Found: C, 57.1; H, 6.8; N, 8.0; S, 8.8.

3

1-p-sulfophenyl-3-n-octyl-4-isonitroso-5-pyrazolone (b). A solution of 2.3 parts of (a) in 100 parts of 50% acetic acid was treated with 0.5 part of sodium nitrite at 30°. After twenty hours the orange product was collected, 1.35 parts (b), melts >250°.

1-p-sulfophenyl-3-n-octyl-4-amino-5-pyrazolone, its diazotization and coupling. The nitrosopyrazolone (b), 1.65 parts, in 100 parts of warm water was reduced over Raney nickel. The catalyst was removed by filtration and the filtrate was run into a flask containing two parts of concentrated hydrochloric acid. The solution was cooled and treated with 0.32 part of sodium nitrite. After a few minutes a solution of (a), 1.6 parts, in 100 parts of 5% sodium carbonate solution was added. After one hour the solution was made acid with hydrochloric acid and concentrated to dryness. The dye was extracted from the residue with absolute alcohol and obtained from the latter by drowning in ether. The product (Example 1) is an amorphous, orange powder, 2 parts, which melts > 200°.

Example 2.—1-(p-sulfophenyl)-3-methyl-4-(1'-phenyl-3'-benzamido-5'-oxo-2'-pyrazolinyl-4'-azo)-5-pyrazolone

1-phenyl-3-benzamido-5-pyrazolone (J. Am. Chem. Soc., 64, 2133 (1942)), 2.8 parts, in 500 parts of 3% sodium carbonate solution was treated with 3 parts of 1-p-sulfophenyl-3-methyl-5-pyrazolone-4-diazonium enol betaine sodium salt (U. S. Patent 2,420,791). The mixture was warmed to 60° C., then made sufficiently acid with hydrochloric acid that the dye precipitated. It was separated by decanting. The dye was triturated with concentrated hydrochloric acid, which caused it to solidify. It was collected and dried, 1 part, amorphous, M. ca. 180° C.

Example 3.—1-(4-tert-butylphenoxyphenyl)-3-[α-(4-tert-butylphenoxy) propionamido]-4-(1'-p-sulfophenyl-3'-methyl-5'-oxo-2'-pyrazolinyl-4'-azo)-5-pyrazolone

Prepared as above from 1-p-tert-butylphenoxyphenyl-3-α-p-tert-butylphenoxypropionamido-5-pyrazolone (U. S. Patent 2,343,702, Example 47). M. P. 184–185° from an aqueous acetic acid-sodium acetate solution.

Example 4.—4-azobis-1-p-sulfophenyl-3-methyl-5-pyrazolone

Prepared as above from 1-p-sulfophenyl-3-methyl-5-pyrazolone. M. P. > 250°.

Example 5.—2,2'-di-(2,4-di-tert-amylphenoxy acetamido)-5,5'-dimethyl-6,6'-dichloro-azodiphenol

Five parts of 2-(diamylphenoxy)-acetamido-4,6-dichloro-5-methylphenol were dissolved in a solution of 10 parts of conc. HCl in 50 parts of acetic acid. After 20 hours the precipitate of 2-(2,4-di-t-amylphenoxyacetamido)-5-methyl-6-chloroquinone was collected, washed with water and recrystallized from methanol. Yield: 2.5 parts, M. P. 107–108. Anal. calcd. for C₁₅H₂₂ClNO₄; N, 8.0. Found, 7.7. This was converted by treatment with hydroxylamine hydrochloride in alcohol to 2-(2,4-di-t-amylphenoxyacetamido)-4-nitroso-5-methyl-6-chlorophenol. Yield: 2 parts, M. P. 203° C. This was reduced to 2-(2,4-di-t-amylphenoxyacetamido)-4-amino-5-methyl-6-chlorophenol. Yield: 1.5 parts, M. P. 156.

This amine when diazotized autocouples. M. P. > 250° C.

2-(2,4-DIAMYLPHENOXY)-ACETAMINO-4,6-DICHLORO-5-METHYLPHENOL

In a 500-cc. 3-necked flask provided with a mechanical stirrer and thermometer was added 400 cc. of 80% acetic acid and 31 g. (0.38 mole) of anhydrous sodium acetate. To the solution was added 23 g. (.10 mole) of 2-amino-4,6-dichloro-5-methylphenol hydrochloride. After 15 minutes of stirring, to this mixture was added 33 g. (0.11 mole) of diamylphenoxyacetyl chloride. The temperature of the mixture rose from 26° C. to 33° C. After 1

4

hour of stirring, the slurry was diluted with 400 cc. of water, filtered by suction and the product washed on the filter with 1 l. of water. Solid was dried overnight at 50° C.

This product was dissolved by stirring on a steam bath with 2 l. of 80% acetic acid, treated with 5 g. of activated carbon and filtered by suction through 5 g. of activated carbon. A white product crystallized from the pale orange liquor. Yield: 29 g. (62%), M. P. 151–152° C.

Example 6.—1-hydroxy-2',5'-dibutoxy-4-(4-hydroxy-2-n-pentadecyl-phenylazo)-2-naphthanilide

4-amino-2-pentadecylphenol, 3.2 parts, in 100 parts of acetic acid was treated at 0° C. with a solution of 0.7 part of sodium nitrite in ten parts of water. This diazonium solution was allowed to stand twenty hours at 0° C. before use.

The coupler 1-hydroxy-2',5'-dibutoxy-2-naphthanilide, prepared by condensation of phenyl-1-hydroxy-2-naphthoate with aminohydroquinone dibutyl ether, 4.1 parts, was dissolved in 300 parts of pyridine and cooled to 0° C. The diazonium solution was added and the mixture was allowed to stand one hour before being drowned in ice and hydrochloric acid. The solid was collected and recrystallized twice from ligroin, orange dye, M. P. 74–75°.

My compounds are particularly useful in a process, such as that of Hanson U. S. Patent 2,449,966, granted September 21, 1948. The Hanson process involves a color correction method in which a colored coupler is incorporated in the photographic emulsion layer prior to exposure and upon development is converted into a colored image where the layer was exposed. The coupler remaining in the unexposed portions of the layer retains its original color, and by suitable choice of the color of the original coupler and the color of the final dye image, a masking or correction effect can be obtained.

The following example illustrates the method of incorporating the azo-bis couplers in a silver halide layer:

3.6 grams of coupler No. 1 was dissolved in a mixture of 15 ml. of ethanol and 7.5 ml. of 20% aqueous sodium hydroxide solution. The resulting clear solution was diluted with 200 ml. of water and the pH adjusted to 6.5 by the addition of the necessary quantity of a 2.5% aqueous citric acid solution. This produced a clear orange-red solution which was mixed with 250 ml. of a melted sensitized silver halide emulsion. Coatings were prepared in the normal way on a transparent film support. When this coating was submitted to standard color processing, a bright magenta dye image was produced, and the yellow colored coupler was retained in the unexposed areas, serving as a color-correcting dye image.

Various photographic developing agents can be employed with the couplers of my invention. The primary aromatic amino developing agents are generally suitable including the phenylenediamines and aminophenols. The alkyl phenylenediamines may be substituted in the amino group as well as in the ring. Suitable compounds are diethylparaphenylenediamine, monomethyl paraphenylenediamine, dimethyl paraphenylenediamine and para-amino-phenol. These compounds are usually employed in the salt form, such as the hydrochloride or the sulphate which are more stable than the free amines. All of these compounds have a primary amino group which enables the oxidation product of the developer to couple with the color-forming compounds to form dye images.

The following developing solution is suitable for developing gelatino silver halide layers containing colored couplers according to my invention.

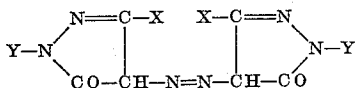
	Grams
2-amino-5-diethyl-amino toluene HCl	2
Sodium sulphite	2
Sodium carbonate	20
Potassium bromide	2
Water to 1 liter.	

5

It will be understood that the examples and modifications set forth herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

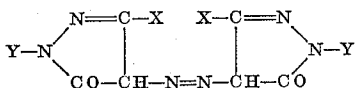
I claim:

1. The method of developing a colored image in a silver halide emulsion layer which comprises incorporating in said layer a coupler compound having the formula:



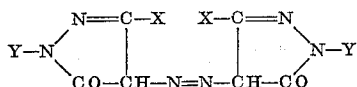
where X is selected from the class consisting of alkyl radicals and acylamino radicals and Y is a mononuclear aryl radical, exposing said layer and developing it with a primary aromatic amino developing agent, thereby splitting the azo group and coupling both residual portions of said coupler compound at the point of splitting, with the oxidation product of said developing agent to form a dye image, leaving the coupler compound intact in the undeveloped regions of said layer.

2. An unexposed gelatino-silver halide emulsion layer containing a coupler compound having the formula:



where X is selected from the class consisting of alkyl radicals and acylamino radicals and Y is a mononuclear aryl radical.

3. The method of developing a colored image in a silver halide emulsion layer which comprises incorporating in said layer a coupler compound having the formula:

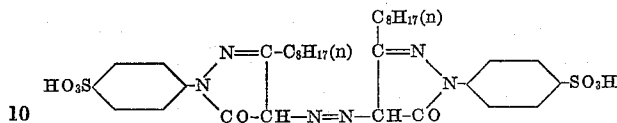


where X is an alkyl radical and Y is a mononuclear aryl radical) exposing said layer and developing it with a primary aromatic amino developing agent, thereby splitting the azo group and coupling both residual portions of said coupler compound at the point of splitting, with the oxidation product of said developing agent to form a dye

6

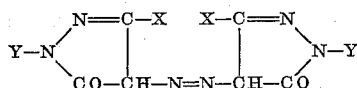
image, leaving the coupler compound intact in the undeveloped regions of said layer.

4. The method of developing a colored image in a silver halide emulsion layer which comprises incorporating in said layer a coupler compound having the formula:



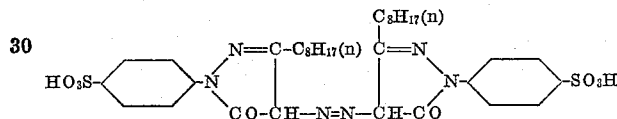
exposing said layer and developing it with a primary aromatic amino developing agent, thereby splitting the azo group and coupling both residual portions of said coupler compound at the point of splitting, with the oxidation product of said developing agent to form a dye image, leaving the coupler compound intact in the undeveloped regions of said layer.

5. An unexposed gelatino-silver halide emulsion layer containing a coupler compound having the formula:



where X is an alkyl radical and Y is a mononuclear aryl radical.

6. An unexposed gelatino-silver halide emulsion layer containing a coupler compound having the formula:



References Cited in the file of this patent

UNITED STATES PATENTS

2,455,169	Glass et al.	Nov. 30, 1948
2,455,170	Glass et al.	Nov. 30, 1948

FOREIGN PATENTS

586,211	Great Britain	Mar. 11, 1947
599,377	Great Britain	Mar. 11, 1948
627,814	Great Britain	Aug. 16, 1949