Patented Oct. 27, 1953

2,657,134

UNITED STATES PATENT OFFICE

2,657,134

PHOTOGRAPHIC EMULSION WITH COLORED COUPLERS CONTAINING ISOPHTHALIC ESTER GROUPS

Bruce Graham, Paul W. Vittum, and Arnold Weissberger, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application December 5, 1951, Serial No. 260,098

8 Claims. (Cl. 95—6)

1

This invention relates to color photography and particularly to color couplers 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 of 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 certain colored couplers have been used in this way.

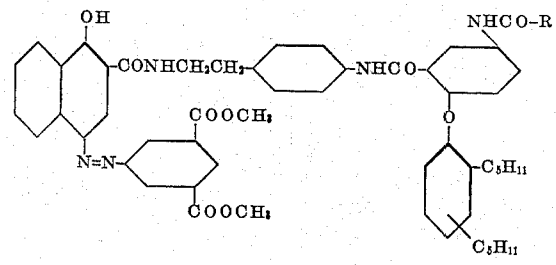
Couplers which are in themselves more or less strongly colored, and which contain a chromophore group which is split off or destroyed during and by means of the coupling reaction, with the result that the original color of the coupler is destroyed and a new dye is formed upon coupling, are disclosed in Glass, Vittum and Weissberger U. S. Patents 2,453,661; 2,455,169; 2,455,170 and 2,521,903.

We have now found a class of colored couplers derived from diazotized aminoisophthalic acid or diazotized aminoisophthalic ester which possess valuable and novel properties. These couplers are miscible with aqueous colloid emulsion carriers, such as gelatin or polyvinyl alcohol, and can therefore be incorporated directly into the usual photographic emulsions. When incorporated directly in this way, the couplers must be hydrolyzed to the free acid form before or during incorporation in the emulsion. They

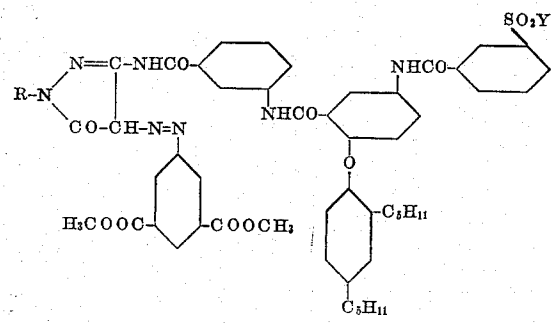
2

may also be used in the ester form in processes such as those of Mannes and Godowsky U. S. Patent 2,304,940 and Jelley and Vittum, U. S. Patent 2,322,027.

The couplers of our invention have the general formula:



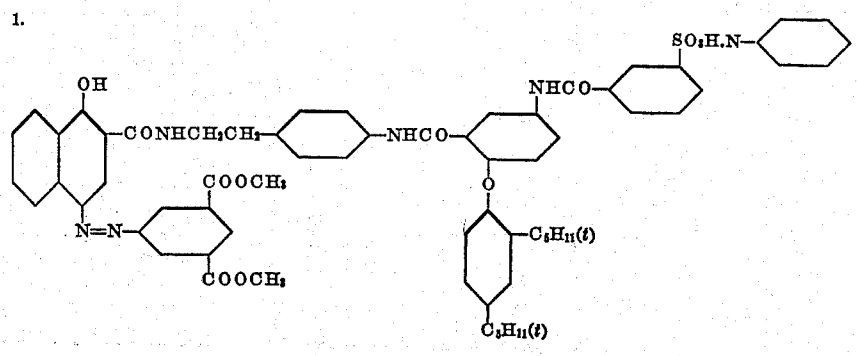
or



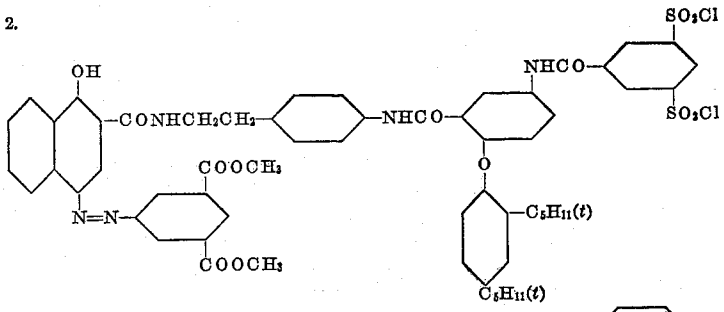
where R is a mononuclear aryl radical, e. g., phenyl and substituted phenyl, and Y is a hydroxyl or an arylamino group.

The following examples illustrate couplers which may be used according to our invention:

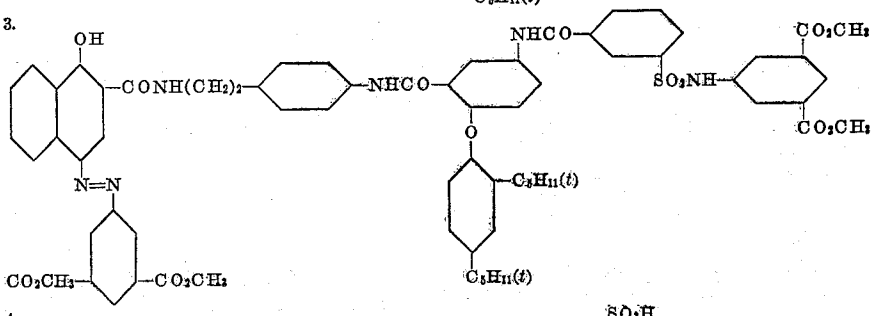
1.



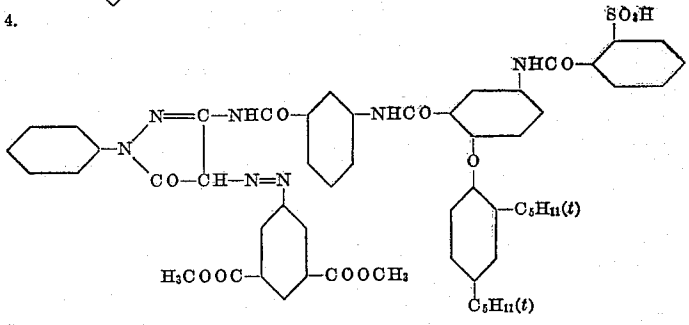
2.



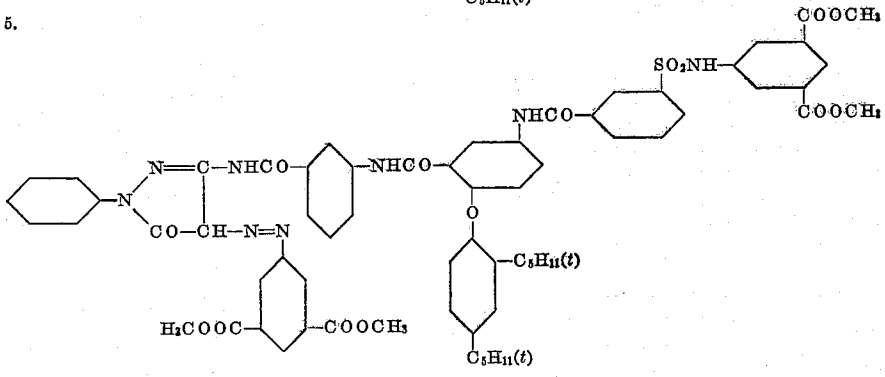
3.



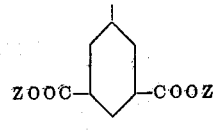
4.



5.



When these compounds are to be incorporated directly in the gelatin of a gelatino-silver halide emulsion, the esters must be hydrolyzed to the free acid before, or at the time of, incorporation in the emulsion. The compounds are then introduced into the emulsion as an alkali metal salt, usually the sodium salt. The isophthalic acid or ester portion of the couplers may, therefore, have the structure



where Z is an alkali metal, e. g., sodium or potassium, or a methyl radical, depending on whether the coupler is introduced directly into the emulsion or is incorporated in a solvent which is then dispersed in the emulsion, as in U. S. Patent 2,304,940 or 2,322,027 referred to above.

Our couplers are intended to be incorporated in one of the emulsion layers of a multi-layer coating in order to secure the masking effects described in Hanson U. S. Patent 2,449,966. 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 to a colored image where the layer is 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 compounds of our invention may be prepared in general, by reaction of the uncolored coupler with the appropriate diazonium compound.

Compound 1 was prepared as follows:

1 - hydroxy - N - {4 - [2 - (2,4 - diamylphenoxy) - 5 - (3 - sulfobenzamido) - benzamido]-phenethyl}-2-naphthamide was prepared by the following steps:

(*a*) Phenyl 1-hydroxy-2-naphthoate was condensed at 150° for one-half hour with an equi-

molecular quantity of p-nitrophenethylamine yielding 1 - hydroxy - N - (p - nitrophenethyl) - 2-naphthamide.

(*b*) The nitro compound was reduced catalytically in the presence of Raney nickel to the amine.

(*c*) 1 - hydroxy - N-(p-aminophenethyl) - 2-naphthamide was condensed in acetic acid and sodium acetate at room temperature with an equimolecular quantity of 2-(2,4-diamylphenoxy)-5-nitrobenzoyl chloride.

(*d*) 1 - hydroxy - N - {4' - [2'''-(2''',4''' - diamylphenoxy) - 5'' -amino - benzamido] phenethyl}-2-naphthamide was prepared by the catalytic reduction in the presence of Raney nickel of the nitro compound obtained in step (*c*).

(*e*) 1 - hydroxy - N - {4 - [2 - (2,4 - diamylphenoxy) - 5 - (3 - sulfobenzamido) - benzamido]-phenethyl}-2-naphthamide was prepared by the condensation of an equimolecular quantity of 3-sulfobenzoylchloride and the amine of step (*d*) in dioxane and quinoline.

The final compound was prepared by the simple treatment of 1 - hydroxy - N - {4 - [2 - (2,4 - diamylphenoxy) - 5 - (3 - sulfobenzamido) - benzamido] - phenethyl} - 2 - naphthamide with isophthalic methyl ester diazonium chloride. The compound was amorphous, melting slowly above 150° C.

Compound 2 was prepared in the same way as compound 1, using 2 - (2,4 - diamylphenoxy) - 5 - nitrobenzoyl chloride in step (*c*) and 3,5-dichlorosulfonyl benzoyl chloride in step (*e*). The compound was amorphous and hygroscopic.

Compound 3 was prepared as follows:

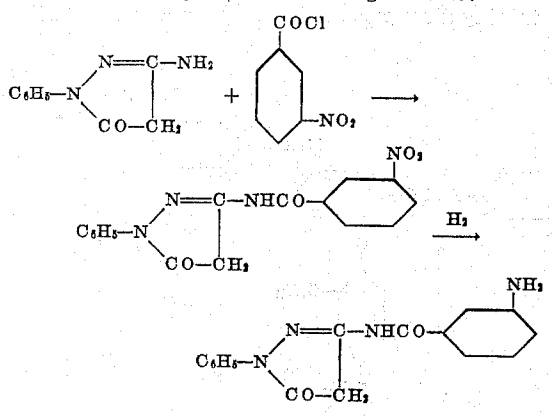
1 - hydroxy - N - {4' - [" - (2''',4''' - diamylphenoxy) - 5'' - aminobenzamido] - phenethyl}-2-naphthamide was (Compound 1*d*.) acylated with m-chlorosulfonylbenzoyl chloride to give 1-hydroxy - 2 - {4' - [2'' - (2''',4 - diamylphenoxy) - 5'' - (3'''' - chlorosulfonylbenzamido) - benzamido] - phenethyl} - naphthamide. (M. P. 150–155° C.)

This sulfonyl chloride is used to acylate methyl-5-aminoisophthalate to give 1-hydroxy-2-{4'-{2'' - [2''',4 - diamylphenoxy] - 5'' - [3''''-(3''''',5 - dicarbomethoxyphenyl) - sulfamylbenzamido] - benzamido} - phenethyl} - naphthamide (M. P. 150–153° C.).

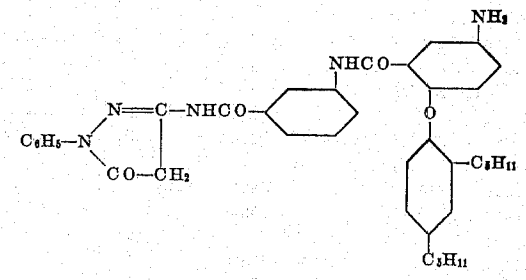
Compound 3 results when the above coupler is treated with 3,5 - dicarbomethoxybenzenediazonium chloride. (M. P. 165–167° C., orange dye.)

Compound 4 was prepared as follows:

(*a*) 1-phenyl-3-amino-5-pyrazolone was condensed with m-nitro-benzoyl chloride, and the nitro group was reduced catalytically with Raney nickel, according to the following scheme:



(*b*) The compound obtained in (*a*) was condensed in acetic acid and sodium acetate at room temperature with an equimolecular quantity of 2 - (2,4 - diamyl - phenoxy) - 5 - nitrobenzoyl chloride, and this compound treated with Raney nickel to reduce the nitro group, resulting in a compound of the following structure:



(*c*) The 1-phenyl-3{3'-[2''-(2''',4'''-di-tert.-amylphenoxy) - 5'' - aminobenzamido] - benzamido}-5-pyrazolone obtained in step (*b*) was coupled with 3,5-dicarbomethoxybenzene diazonium chloride to yield the amino dye 1-phenyl-3{3' - [2'' - (2''',4'''-di-tert.-amylphenoxy) - 5''-aminobenzamido] - benzamido} - 4 - (3'''',5''''-dicarbomethoxyphenylazo)-5-pyrazolone whose melting point is 209–212° C. when recrystallized from xylene.

(*d*) The final compound was obtained by acylating the amino dye obtained in (*c*) with orthosulfobenzoic anhydride in boiling, dry xylene. The final compound softens and melts at 175–180° C.

Compound 5 was prepared in the same way as compound 4, except that in (*d*) m-chlorosulfonylbenzoyl chloride was used in place of o-sulfobenzoic anhydride. The compound thus obtained was used to acylate methyl-5-amino-isophthalate to yield the final compound, M. P. 185–190° C.

The following example illustrates the method of hydrolysis of the ester of the coupler and incorporation in a gelatin emulsion:

Three grams of compound 1 were dissolved in a mixture of 15 cc. of 95 per cent ethyl alcohol and 7.5 cc. of 20 per cent sodium hydroxide solution. The mixture was warmed gently if necessary to complete solution of the coupler and then poured into 200 cc. of water at 40° C. If desired, the mixture may be added directly to a gelatin solution. The resulting solution was brought to a pH of 6 to 7 by addition of 2 per cent citric acid solution. The coupler solution was then mixed with a suitable amount of melted silver halide emulsion e. g. 400 cc. of a positive type gelatino silver halide emulsion at 40° C. After coating, the emulsion layer thus obtained may be subjected to the usual exposure and processing steps of color photography.

In hydrolyzing the couplers other means may be used such as acid or alkaline hydrolysis in lower aliphatic alcohol or aqueous media provided that the conditions employed do not cause splitting of the coupler at points in the molecule such as at the —NHCO— linkage.

The following example illustrates incorporation of the methyl ester of the coupler in solvent dispersion in a gelatin emulsion:

A solution of 7.5 grams of compound 3 in 15 grams of 1,2-dimethoxy benzene was added to 200 cc. of 5 percent gelatin solution containing 2.0 grams of the wetting agent Gardinol WA. The whole mixture was stirred to effect preliminary emulsification then passed through a colloid mill several times while the temperature of the solution and the mill was maintained at about

20° C. In this way a very stable and very fine emulsion was obtained which was added to 1000 cc. of a melted silver halide gelatin emulsion. The emulsion containing the added coupler dispersion was coated on a suitable support, set and dried in the usual manner. On exposure and development of this emulsion with a developing solution employing 2-amino-5-diethylaminotoluene as the developing agent and subsequent removal of silver, a cyan dye image was obtained.

Various photographic developing agents can be employed with the couplers of our 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 diethyl paraphenylenediamine, monomethyl paraphenylenediamine, dimethyl paraphenylenediamine and para-aminophenol. 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.

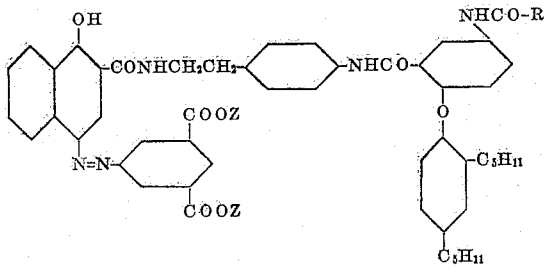
The following developing solution is suitable for developing gelatino-silver halide layers containing colored couplers according to our invention incorporated either directly in the emulsion or in solvent dispersion:

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

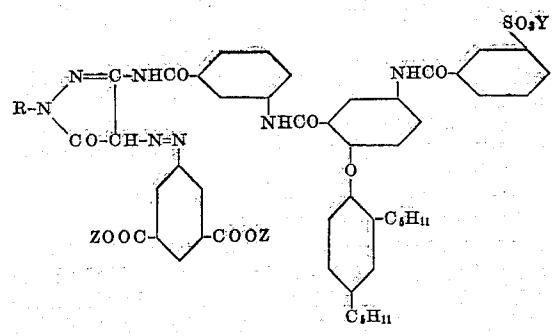
It will be understood that the examples and modifications set forth herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A gelatino-silver halide emulsion layer containing a coupler compound having a formula selected from the class consisting of

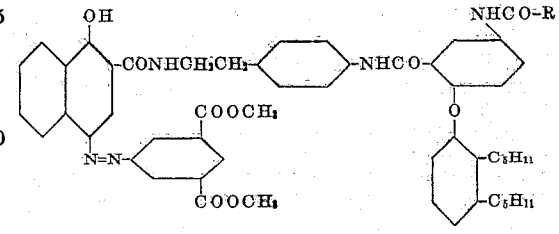


and



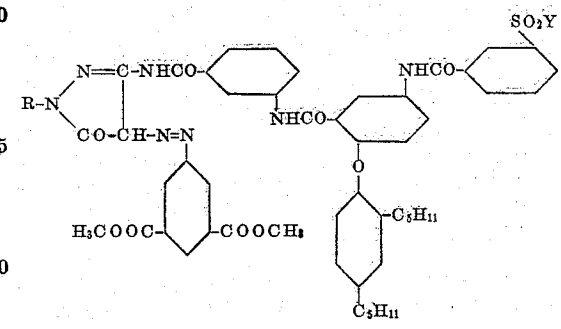
where R is a mononuclear aryl radical, Y is selected from the class consisting of hydroxyl and arylamino groups, and Z is selected from the class consisting of an alkali metal and a methyl radical.

2. A gelatino-silver halide emulsion layer containing the sodium salt of the free acid of a coupler compound having the formula:



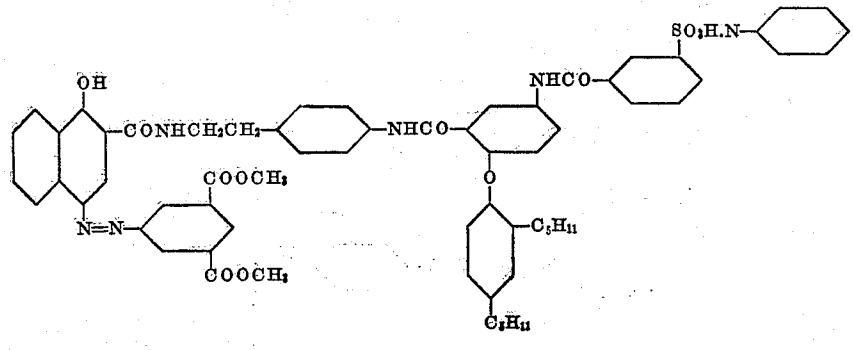
where R is a mononuclear aryl radical.

3. A gelatino-silver halide emulsion layer containing a coupler compound having the formula:

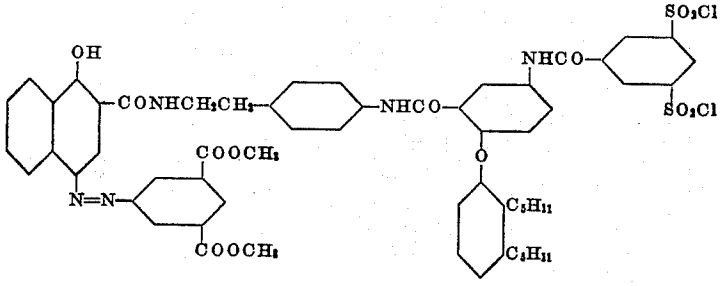


where R is a mononuclear aryl radical and Y is selected from the class consisting of hydroxyl and arylamino groups.

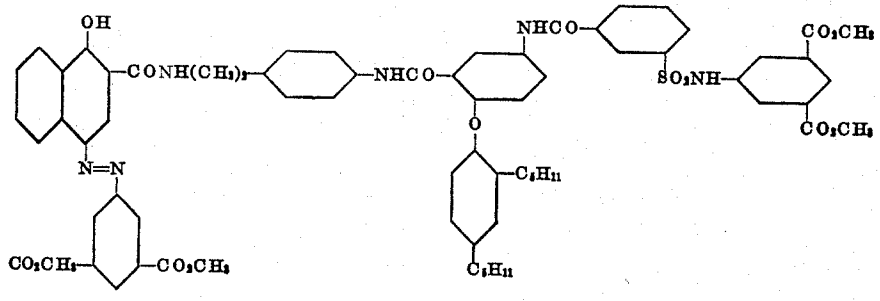
4. A gelatino-silver halide emulsion layer containing a coupler compound having the formula:



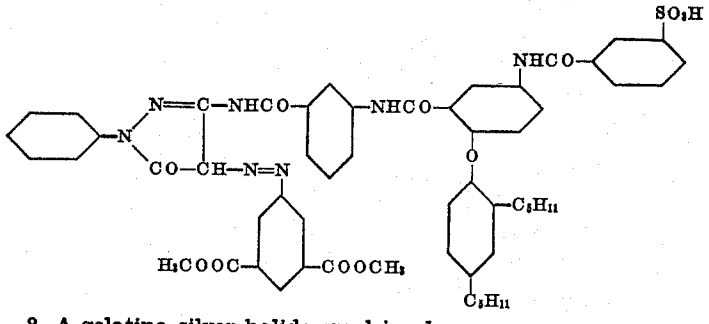
5. A gelatino-silver halide emulsion layer containing a coupler compound having the formula:



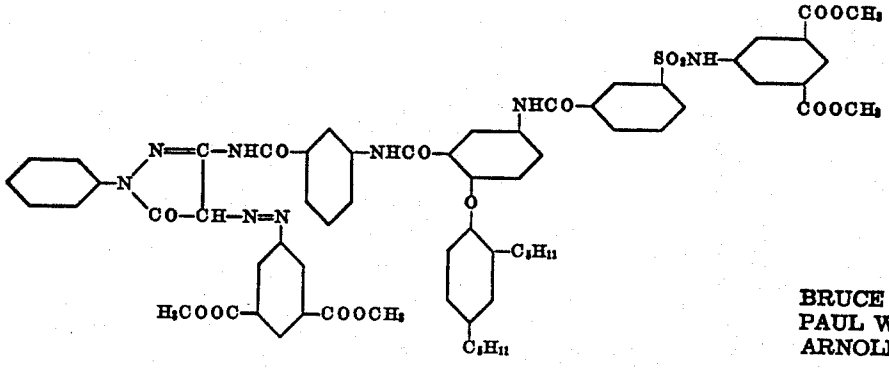
6. A gelatino-silver halide emulsion layer containing a coupler compound having the formula:



7. A gelatino-silver halide emulsion layer containing a coupler compound having the formula:



8. A gelatino-silver halide emulsion layer containing a coupler compound having the formula:



BRUCE GRAHAM.
PAUL W. VITTUM.
ARNOLD WEISSBERGER.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,179,239	Wilmanns et al.	Nov. 7, 1939
2,186,717	Eggert et al.	Jan. 9, 1940
2,369,489	Porter et al.	Feb. 13, 1945

FOREIGN PATENTS

Number	Country	Date
890,863	France	Nov. 19, 1943