Oct. 24, 1961 D. G. SAUNDERS ET AL 3,005,712

YELLOW-COLORED MAGENTA-FORMING COUPLERS

Filed Sept. 26, 1958 2 Sheets-Sheet 1

Fig. 1

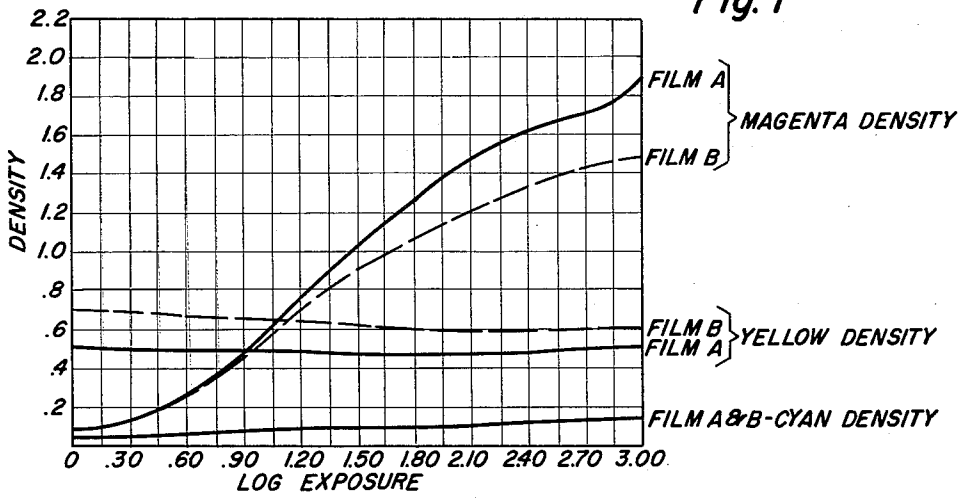
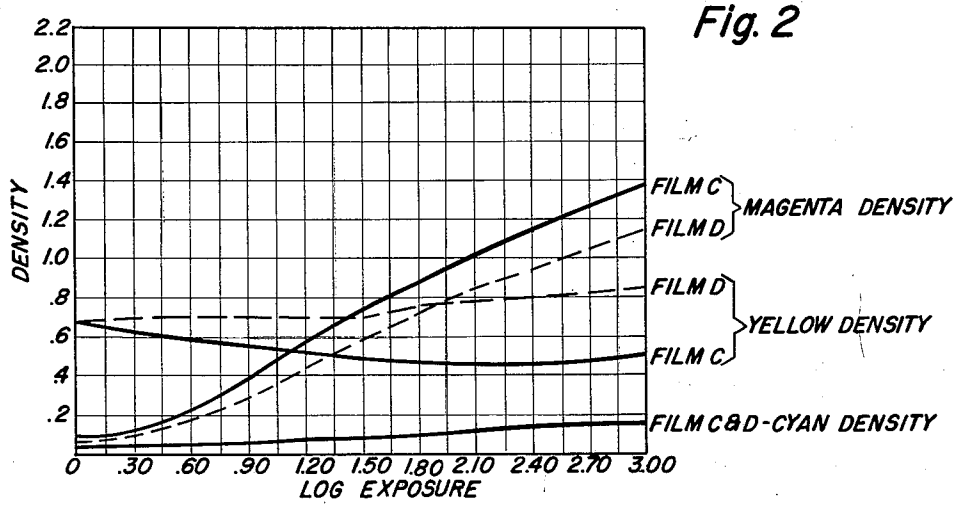


Fig. 2



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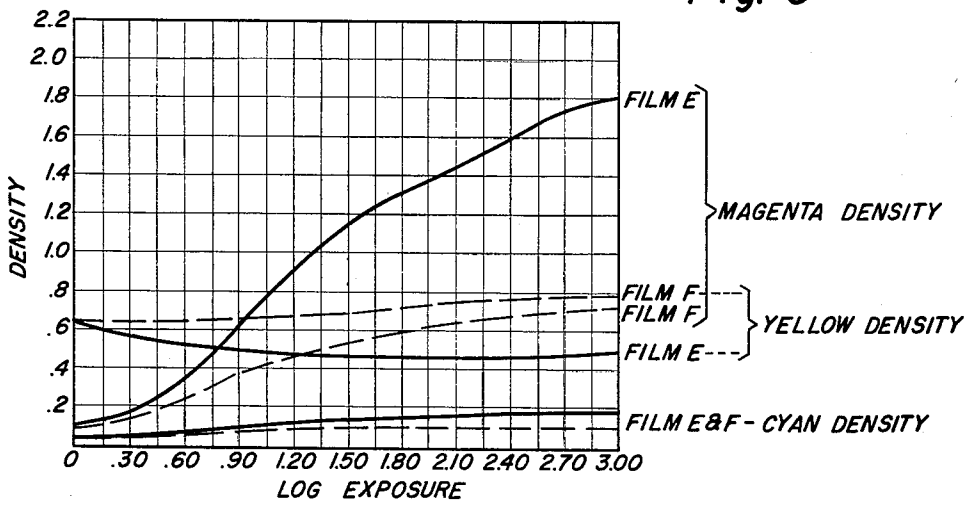
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Fig. 3



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3,005,712
YELLOW-COLORED MAGENTA-FORMING COUPLERS

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11 Claims. (Cl. 96—100)

This invention relates to color photography and particularly to colored 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 when the coupler is to be incorporated in the emulsion layer and the unused coupler remains after formation of the colored image.

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, 2,455,170, Hansen 2,449,966, and Heimbach et al., 2,688,539.

Upon development of an emulsion layer containing one of these colored couplers, the coupler color is usually destroyed and a new color is formed by the coupling reaction at those points where development occurs. There is formed in this way a dye image consisting of the new dye and the residual colored coupler on a background consisting of the colored coupler. The theory of color correction requires that the sum of the absorption of the residual colored coupler and the undesired absorption of the image dye should be constant. This requirement is not always fulfilled by colored couplers in use so errors are introduced in the process of color correction.

Magenta dyes produced upon color development have an undesired absorption of light in the blue region of the spectrum. Therefore, it is desirable to have yellow-colored magenta-forming coupler compounds that can be used to correct for this unwanted blue absorption.

Yellow-colored magenta-forming coupler compounds known before have slow coupling rates with oxidized primary aromatic amino developing agents as compared to the coupling rates of the uncolored magenta-forming coupler compounds with the same oxidized developing agent when used in the coupler to coupler incorporating solvent ratio of 1:¼. This has limited the usefulness of these compounds for correcting the unwanted blue light absorption of the magenta dye.

It is, therefore, an object of the present invention to provide a class of novel yellow-colored magenta-forming couplers for use with uncolored magenta-forming couplers to correct for the deficiencies in the magenta dye produced upon color development. A further object is to provide a class of yellow-colored magenta-forming couplers which couple with an oxidized color developer such as a primary aromatic amino developing agent at rates more nearly equal to the coupling rates of the uncolored magenta-forming coupler and which therefore are superior for correcting the unwanted blue absorption of the magenta dye formed. A still further object is to provide a yellow-colored magenta-forming coupler which is particularly active compared to the aryl azo analogue when used in a dispersion at a higher coupler to coupler incorporating solvent ratio thus making it possible to reduce the thickness of the green-sensitive layer when our couplers are used in them. Other objects will appear from the following description and claims.

These and other objects are accompanied by means of this invention as described hereinafter. We have discovered that couplers having a 3,5-dimethylpyrazolyl-4-azo group or a 3,5-dimethylisoxazolyl-4-azo group attached to the carbon of the active methylene group on a 1,3-substituted 5 pyrazolone have the common characteristic of being yellow colored before development and of forming magenta dye upon development. They are all further characterized by having coupling rates that are more nearly equal to the coupling rates of the uncolored magenta-forming couplers and of being particularly active compared to the arylazo analogues when used in emulsion dispersions at higher coupler to coupler incorporating solvent ratios. These reaction rate effects are illustrated by curves on the accompanying drawing which are described below.

FIGURE 1 is a plot showing the relationship of the optical densities of processed photographic images to log exposure for film samples A and B. The optical densities are expressed in terms of magenta density, yellow density and cyan density as measured by the absorption of green, blue and red light respectively by the image. Solid-line curves show these data for sample A and broken-line curves for sample B. Film sample A has a light-sensitive emulsion containing the uncolored magenta-forming coupler 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-amylphenoxyacetamido)benzamido]-5 - pyrazolone in admixture with an equal amount of our yellow-colored magenta-forming coupler 1-(2',4',6'-trichlorophenyl)-3-[3''(2''',4''' - di - tertiaryamylphenoxyacetamido)benzamido]-4-[4-(3,5-dimethylpyrazolylazo)]-5 - pyrazolone. Film sample B has a light-sensitive emulsion containing equal amounts of the same uncolored magenta-forming coupler as in A and the yellow-colored magenta-forming coupler 1(2',4',6' - trichlorophenyl) - 3 - [3''-(2''',4''' diamylphenoxyacetamido)benzamido] - 4 - (4 - methoxyphenylazo)-5-pyrazolone. The couplers in each film sample were incorporated in the emulsion with tri-o-cresyl phosphate as an incorporating solvent at a coupler to coupler solvent ratio of 1:2. The films were each given a sensitometric exposure and developed in a color developer containing 2-amino-5(N-ethyl-N-β-methanesulfonamidoethylamino)toluene sulfate.

FIGURE 2 is a similar plot for two other film samples C and D containing the same couplers as samples A and B respectively. Solid-line curves depict data for film sample C and the broken-line curves depict data for sample D. The couplers in film samples C and D were incorporated in the emulsion with tri-o-cresyl phosphate as an incorporating solvent at a coupler to coupler solvent ratio of 1:¼. After receiving sensitometric exposures these samples were developed with the same developer used to develop samples A and B.

FIGURE 3 is a similar plot for film samples E and F which contain the same couplers as film samples C and D respectively incorporated with tri-o-cresyl phosphate at a coupler to coupler solvent ratio of 1:¼ but which after sensitometric exposure were developed in a developer containing 4-amino-N-N-diethyl-m-toluidene hydrochloride.

A comparison of the two sets of curves in each figure illustrates that our couplers react with oxidized color developer at a rate that is closer to the reaction rate of the uncolored magenta-forming coupler with the oxidized color developer than does the methoxyphenyl type colored coupler. For example, the difference in the yellow density curves for film samples A and B in FIG. 1 is a measure of the relative amounts of unreacted yellow-colored magenta-forming coupler in these developed film samples since both film samples have the same amount of unwanted yellow density contributed by the magenta

dye. Our colored coupler reacts more completely as is shown by the lower yellow densities.

FIGURE 1 shows that film sample A which contains our coupler has up to 28% less yellow dye than film sample B.

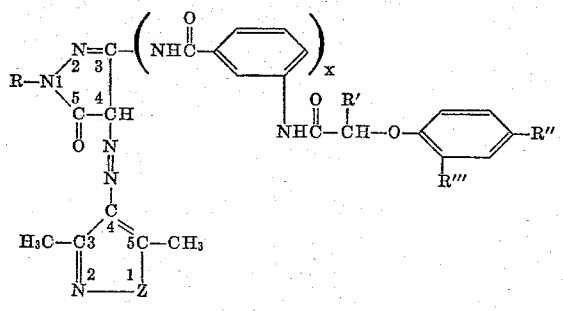
FIGURE 2 shows that film sample C which contains our coupler has up to 39% less yellow dye in its image than film sample D indicating that our coupler is considerably more reactive than the other coupler when both are incorporated with a coupler to coupler solvent ratio of 1:¼.

FIGURE 3 shows that film sample E has up to 36% less yellow dye in its image than film F.

In a similar fashion the magenta density curves may also be used as a measure of the unreacted yellow-colored magenta-forming coupler because the unreacted coupler does not contribute to the magenta density. A comparison of the magenta curves in each figure shows that the film samples A, C and E which contain our coupler have a higher conversion of the colored coupler to the magenta dye.

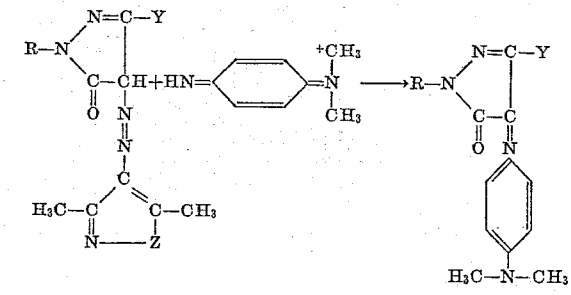
Our coupler as used in film sample A is particularly desirable since the developed yellow density is relatively low and almost constant for all values of log exposure and the magenta curve has a long straight line portion extending for about ⅓ the length of the curve in the middle of the sensitometric scale.

The preferred embodiments of this invention have the formula:



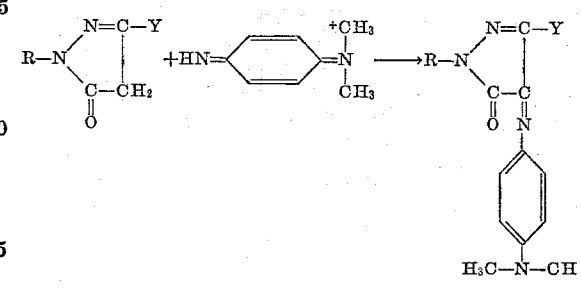
wherein R is a substituted or unsubstituted monocyclic aryl group of the benzene series; R′ represents a hydrogen atom or an alkyl group having from 1 to 3 carbon atoms; X is either 0 or 1; R″ is an alkyl group having from 4 to 6 carbon atoms and R‴ is from the group consisting of a hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; and Z is an oxygen atom or a =NH radical.

The yellow color of our couplers is destroyed upon reaction with an oxidized primary aromatic amino developing agent and a magenta-colored dye is formed. Although the exact mechanism of this reaction is not completely understood, it appears as though the reaction may proceed as follows:



wherein R and Z represent the groups described for the general formula and Y represents the groups described as being substituted on the 3 position of the 5-pyrazolone of the general formula.

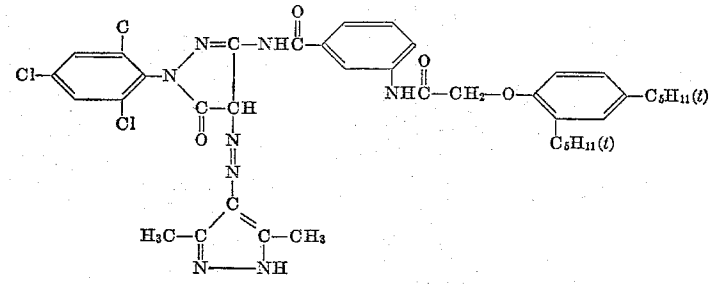
The compounds of this invention can be used in admixture with uncolored couplers which appear to react as follows:



wherein R and Y represent the groups defined above.

Typical compounds embodying the invention and which can be used according to our invention include the follower which illustrate the invention but to which the invention is not limited:

COUPLER I



1-(2′,4′,6′-trichlorophenyl)-3-[3″-(2‴,4‴-di-tertiary-amylphenoxyacetamido)benzamido]-4[4-(3,5-dimethylpyrazolyl)-azo]-5-pyrazolone

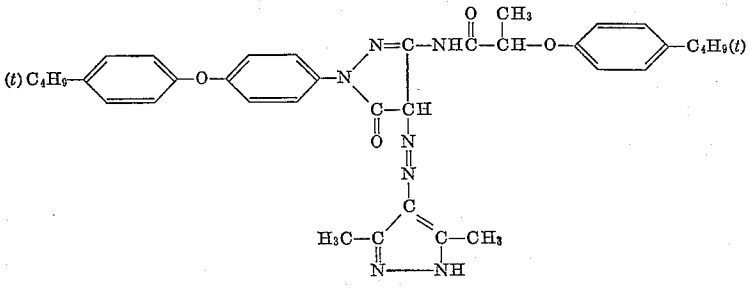
A typical process for preparing Coupler I is as follows: 1.8 gms. (.01 mole) of 4-amino-3:5-dimethylpyrazole dihydrochloride are dissolved in 4 cc. of water and 2.5 cc. of concentrated hydrochloric acid at 0° C. and diazotized with a solution of 0.8 gm. of sodium nitrite in 2.5 cc. of water below 5° C.

The diazonium solution is added to 6.7 gms. (.01 mole) of coupler compound 1-(2′,4′,6′-trichlorophenyl)-3-[3″-(2‴,4‴-di-tertiary-amylphenoxyacetamido)benzamido]-5-pyrazolone dissolved in 35 cc. of pyridine at 0° C. The preparation of this latter coupler is described as Compound VII of Lori et al. U.S. Patent 2,600,788, column

5, lines 9, 10 and 11. The mixture is stirred occasionally for 30 minutes while being cooled by an ice bath. It is then poured into 100 cc. of water and the viscous red gum obtained is filtered off. The gum is dissolved in alcohol, a little benzene added and the solution boiled to remove water as an azeotrope. More benzene is added and the process is repeated several times.

All the benzene is boiled off and the alcoholic solution remaining concentrated to about 50 cc. The concentrated solution is poured into a liter of well-stirred petroleum ether (boiling range 40–60° C.) The fine orange colored precipitate is filtered and air dried. A yield of 7.7 grams (97% yield) is obtained, having a melting point of 152° C. with decomposition and an analytical composition very close to the calculated theoretical.

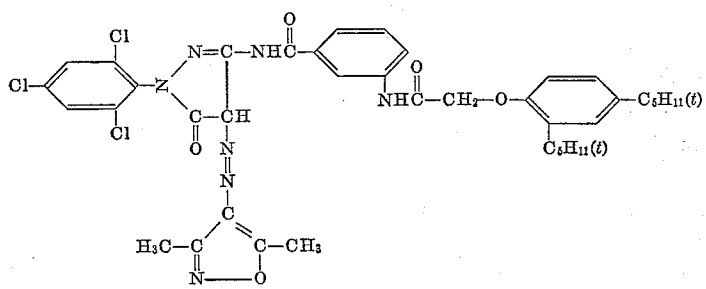
COUPLER II



1-[4' - (4''-tertiarybutylphenoxy)phenyl] - 3 - [α-(4'''-tertiarybutylphenoxy)propionamido]-4-[4-(3,5 di-methylpyrazolyl) azo]-5-pyrazolone

This coupler is prepared as described for Coupler I except that the diazonium solution formed from .01 mole of 4-amino-3,5-dimethylpyrazole di-hydrochloride is reacted with .01 mole of 1-[4'-(tertiarybutylphenoxy)-phenyl] - 3 - [α - (4'' - tertiarybutylphenoxy)propionamido]-5-pyrazolone which is described as Coupler No. 47 in Porter et al. U.S. Patent 2,369,489. The coupler made has a melting point of 213.5° C. with decomposition and an analytical composition that is very close to the calculated theoretical.

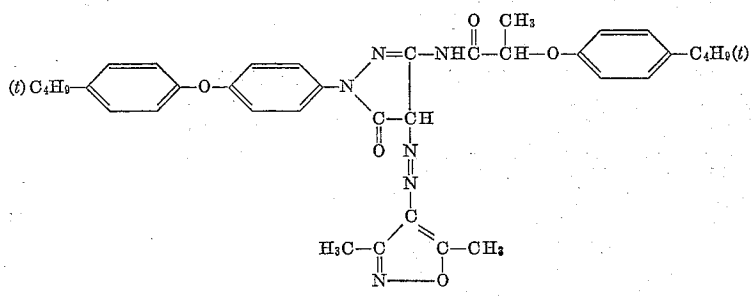
COUPLER III



1-(2',4',6' - trichlorophenyl)-3-[3''-(2''',4'''-di-tertiaryamylphenoxyacetamido)benzamido] - 4 - [4-(3,5-dimethylisoxazolyl)-azo]-5-pyrazolone

This coupler is prepared as described for Coupler I except that the diazonium solution formed from .01 mole of 4-amino-3,5-di-methylisoxazolyl di-hydrochloride is reacted with .01 mole of the coupler compound 1 - (2',4',6'-trichlorophenyl) - 3 - [3'' - (2''',4''' - di-tertiaryamylphenoxyacetamido)benzamido] - 5 - pyrazolone.

COUPLER IV



1-[4'-(4''-tertiarybutylphenoxy)phenyl] - 3 - [α-(4'''-tertiarybutylphenoxy)propionamido]-4-[4-(3,5 dimethylisoxazolyl) azo]-5-pyrazolone

This compound is prepared as Coupler II except that the diazonium solution formed from .01 mole of 4-amino-3,5-dimethylisoxazolyl di-hydrochloride is reacted with .01 mole of 1-[4-(tertiarybutylphenoxy)phenyl]-3[α - (4'' - tertiarybutylphenoxy)propionamido] - 5-pyrazolone.

Our yellow-colored magenta-forming coupler compounds can be used in any photographic emulsion where magenta-forming couplers are used or can be used. Usually these couplers are used in admixture with uncolored magenta-forming couplers. Colored and uncolored couplers are selected which form either the same magenta dye upon color development or a magenta dye of the same hue. In this way the color correcting mask effects can be obtained as described in Vittum and Arnold U.S. Patent 2,428,054 and Hanson U.S. Patent 2,449,966. These photographic emulsions producing color corrected magenta images can be used alone, however, they are usually used in combination with photographic elements forming a yellow image, and a cyan or corrected cyan image to produce a colored picture.

The coupler compounds may be dispersed in gelatin or in synthetic vehicles used for making photographic emulsions such as collodion, organic esters of cellulose or synthetic resins. Photographic emulsions containing our couplers may be coated on transparent supports such as glass, cellulose esters, or on a non-transparent

reflecting material such as paper or opaque cellulose ester.

The following examples illustrate a typical way in which our couplers can be incorporated and used in color photographic material:

Example I

0.25 gram of 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''', 4''' - ditertiary - amylphenoxyacetamido)benzamido]-5-pyrazolone and 0.25 gram of 1-(2',4',6'-trichlorophenyl) - 3 - [3'' - (2''',4''' - ditertiaryamylphenoxyacetamido)benzamido] - 4 - [4 - (3,5-dimethylpyrazolyl)-azo-5-pyrazolone were dissolved in 1 gram of tri-o-cresyl phosphate by heating to about 110° C. with stirring. This solution was intimately mixed with and dispersed in one containing 22 ml. of 10% gelatin and 2 ml. of 5% alkanol B. To this mixture was added 2 ml. of 7½% saponin and 15 ml. of water. 25 ml. of this dispersion was added to 5 ml. of a medium speed silver bromoiodide emulsion and the mixture was coated on a cellulose acetate support and dried.

The coating was exposed under an image and developed in a 2-amino-5-(N-ethyl-N-β-methanesulfonamidoethylamino)toluene sulfate developing composition to form a negative silver and magenta dye image. The silver image and the residual silver halide were removed by treatment with an alkali ferricyanidebromide bleach followed by a hypo fixing bath leaving a magenta-colored negative image having a maximum absorption at a wavelength of 545 mμ and a yellow-colored coupler positive image having a maximum absorption at a wavelength of 436 mμ.

Example II

Similar results were obtained using a dispersion made by dissolving 0.25 gram of each of the couplers in Example I in 0.125 gram of tri-o-cresyl phosphate and 4 ml. of ethyl acetate. This solution was added to the same amount of gelatin solution and emulsion as in Example I and coated in the same manner. The ethyl acetate evaporates from the coating on drying. Following exposure under an image, the same color development, bleaching and fixing produces a negative dye image having a maximum absorption at a wavelength of 551 mμ and a positive yellow image with a maximum absorption at a wavelength of 432 mμ.

Multilayer, multicolor films are made by combining a single layer emulsion such as just described, with an emulsion layer containing a yellow-forming coupler, and an emulsion layer containing a cyan-forming coupler or a cyan-forming coupler in admixture with a colored cyan-forming coupler. These emulsion layers may be arranged in any order upon the support which may be either a transparent or an opaque reflecting material. A gelatin dispersion of a higher alkyl substituted hydroquinone or a higher alkyl substituted catechol dissolved in tricresyl phosphate can be coated as an interlayer separating the differently sensitized emulsion layers. These multilayer color films are exposed, and processed in the same manner as the single layer material described above to yield a color-corrected dye image.

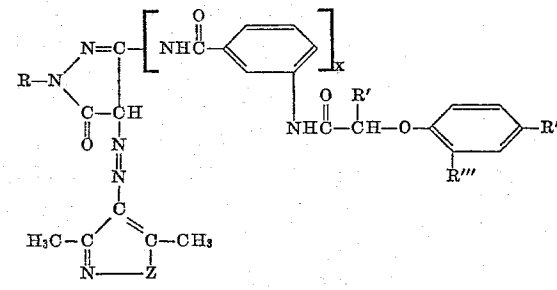
Our yellow-colored magenta-forming couplers described hereinabove are superior to the colored magenta-forming couplers known and used before to correct the undesired blue absorption of the magenta dye formed upon color development. The faster coupling rates of our couplers with the oxidized color developer make it possible to get more complete color correction than with prior art couplers. Our couplers are also valuable because their high activity makes it possible to use them in dispersions having higher coupler to coupler incorporating solvent ratios. This means that our couplers can be used at higher concentrations in emulsions and that the emulsions containing them can be coated thinner. Thinner emulsion coatings not only reduce manufacturing costs but give photographic products that will produce images with higher definition and improved resolution.

Our yellow-colored magenta-forming couplers are most useful in color photography where they are used to dye the gelatin or synthetic vehicle in which they are dispersed, however they can also be used to dye any other materials which are dyed with azo dyes.

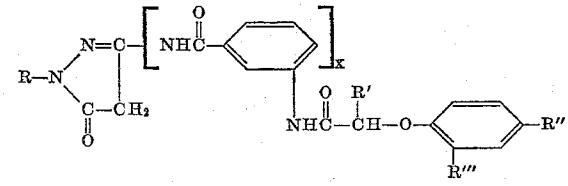
The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic silver halide emulsion containing (*a*) a yellow-colored magenta-forming coupler compound selected from the group consisting of compounds with the formula:

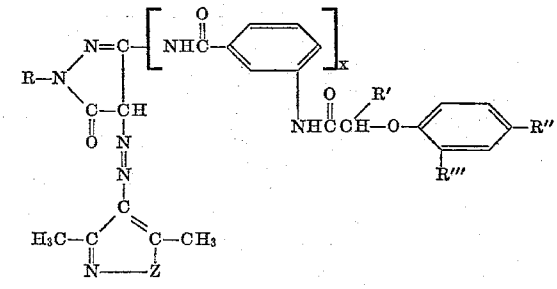


and (*b*) an uncolored magenta-forming coupler selected from those having the formula:



wherein R is a member selected from the group consisting of a 2,4,6-trichlorophenyl radical and a 4-tertiarybutylphenoxyphenyl radical; R' represents a member selected from the group consisting of a hydrogen atom and an alkyl group having from 1 to 3 carbon atoms inclusively; X is an integer from 0 to 1; R'' is an alkyl group having from 4 to 6 carbon atoms; R''' is a member selected from the group consisting of a hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; and Z is a group selected from the class consisting of an oxygen atom and a =NH radical.

2. A photographic silver halide emulsion containing a yellow-colored magenta-forming coupler compound selected from the group consisting of compounds with the formula:



wherein R is a member selected from the group consisting of a 2,4,6-trichlorophenyl radical and a 4-tertiarybutylphenoxyphenyl radical; R' represents a member selected from the group consisting of a hydrogen atom and an alkyl group having from 1 to 3 carbon atoms inclusively; X is an integer from 0 to 1; R'' is an alkyl group having from 4 to 6 carbon atoms; R''' is a member selected from the group consisting of a hydrogen atom

and an alkyl group having from 1 to 6 carbon atoms; and Z is a group selected from the class consisting of an oxygen atom and a =NH radical.

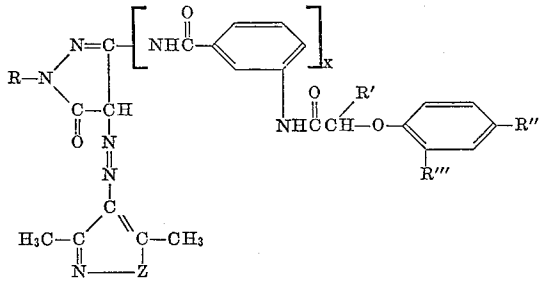
3. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2',4',6'-tri-chlorophenyl) - 3 - [3''-(2''',4'''-di-tertiary-amylphenoxyacetamido)benzamido] - 4 - [4-(3,5-di-methylpyrazolyl)-azo]-5-pyrazolone.

4. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2',4',6'-tri-chlorophenyl)-3-[3''-(2''',4'''-di-tertiarylamyl phenoxyacetamido) - benzamido]-4-[4-(3,5-dimethylisoxazolyl)azo]-5-pyrazolone.

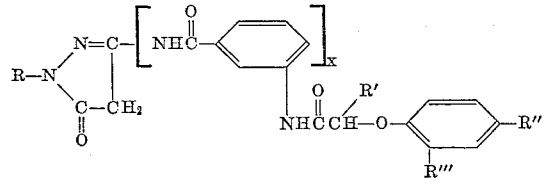
5. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-[4'-(4''-tertiarybutylphenoxy)phenyl] - 3 - [α - (4'''-tertiarybutylphenoxy)-propionamido] - 4 - [4-(3,5-dimethylisoxazolyl)azo]-5-pyrazolone.

6. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-[4'-(4''-tertiarybutylphenoxy)phenyl] - 3 - [α-(4'''-tertiarybutylphenoxy) - propionamido]-4-[4-(3,5 di-methylpyrazolyl)azo]-5-pyrazolone.

7. A photographic silver halide emulsion containing a yellow-colored magenta-forming coupler compound selected from the group consisting of compounds with the formula:



and an uncolored magenta-forming coupler which both form the same magenta dye upon coupling with the development product of a primary amino developing agent, said uncolored coupler having the formula:



wherein R is a member selected from the group consisting of a 2,4,6-trichlorophenyl radical and a 4-tertiarybutylphenoxyphenyl radical; R' represents a member selected from the group consisting of a hydrogen atom and an alkyl group having from 1 to 3 carbon atoms inclusively; X is an integer from 0 to 1; R'' is an alkyl group having from 4 to 6 carbon atoms; R''' is a member selected from the group consisting of a hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; and Z is a group selected from the class consisting of an oxygen atom and a =NH radical.

8. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler 1-(2',4',6'-trichlorophenyl) - 3 - [3''-(2''',4''' - di-tertiaryamylphenoxyacetamido)benzamido] - 4 - [4 - (3,5-di-methylpyrazolyl)-azo] - 5 - pyrazolone, and the uncolored magenta-forming coupler 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''', 4''' - di - tertiarylamylphenoxyacetamido)benzamido]-5-pyrazolone.

9. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler 1-(2',4',6'-trichlorophenyl) - 3 - [3''-(2''',4''' - di-tertiaryamylphenoxyacetamido)benzamido] - 4[4 - (3,5 - dimethylisoxazolyl)azo] - 5 - pyrazolone, and the uncolored magenta-forming coupler 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''', 4''' - di - tertiaryamylphenoxyacetamido)benzamido]-5-pyrazolone.

10. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler 1-[4'-(4''-tertiarybutylphenoxy)phenyl] - 3 - [α-(4'''-tertiarybutylphenoxy)propionamido] - 4 - [4-(3,5 dimethylisoxazolyl)-azo]-5-pyrazolone, and the uncolored magenta-forming coupler 1 - [4' - (4''-tertiarybutylphenoxy)phenyl]-3-[α-(4'''-tertiarybutylphenoxy)propionamido]-5-pyrazolone.

11. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler 1-[4'-(4''-tertiarybutylphenoxy)phenyl] - 3 - [α-(4'''-tertiarybutylphenoxy)propionamido]-4-[4 - (3,5 di-methylpyrazolyl)-azo]-5-pyrazolone, and the uncolored magenta-forming coupler 1 - [4' - (4''-tertiarybutylphenoxy)phenyl]-3-[α-(4'''-tertiarybutylphenoxy)propionamido]-5-pyrazolone.

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2,472,109	Hendermann	June 7, 1949
2,584,349	Heimbach	Feb. 5, 1952
2,725,291	Graham	Nov. 29 1955