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YELLOW-COLORED MAGENTA-FORMING COUPLERS

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13 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.

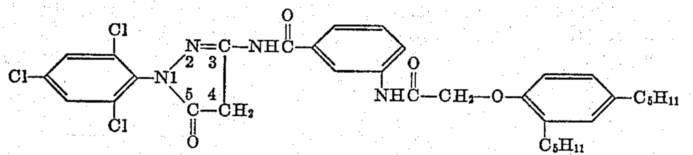
Couplers which are in themselves more or less strongly colored and which contain a chromophore group which is split off or destroyed during and by means of the coupling reaction with the result that the original color of the coupler is destroyed and a new dye is formed upon coupling are disclosed in 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 of those points where development occurs.

There is formed in this way a dye image consisting of the new dye and the residual colored coupler. The theory of color correction requires that 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.

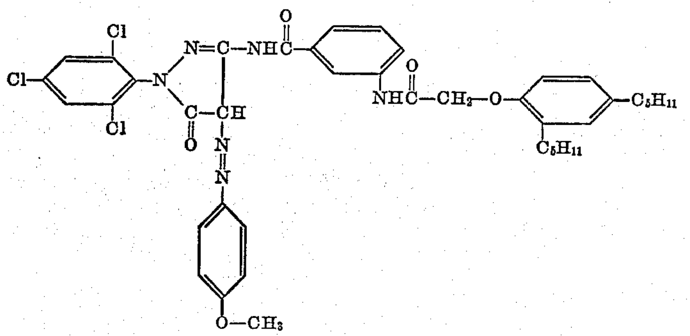
Magenta dyes produced upon color development have an undesired absorption of light in the blue region of the spectrum. Therefore, it is desirable to have yellow-colored magenta-forming coupler compounds that can be used to correct for this unwanted blue absorption.

Yellow-colored magenta-forming coupler compounds made from colorless magenta-forming coupler compounds that are incorporated in certain color negative materials are insufficiently reactive to give the desired color corrective masking effects. For example, in a typical case, an unwanted blue absorption of 0.28 density units is produced by the magenta dye formed from the reaction of the oxidized primary aromatic amino developing agent with the uncolored magenta-forming Coupler A:



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

In an ideal situation enough blue absorbing colored coupler is mixed with the colorless coupler to compensate for this unwanted absorption as described in Vittum and Arnold, U.S. Patent 2,428,054 and Hansen, U.S. Patent 2,449,966. However, the yellow-colored magenta-forming Coupler B:



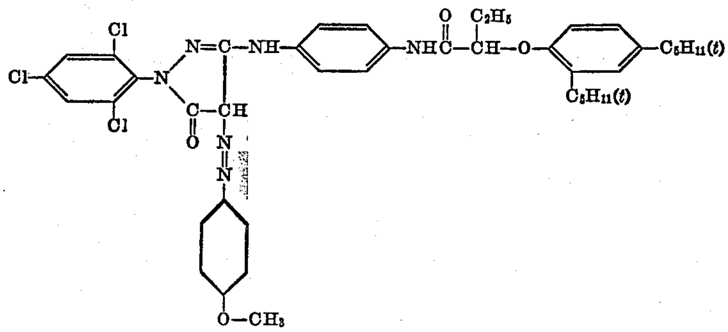
1(2',4',6'-trichlorophenyl)-3[3''-(2''',4'''-di-amylphenoxyacetamido)benzamido]-4-(4-methoxyphenylazo)-5-pyrazolone

derived from uncolored coupler is insufficiently reactive and a residual amount raises the blue absorption in the exposed area from 0.28 to 0.43 density units. Consequently, the colored Coupler B must be used in a concentration that is sufficient to give a density of 0.43 in unexposed regions. This situation prevails when the ratio of Coupler B to coupler incorporating solvent is 1:2. At the desired ratio of 1:¼ the colored Coupler B is completely unreactive and gives no color correction.

Furthermore, it is desired to have yellow-colored magenta-forming couplers with higher extinction coefficients than the available colored couplers.

It is, therefore, an object of the present invention to provide a class of 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 are sufficiently reactive to give complete compensation for the unwanted blue absorption of the magenta dye produced upon colored development at the desired coupler to coupler incorporating solvent ratio of 1:¼. A still further object is to provide a yellow-colored magenta-forming coupler with a higher extinction coefficient than the available colored magenta-forming couplers. A still further object is to provide a class of yellow-colored magenta-forming couplers which because of their superior characteristics can be used for color correction in color photographic products in thinner emulsion coatings to give a photographic product having a lower minimum density than would be possible with known colored magenta-forming couplers. Other objects will appear from the following description and claims.

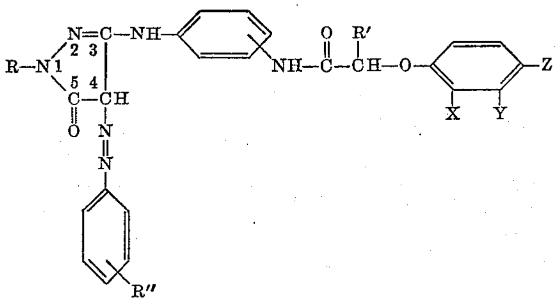
These and other objects are accomplished by means of this invention as described hereinafter. We have discovered that couplers of the 3-anilino-4-arylazo-5-pyrazolone type are valuable yellow-colored magenta-forming couplers. Our couplers are not only yellow-colored but are characterized by being completely reactive with the oxidized primary aromatic amino developing agents, even when used at a coupler to coupler incorporating solvent ratio of 1:¼. For example, our Coupler I is completely reactive at a coupler to coupler incorporating solvent ratio of 1:¼ and gives complete compensation for the unwanted blue absorption of the magenta dye when incorporated in sufficient amount to have the density of 0.28 units to blue light. These characteristics are entirely unexpected because of the vary small chemical differences between our Coupler I and Coupler B which is completely unreactive at coupler to coupler incorporating solvent ratios of 1:¼ and therefore gives no color correction.



Our couplers are not only valuable because of their reactivity but because they have higher extinction co-efficients than do the corresponding 3-benzamido-5-pyrazolone type of coupler. For example, our Coupler I has an extinction co-efficient of 2.8×10^4, in butyl acetate as compared to an extinction coefficient of 1.5×10^4 in butyl acetate given by Coupler B.

The characteristics shown by our couplers give their user valuable advantages over one using the yellow-colored magenta-forming coupler compounds known before. For example, smaller amounts of our coupler can be used than similar couplers outside the invention. In addition to this, the products in which our couplers are used are improved because they have a lower minimum density and because our couplers can be coated in thinner emulsion layers. Thinner emulsion layers are often desirably employed for giving images with improved definition and resolution.

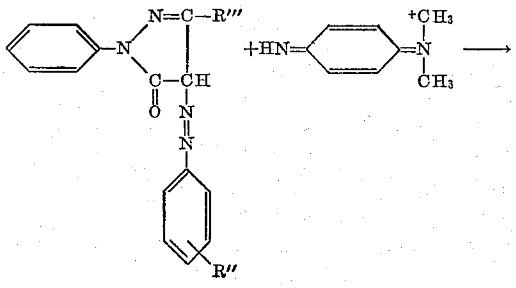
The preferred embodiments of this invention have the formula:

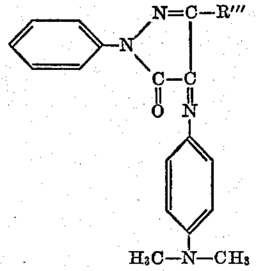


wherein R is an aryl group such as a phenyl radical or a phenyl radical substituted at the 2,4, and 6 carbons with halogen atoms, such as a 2,4,6-trichlorophenyl, a 2,4,6-tribromophenyl, a 2,4,6-triiodophenyl or a 2,4,6-trifluorophenyl group; R′ is a hydrogen atom or an alkyl group having from 1–8 carbon atoms but preferably from 1–4 carbon atoms; X, Y and Z are hydrogen atoms and alkyl radicals usually having from 1–20 carbon atoms but preferably 1–15 with at least one of the substituents X, Y and Z being an alkyl radical; R″ is a hydrogen atom, an alkyl or an alkoxy radical usually having from 1–10 carbon atoms but preferably from 1–6 carbon atoms.

In addition to the preferred embodiments defined above, this invention also includes compounds of the above formula wherein R is a phenyl group substituted at the 2, 4, and 6 carbons with alkyl or alkoxy radicals usually having from 1–6 carbon atoms, aryl groups, aryloxy groups, cyano groups, carbalkoxy groups, or nitro groups; and where R″ is an acylamido group, a carbalkoxy group, a dialkylamino group, an arylether group or other electron-donating substituent.

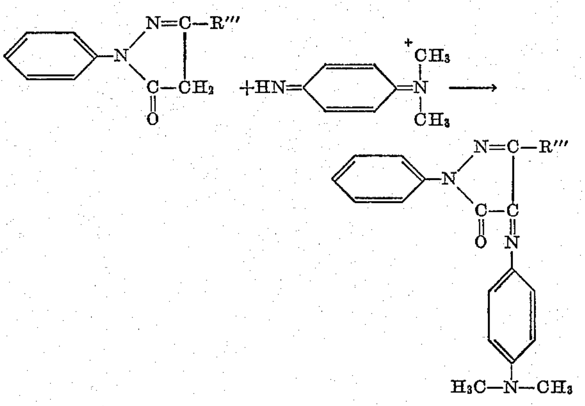
The yellow color of our couplers is destroyed upon reaction with an oxidized primary aromatic amino developing agent and a magenta-colored dye is formed. Although the exact mechanism of this reaction is not completely understood, it appears as though the reaction may proceed as follows:





wherein R'' represents the groups described by the general formula and R''' represents the groups described as being substituted on the carbon atom in the 3 position of the 5-pyrazolone of the general formula.

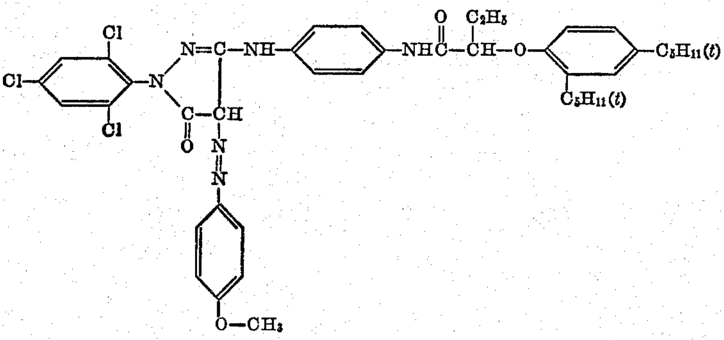
The compounds of this invention can be used in admixture with the uncolored couplers which appear to react as follows:



wherein R''' represent the groups defined above.

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

COUPLER I



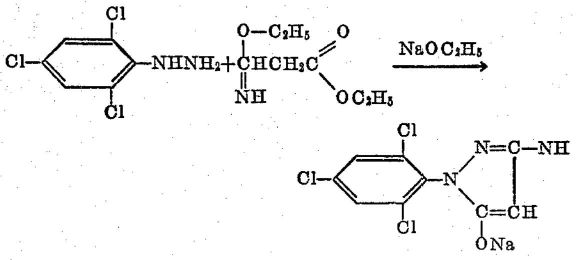
1-(2',4',6'-trichlorophenyl)-3-{4''-[α(2''',4'''-di-tertiaryamylphenoxy)-butyramido]anilino}-4-(4''''methoxyphenyl)azo-5-pyrazolone

[Melting point, 218.5–221° C.]

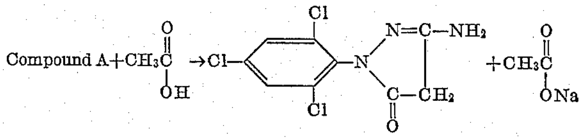
Percent Composition	Calculated	Found
C	62.6	62.9
H	5.9	6.2
N	10.4	11.1
Cl	13.1	11.3

A typical process for preparing Coupler I is as follows:

Step 1.—1-(2,4,6-trichlorophenyl)-3-amino-5-pyrazolone is prepared by the reaction



Compound A

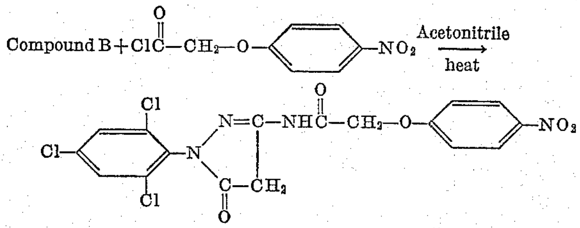


Compound B

Procedure

In a 5-l. flask equipped with a reflux condenser is placed 317 g. (1.5 moles) of 2,4,6-trichlorophenylhydrazine, 249 g. (1.65 moles) of ethyl β-ethoxy-β-iminopropionate, 950 cc. of absolute ethanol, and 5 cc. of glacial acetic acid. The reaction is refluxed 2.5 hours. Meanwhile, 69 g. (3.0 moles) of sodium is reacted with 1100 cc. of absolute ethanol and added cautiously through the condenser after the original reflux. The alkaline solution is refluxed 1 hour, diluted with 1 l. of warm water, acidified with 190 cc. of glacial acetic acid, and cooled to 5°. The solid is filtered, washed with cold water and dried. The yield is 317 g. of pink crystals, melting at 222–224°. Concentration of the liquors to ¼ volume and dilution with 500 cc. of water gives 51 g. of pink solid melting at 218–220°.

Step 2.—1-(2',4',6'-trichlorophenyl)-3-(4''-nitrophenoxy)acetamido-5-pyrazolone is prepared by the reaction

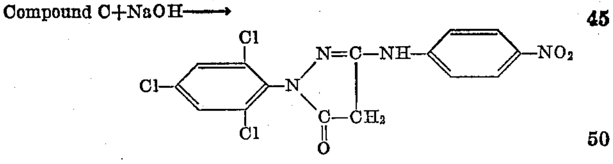


Compound C

Procedure

A 500-ml. 3-necked flask is equipped with a stirrer, dropping funnel and water-cooled condenser. The flask is charged with 55.6 g. (.2 mole) of 1-(2,4,6-trichlorophenyl)-3-amino-5-pyrazolone, and 200 ml. of dry acetonitrile and heated at reflux over a steam bath with mechanical stirring. A solution of 47 g. (.2 mole) of α-(p-nitrophenoxy)acetyl chloride, in 100 ml. of dry acetonitrile is added from the dropping funnel in 30 min. Solution is complete at this point, but soon a precipitate starts to form. After 4 hours the precepitate is filtered from the hot mixture, and washed on the funnel first with 100 ml. of fresh acetonitrile and then with about 2 liters of water. The crude 1-(2′,4′,6′-trichlorophenyl)-3-[α-(4″-nitrophenoxy)acetamido]-5-pyrazolone is crystallized from 90 percent acetic acid (50 ml./g.) to give a purified product melting at 245–6° C.

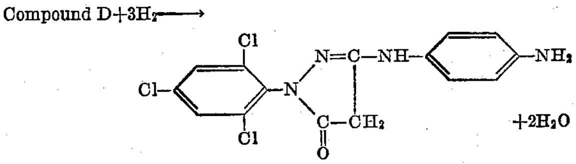
Step 3. — 1-(2′,4′,6′-trichlorophenyl)-3-(4″-nitroanilino)-5-pyrazolone is prepared by the reaction—


Compound D

Procedure

A 12-liter flask equipped with a mechanical stirrer is charged with 840 cc. of water, 3.2 l. of 3-A alcohol and 352 g. (8.8 moles) of freshly opened sodium hydroxide (c.p.). The solution formed on stirring is cooled to room temperature and 2 Kg (4.38 moles) of 1-(2′,4′,6′-trichlorophenyl)-3-[α-(4″-nitrophenoxy)acetamido] - 5 - pyrazolone is added. After being stirred overnight the reaction mixture is filtered and the solid washed on the funnel with 3–A alcohol unit most of the red color is washed out. The combined filtrate and washings are neutralized with glacial acetic acid, the product is collected on a Lapp funnel, washed with acetic acid, and air dried. This crude product is recrystallized by dissolving in 3 l. of warm N,N-dimethylformamide and adding 30 l. of 3–A alcohol at room temperature, yielding 1240 g. with a M.P. of 299–304°.

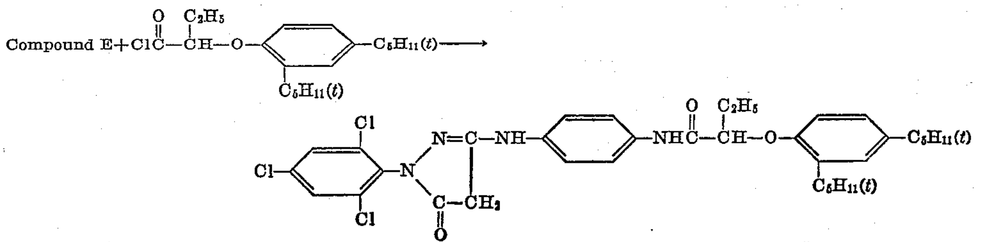
Step 4. — 1 - (2′,4′,6′ - trichlorophenyl) - 3 - (4″ - aminoanilino)-5-pyrazolone is prepared by the reaction—


Compound E

Procedure

A solution of 10 g. (0.025 mole) of 1-(2′,4′,6′-trichlorophenyl)-3-(4″-nitroanilino)-5-pyrazolone in 200 cc. of alcholo is hydrogenated for 3 hours at 40 p.s.i. and 40°. The catalyst is filtered off and the filtrate concentrated to 50 cc. under vacuum. The solid is redissolved on heating then separated on cooling giving 5.1 g. of 1-(2′,4′,6′-trichlorophenyl)-3-(4″-aminoanilino)-5 - pyrazolone with a M.P. of 173–6° C.

Step 5. — From this compound 1-(2′,4′,6′-trichlorophenyl) - 3 - {4″[α-(2‴,4‴-di-tert. amylphenoxy)butyramido]anilino}-5-pyrazolone is made by the reaction—


Compound F

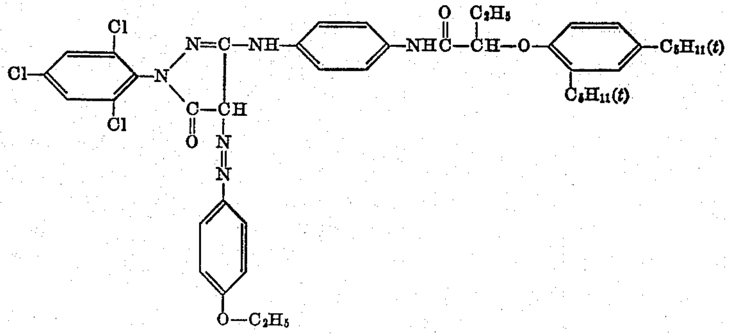
Procedure

A mixture of 5.7 g. (0.154 mole) of 1-(2′,4′,6′-trichlorophenyl)-3 - (4″ - aminoanilino) - 5 - pyrazolone and 5.23 g. (0.154 mole) of α-(2,4-di-tertiaryamylphenoxy) butyryl chloride in 250 cc. of acetonitrile is refluxed for 7½ hours then allowed to stand for 16 hours followed by 2 hours additional refluxing. The reaction mixture is evaporated to dryness in vacuo. The residue is dissolved in 25 cc. of acetone and 200 cc. of "hexane" (from petroleum) is added. The mixture is digested in a steam bath until crystallization occurs. On cooling the crude product separates. Alternating recrystallization from acetone-hexane and from acetonitrile gives 6.0 g. of tiny white crystals melting at 188.5–189°.

Step 6.—Coupler I is made by the reaction—

To a solution of 1.34 g. (0.002 mole) of 1-(2′,4′,6′-trichlorophenyl) - 3 - {4″ - [α(2‴,4‴ - di - tertiaryamylphenoxy)-butyramido]anilino}-5-pyrazolone in 27 cc. of pyridine is added during ½ hour at 0–5° to the theoretical amount of diazotized 4-methoxyaniline. The mixture is stirred for 3 hours then drowned in ice and water to give 1.6 g. of crude product. This solid is crystallized twice from acetonitrile giving 0.6 g. of 1-(2′,4′,6′-trichlorophenyl) - 3 - {4″ - [α(2‴,4‴ - di - tertiaryamylphenoxy)butyramido]anilino}-4-(4 - methoxyphenyl)azo 5-pyrazolone, with a M.P. of 218.5–221° C.

COUPLER II

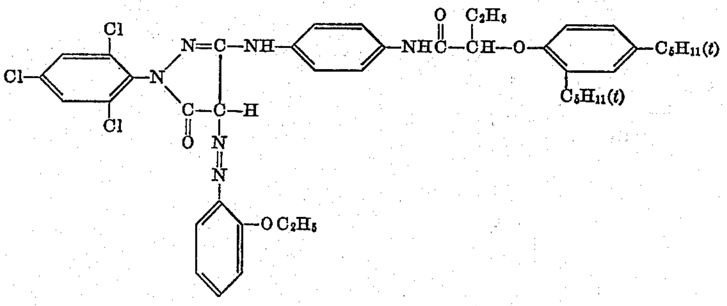


1 - (2',4',6' - trichlorophenyl) - 3 - {4'' - [α - 2''',4''' - di - tertiaryamylphenoxy)butyramido]anilino} - 4 - (4'''' - ethoxyphenyl)azo-5-pyrazolone

[Melting point, 140.-144.° C.]

Percent Composition	Calculated	Found
C	62.9	62.9
H	6.0	6.3
N	10.2	10.7
Cl	13.0	13.4

COUPLER III

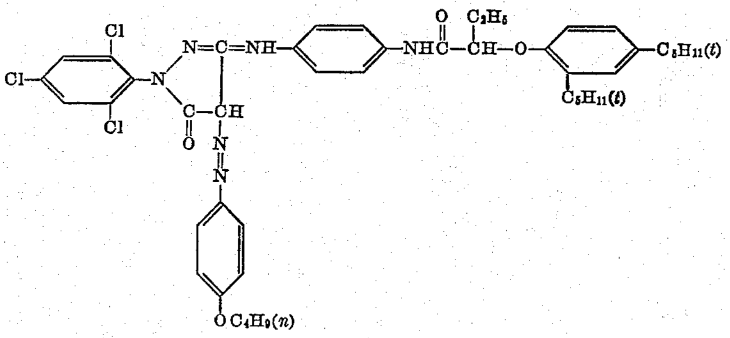


1 - 2',4',6' - trichlorophenyl) - 3 - {4''[α - (2''',4''' - di - tertiaryamylphenoxy)butyramido]anilino} - 4 - (2'''' - ethoxyphenyl)azo-5-pyrazolone

[Melting point, 209.-210.° C.]

Percent Composition	Calculated	Found
C	62.9	62.4
H	6.0	6.0
N	10.2	10.3
Cl	13.0	12.9

COUPLER IV

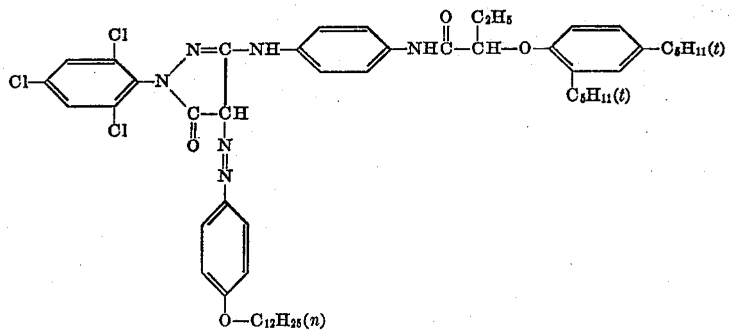


1 - (2'4',6' - trichlorophenyl) - 3 - {4'' - [α(2''',4''' - di - tertiaryamylphenoxy) - butyramido]anilino} - 4 - (4'''' - butoxyphenyl)azo-5-pyrazolone

[Melting point, 142.-145.° C.]

Percent Composition	Calculated	Found
C	63.7	63.4
H	6.3	6.2
N	9.9	10.0
Cl	12.6	13.1

COUPLER V



1 - (2',4',6' - trichlorophenyl) - 3 - {4'' - [α(2''',4''' - di - tertiaryamylphenoxy)butyramido]anilino} - 4 - (4'''' - dodecoxyphenyl)azo-5-pyrazolone

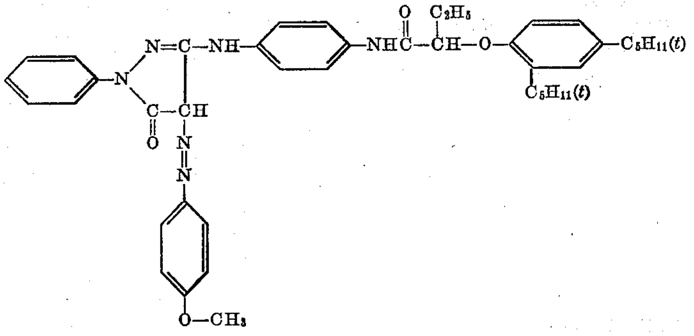
[Melting point, 98.-102.° C.]

Percent Composition	Calculated	Found
C	66.3	66.7
H	7.3	7.3
N	8.8	9.3
Cl	11.1	11.0

Couplers II, III, IV and V are prepared according to the procedure described for Coupler I excepting that Compound F is reacted in Step 6 with the appropriate diazonium chloride compound as shown in the following table:

Coupler	Diazonium Chloride Used in Step 6 of Synthesis
II	4-ethoxy benzene diazonium chloride.
III	2-ethoxy benzene diazonium chloride.
IV	4-butoxy benzene diazonium chloride.
V	4-dodecoxy benzene diazonium chloride.

COUPLER VI



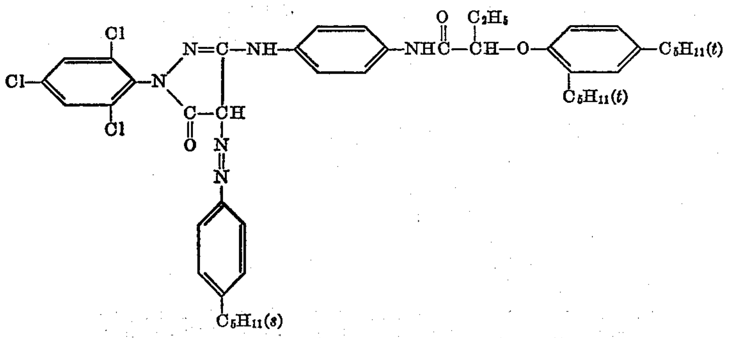
1-phenyl-3-{4''[α(2''',4'''-di-tertiaryamylphenoxy)butyramido]anilino}-4-(4''''methoxyphenyl)azo-5-pyrazolone

[Melting point, 166.-168.) C.]

Percent Composition	Calculated	Found
C	71.7	71.4
H	7.1	7.0
N	12.0	12.2
O	9.1	9.6

Coupler VI is prepared by the procedure described for Coupler I except that in Step 1 phenyl hydrazine is used in place of the 2,4,6-trichlorophenylhydrazine used for the Coupler I synthesis.

COUPLER VII



1 - (2',4',6' - trichlorophenyl) - 3 - {4'' - [α(2''',4''' - di - tertiaryarylamylphenoxy)butyramido]anilino} - 4 - (4'''' - secondary amylphenyl)azo - 5 - pyrazolone

[Melting point, 144.-148.° C.]

Percent Composition	Calculated	Found
C	65.5	65.3
H	6.6	6.5
N	10.0	10.3
Cl	12.6	12.8

Coupler VII is prepared by the procedure described for Coupler I excepting that Compound F is reacted in Step 6 with 4-secondary amyl benzene diazonium chloride.

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. 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 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 our yellow-colored magenta-forming Coupler I and 0.25 gram of the uncolored magenta-forming coupler 1(2′,4′,6′-trichlorophenyl)-3[3″-(2‴,4‴-diamylphenoxyacetamido) benzamido]-5-pyrazolone were dissolved in 1 gram of tri-o-cresyl phosphate with stirring at 110° C. This solution was intimately mixed with and dispersed in a solution containing 22 ml. of 10% gelatin and 2 ml. of .5% Alkanol B. 2 ml. of 7.5% saponin and 15 ml. of water were added to this dispersion. 25 ml. of this dispersion was added to 5 ml. of a medium speed silver bromoiodide emulsion and this was coated on a cellulose acetate support and dried.

The coating was given an image exposure and developed in an alkaline developer solution containing 2-amino-5-(N-ethyl-N-β-methane sulfonamidoethyl)toluene sulfate, to form a negative silver and magenta dye image and a yellow-positive dye image. The silver image and the residual silver halide were removed by treating film in a ferri cyanide bleach followed by hypo fix. This left a negative image in magenta dye having maximum absorption at a wavelength of 534 mμ, and a positive image in residual yellow-colored coupler having a maximum absorption at 430 mμ.

EXAMPLE II

Similar results were obtained by using a dispersion made by dissolving 0.25 gram of our yellow-colored magenta-forming Coupler I and 0.25 gram of the uncolored magenta-forming coupler 1(2′,4′,6′-trichlorophenyl) - 3 - [3″-(2‴,4‴-diamylphenoxyacetamido)-benzamido]-5-pyrazolone 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 the emulsion as in Example I, and coated in the same manner. The ethyl acetate evaporated from the coating on drying. The same exposure and processing conditions yielded a negative magenta dye image having maximum absorption of at least 540 mμ and a positive yellow image with maximum at 430 mμ.

The couplers of our invention are used in photographic emulsions of the developing out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944; Sheppard and Punnett U.S. Patent 1,623,499; and Sheppard and Brigham U.S. Patent 2,410,689.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller, Collins, and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925), or bis(β-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301; 1,846,302; and 1,942,854; White U.S. Patent 1,990,507; Brooker and White U.S. Patents 2,112,140; 2,165,338; 2,493,747; and 2,739,964; Brooker and Keyes U.S. Patent 2,493,748; Sprague U.S. Patents 2,503,776 and 2,519,001; Heseltine and Brooker U.S. Patent 2,666,761; Hesseltine U.S. Patent 2,734,900; VanLare U.S. Patent 2,739,149; and Kodak Limited British 450,958.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers, and Murray U.S. Patent 2,728,663; Carroll and Murray U.S. Patent 2,728,664, and Leubner and Murray U.S. Patent 2,728,665; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606; Heimbach U.S. Patents 2,444,607 and 2,450,397; Heimbach and Clark U.S. Patent 2,444,609; Allen and Reynolds U.S. Patents 2,713,541 and 2,743,181; Carroll and Beach U.S. Patent 2,716,062; Allen and Beilfuss U.S. Patent 2,735,769; Reynolds and Sagai U.S. Patent 2,756,147; Allen and Sagura U.S. Patent 2,772,164, and those disclosed by Birr in the Z. wiss. Phot. 47, 2(1952); the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038; and the zinc and cadmium salts of Jones U.S. Patent 2,839,405.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623; Carroll and Allen U.S. Patent 2,288,226; and Carroll and Spence U.S. Patent 2,334,864; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in U.S. application Serial No. 588,951 of Milton and Murray; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in U.S. application Serial No. 662,564 of Milton; bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. Patent 2,940,854 or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Long U.S. Patent 2,852,386. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in U.S. Patent 2,080,019 of White; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2)-7-octene - 2,3,5,6 - tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-

disulfonyl chloride as described in U.S. Patents 2,725,294 and 2,725,295 of Allen and Carroll; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in U.S. Patent 2,725,305 of Allen and Byers; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)-ethane as described in U.S. Patent 2,726,162 of Allen and Laakso; 1,3-dihydroxymethylbenzimidazole-2-one as described in U.S. Patent 2,732,316 of July, Knott and Pollak; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms such as β-methyl glutaraldehyde bis-sodium bisulfite as described in U.S. application Serial No. 556,031 of Allen and Burness; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in U.S. application Serial No. 599,891 of Allen and Webster; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013.

The emulsions may have been supplied with a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in U.S. Patent 2,831,766 of Knox and Davis; a salt of a sulfated and alkylated polyethylene glycol ether as described in U.S. Patent 2,719,087 of Knox and Davis; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in U.S. Patent 2,739,891 of Knox, Twardokus, and Davis; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg, and Wilson U.S. Patent 2,843,487; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in U.S. Patent 2,823,123 of Knox and Fowler; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert.octylphenoxypentaethoxy) glutamate as described in U.S. application Serial No. 600,679 of Knox and Wilson; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in U.S. application Serial No. 691,125 of Knox and Stenberg.

The couplers which we have described may be used in various kinds of photographic emulsions. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The couplers can be used in emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,696,794 or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in U.S. Patent 2,286,215 of Lowe; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, a water-soluble ethanolamine cellulose acetate as described in U.S. Patent 2,322,085 of Yutzy; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in U.S. Patent 2,541,474 of Lowe, Minsk and Kenyon; zein as described in U.S. Patent 2,563,791 of Lowe; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in U.S. Patent 2,768,154 of Unruh and Smith, or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in U.S. Patent 2,808,331 of Unruh, Smith, and Priest; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth, Dann, and Gates U.S. Patent 2,852,382.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation.

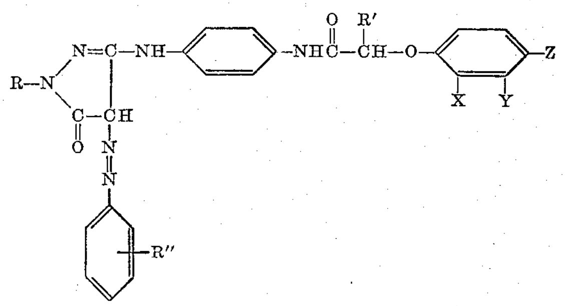
Photographic emulsions containing our couplers may be coated on transparent supports such as glass, cellulose esters, or on a non-transparent reflecting material such as paper or opaque cellulose ester.

Our yellow-colored magenta-forming 3-anilino-4-arylazo-5-pyrazolone 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. They are characterized by being completely reactive with oxidized primary aromatic amino developing agents when they are used in emulsion dispersions having a coupler to coupler incorporating solvent ratio of 1:¼ and give complete compensation for unwanted blue absorption of the magenta dye when incorporated in the proper amount. This valuable characteristic is very unexpected since the corresponding 3-benzamido-4-arylazo-5-pyrazolone couplers which are very similar chemically to our couplers are completely unreactive at the desired coupler-to-coupler incorporating solvent ratio of 1:¼ and give no color correction. Furthermore, our couplers are characterized by having an extinction coefficient of 2.8×10^4 in butyl acetate which is surprisingly higher than the extinction coefficient of 1.5×10^4 in butyl acetate for the corresponding 3-benzamido-4-arylazo-5-pyrazolone couplers referred to above. These valuable characteristics of our couplers make it possible to get complete color correction in emulsions containing them with smaller amounts of coupler than is possible with couplers used before. Our couplers can be coated in thinner layers which makes it possible to produce images with lower minimum densities and thus produce pictures with whiter highlights. Thinner emulsion layers are often desirably employed for producing images with improved definition and resolution.

This 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 spiirt and scope of the invention as described hereinabove and as defined in the appended claims.

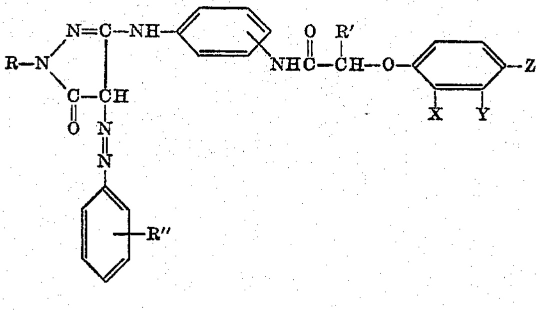
We claim:

1. A photographic silver halide emulsion containing a yellow-colored magenta-forming coupler compound selected from those having the formula:

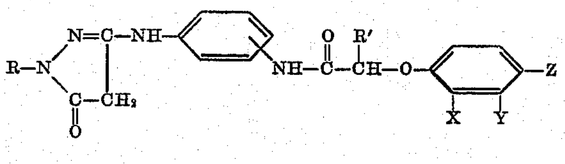


wherein R is a member selected from the group consisting of a phenyl radical and halogen substituted phenyl radicals; R′ is a member selected from the group consisting of hydrogen atoms and alkyl radicals having 1 to 4 carbon atoms; X, Y, and Z are selected from the group consisting of hydrogen atoms and alkyl radicals having 1 to 20 carbon atoms and where at least one of the substituents X, Y, and Z is said alkyl radical; and R″ is selected from the group consisting of alkyl radicals having 1 to 10 carbon atoms and alkoxy radicals having 1 to 10 carbon atoms, and an uncolored magenta-forming pyrazolone coupler which forms a dye of the same hue as formed by the yellow-colored magenta-forming coupler upon coupling with an oxidized primary aromatic amino developing agent.

2. A photographic silver halide emulsion containing (1) a yellow-colored magenta-forming coupler compound selected from those having the formula:

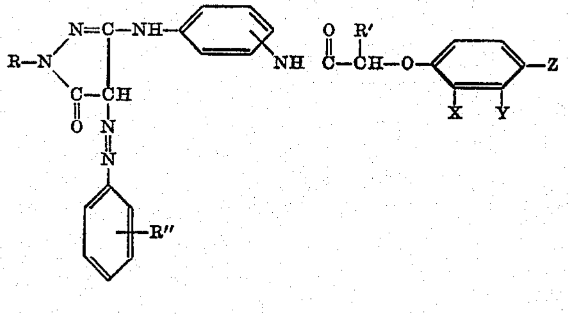


wherein R is a member selected from the group consisting of a phenyl radical and halogen substituted phenyl radicals; R′ is a member selected from the group consisting of hydrogen atoms and alkyl radicals having 1 to 4 carbon atoms; X, Y, and Z are selected from the group consisting of hydrogen atoms and alkyl radicals having 1 to 20 carbon atoms and where at least one of the substituents X, Y, and Z is said alkyl radical; R″ is selected from the group consisting of alkyl radicals having from 1 to 10 carbon atoms and alkoxy radicals having 1 to 10 carbon atoms, and (2) an uncolored magenta-forming coupler which both form the same magenta dye, said uncolored coupler having the formula:



wherein R, R′, X, Y, and Z are as defined above and where at least one of the substituents X, Y, and Z is said alkyl radical.

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



wherein R is a member selected from the group consisting of phenyl radicals and halogen substituted phenyl radicals; R′ is a member selected from the group consisting of hydrogen atoms and alkyl radicals having 1 to 4 carbon atoms; X, Y and Z are selected from the group consisting of hydrogen atoms and alkyl radicals having 1 to 20 carbon atoms and where at least one of the substituents X, Y, and Z is said alkyl radical; R″ is selected from the group consisting of alkyl radicals having from 1 to 10 carbon atoms and alkoxy radicals having from 1 to 10 carbon atoms.

4. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (4⁗-methoxyphenyl)azo-5-pyrazolone.

5. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 (2⁗-ethoxyphenyl)azo-5-pyrazolone.

6. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (4⁗-dodecoxyphenyl)azo-5-pyrazolone.

7. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-phenyl - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (4⁗-methoxyphenyl(azo-5-pyrazolone.

8. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryarylamylphenoxy)-butyramido]anilino} - 4 - (4⁗-secondaryamylphenyl)azo-5-pyrazolone.

9. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (4⁗-methoxyphenyl)azo-5-pyrazolone and the uncolored magenta-forming coupler compound 1-(2′,4′,6′-trichlorophenyl)-3-{4″ - [α-(2‴,4‴ - di-tertiaryamylphenoxy)butyramido]-anilino}-5-pyrazolone.

10. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (2⁗-ethoxyphenyl)azo-5-pyrazolone, and the uncolored magenta-forming coupler compound 1-(2′,4′,6′-trichlorophenyl)-3-{4″ - [α-(2‴,4‴-di-tertiaryamylphenoxy)butyramido]-anilino}-5-pyrazolone.

11. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (4⁗-dodecoxyphenyl)azo-5-pyrazolone and the uncolored magenta-forming coupler compound 1-(2′,4′,6′-trichlorophenyl)-3-{4″-[α-(2‴,4‴ - di - tertiaryamylphenoxy)butyramido]anilino}-5-pyrazolone.

12. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-phenyl - 3 - {4″-[α-(2‴,4‴-di-tertiaryamylphenoxy)-butyramido]anilino} - 4 - (4⁗-methoxyphenyl)azo-5-pyrazolone and the uncolored magenta-forming coupler compound 1-phenyl-3-{4″-[α-(2‴,4‴-di-tertiaryarylamylphenoxy)butyramido]anilino}-5-pyrazolone.

13. A photographic silver halide emulsion containing the yellow-colored magenta-forming coupler compound 1-(2′,4′,6′,trichlorophenyl) - 3 - {4″-[α-(2‴,4‴-di-tertiaryarylamylphenoxy)butyramido]anilino} - 4 - (4⁗-secondaryamylphenyl)azo-5-pyrazolone, and the uncolored magenta-forming coupler compound 1-(2′,4′,6′-trichlorophenyl) - 3 - {4″ - [α-(2‴,4‴ - di-tertiaryamylphenoxy)-butyramido]anilino}-5-pyrazolone.

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