United States Patent Office

3,006,759

Patented Oct. 31, 1961

3,006,759

TWO-EQUIVALENT MAGENTA-FORMING COUPLERS FOR COLOR PHOTOGRAPHY

Anthony Loria, Warren A. Reckhow, and Ilmari F. Salminen, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Aug. 3, 1959, Ser. No. 831,006

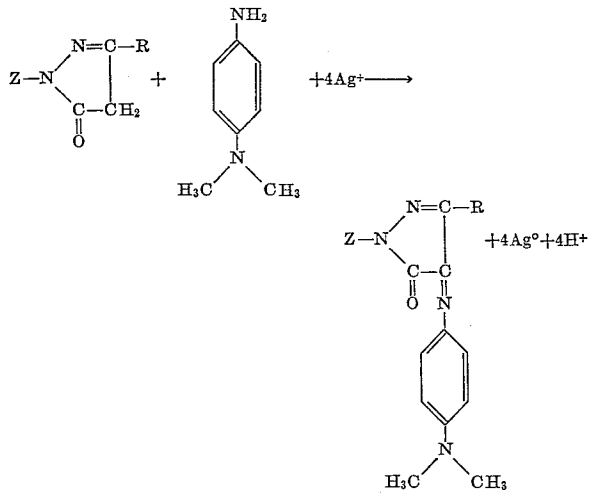
14 Claims. (Cl. 96—55)

This invention relates to photography and particularly to compounds which form dyes on coupling with the oxidized developing agent to produce magenta colored images.

The formation of colored photographic images by the coupling of oxidized aromatic amino developing agents with color forming or coupling compounds is well known. In these processes the subtractive process of color formation is ordinarily used and the image dyes are intended to be cyan, magenta, and yellow, the colors that are complementary to the primary colors. The couplers which produce the cyan dyes are usually phenols or naphthols. Those producing the magenta dyes are ordinarily pyrazolones, and those producing the yellow dyes are ordinarily compounds containing a methylene group having 2-carbonyl groups attached to it. The dyes produced by coupling are azomethines, indamines, or indophenols depending upon the composition of the coupler and of the developer.

The use of various 5-pyrazolone (i.e. pyrazolin-5-one) derivatives for the production of magenta images in color photography is old. Although the exact mechanism of this magenta dye forming reaction is not completely understood, it is thought that the overall reaction can be illustrated as follows:

EQUATION I



This equation summarizes a series of intermediate reaction steps by which the silver ions from four exposed silver halide molecules are reduced to metallic silver, while the developing agent, p-dimethylaminoaniline, undergoes a series of oxidation-reduction reactions which in effect result in the ionization of 4 hydrogen atoms, two of these being on the primary amine group of the developer and two on the 4 carbon of the 5-pyrazolone ring, and the subsequent coupling of the activated coupler and oxidized developer molecule to form one molecule of dye.

These conventional magenta-forming couplers are called 4-equivalent couplers since four molecules of exposed silver halide must be developed in order that one molecule of the coupler can react with a molecule of oxidized developer to form a molecule of magenta dye.

It is, therefore, an object of the present invention to provide a novel class of 2-equivalent couplers for forming magenta dye images in color photography which require the development of only two exposed silver halide molecules to produce one molecule of magenta dye.

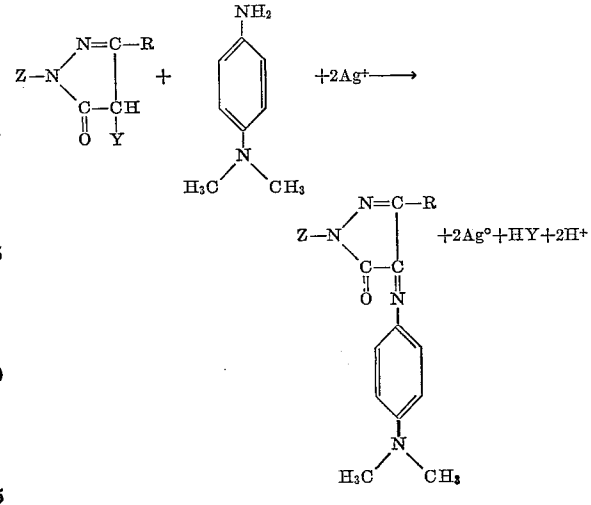
A further object of the invention is to provide a novel class of magenta-forming couplers which are not only 2-equivalent but which are characterized by having all of the desirable features of prior art magenta-forming couplers.

A still further object of the invention is to provide a novel class of magenta-forming couplers which are not only 2-equivalent couplers, but are couplers which upon coupling with oxidized developing agents to form the magenta dye, release development inhibiting materials.

Other objects will become apparent from the following description.

These and other objects are accomplished by means of this invention as described hereinafter. We have discovered that couplers of the 4-chloro-, 4-bromo-, 4-iodo-5-pyrazolone type are valuable magenta-forming couplers. Our couplers are characterized by being 2-equivalent couplers in contrast to the conventional couplers which are 4-equivalent. The couplers of our invention require one-half the amount of exposed silver halide heretofore required to produce a given amount of dye. Although the exact mechanism of this reaction is not completely understood, it appears as though a series of intermediate reactions may be summarized in the following equation:

EQUATION II



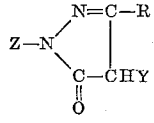
where Y is a halogen atom such as iodine, bromine, or chlorine. From Equation II it can be seen that only two silver ions must be reduced to silver in order that one molecule of magenta dye be formed from one molecule of a 2-equivalent coupler.

2-equivalent couplers have several important and distinctive advantages over the conventional or 4-equivalent couplers. For example, the amount of silver halide conventionally used can be reduced 50%. This not only reduces the cost of producing emulsions containing our magenta-forming couplers but results in improved quality of pictures made using these emulsions. The reduced silver halide requirements make possible thinner emulsion layers. It is known that improved resolving power and image definition result from reducing the thickness of emulsion layers. Reductions of emulsion thickness have

the further advantage of decreasing the optical opacity of the emulsion layer which allows more light to penetrate into emulsion layers underneath the emulsion layer containing our coupler.

Certain of the couplers of the invention are further characterized by releasing development inhibiting materials. From Equation No. II it can be seen that each coupler molecule upon reaction with oxidized developer and the formation of a magenta dye molecule, releases the halogen atom attached to the carbon in the 4-position of the pyrazolone ring as a soluble halide. It is known that iodide ions in particular, and bromide ions to a lesser degree inhibit the photographic development reaction. Thus, it is apparent that our couplers which have iodo or bromo substituents in the 4-position of the pyrazolone ring are especially valuable for use in color photography wherever it is desired to have development inhibitors released where color development occurs. It is also apparent that the strength of the inhibiting effect produced may be controlled by using appropriate mixtures of the 4-iodo, 4-bromo and 4-chloro derivatives of our couplers. For example, blends of the 4-iodo- and 4-bromo-5-pyrazolone coupler can be used to produce a development inhibitor effect that would be less than that produced by the 4-iodo- alone and more than that produced by the 4-bromo-coupler alone.

The couplers of our invention have the general formula:

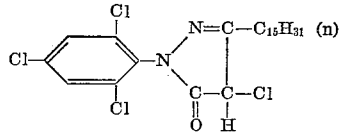


wherein Z represents hydrogen or any of the radicals which are substituted at the 1-position of known 5-pyrazolone couplers including such radicals as alkyl having from 1–10 carbon atoms, a phenyl ring, a phenyl ring substituted with at least one member of the group consisting of alkyl radicals having from 1–10 carbon atoms, alkoxy radicals having from 1–10 carbon atoms, aryl radicals, aryloxy radicals such as phenoxy, methylphenoxy and butylphenoxy radicals, cyano radicals, halo radicals, sulfo radicals, amido radicals, acyl radicals such as acetyl, valeryl, methoxyacetyl, phenoxyacetyl, and benzoyl radicals, isocyclic radicals and heterocyclic radicals such as 2-benzothiazolyl, α-quinolyl, and α-pyridyl; R is an alkyl group having from 1–20 carbon atoms, a substituted or unsubstituted aryl group, or a heterocyclic group; and Y is a halogen atom.

Especially useful couplers of our invention are those in which Z is a di- or trihalogenated (e.g. chlorine or bromine substituted, etc.) aryl group such as 2,4-dihalophenyl, 2,5-dihalophenyl, 2,4,6-trihalophenyl, 2,4,5-trihalophenyl, etc; R is an alkyl group having from 1 to 20 carbon atoms such as methyl, amyl, octyl, undecyl, pentadecyl, heptadecyl, phytyl, etc., an unsubstituted phenyl group, an alkyl substituted phenyl group in which the alkyl group has from 1 to 10 carbon atoms such as methyl, ethyl amyl, octyl, decyl, etc., or a heterocyclic group such as furyl and Y is a chlorine, bromine or iodine atom.

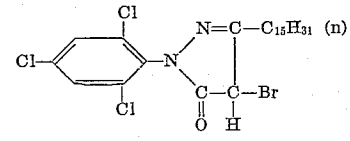
Typical compounds embodying the invention that are used according to the invention include the following which illustrate but are not intended to limit the invention.

Coupler 1



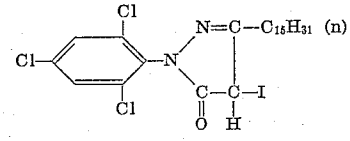
1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-chloro-5-pyrazolone

Coupler 2



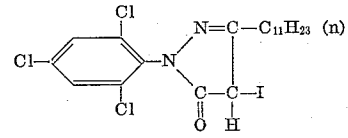
1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-bromo-5-pyrazolone

Coupler 3



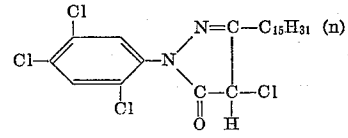
1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-iodo-5-pyrazolone

Coupler 4



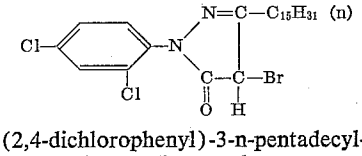
1-(2,4,6-trichlorophenyl)-3-n-undecyl-4-iodo-5-pyrazolone

Coupler 5



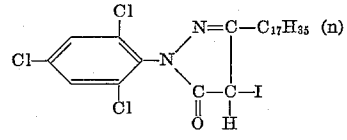
1-(2,4,5-trichlorophenyl)-3-n-pentadecyl-4-chloro-5-pyrazolone

Coupler 6



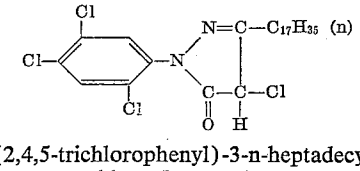
1-(2,4-dichlorophenyl)-3-n-pentadecyl-4-bromo-5-pyrazolone

Coupler 7



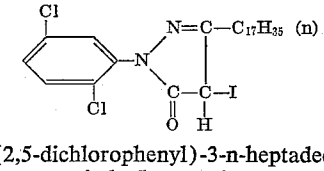
1-(2,4,6-trichlorophenyl)-3-n-heptadecyl-4-iodo-5-pyrazolone

Coupler 8



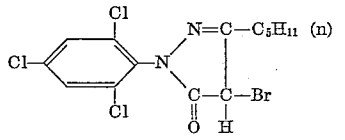
1-(2,4,5-trichlorophenyl)-3-n-heptadecyl-4-chloro-5-pyrazolone

Coupler 9



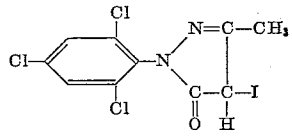
1-(2,5-dichlorophenyl)-3-n-heptadecyl-4-iodo-5-pyrazolone

Coupler 10



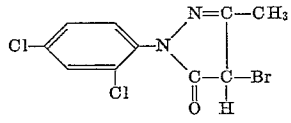
1-(2,4,6-trichlorophenyl)-3-n-amyl-4-bromo-5-pyrazolone

Coupler 11



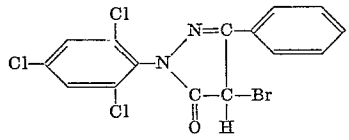
1-(2,4,6-trichlorophenyl)-3-methyl-4-iodo-5-pyrazolone

Coupler 12



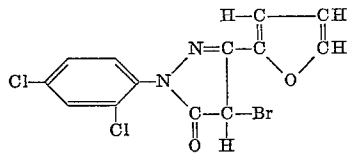
1-(2,4-dichlorophenyl)-3-methyl-4-bromo-5-pyrazolone

Coupler 13



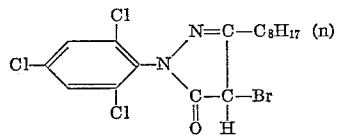
1-(2,4,6-trichlorophenyl)-3-phenyl-4-bromo-5-pyrazolone

Coupler 14



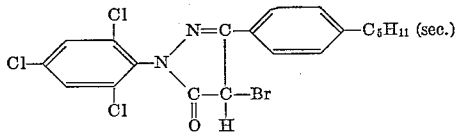
1-(2,4-dichlorophenyl)-3-furyl-4-bromo-5-pyrazolone

Coupler 15



1-(2,4,6-trichlorophenyl)-3-n-octyl-4-bromo-5-pyrazolone

Coupler 16



1-(2,4,6-trichlorophenyl)-3-(p-sec. amylphenyl)-4-bromo-5-pyrazolone

Our magenta-forming coupler compounds were prepared by halogenating the appropriate parent 1-polyhalophenyl-3-substituted-5-pyrazolone coupler.

Descriptions of the preparations used to make the parent couplers from which the couplers 1 through 15 of our invention were made are found in the literature as follows:

Parent of coupler No:	Reference
1 through 9	U.S. Serial 608,210.
10	Mouren, Lazannec, CR 142, 1534; B1 [3] 35,850.
11, 12	F. D. Chattaway and C. R. N. Strouts, J. Chem. Soc. 125, 2423 (1924).
13	Prepared by the method given for coupler 11 using ethyl benzoylacetate in place of ethyl acetoacetate.
14	S. S. Sandelin, Ber., 33, 493 (1900).
15	Asahina, Nakayama, J. Pharm. Japan, 1925, No. 526, S4; C. (1926), 2670.

The parent coupler of our coupler 16 was prepared by the steps described below:

STEP 1

p-Sec.-amylacetophenone.—To a solution of 500 g. (3.37 mole) of sec-amylbenzene in 1 liter of CS_2 stirred in an ice bath was added 275 g. (3.50 moles) of acetyl chloride. Then 500 g. (3.75 moles) of $AlCl_3$ was added as rapidly as frothing would permit (1 hour). Stirring was continued for 3 hours. The reaction mixture was decomposed in ice water, the CS_2 layer was separated and washed free of acid with water and dried. The CS_2 was removed and the residue was distilled in vacuo.

STEP 2

Ethyl-p-sec. amylbenzoylacetate.—To 9 g. (0.25 mole) of sodamide in 500 cc. of ligroin was added 36 g. (0.20 mole) of p-sec-amylacetophenone and 95 g. (0.80 mole) of ethylcarbonate and the reaction mixture was stirred at room temperature for 2 hours. It was then acidified with iced acetic acid and the ligroin layer separated, washed free of acid and dried. The ligroin was distilled off and the residue distilled in vacuo.

STEP 3

1-(2,4,6 - trichlorophenyl)-3-p-sec. amylphenyl-5-pyrazolone.—10 g. (.038 mole) of ethyl-p-sec. amylbenzoylacetate and 8.1 g. (.038 mole) of 2,4,6-trichlorophenylhydrazine (prepared as given in Loria et al. U.S. Patent 2,600,788, June 17, 1952), were mixed and allowed to stand at room temperature for 1 hour (ethyl p-sec-amylbenzoylacetate condensed with itself readily on the steam bath). The mixture clouded ($H_2O\downarrow$). It was then heated on the steam bath for 1 hour, ethanol distilling off. After cooling, the product (viscous oil) was taken up in 15 cc. of ether, a few crystals appeared, and on cooling in an ice bath the mass set solid. The solid was filtered and washed with petroleum ether. This gave 4.3 g. of the parent coupler (used to make our coupler 16), which was crystallized from 40 cc. of ligroin, by cooling in an ice bath.

Our coupler No. 1 was prepared from its parent coupler by the chlorination reaction described by the following process:

One-tenth of a mole, 47.3 g., of 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone was suspended in 500 ml. of acetic acid (HOAc), and while stirring first 8.5 g. of sodium acetate, then 13.9 g. (0.1 mole) of sulfuryl chloride were added through a dropping funnel (30 min.). The temperature was kept at 20°–25° C. and stirred for 30 min. before pouring the mixture into cold water.

The solid which precipitated was filtered and washed free of HOAc with water, then air dried. Crystallizing

three times from methyl alcohol produced a product which had a melting point of 84°–86° C.

	C	H	Cl	N
Calc.	56.8	6.7	27.9	5.5
Found	57.1	7.0	27.7	5.6

The above process is typical of one method used to chlorinate the parent couplers to make our couplers No. 5 and 8.

Our coupler No. 2 was prepared by brominating its parent coupler according to the following process:

One-hundredth of a mole, 4.73 g., of 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone was suspended in 50 ml. of HOAc and while stirring 0.01 mole of Br_2 (1.6 g. or .5 ml.) in 25 ml. of HOAc was added slowly from a dropping funnel. One gram of sodium acetate was added to the mixture before the addition of the bromine was started. The mixture warmed up about 4° during the addition. It was stirred for one hour longer and then added to cold water.

The solid which precipitated was filtered, washed several times with water, until free of HOAc and then air dried. Crystallizing twice from acetonitrile, and once from methyl alcohol using carbon black produced a white product which had a melting point 92°–94° C.

	C	H	Br	Cl	N
Calc.	52.2	6.2	14.5	19.2	5.1
Found	52.0	6.0	14.0	19.0	5.1

In a similar manner our couplers 6, 10, and 12 through 16 were prepared by brominating their respective parent couplers.

Our coupler No. 3 was prepared as follows:

One-hundredth of a mole, 4.73 g. of 1-(2,4,6-trichlorophenyl)-3-pentadecyl-5-pyrazolone was suspended in 50 ml. of HOAc and while stirring first one gram of sodium acetate then 2.55 g. (0.01 mole) of I_2, dissolved in HOAc, were added slowly from a dropping funnel (15 min.). After stirring for one hour the mixture was added to cold water.

The off-white precipitate was filtered, washed with water until free of HOAc and then air dried. Crystallizing twice from acetonitrile, and twice from methyl alcohol using carbon once, produced a white product which had a melting point 90°–92° C.

	C	H	Cl	I	N
Calc.	48.0	5.7	17.7	21.2	4.7
Found	48.0	5.7	17.5	21.2	4.8

Our couplers 4, 7, 9 and 11 were prepared by a similar process to that used to make coupler 3.

Our couplers are incorporated in sensitive silver halide emulsion layers as described in Mannes and Godowsky U.S. Patent 2,304,940 or Jelley and Vittum U.S. Patent 2,322,027.

The following example illustrates the use of coupler No. 1 in an emulsion layer.

Example 1

25 ml. of a dispersion of 1 gram of coupler No. 1 in 3 grams of tri-o-cresyl phosphate and 2.2 grams of gelatin was mixed with 2½ ml. of a conventional medium-speed silver halide emulsion and the mixture was coated on a suitably subbed cellulose acetate support. After being dried, the coating was exposed under an image and developed in a conventional 2-amino-5-diethylamino-toluene HCl developing composition to form a negative silver and magenta dye image. The silver image and the residual silver halide were removed by treatment with a conventional ferricyanide bleach followed by a hypo fixing bath leaving a magenta colored negative image. This image possessed not only very good absorption characteristics having a maximum absorption or λ max. value at 535 mμ but showed improved resolving power and image definition.

Example 2

Exposed emulsion of Example 1 was processed as in Example 1, but with a developer which had N-ethyl-β-methane sulfonamido-ethyl-3-methyl-4-aminoaniline sulfate in place of 2-amino-5-diethylamino toluene hydrochloride. The resulting magenta dye image had very good absorption characteristics with a λ max. value of 537 mμ, and resolving power and image definition improvements which are similar to those obtained in Example 1.

In a manner similar to that illustrated in Example 1 above, molecularly equivalent amounts of other couplers useful in practicing our invention incorporated in the same photographic emulsion followed by identical exposure and processing, produced dye images having the λ max. values shown in Table I.

The dye images formed from these couplers also showed improved resolving power and definition.

TABLE I

Example	Coupler	λ max. value in mμ of magenta dye image formed from coupler and oxidized 2-amino-5-diethylamino toluene HCl
3	2	539
4	3	540
5	4	539
6	5	541
7	6	540
8	7	540
9	8	542
10	9	539
11	10	536
12	11	540
13	12	540
14	13	550
15	14	558
16	15	536
17	16	554

Some of our couplers in which R of the general formula is a lower alkyl group, are diffusible in developer solutions and are therefore useful when incorporated in color developers for developing the magenta image in photographic emulsion layers.

The emulsions used in the photographic element of our invention 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 mecrocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301; 1,846,302; 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; Heseltine U.S. Patent 2,734,900; Van Lare 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 Hemibach 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 Sagal 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, filed March 8, 1955; the 5-thioctic acid of Kodak Belgian Patent 569,317, issued July 31, 1958, and the bis-quaternary salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene bis-benzothiazolium perchlorate, etc.).

The emulsions may also contain speed-increasing compound 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, now U.S. Patent 2,960,404, issued November 15, 1960; 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, now U.S. Patent 2,904,434, issued September 15, 1959; bis-(ethoxy diethylene glycol) succinate as described in U.S. application Serial No. 604,333 of Gray, now U.S. Patent 2,940,854, issued June 14, 1960, 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 Tong 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, now U.S. Patent 2,950,197, issued August 23, 1960; 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-oloeoyl-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 of our invention 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 2,698,794 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 cyanoacetyl 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 of our invention 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 color developing agent can be any of the well-known primary aromatic amino silver halide developing agents such as the phenylenediamines including the alkyl phenylenediamines and the alkyl toluenediamines. These are generally used in the salt form such as the hydrochloride or sulfate. The p-amino phenols and their substitution products may also be used where the amino group is unsubstituted. All of the developing agents have an unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming compounds to form a dye image.

The novel 4-iodo, 4-bromo, and 4-chloro-5-pyrazolone magenta-forming couplers of our invention are characterized by being 2-equivalent couplers. They are valuable for use in making photographic emulsions for color photography because emulsions containing our couplers require only one-half the amount of silver halide required in conventional emulsions in which the prior art magenta-forming couplers are used. The thinner emulsion coatings which this makes possible are very advantageous in color photography since images of improved resolving power and definition can be produced in emulsions containing our coupler. In addition to these advantages the reduced optical opacity of thinner emulsion layers makes it possible for more light to penetrate into emulsions coated under our emulsion which makes it possible to produce photographic products of higher speeds.

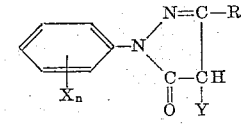
Our couplers are further characterized by possessing the desirable features of prior art magneta couplers, since it is possible to substitute at the 1-carbon of the pyrazolone ring of our couplers, the corresponding substituents from any of the prior art magneta couplers.

The 4-iodo and 4-bromo-5-pyrazolone couplers of our invention are still further characterized by being development inhibitor releasing couplers. Their release of soluble iodides and/or bromides upon color development makes them especially valuable for use in photographic emulsions when it is desired to have development inhibitors released in the emulsion layer where color development occurs. The amount of developer inhibiting effect that will be produced upon development of an emulsion containing our couplers can be conveniently predetermined when the emulsion is made by varying the relative amounts of the 4-iodo-, 4-bromo- and 4-chloro- derivatives of a 5-pyrazolone coupler or couplers in mixtures of these couplers.

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 affected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

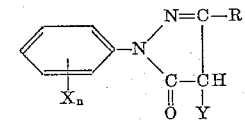
We claim:

1. A method of producing a magenta-colored image in an exposed photographic silver halide emulsion layer by developing said emulsion layer with a primary aromatic amino developing agent in the presence of a novel magenta-forming coupler having the formula:



wherein X is a halogen atom; *n* is an integer of 2 to 3; R is a group selected from the class consisting of alkyl radicals having from 1 to 20 carbon atoms, a phenyl radical, an alkyl substituted phenyl radical in which the alkyl group has from 1 to 10 carbon atoms of the benzene series, and a furyl radical; and Y is a halogen atom.

2. A silver halide emulsion containing a novel magenta-forming coupler having the formula:



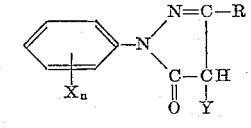
wherein X is a halogen atom; *n* is an integer of 2 to 3; R is a group selected from the class consisting of alkyl radicals having from 1 to 20 carbon atoms, a phenyl radical, an alkyl substituted phenyl radical in which the alkyl group may have from 1 to 10 carbon atoms and a furyl radical; and Y is a halogen atom.

3. A silver halide emulsion of claim 2 in which the R group of the novel magenta-forming coupler is an alkyl radical having from 1 to 20 carbon atoms.

4. A silver halide emulsion of claim 2 in which the R group of the novel magenta-forming coupler is a phenyl radical.

5. A silver halide emulsion of claim 2 in which the R group of the novel magenta-forming coupler is an alkyl substituted phenyl radical in which the alkyl group may have from 1 to 10 carbon atoms.

6. A method of producing a magenta-colored image in an exposed photographic silver halide emulsion layer by developing said emulsion layer with a primary aromatic amino developing agent in the presence of a novel magenta-forming coupler having the formula:



wherein X is a halogen atom; *n* is an integer of 2 to 3; R is a group selected from the class consisting of alkyl radicals having from 1 to 20 carbon atoms, a phenyl radical, an alkyl substituted phenyl radical in which the alkyl group may have from 1 to 10 carbon atoms, and a furyl radical; and Y is a halogen atom.

7. A method of producing a magenta-colored image of claim 6 in which the R group of the novel magenta-forming coupler is an alkyl radical having from 1 to 20 carbon atoms.

8. A method of producing a magenta-colored image of claim 6 in which the R group of the novel magenta-forming coupler is a phenyl radical.

9. A method of producing a magenta-colored image of claim 6 in which the R group is an alkyl substituted phenyl radical in which the alkyl group may have from 1 to 10 carbon atoms.

10. A silver halide emulsion containing the magenta-forming coupler 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-chloro-5-pyrazolone.

11. A silver halide emulsion containing the magenta-forming coupler 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-bromo-5-pyrazolone.

12. A silver halide emulsion containing the magenta-forming coupler 1-(2,4,6-trichlorophenyl)-3-pentadecyl-4-iodo-5-pyrazolone.

13. A silver halide emulsion containing the magenta-

forming coupler 1-(2,4,6-trichlorophenyl)-3-phenyl-4-bromo-5-pyrazolone.

14. A silver halide emulsion containing the magenta-forming coupler 1-(2,4-dichlorophenyl)-3-furyl-4-bromo-5-pyrazolone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,600,788 Loria et al. ---------- June 17, 1952