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3,311,476

TWO-EQUIVALENT COUPLERS FOR COLOR PHOTOGRAPHY

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10 Claims. (Cl. 96-100)

This invention relates to photography and particularly to compounds which form dyes upon coupling with oxidized color developing agent and to photographic elements containing these compounds.

The formation of colored photographic images by the coupling of oxidized aromatic primary 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. Usually phenol or naphthol couplers are used to form the cyan dye image, pyrazolone couplers are used to form the magenta dye image and couplers containing a methylene group having one or two carbonyl groups attached to it are used to form the yellow dye image.

In these color developing processes the color forming coupler may be either in the developer solution or incorporated in the light-sensitive photographic emulsion layer so that during development it is available in the emulsion layer to react with the color developing agent that is oxidized by silver image development. Diffusible type couplers are used in color developer solutions. Fischer-type couplers and hydrophobic couplers are incorporated in photographic emulsion layers. When the dye image formed is to be used in situ, couplers are selected which form nondiffusing dyes. The dye image used for image transfer processes should be diffusible but capable of being mordanted or fixed in the receiving sheet. For this purpose a coupler is selected which will produce this type of dye.

Conventional color-forming couplers are four-equivalent, that is, they require the development of four molecules of exposed silver halide in order to supply one molecule of oxidized color developing agent that is free to couple and form one molecule of dye. Two-equivalent couplers require the development of only two molecules of exposed silver halide to bring about the formation of one molecule of dye. Two-equivalent couplers are very desirable for color photography, since only one-half the usual amount of silver halide is needed and the light-sensitive coatings can thus be made thinner. Certain of the available two-equivalent couplers tend to produce more stain than is desired, and others have not had the desired coupling reactivity. New classes of two-equivalent couplers are needed.

It is, therefore, an object of my invention to provide a new class of colorless two-equivalent cyan-forming and magenta-forming couplers which have a high degree of reactivity.

Another object of my invention is to provide valuable acyloxy substituted two-equivalent couplers for forming cyan dye images and magenta dye images that have good spectral absorption characteristics, and good stability to prolonged exposure to light, heat and high humidity.

Another object is to provide acyloxy substituted two-equivalent couplers which have good coupling reactivity and which include the diffusible type coupler, the Fischer type and the hydrophobic type couplers which are readily incorporated in light-sensitive hydrophilic colloid-silver halide emulsion layers in a wide range of coupler to solvent ratios.

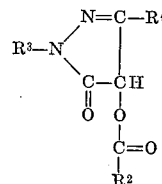
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Still another object is to provide photographic hydrophilic colloid-silver halide emulsion layers containing my acyloxy substituted two-equivalent couplers.

Still further objects will be apparent from the following specification and claims.

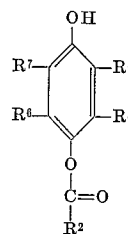
These and other objects are accomplished by the use of my acyloxy substituted two-equivalent couplers. My new class of couplers include the magenta-forming couplers of formula:

(I)

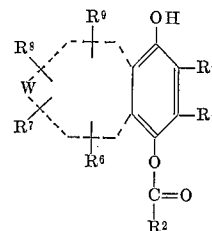


and the cyan-forming couplers of the formulas:

(II)



(III)



wherein R² represents a group selected from the class consisting of an alkyl group having from 1 to 22 carbon atoms, e.g., methyl, 3-pentadecylphenoxyethyl, ethyl, phenylethyl, n-propyl, isopropyl, α-(2,4-di-tert-amylphenoxy)propyl, δ-sulfobutyl, sec-butyl, tert-butyl, docosyl, chloromethyl, trifluoromethyl, 2-hydroxymethyl, β-carboxethyl, 2-(2,4,6-trichlorophenyl)ethyl, 2-aminoethyl, α,α-dimethylbutyl, α-methoxy-α-methylloctyl, α-propyl-α-octyldocosyl, α,α-diethyldecyl, α,α-di-decylundecyl, α,α-di-tert-butyldecyl, α,α-di-sec-butylpentadecyl, etc., a terphenyl group, e.g., 7,7-dimethylnorbornyl, 2-alkyl-7,7-dimethylnorbornyl radicals in which the alkyl group has from 1 to 18 carbon atoms, such as methyl, butyl, octadecyl, etc., for example, 2-methyl-7,7-dimethylnorbornyl, 2-octadecyl-7,7-dimethylnorbornyl, etc., a 2-aryl-7,7-dimethylnorbornyl radical, such as 2-phenyl-7,7-dimethylnorbornyl, 2-tolyl-7,7-dimethylnorbornyl, etc., an aryl group, e.g., phenyl, 3-(2-carboxybenzamido)phenyl, 3-(β-sulfopropionamido)phenyl, α-naphthyl, β-naphthyl, 2,4,6-trichlorophenyl, 4-ethoxyphenyl, 4-bromophenyl, 4-fluorophenyl, 3-[α-(2,4-di-tert-amylphenoxy)butyramido]phenyl, 3-[γ-(2,4-di-tert-amylphenoxy)butyramido]phenyl, etc., a heterocyclic radical, e.g., a benzofuranyl group, a furanyl group, a thiazolyl group, a benzothiazolyl group, a naphthothiazolyl group, an oxazolyl group, a benzoxazolyl group, an imidazolyl group, a benzimidazolyl group, a quinolinyl group, etc.; R³ represents the hydrogen atom, a primary, secondary or tertiary alkyl group having from 1 to 22 carbon atoms, e.g., methyl, propyl, isopropyl, n-butyl, secondary butyl, tertiary butyl, hexyl, dodecyl, docosyl, 2-chlorobutyl, 2-hydroxyethyl, 2-phenylethyl, 2-(2,4,6-trichlorophenyl)ethyl, 2-aminoethyl, etc., an aryl group, e.g., phenyl, 4-methylphenyl, 2,4,6-trichlorophenyl,

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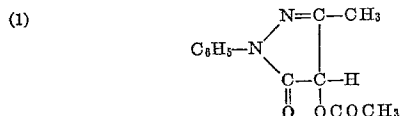
3,5-dibromophenyl, 4-trifluoromethylphenyl, 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, naphthyl, 2-chloronaphthyl, 3-ethylnaphthyl, etc., a heterocyclic group, e.g., a benzofuranyl group, a furanyl group, a thiazolyl group, a benzothiazolyl group, a naphthothiazolyl group, an oxazolyl group, a benzoxazolyl group, a naphthoxazolyl group, a pyridyl group, a quinolinyl group, etc.; R^4 represents the hydrogen atom, a primary, secondary or tertiary alkyl group having from 1 to 22 carbon atoms as defined for R^3 , an aryl group as defined for R^3 , a heterocyclic group as defined for R^3 attached directly to the coupler molecule, an amino group, e.g., amino, methylamino, diethylamino, docosylamino, phenylamino, tolylamino, 4-(3-sulfobenzamido)anilino, 4-cyanophenylamino, 2-trifluoromethylphenylamino, benzothiazolamino, etc., a carbonamido group, e.g., an alkylcarbonamido group, such as ethylcarbonamido, decylcarbonamido, phenylethylcarbonamido, etc., an arylcarbonamido group, such as phenylcarbonamido, 2,4,6-trichlorophenylcarbonamido, 4-methylphenylcarbonamido, 2-ethoxyphenylcarbonamido, 3-[α -(2,4-di-tert-amylphenoxy)acetamido]benzamido, naphthylcarbonamido, etc., a heterocyclic carbonamido group, such as thiazolylcarbonamido, benzothiazolylcarbonamido, naphthothiazolylcarbonamido, oxazolylcarbonamido, benzoxazolylcarbonamido, imidazolylcarbonamido, benzimidazolylcarbonamido, etc., a sulfonamido group, e.g., an alkylsulfonamido group, such as butylsulfonamido, docosylsulfonamido, phenylethylsulfonamido, etc., an arylsulfonamido group, such as phenylsulfonamido, 2,4,6-trichlorophenylsulfonamido, 2-methoxyphenylsulfonamido, 3-carboxyphenylsulfonamido, naphthylsulfonamido, etc., a heterocyclic-sulfonamido group, such as thiazolylsulfonamido, benzothiazolylsulfonamido, imidazolylsulfonamido, benzimidazolylsulfonamido, pyridylsulfonamido, etc., an alkylsulfamyl group, e.g., propylsulfamyl, octylsulfamyl, pentadecylsulfamyl, octadecylsulfamyl, etc., an arylsulfamyl, such as phenylsulfamyl, 2,4,6-trichlorophenylsulfamyl, 2-methoxyphenylsulfamyl, naphthylsulfamyl, etc., a heterocyclic sulfamyl group, such as a thiazolylsulfamyl, a benzothiazolylsulfamyl, an oxazolylsulfamyl, a benzimidazolylsulfamyl, a pyridylsulfamyl group, etc., an alkylcarbaryl, such as ethylcarbaryl, octylcarbaryl, pentadecylcarbaryl, octadecylcarbaryl, etc., an arylcarbaryl, such as phenylcarbaryl, 2,4,6-trichlorophenylcarbaryl, etc., a heterocyclic carbaryl group, such as a thiazolylcarbaryl, a benzothiazolylcarbaryl, an oxazolylcarbaryl, an imidazolylcarbaryl, a benzimidazolylcarbaryl group, etc.; R^5 , R^6 , R^7 , R^8 and R^9 each represent any of the groups defined by R^4 and W represents the nonmetallic atoms necessary to form a fused 5- or 6-membered ring, such as a benzene ring, a cyclohexene ring, a cyclopentene ring, a thiazole ring, an oxazole ring, an imidazole ring, a pyridine ring, a pyrrole ring, a tetrahydropyridine ring, etc.

My two-equivalent couplers are characterized by having an acyloxy group on the coupling position of the coupler which gives them good coupling reactivity and other valuable properties. Some of my nondiffusible couplers have good coupling reactivity when incorporated in emulsion layers with no high-boiling coupler solvents, while the others are dispersed to advantage in high-boiling solvents solutions in a wide range of coupler to solvent ratios.

The following representative magenta-forming and cyan-forming couplers will illustrate but not limit my invention.

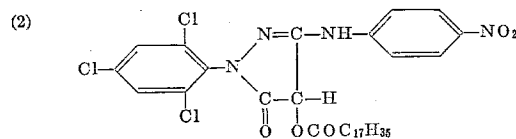
MAGENTA DYE-FORMING COUPLERS

1-phenyl-3-methyl-4-acetoxy-5-pyrazolone

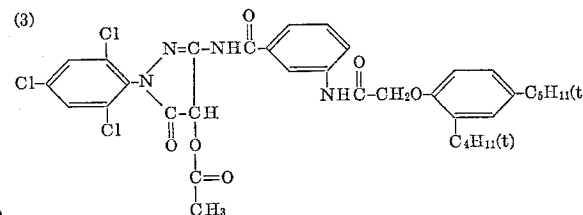


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1-(2,4,6-trichlorophenyl)-3-(4-nitroanilino)-4-stearoyloxy-5-pyrazolone

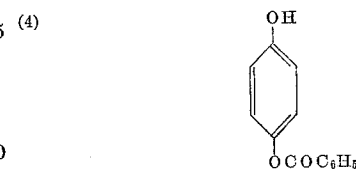


1-(2,4,6-trichlorophenyl)-3-(3-[α -(2,4-di-tert-amylphenoxy)acetamido]benzamido)-4-acetoxy-5-pyrazolone

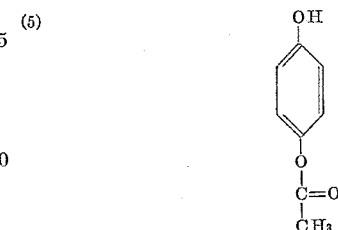


CYAN DYE-FORMING COUPLERS

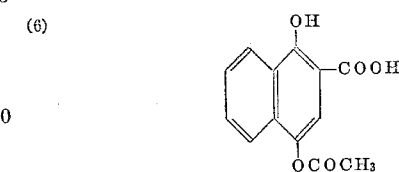
4-benzoyloxyphenol



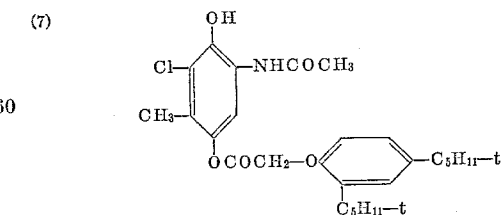
4-acetoxyphenol



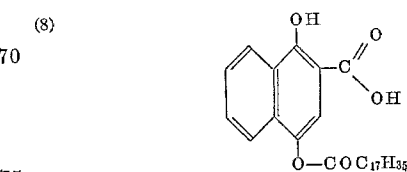
1-hydroxy-4-acetoxy-2-naphthoic acid



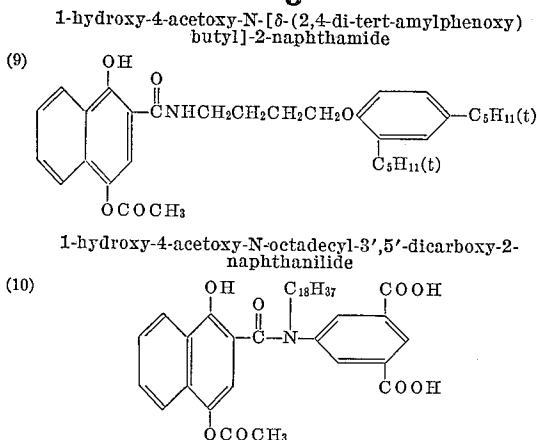
6-acetamido-2-chloro-4-[α -(2,4-tert-amylphenoxy)acetoxy]-3-methylphenol



1-hydroxy-4-stearoyloxy-2-naphthoic acid



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The diffusible couplers of my invention, such as magenta-forming couplers Nos. 1 and 2 and cyan-forming couplers Nos. 4 and 5 are used to advantage in color developer solutions used to color develop light-sensitive elements used for color photography which do not contain the color-forming coupler. Any of the well known primary aromatic amino color-forming silver halide developing agents such as the phenylenediamines, e.g., diethyl-p-phenylenediamine hydrochloride, monomethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-diethylaminotoluene hydrochloride, 2-amino-5(N-ethyl-N-lauryl)toluene, N-ethyl- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, N-ethyl- β -methanesulfonamidoethyl-4-aminoaniline, 4-N-ethyl-N- β -hydroxyethylaminoaniline, etc., the p-aminophenols and their substitution products where the amino group is unsubstituted may be used in the alkaline developer solution with my couplers. Various other materials may be included in the developer solutions depending upon the particular requirements, for example, an alkali metal sulfite, carbonate, bisulfite, bromide, iodide, etc., and the thickening agents used in viscous developer compositions such as are described in copending Whitmore and Mader U.S. Ser. No. 222,105, filed Sept. 7, 1962, now U.S. Patent 3,227,550. The following is a typical developer solution given to illustrate but not limit the invention.

2-amino-5-diethylaminotoluene HCl	2.0
Sodium sulfite (anhydrous)	2.0
Sodium carbonate (anhydrous)	20.0
Potassium bromide	1.0
Coupler	2.0
Water to 1000.0 ml.	

The diffusible couplers of my invention are used to advantage in emulsion layers when incorporated by the methods described by Mannes et al. U.S. Patent 2,304,940, issued Dec. 15, 1940.

Cyan coupler No. 6 illustrates a type of coupler that is used to advantage in color developer solutions (with image-forming couplers) as competing couplers, since the dyes formed are diffusible and are washed out of the emulsion layer during processing. Similarly, other couplers of my invention can be used as competing couplers providing a solubilizing group or groups are present on the R³, R⁴, R⁵, R⁶, R⁷, R⁸ or R⁹ groups.

The other coupler examples used to illustrate my invention are nondiffusing and are used to advantage in photographic emulsion layers. Cyan couplers No. 8 and No. 10 illustrate those that are incorporated as Fischer type couplers. The other nondiffusing couplers are incorporated in emulsion layers by methods such as are described by Mannes et al. U.S. Patent 2,304,939, issued Dec. 15, 1942, Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, etc., in which high-boiling organic solvents are

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used to dissolve the coupler, and by methods described in Vittum et al. U.S. Patent 2,801,170, and Fierke et al. U.S. Patent 2,801,171, both issued July 30, 1957, and Julian U.S. Patent 2,949,360, issued Aug. 16, 1960 in which low-boiling or water-soluble organic solvents are used with or in place of the high-boiling solvent. Not only can emulsion layers containing my couplers be made thinner because they require only one-half the silver halide required by conventional couplers (i.e., four-equivalent couplers) but some of my couplers are sufficiently reactive that they do not require any high-boiling coupler solvent that is usually required by couplers. Thin image-forming layers are very desirable because they cause less light scattering and produce sharper images.

My nondiffusing cyan coupler No. 8 forms diffusible dye images upon color development and is used to advantage either in image transfer elements or in emulsion layers that contain my coupler as a nonimage-forming competing coupler along with an image-forming coupler.

The other nondiffusing couplers used to illustrate my invention form nondiffusing dyes and are used to advantage in any photographic element where incorporated image-forming couplers are desired.

My couplers are used in the color development of photographic hydrophilic colloid-silver halide emulsion layers of the developing-out type either in the color developer solution or in the emulsion layer. The emulsions may contain silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide, etc., as the light-sensitive material.

Hydrophilic colloids used to advantage include gelatin, 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 ethanalamine 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 cyano-acetate 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 U.S. Patent 2,852,382 of Illingsworth, Dann and Gates.

The emulsions used in the photographic element of my 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 chloropalladate, 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-aurosulfo-benzothiazole 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; Heseltine U.S. Patent 2,734,900; Van Lare U.S. Patent 2,739,149; and Kodak Limited British 450,958.

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 above-described emulsions can be coated on a wide variety of photographic emulsion supports. Typical supports include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polyethylene film, polypropylene film, and related films of resinous materials, as well as paper, glass and others.

Usually my emulsions are coated on photographic supports in the form of multilayer color photographic elements wherein at least three differently sensitized emulsion layers are coated over one another on the support. Usually the support is coated in succession with a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer either with or without a Carey Lea filter layer between the blue-sensitive and green-sensitive layers. The three differently color sensitized layers may be arranged in any other order over one another that is desirable; however, the Carey Lea filter layer obviously would not be put over the blue-sensitive layer. Preferably, these light-sensitive layers are arranged on the same side of the support.

Elements made for image transfer processing may use a separate reception sheet which is contacted with the light-sensitive layer during its development or the reception layer may be an integral part of the light-sensitive element. Any of the support materials mentioned previously may be used for a separate reception sheet. The reception layer comprises a hydrophilic colloid layer containing a cationic mordant, e.g., the polymers of amino guanidine derivatives of vinyl methyl ketone such as described in Minsk U.S. Patent 2,882,156, granted Apr. 14, 1959. Other mordants include the 2-vinyl pyridine polymer metho-p-toluene sulfonate and similar compounds described in Sprague et al. U.S. Patent 2,484,430, granted Oct. 11, 1949, and cetyl trimethyl ammonium bromide, etc. Particularly effective mordanting compositions are described in copending applications of Knechel et al. U.S. Ser. No. 211,095, filed July 19, 1962, now U.S. Patent 3,271,148, and Bush U.S. Ser. No. 211,094, filed July 19, 1962, now U.S. Patent 3,271,147. Additional variations of the image transfer elements and processes in which couplers of my invention (such as 8) can be used to advantage, are described in copending application of Whitmore and Mader U.S. Ser. No. 222,103, filed Sept. 7, 1962, now U.S. Patent 3,227,550.

The following Examples 1 and 2 will serve to illustrate the use of my magenta-forming couplers but it is understood that my invention is not to be limited thereby.

EXAMPLE 1

A magenta-forming developer solution having the formula:

	G.
Sodium sulfite -----	2
2-amino-5-diethylaminotoluene HCl -----	2
Sodium carbonate -----	20
Potassium bromide -----	2
Magenta coupler No. 1 -----	2
Water to 1 l.	

(pH adjusted to 11.5 with NaOH)

was used to color develop a magenta image in a strip of light image exposed silver halide emulsion. The silver in the strip was converted to silver halide by treating it with a ferricyanide-bromide bleach and then the silver halide was removed by treating the strip with a hypo fix bath to leave a good magenta dye image.

EXAMPLE 2

Good magenta dye images are obtained by color developing light image exposed single layer gelatino-silver bromide emulsions containing my magenta-forming couplers No. 2 and No. 3 dissolved in coupler solvent, tri-o-cresyl phosphate. The coatings contain 400 mg. gelatin/ft.², 150 mg. Ag/ft.², 60 mg. of coupler/ft.² and 30 mg. of solvent/ft.².

The process and formula are as follows.

Processing solution:	Time in minutes
Color developer -----	11.5
Acid stop bath -----	6.0
Formalin hardener -----	4.0
Water wash -----	4.0
Ferricyanide bleach -----	6.5
Water wash -----	4.0
Hypo fix -----	4.5
Water wash -----	8.0

Color developer

Benzyl alcohol -----	ml.	5.00
Sodium hexametaphosphate -----	g.	2.50
Sodium sulfite -----	g.	1.85
Sodium bromide -----	g.	1.40
Potassium bromide -----	mg.	0.50
Sodium hydroxide -----	g.	13.10
Borax -----	g.	39.60
4-amino-N-ethyl-3-methyl-N- β -methyl-sulfonamidoethylaniline -----	g.	50.00
Water to make, 1000.00 ml.		

Acid stop bath

Acetic acid (glacial) -----	ml.	8.6
Water to make, 1000.0 ml.		

Formaline hardener

Formalin (37% by weight formaldehyde in water) -----	ml.	20.00
Sodium bisulfite -----	g.	5.00
Borax -----	g.	3.82
Sodium hydroxide -----	g.	4.50
Water to make, 1000.00 ml.		

Ferricyanide bleach

Potassium ferricyanide -----	G.	18.0
Sodium bromide -----		12.8
Borax -----		7.3
Boric acid -----		15.0
Water to make, 1000.0 ml.		

Hypo fix

	G.
Sodium sulfite -----	5.90
Sodium thiosulfate -----	320.00
Sodium bisulfite -----	1.47
Water to make, 1000.00 ml.	

Examples 3, 4 and 5 will serve to illustrate the use of my cyan-forming couplers, but are not to limit the invention.

EXAMPLE 3

A cyan-image-forming developer solution having the formula:

	G.
Sodium sulfite -----	2
2-amino-5-diethylaminotoluene HCl -----	2
Sodium carbonate -----	20
Potassium bromide -----	2
Cyan coupler No. 4 -----	2
Water to 1 l.	

(pH adjusted to 11.5 with NaOH)

was used to develop a cyan image in a light image exposed silver halide emulsion layer. The developed layer was treated with a conventional bleach and hypo fix to leave a good cyan dye image.

EXAMPLE 4

Cyan-forming coupler No. 7 dispersed in coupler solvent underwent a coupling reaction with oxidized color developing agent to form a nondiffusing cyan image dye.

EXAMPLE 5

A good cyan dye image is obtained by color developing a light image exposed gelatino-silver bromide emulsion containing my cyan-forming coupler No. 9 dissolved in tri-o-cresylphosphate. The coating contains 400 mg. gelatin/ft.², 150 mg. Ag/ft.², 60 mg. coupler/ft.² and 30 mg. solvent/ft.². The process is described in Example 2.

Similarly, a good cyan dye image is produced by color developing a light image exposed emulsion containing my cyan-forming coupler No. 10. This is a Fischer-type coupler and does not require coupler solvent for incorporating it in the emulsion. The emulsion is like that described previously in this example except that no coupler solvent is used.

A light-image exposed emulsion containing cyan-forming coupler No. 8 instead of No. 10 produces a good diffusible cyan dye image when it is processed by contacting it for 7 minutes at 80° F. with a mordant containing receiving sheet that is presoaked in the following developer solution.

	G.
Sodium carbonate monohydrate -----	22.000
Ascorbic acid -----	0.385
Potassium bromide -----	0.825
Sodium sulfite -----	2.000
4-N-ethyl-n-β-hydroxyethylamino aniline -----	11.000
Water to 1100.000 ml.	

(pH 11.0)

The preparation of my magenta-forming couplers having Formula I is illustrated by the preparation of coupler 1 starting with the four-equivalent parent pyrazolone couplers as follows:

1-phenyl-3-methyl-4-(4-dimethylaminophenylimino)-5-pyrazolone

To a solution of 261 g. of 1-phenyl-3-methyl-5-pyrazolone (U.S. Patent 1,969,479) in 2 l. of ethyl alcohol was added 8 ml. of 5% sodium carbonate solution and a solution of 225 g. of 4-nitrosodimethylaniline in 1.5 l. of boiling alcohol. The mixture was refluxed for 1 hour after which time it was refrigerated for 12 hours. The green solid which separated was collected and recrystallized three times from acetone, yielding 71 g. of product, M.P. 188–190° C.

1-phenyl-3-methyl-4-keto-5-pyrazolone

To a mixture of 145 g. of 1-phenyl-3-methyl-4-(4-dimethylaminophenylimino)-5-pyrazolone in 2 l. of ethyl ether was added a solution of 100 ml. of concentrated sulfuric acid in 1 liter of water. This mixture was stirred at room temperature for 1 hour and filtered. The ether layer was separated, washed with water and dried over anhydrous magnesium sulfate. It was then concentrated in vacuo and the residue was recrystallized from a 50:50 mixture of benzene and ligroin, yielding 55 g. of product, M.P. 120–121° C.

1-phenyl-3-methyl-4-hydrazono-5-pyrazolone
(Intermediate A)

To a solution of 2 g. of 1-phenyl-3-methyl-4-keto-5-pyrazolone in 20 ml. of glacial acetic acid, which had been preheated on steam, was added a solution of 2 ml. of hydrazine hydrate in 5 ml. of glacial acetic acid. The resulting clear reaction mixture was heated on steam for 15 minutes after which time it was poured into 150 ml. of ice water whereupon a yellow solid separated. The solid was collected and recrystallized from ligroin, yielding .5 g. of product, M.P. 103–105° C.

1-phenyl-3-methyl-4-diazonium-5-pyrazolone
(Intermediate B)

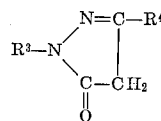
To a mixture of 5 g. of Intermediate A above, 11 g. of yellow mercuric oxide and 5 g. of anhydrous sodium sulfite in 200 ml. of ethyl ether was added 1.5 ml. of a saturated alcoholic potassium hydroxide solution. This mixture was agitated at room temperature for 1 hour, filtered, and the filtrate was concentrated to dryness. The solid residue was recrystallized from ligroin, yielding 2 g. of product, M.P. 97–99° C.

1-phenyl-3-methyl-4-acetoxy-5-pyrazolone

A solution of 5 g. of Intermediate B above and 2 ml. of fluoroboric acid (HBF₄) in 25 ml. of glacial acetic acid was heated on steam for 16 hours. This mixture was then poured into 100 ml. of ice water whereupon a solid separated, was collected, and dried. This solid was recrystallized from aqueous acetonitrile, yielding 1.5 g. of product, M.P. 190–191° C.

Similarly any of the other couplers of Formula I are prepared as coupler 1 starting in each instance with the appropriate four-equivalent parent 5-pyrazolone coupler having the formula:

(IV)



where R³ and R⁴ are as defined previously, then proceeding with the synthesis to form the corresponding 4-diazonium-5-pyrazolone and reacting it with the appropriate organic acid and acylating agent.

Coupler 2, for example, is prepared like coupler 1 by using 1 - (2,4,6-trichlorophenyl)-3-(4-nitroanilino)-5-pyrazolone as the parent coupler and reacting the corresponding 4-diazonium-5-pyrazolone with stearic acid.

Coupler 3 is prepared like coupler 1 by using the parent coupler 1 - (2,4,6-trichlorophenyl) - 3-{3-[α-(2,4-di-tert-amylophenoxy) - acetamido]benzamido}-5-pyrazolone and the acylating agent glacial acetic acid.

The preparation of my cyan-forming couplers of Formulas II and III is illustrated by the following preparation of coupler 7:

Intermediate A: 5-acetamido-4-benzyloxy-3-chloro-2-methylphenol.—In 200 volumes of dry acetone containing 6.5 g. of potassium carbonate was placed 10 g. of 5-

acetamido-3-chloro-2-methylhydroquinone and 8 g. of α -bromotoluene. The mixture was refluxed for 1½ hours, cooled, poured into 500 volumes of an equivolume mixture of ether and 3% aqueous sodium bicarbonate. The ether layer was withdrawn, dried, and then removed under reduced pressure. The resulting solid was recrystallized from acetonitrile, yielding 4.2 g. of product.

Intermediate B: 2-benzyloxy-3-chloro-5-[α -(2,4-di-tert-amylphenoxy)-acetoxy]-4-methylacetanilide.—A solution of 3 g. of Intermediate A above and 7 g. of α -(2,4-di-tert-amylphenoxy)acetic anhydride in 100 ml. of pyridine was held at room temperature for 72 hours, after which time it was heated on steam for ½ hour. The resultant solution was diluted with an equal volume of ether, which was then washed twice with dilute sodium carbonate solution. The ether layer was separated, dried, and concentrated in vacuo. The residual oil was slurried in 150 ml. of water and the solid which formed was filtered and air dried, yielding the product, M.P. 123–126° C.

Coupler 7

A solution of 2 g. of Intermediate B above in 100 ml. of ethyl acetate containing .1 g. of palladium on charcoal was reduced at 40 lb. p.s.i. hydrogen pressure, at room temperature. The solution was filtered, washed twice with dilute sodium carbonate solution, dried, concentrated in vacuo, yielding the product.

Coupler 9 is prepared by the method used for coupler 6 by starting with the compound 1,4-dihydroxy-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide and then acylating it with acetic anhydride.

Couplers 4 (M.P. 162–164° C.), 5 (M.P. 62–63° C.) and 6 (M.P. 194° C.) were prepared by the synthesis described by Wilt and Johnson Ber. 26, 1910; Olcott, J.A.C.S. 59, 392 (1937), and Desai and Sethna J. Ind. Chem. Soc. 28, No. 4, 213–217 (1951), respectively.

Coupler 8 is prepared like coupler 6 by using stearyl chloride in place of acetic anhydride as the acylating agent.

Coupler 10 is prepared by reacting phenyl 1,4-dihydroxy-2-naphthoate (formed by reacting 1,4-dihydroxy-2-naphthoic acid with phenol) with N-(3,5-dicarboxyphenyl)-N-stearylamine to form 1,4-dihydroxy-N-octadecyl-3',5'-dicarboxy-2-naphthanilide which is hydrolyzed, then acetylated with acetic anhydride to produce 1-hydroxy-4-acetoxy-N-octadecyl-3',5'-dicarboxy-2-naphthanilide.

The two-equivalent image-forming couplers of my invention are distinguished from other two-equivalent couplers by having an acyloxy group substituted on the coupling position of the coupler molecule. My nondiffusing couplers are dispersed readily in emulsion layers as a coupler solvent solution having a wide range of coupler to solvent ratios.

My couplers are not only valuable for the reasons cited but because photographic emulsion layers color developed with them require only ½ the amount of silver halide required by four-equivalent couplers. Of particular value are certain of my nondiffusing couplers which have high coupling reactivity when dispersed in photographic emulsion layers without any high-boiling solvent. These couplers are coated to advantage in particularly thin layers that produce very sharp images.

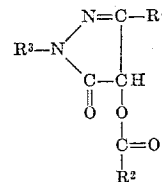
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A light-sensitive photographic element comprising a support and at least one light-sensitive layer comprising a hydrophilic colloid-silver halide emulsion having dispersed therein an uncolored dye image-forming two-

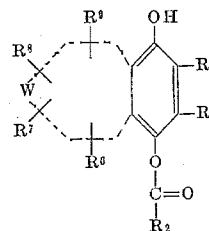
equivalent coupler selected from the couplers represented by the formulas:

(I)



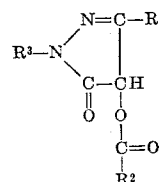
and

(II)



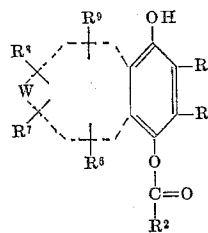
wherein R² represents a group selected from the class consisting of an alkyl group having from 1 to 22 carbon atoms, a phenyl group, and a naphthyl group; R³ represents a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group and a heterocyclic group; R⁴, R⁵, R⁶, R⁷, R⁸, and R⁹ each represents a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an amino group, a carbonamido group, a sulfonamido group, a sulfamyl group and a carbamyl group; and W represents the nonmetallic atoms necessary to form a fused 5- or 6-membered ring, said couplers represented by Formula I forming magenta dye images and said couplers represented by Formula II forming cyan dye images.

2. A light-sensitive photographic element comprising a support and at least one light-sensitive layer comprising a hydrophilic colloid-silver halide emulsion having dispersed therein a magenta-forming two-equivalent coupler selected from those having the formula:



wherein R² represents a group selected from the class consisting of an alkyl group having from 1 to 22 carbon atoms, a phenyl group and a naphthyl group; R³ represents a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group and a heterocyclic group; and R⁴ represents a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an amino group, a carbonamido group, a sulfonamido group, a sulfamyl group, and a carbamyl group.

3. A light-sensitive photographic element comprising a support and at least one light-sensitive layer comprising a hydrophilic colloid-silver halide emulsion having dispersed therein a cyan-forming two-equivalent coupler selected from those having the formula:



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wherein R² represents a group selected from the class consisting of an alkyl group having from 1 to 22 carbon atoms, a phenyl group and a naphthyl group; R⁴, R⁵, R⁶, R⁷, R⁸, and R⁹ each represents a group selected from the class consisting of the hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an amino group, a carbonamido group, a sulfonamido group, a sulfamyl group, and a carbamyl group; and W represents the non-metallic atoms necessary to form a fused 5- or 6-membered ring.

4. A light-sensitive photographic element of claim 1 comprising a support, at least one hydrophilic-colloid-silver halide emulsion layer having dispersed therein a two-equivalent magenta image-forming coupler of Formula I and at least one hydrophilic-colloid-silver halide emulsion layer having dispersed therein a two-equivalent cyan image-forming coupler of Formula II.

5. A light-sensitive photographic element comprising a support, and a light-sensitive hydrophilic-colloid-silver halide emulsion layer having dispersed therein the two-equivalent coupler 1-(2,4,6-trichlorophenyl)-3-(4-nitro-anilino)-4-stearoyloxy-5-pyrazolone.

6. A light-sensitive photographic element comprising a support, and a light-sensitive hydrophilic-colloid-silver halide emulsion layer having dispersed therein the two-equivalent coupler 1-(2,4,6-trichlorophenyl)-3-{3-[α -(2,4-di-tert-amylphenoxy) - acetamido]benzamido}-4-acetoxy-5-pyrazolone.

7. A light-sensitive photographic element comprising a support, and a light-sensitive hydrophilic-colloid-silver halide emulsion layer having dispersed therein the two-equivalent coupler 1-hydroxy-4-stearoyloxy-2-naphthoic acid.

8. A light-sensitive photographic element comprising a support, and a light-sensitive hydrophilic-colloid-silver halide emulsion layer having dispersed therein the two-

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equivalent coupler 1-hydroxy-4-acetoxy-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide.

9. A light-sensitive photographic element comprising a support, and a light-sensitive hydrophilic-colloid-silver halide emulsion layer having dispersed therein the two-equivalent coupler 1-hydroxy-4-acetoxy-N-octadecyl-3',5'-dicarboxy-2-naphthanilide.

10. A light-sensitive photographic element comprising a support, and a light-sensitive hydrophilic-colloid-silver halide emulsion layer having dispersed therein the two-equivalent coupler 1-phenyl-3-methyl-4-acetoxy-5-pyrazolone.

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