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3,408,194

SILVER HALIDE EMULSION LAYERS CONTAINING YELLOW DYE FORMING COUPLERS

Anthony Loria, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Continuation-in-part of application Ser. No. 312,894, Oct. 1, 1963. This application July 6, 1965, Ser. No. 469,887

9 Claims. (Cl. 96—100)

ABSTRACT OF THE DISCLOSURE

Open chain reactive methylene two-equivalent yellow-forming couplers in which one of the hydrogen atoms of the active methylene group is replaced with a cyclooxy group are used to advantage in color developer solutions and in light-sensitive photographic emulsion layers for forming yellow dye images in color photography.

This is a continuation-in-part application of Loria U.S. application Ser. No. 312,894, filed Oct. 1, 1963 now abandoned.

This invention relates to photography and particularly to a new class of two-equivalent dye-forming couplers and their use in color photography.

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 or 2-(alpha-cyanoacetyl)-coumarone couplers are used to form the magenta dye image, and open-chain reactive methylene couplers having two carbonyl groups attached to the active methylene group 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. Diffusable type couplers are used in color developer solutions. Fischer type couplers and nondiffusing couplers are incorporated in photographic emulsion layers. When the dye image formed is to be used in situ, couplers are selected which form non-diffusing dyes. The dye image used for image transfer processes should be diffusable but capable of being mordanted or fixed in a receiving layer. 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 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 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 from coupling in areas of the color photographic element being developed where the silver halide grains had not been exposed, and others do not have the desired coupling reactivity, especially for incorporation in photographic emulsion layers at low coupler solvent ratios. Other characteristics required of couplers, that are not always exhibited by other classes of couplers to the desired degree, are low printout, and low yellowing in emulsion layers containing them. Furthermore, the dyes formed from other classes of couplers do not always have the desired spectral absorption characteristics, light fading and low heat fading properties.

It is therefore an object of my invention to provide a new class of colorless two-equivalent dye-forming couplers which have a high degree of reactivity but which do not produce stains caused by nonimage-forming coupling that is a problem with some of the prior art two-equivalent dye-forming couplers.

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

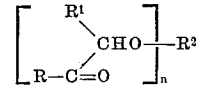
Another object is to provide cyclooxy substituted two-equivalent couplers which have good coupling reactivity and which include the diffusible type coupler, the Fischer type and the nondiffusing type couplers which are readily incorporated in light-sensitive hydrophilic colloid-silver halide emulsion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

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

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

These and other objects are accomplished according to my invention by the preparation and use of my novel class of couplers. The couplers of my invention are open-chain reactive methylene two-equivalent couplers wherein one of the hydrogens of the active methylene group is replaced with a cyclooxy substituent; the cyclooxy group includes, for example, unsubstituted aryloxy, substituted aryloxy, e.g., arylenedioxy, as well as the unsaturated and saturated heterocyclooxy groups such as 4-pyridyloxy and tetrahydropyranyloxy, respectively. My two-equivalent couplers are derived to advantage from any of the known four-equipalent open-chain types, e.g., the alpha-acylacetamides, the 2-(alpha-cyanoacetyl) coumarones and the alpha-acylacetonitriles, etc. The effectiveness of my couplers as two-equivalent couplers is not dependent on the specific composition of the coupler moiety, and it will be understood that this moiety may be varied widely to meet such requirements as spectral absorptivity, reactivity, solubility, and diffusibility, as may be imposed by the photographic system in which the coupler should be used. Typical examples of different classes of couplers which are included in my invention are alpha-acylacetamides, 2-(alpha-cyanoacetyl)coumarones, and alpha-acylacetonitriles, etc.

Included among the couplers of my invention are those represented to advantage by the following formula:

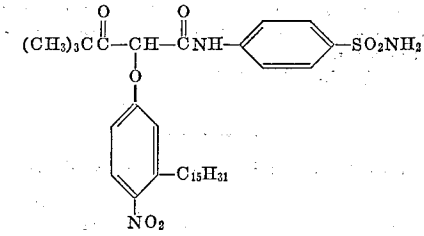


wherein R represents an alkyl radical, either straight or branched chain of from 1 to 30 carbon atoms, a mono- or bicyclic alkyl radical such as cyclohexyl, terpenyl, e.g., a norbonyl radical, etc., the said R group may also represent a substituted alkyl radical containing substituent groups such as halogen, nitro, hydroxyl, carboxyl, amino, substituted amino (N-alkylamino, N,N-dialkylamino, anilino, N-alkylanilino, etc.), a carboxyl ester (e.g. carboalkoxy, carbophenoxy, etc.), sulfo, a sulfo ester (e.g., methoxysulfonyl, butoxysulfonyl, phenoxysulfonyl, etc.), an amido group (e.g., an acetamido, a butyramido, ethylsulfonamido, etc.), a carbamyl group (e.g., carbamyl, an N-alkylcarbamyl group, an N-phenylcarbamyl group, etc.), a sulfamyl group (e.g., sulfamyl, N-alkylsulfamyl, N,N-dialkylsulfamyl, N-phenylsulfamy, etc.), an alkoxy group, an aryl group, an aryloxy group, an alkylsulfonyl group, an arylsulfonyl group, etc., the said R group also represents an aryl group (e.g., phenyl naphthyl, etc.) including substituted aryl groups where the substituents may be any of those that are defined previously for R when substituted alkyl, the said R group also represents a heterocyclic group (e.g., furanyl, benzofuranyl, benzothiazolyl, oxazolyl, imidazolyl, quinolinyl, etc.) each of which heterocyclic groups may be substituted with groups such as previously defined for the substituted alkyl groups; R' represents a carbamyl group (e.g., an unsubstituted carbamyl, an alkylcarbamyl group in which the alkyl group is either straight or branched chain having from 1 to 30 carbon atoms, a mono or bicyclic group such as cyclohexyl, terpenyl, e.g., a norbornyl group, etc., a dialkylcarbamyl group in which a combination of any two of the above mentioned alkyl groups are substituted on the nitrogen atom of the carbamyl group, an arylcarbamyl group in which the aryl group is a group such as phenyl, naphthyl, etc., an aralkylcarbamyl group in which a combination of any two of the above alkyl and aryl groups are substituted on the nitrogen atom of the carbamyl group, e.g., an N-methyl-N-phenylcarbamyl group, an N-butyl-N-tolylcarbamyl group, etc., a heterocyclic carbamyl group in which the heterocyclic group is a group such as a thiazolyl group, a benzothiazolyl group, a naphthothiazolyl group, an oxazolyl group, a pyridinyl group, a quinolinyl group, an alkyl heterocyclic carbamyl group in which a combination of any two of the above alkyl groups and heterocyclic groups, respectively, are substituted on the nitrogen atom of the carbamyl group, e.g., an N-(2-benzothiazolyl)-N-methylcarbamyl group, etc., an N-aryl-N-heterocyclic carbamyl group in which a combination of any two of the above aryl groups and heterocyclic groups, respectively, are substituted on the nitrogen atom of the carbamyl group (e.g., an N-phenyl-N-(2-thiazolyl) carbamyl group, etc.), the said alkyl, aryl, and heterocyclic groups on the carbamyl groups (R') may contain substituent groups such as defined for substituted alkyl in R above, the R' group may also represent the cyano group; *n* is an integer of from 1 to 2; R^2 represent the cyano group such as phenyl, naphthyl, etc., a heterocyclic group (such as a 4-pyridinyl group, a 2-tetrahydropyranyl group, a 2-(1,2,3,4)-tetrahydroquinolinyl group, etc.) when *n* represents the integer 1, and R^2 represents a divalent cyclo group (such as arylene, e.g. 1,3-phenylene, 1,4-phenylene, 1,4-naphthylene, 2,5-pyridyl, etc.), the said cyclo groups may contain substituent groups such as defined for substituted alkyl in R above.

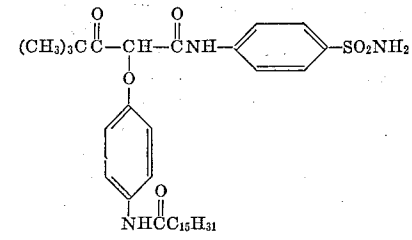
My two-equivalent couplers are characterized by having a cyclooxy group on the coupling position of the coupler which gives them good coupling reactivity and other valuable properties. Non-image-forming but stain-producing reactions characteristic of certain prior art two-equivalent dye-forming couplers are not exhibited by my couplers. Some of my non-diffusible couplers have good coupling reactivity when incorporated in emulsion layers with no high-boiling coupler solvents, while others are dispersed to advantage in high-boiling solvent solutions in a wide range of coupler to solvent ratios.

Included among my novel couplers are the following typical examples which are used to illustrate but not limit my invention.

(1) Alpha-(4-nitro-3-pentadecylphenoxy)-alpha-pivalyl-4-sulfamylacetanilide

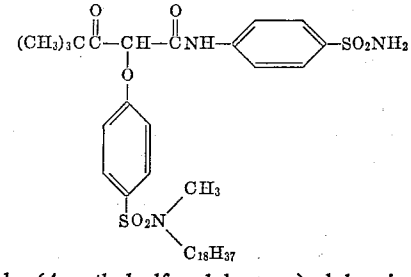


(2) Alpha-(4-palmitamidophenoxy)-alpha-pivalyl-4-sulfamylacetanilide



(3) Alpha-(4-nitro-3-pentadecylphenoxy)-alpha-pivalyl-2-chloro-4-sulfamylacetanilide

(4) Alpha-[4-(N-methyl-N-octadecylsulfamyl)-phenoxy]-alpha-pivalyl-4-sulfamylacetanilide



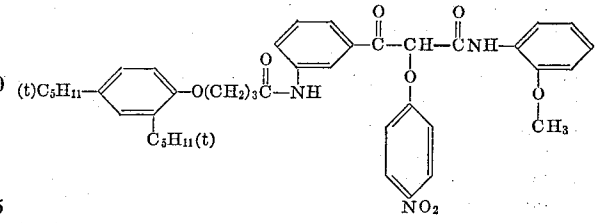
(5) Alpha-(4-methylsulfonylphenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(6) Alpha-pivalyl-alpha-(4-sulfamylphenoxy)-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(7) Alpha-(4-nitrophenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(8) Alpha-benzoyl-alpha(4-nitro-3-pentadecylphenoxy)-2-methoxyacetanilide

(9) Alpha-{3-[γ-(2,4-di-tert-amylphenoxy)butyramido]-benzoyl}-alpha-(4-nitrophenoxy)-2-methoxy-acetanilide



(10) Alpha-(4-acetylphenoxy)-alpha-{3-[γ-(2,4-di-tert-amylphenoxy)-butyramido]benzoyl}-2-methoxyacetanilide

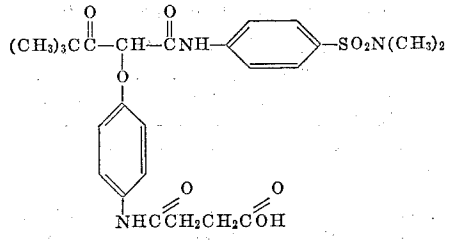
(11) Alpha-{3-[γ-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-alpha-(4-sulfamylphenoxy)-2-methoxy-acetanilide

(12) Alpha-{3-[alpha-(2,4-di-tert-amylphenoxy)-acetamido]benzoyl}-alpha-(4-phenylphenoxy)-2-methoxyacetanilide

(13) Alpha-benzoyl-alpha-[4-(N-methyl-N-octadecylsulfamyl)phenoxy]-2-ethoxyacetanilide

(14) Alpha-(4-methoxybenzoyl)-alpha-(4-methylsulfonylphenoxy)-2-chloro-5-[γ-(2,4-di-tert-amylphenoxy)butyramido]-acetanilide

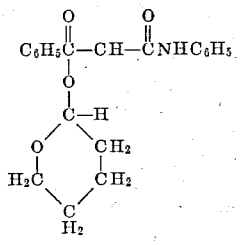
(15) Alpha-[4-(beta-carboxypropionamido)phenoxy]-alpha-pivalyl-4-(N,N-dimethylsulfamyl)-acetanilide



(16) Alpha-(4-nitrophenoxy)-alpha-pivalyl-4-(N,N-dimethylsulfamyl)acetanilide

(17) Alpha-benzoyl-alpha-(4-nitrophenoxy)-2-methoxyacetanilide

(18) Alpha-benzoyl-alpha-(2-tetrahydropyranyloxy) acetanilide



(19) Alpha-(4-carbomethoxyphenoxy)-alpha-benzoyl-2-methoxyacetanilide

(20) Alpha-benzoyl-alpha-(4-sulfamylphenoxy)-2-methoxyacetanilide

(21) Alpha-(4-aminophenoxy)-alpha-benzoyl-2-methoxyacetanilide hydrochloride

(22) Alpha-(4-nitro-3-pentadecylphenoxy)-alpha-pivalyl-4-sulfoacetanilide potassium salt

(23) Alpha-[4-(N-methyl-N-octadecylsulfamyl)-phenoxy]-alpha-pivalyl-4-sulfoacetanilide potassium salt

(24) Alpha-[4-(beta-carboxypropionamido)phenoxy]-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)-acetanilide

(25) Alpha-pivalyl-alpha-(4-sulfophenoxy)-4-(N-methyl-N-octadecylsulfamyl)acetanilide potassium salt

(26) Alpha-(4-carbomethoxyphenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(27) Alpha-(4-carboxyphenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(28) Alpha-[4-(N-methyl-N-octadecylsulfamyl)-phenoxy]-alpha-pivalyl-4-acetylacetanilide

(29) Alpha-[4-(4-hydroxyphenylsulfonyl)phenoxy]-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)-acetanilide

(30) Alpha-pivalyl-alpha-(4-sulfophenoxy)-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide potassium salt

(31) Alpha[4-(4-hydroxyphenylsulfonyl)phenoxy]-alpha-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy) butyramido]acetanilide

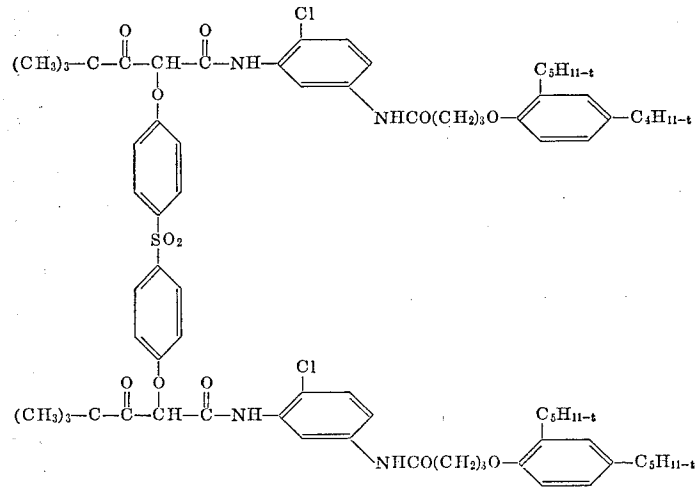
(32) Alpha-(4-carboxyphenoxy)-alpha-pivalyl-3-(N-methyl-N-octadecylsulfamyl)acetanilide

(33) Alpha-(4-carbobenzyloxyphenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(34) Alpha-(4-carboxyphenoxy)-alpha-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide

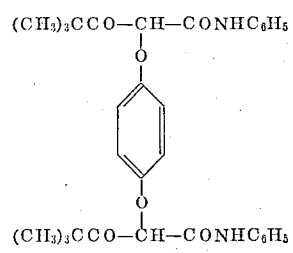
(35) Alpha-pentafluorophenoxy-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide

(36) 4,4'-bis[alpha-pivalyl-alpha-{2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]phenylcarbamyl} methoxy]diphenylsulfone



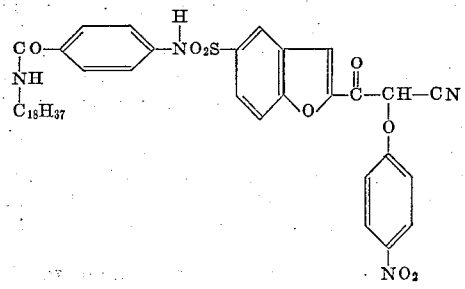
(37) 4,4'-bis[alpha-benzoyl-alpha-(N-phenylcarbamyl)-methoxy]diphenylsulfone

(38) 1,4-bis[alpha-pivalyl-alpha-(N-phenylcarbamyl)-methoxy]benzene

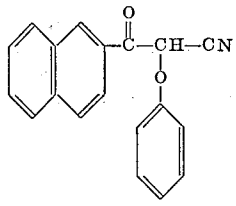


(39) 2-[alpha-cyano-alpha-(4-sulfamylphenoxy)-acetyl]coumarone

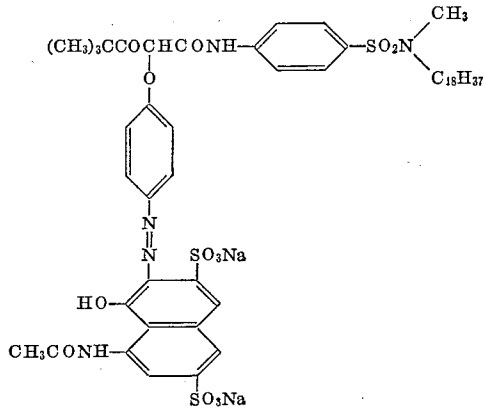
(40) 2-[alpha-cyano-alpha-(4-nitrophenoxy)acetyl]-5-[4-(N-octadecylcarbamyl)phenylsulfamyl] coumarone



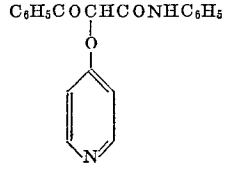
(41) Alpha-(2-naphthoyl)-alpha-phenoxyacetonitrile



(42) Alpha-[4-(8-acetamido-3,6-disulfo-1-hydroxy-2-naphthylazo)phenoxy]-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide disodium salt



(43) Alpha-benzoyl-alpha-(4-pyridinyloxy)acetanilide



(44) Alpha-benzoyl-alpha-[4-(N,N-dimethylsulfamyl) phenoxy]-2-decyloxyacetanilide

The diffusible couplers of my invention, such as couplers 15 through 21 and 39, 41, and 43 are used to advantage in color developer solutions used to color develop light-sensitve 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-laurylamino)-toluene, N - ethyl - N - (beta - methanesulfonamidoethyl) - 3-methyl-4-aminoaniline sulfate, N-ethyl-N-(beta-methanesulfonamidoethyl) - 4 - aminoaniline, 4-[N-ethyl-N-(beta-hydroxyethyl)amine]aniline, 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, carboxymethyl cellulose, carboxyethyl cellulose, gelatin, etc. The following is a typical developer solution given to illustrate but not limit the invention.

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

The other coupler examples used to illustrate my invention are nondiffusing and are used to advantage in photographic emulsion layers. Couplers such as 22, 23, 27, 30, 32, 34, and 42 illustrate those that are incorporated as Fischer type couplers. The other nondiffusing couplers, e.g., 1 through 14, 24, 25, 26, 28, 29, 31, 33, 35, 36, 37, 38, 40, are incorporated in emulsion layers by methods such as are described by Mannes et al., U.S. Patent No. 2,304,939, issued Dec. 15, 1942, Jelley et al., U.S. Patent 2,322,027, isued June 15, 1943, etc., in which high-boiling organic solvents are 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 No. 2,801,-171, both issued July 30, 1957 and Julian, U.S. Patent No. 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 couplers 1, 2, 3 and 4 each have a sulfamyl group (on a noncoupling position) which ionizes and forms a diffusible dye upon color development at a pH above 12.

The other nondiffusing couplers 5 through 14, 24, 25 and 44 used to illustrate my invention form nondiffusing dyes and are used to advantage in any photographic element where incorporated image-forming couplers are desired. Couplers 1, 2, 3 and 4 when developed with a color developer with a pH lower than 12 will produce nondiffusing dye images.

Coupler 42 contains a preformed dye attached to the coupler on the aryloxy group. This dye is eliminated on the coupling of the coupler with oxidized color developer and diffuses out of the film. This coupler can be used as a magenta colored coupler for the purpose of correcting for the unwanted blue absorption of yellow image dyes, i.e., that formed from the coupler itself as well as that formed from other yellow couplers. Generally, such a coupler as this would be used in combination with another image-forming yellow coupler in the same layer.

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 described in Lowe, U.S. Patent 2,286,-215, issued June 16, 1942; a far hydrolyzed cellulose

ester, such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in Lowe et al., U.S. Patent 2,327,808, issued Aug. 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy, U.S. Patent 2,322,085, issued June 15, 1943; 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 Lowe et al., U.S. Patent 2,541,474, issued Feb. 13, 1951; zein as described in Lowe, U.S. Patent 2,563,-791, issued Aug. 7, 1951, a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh et al., U.S. Patent 2,768,154, issued Oct. 23, 1956, or containing cyano-acetyl groups, such as the vinyl alcohol-vinyl cyano-acetate copolymer as described in Unruh et al., U.S. Patent 2,808,331, issued Oct. 1, 1957; 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 et al., U.S. Patent 2,852,382, issued Sept. 16, 1958.

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, issued Mar. 2, 1926; Sheppard et al., U.S. Patent 1,623,499, issued Apr. 5, 1927; and Sheppard et al., U.S. Patent 2,410,689, issued Nov. 5, 1946.

The emulsions can also be treated with salts of the noble metals, such as ruthenium, rhodium, palladium, iridium and platinum, as described in Smith et al., U.S. Patent 2,448,060, issued Aug. 31, 1948 and as described in Trivelli et al., U.S. Patents 2,566,245 and 2,566,263, both issued Aug. 28, 1951.

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker, U.S. Patents 1,846,301 and 1,846,302, both issued Feb. 23, 1932; and 1,942,854, issued Jan. 9, 1934; White, U.S. Patent 1,990,507, issued Feb. 12, 1935; Brooker and White, U.S. Patents 2,112,140, issued Mar. 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued Jan. 10, 1950; and 2,739,964, issued Mar. 27, 1956; Brooker et al., U.S. Patent 2,493,748, issued Jan. 10, 1950; Sprague, U.S. Patents 2,503,776, issued Apr. 11, 1950, and 2,519,001, issued Aug. 15, 1950; Heseltine et al., U.S. Patent 2,666,761, issued Jan. 19, 1954; Heseltine, U.S. Patent 2,734,900, issued Feb. 14, 1956; Van Lare, U.S. Patent 2,739,149, issued Mar. 20, 1956; and Kodak Limited, British 450,958, accepted July 15, 1936.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll, U.S. Patent 2,271,623, issued Feb. 3, 1942; Carroll et al., U.S. Patent 2,288,226, issued June 30, 1942; and Carroll et al., U.S. Patent 2,334,864, issued Nov. 3, 1943; and the polyethylene glycol type of Carroll et al., U.S. Patent 2,708,-162, issued May 10, 1955.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al., U.S. Patent 2,399,-083, issued Apr. 23, 1946 or stabilized with gold salts as described in Damschroder, U.S. Patent 2,597,856, issued May 27, 1952; and Yutzy et al., U.S. Patent 2,597,-915, issued May 27, 1942. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The couplers of my invention may also be used to advantage in image-forming layers, either alone or with image-forming compounds other than silver halide, such as ZnO, ZnS, CdS, CdSe, NiS, etc., either with or without binders such as gelatin, polyvinyl alcohol, etc.

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 Kneckel 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 1, 2, 3, 4, 22 and 23) can be used to advantage, are described in copending application of Whitmore and Mader, U.S. Ser. No. 222,105, filed Sept. 7, 1962, now U.S. Patent 3,227,550.

My invention is still further illustrated by the following typical examples.

Example 1

Single layer gelatino-silver bromoiodide emulsions containing yellow-forming coupler and the coupler solvent di-n-butylphthalate were made for my couplers 1, 2, 3, 4, 5, 11, 24 and 25. The amounts of gelatin, silver bromoiodide, and coupler solvent used in the coatings are listed in Table 1. The each instance the coupler was used so as to be coated at 60 mg./ft.^{2}.

Strips of the coatings were given identical exposures to a 0.3 neutral density step tablet in a 1B intensity scale sensitometer and processed through the following process:

Process steps:	Time
Water dip	min. 30
Development	sec. 10
Stop bath	sec. 5
Ferricyanide bleach	sec. 5
Wash	sec. 5
Fixing bath	sec. 5
Wash	sec. 10
Photo-Flo (wetting agent solution)	min. 30
Dry.	

The following developer solutions were used in this process:

Developer 1

Sodium sulfite	g. 2
2-amino-5-diethylamino-toluene HCl	g. 2
Sodium carbonate	g. 20
Potassium bromide	g. 2
Water to	l. 1

pH 10.86.

Developer 2

Benzyl alcohol	ml	4.00
Sodium sulfite	g	2.00
N-ethyl-β-methanesulfonamido - ethyl-4-aminoaniline sulfate	g	5.00
Sodium carbonate	g	50.00
Sodium bromide	g	0.86
Sodium hydroxide (20% solution)	ml	4.00
Sodium hexametaphosphate	g	0.50
Water to	l	1.00

pH 10.75.

Conventional acid stop bath, potassium ferricyanide bleach, sodium thiosulfate fixing baths were used in this process.

Spectrophotometric curves were made to determine the λ_{max} and the D_{max} (at λ_{max}) for the yellow dye images in each coating. Light fade, printout, heat fade and yellowing data were also obtained for each processed coating. The fading measurements were made at an original dye density of about 1.2 by determining the density decrease produced in the spectrophotometric curve by 30 hours exposure to a Xenon arc (light fade), and the density decrease produced in the spectrophotometric curve by storage in an oven at 140° F. at 70% RH for one week (heat fade). The printout values, that is, the percent change in transmission produced in an area of the processed element having no exposure by 30 hours exposure to a Xenon arc were determined for each coating. The yellowing values, that is, the percent decrease in transmission produced in an unexposed area of the processed element by storage at 140° F. and 70% RH for one week were determined for each coating. The data are listed in Table 1.

and for α-benzoyl-2-methoxyacetanilide as a control. The alkaline color developer comprised:

Na_2SO_3	g	10.0
Diethyl-p-phenylenediamine hydrochloride	g	3.0
Coupler	m	0.01
Alkali (to give a pH of 11.5).		
Water to	l	1.0

Strips of a multilayer structure containing a layer of light-sensitive silver halide emulsion were given sensitometric exposure with the 1B sensitimeter mentioned in Example 1. These strips were given the following processing steps: 1 minute, 5 seconds in a conventional formalin-sodium bisulfide prehardener, water washed, 2½ minutes' development in a conventional hydroquinone p-methylaminophenol sulfate developer, water washed, fogged, 5 minutes yellow color development, water washed, 3 minutes in a conventional potassium ferricyanide bleach bath, 2 minutes of conventional sodium thiosulfate fixing, water washing and drying. The λ_{max} in mμ was measured at a density of 1 and the percent of yellow dye fading (at a density of 1) produced by exposure to tungsten light and storage in an oven was determined for the processed strips. The results are summarized in Table 2.

TABLE 2

Coupler Used in Color Developer	λ_{max} in mμ	3 Day Tungsten Fade (percent)	2 Weeks' Oven Fade at 70% RH and 140° F. (percent)
Control	441	38	8
No. 19	441	28	8
No. 20	441	28	6

The results show that my couplers produced good

TABLE 1

Coating No.	Gelatin, mg./ft.²	Silver Bromoiodide, mg./ft.²	Coupler No.	Ratio of Coupler to Coupler Solvent	Developer Formula	Photographic Data					
						λ_{max} in mμ	D_{max}.	Light Fade	Print Out, Percent	Heat Fade	Yellowing, Percent
1	250	100	2	1:1	1	451	1.64	.33	+4	.13	5
2	250	100	4	1:1	1	452	2.72	.33	+6	.08	3
2	250	100	4	1:1	2	448	2.60	.14	+3	.18	5
3	250	100	5	2:1	1	451	1.90	.23	+8	.08	2
3	250	100	5	2:1	2	448	1.74	.10	+8	.10	4
4	250	100	11	2:1	1	447	3.28	.38	+1	.02	6
5	300	150	24	2:1	1	450	2.42	.05	+6	.05	2
5	300	150	24	2:1	2	446	2.26	.02	+9	.12	6.5
6	300	150	24	1:0	1	---	2.64	(Essentially the same as for Coating 5)			
6	300	150	24	1:0	2	---	2.21				
7	300	150	25	2:1	1	449	1.94	.05	0	.04	2.5
7	300	150	25	2:1	2	445	1.76	.04	0	.05	5
8	300	150	25	1:0	1	---	2.08	(Essentially the same as for Coating 7)			
8	300	150	25	1:0	2	---	1.84				

The data show that my representative couplers used in the photographic elements produced good yellow dye images upon color development following exposure to a light image. D_{max} and λ_{max} values are good. The yellow dye images have good stability to prolonged exposure to a high intensity light and good stability when stored under high temperature and humidity conditions. The residual coupler in the minimum density areas of the processed emulsion layers exhibited a low amount of printout and yellowing. The data show that the coupler:coupler solvent can be used over a wide range, i.e., from 1:0 to 1:1 and that couplers such as 24 and 25 give good reactivity even in the absence of the high boiling coupler solvent.

Similar results are obtained when my yellow-forming couplers are incorporated in a multilayer multicolor photographic element such as are used in color photography.

Example 2

A yellow color developer solution was prepared for each of my representative diffusible couplers 19 and 20 yellow dye images that faded substantially less than the dye from the control coupler and which were equivalent or better for fading upon prolonged storage at elevated temperature and humidity.

Example 3

Samples of coatings 1 and 2 of Example 1 and coatings made like said coatings but containing coupler No. 1, No. 3 and No. 22 were exposed to a light image and processed in an aqueous alkaline developer solution having a pH of 13 and comprising 2 g./l. of Na_2SO_3, and 11 g./l. of 4-N-ethyl-N-β-hydroxyethylamino aniline in contact with a receiving sheet containing the mordant, dimethyl-β-hydroxyethyl-γ-stearamidopropyl ammonium dihydrogen phosphate, for three minutes at 75° F. After development the receiving sheets were separated from the respective coatings showing that the yellow dye images formed in the coatings were transferred to and were mordanted in the respective receiving sheets.

Example 4

Single layer gelatin silver bromoiodide coatings were prepared containing couplers 26, 28, 29, 31, 33, 35, 36, and 40, respectively. Each of these couplers were dispersed in said coatings in the form of a finely dispersed solution of the coupler in coupler solvent, di-n-butylphthalate.

These coatings contained 10 parts of gelatin, 5 parts of silver, 2 parts of coupler, and 1 part of coupler solvent. Samples of the above mentioned coatings were given 1/25 second exposure on a 1B intensity scale sensitometer and processed in a conventional manner to color negatives, respectively, using the following developer solution:

Sodium sulfide (anhydrous)	g.	2.0
2-amino-5-diethylaminotoluene HCl	g.	2.0
Sodium carbonate monohydrate	g.	20.0
Potassium bromide	g.	2.0
Water to	l.	1.0

pH to 10.86.

Each of the processed strips which contained the respective yellow couplers contained high quality yellow dye images. The one strip containing the magenta dye-forming coupler 40 contained a high quality magenta dye image.

The preparation of my couplers is illustrated by a description of representative couplers of my invention.

Coupler 1

A mixture of 33 g. of α-pivalyl-α-chloro-4-sulfamylacetanilide and 40 g. of 4-nitro-3-pentadecylphenol sodium salt in 300 ml. of acetonitrile was refluxed overnight, after which time the mixture was filtered and the filtrate was cooled to room temperature, whereupon a solid separated. The solid was collected and recrystallized four times from acetonitrile, yielding 25 g. of coupler 1, M.P. 130–138° C.

Coupler 2

To a solution of 4 g. of α-pivalyl-α-(p-aminophenoxy)-4-sulfamylacetanilide, Intermediate No. 2, and 3 g. of triethylamine in 25 ml. of dioxane was added a solution of 2.8 g. of palmitoyl chloride in 25 ml. of dioxane with stirring at room temperature over a period of ½ hour. The resultant mixture was stirred at room temperature overnight, filtered, and the filtrate concentrated in vacuo, whereupon a solid was obtained. This solid was recrystallized twice from acetonitrile and twice from ethanol, yielding 2.5 g. of coupler 2, M.P. 207–214° C.

Intermediate No. 1

α-Pivalyl-α-(4-nitrophenoxy)-4-sulfamylacetanilide

A mixture of 16.7 g. of α-pivalyl-α-chloro-4-sulfamylacetanilide, 7.7 g. of 4-nitrophenol and 5.4 g. of triethylamine in 150 ml. of acetonitrile was refluxed overnight, after which time the clear solution was concentrated in vacuo. The residual oil was triturated with diethyl ether, whereupon it solidified. This solid was recrystallized several times from ethanol, yielding 10 g. of product.

Intermediate No. 2

α-Pivalyl-α-(4-aminophenoxy)-4-sulfamylacetanilide

A mixture of 10.8 g. of Intermediate No. 1 and 150 ml. of ethyl alcohol was hydrogenated in a Parr hydrogenation apparatus at room temperature under a hydrogen atmosphere of 30 p.s.i. using palladium on charcoal as the catalyst. The time required for the reduction was four hours, after which time the solution was heated to boiling. Catalyst was removed by filtration and the filtrate concentrated in vacuo. The solid residue was recrystallized from methanol, yielding 4 g. of product.

Coupler 3

This coupler was prepared by the method used for coupler 1 excepting that an equimolar amount of α-pivalyl-α-chloro-2-chloro-4-sulfamylacetanilide was used in place of α-pivalyl-α-chloro-4-sulfamylacetanilide. The recrystallized and dried coupler had a M.P. of 116–118° C.

Coupler 4

A mixture of 10 g. of 4-(N-methyl-N-octadecyl-sulfamyl)phenol sodium salt and 6.7 g. of α-pivayl-α-chloro-4-sulfamylacetanilide in 100 ml. of acetonitrile was refluxed overnight. The mixture was filtered and the filtrate cooled in ice for several hours, whereupon a white solid separated. This solid was collected and recrystallized from ethanol, yielding 3 g. of product, M.P. 99–111° C.

Coupler 5

This coupler was prepared by the method used for coupler 4 excepting that an equivalent amount of 4-methylsulfonylphenol sodium salt and α-pivalyl-α-chloro-4-(N-methyl-N-octadecylsulfamyl)acetanilide were used. The product had a M.P. of 82–89° C.

Coupler 6

This coupler was prepared by the method used for coupler 4 but substituting equivalent amounts of 4-sulfamylphenol sodium salt and α-pivalyl-α-chloro-4-(N-methyl-N-octadecylsulfamyl)acetanilide. The product had a M.P. of 85–88° C.

Coupler 7

This coupler was prepared by the method used for coupler 4 but substituting equivalent amounts of 4-nitrophenol sodium salt and α-pivalyl-α-chloro-4-(N-methyl-N-octadecylsulfamyl)acetanilide. The coupler had a M.P. of 99–101° C.

Coupler 8

A mixture of 12 g. of 4-nitro-3-pentadecylphenol sodium salt and 9 g. of α-benzoyl-α-chloro-2-methoxyacetanilide in 130 ml. of acetonitrile was refluxed overnight, after which time the clear solution was cooled to room temperature, whereupon a solid separated. This solid was collected and recrystallized twice from hexane, yielding 3 g. of coupler, M.P. 104–106° C.

Coupler 9

A mixture of 4 g. of 4-nitrophenol sodium salt and 12.5 g. of α-{3-[γ-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-α-chloro-2-methoxyacetanilide in 120 ml. of acetonitrile was refluxed overnight, after which time the mixture was filtered hot. The filtrate was cooled and concentrated in vacuo. The residual oil was triturated with a diethyl ether-petroleum ether mixture, whereupon it solidified. This solid was recrystallized twice from a 50:50 mixture of hexane and ethylacetate and 3 times from acetonitrile, yielding 4 g. of product, M.P. 153–160° C.

Coupler 10

This coupler was prepared by the method used to prepare coupler 9 but using an equivalent amount of 4-acetylphenol sodium salt in place of 4-nitrophenol sodium salt. The coupler had a M.P. of 142–148° C.

Coupler 11

This coupler was prepared by the method used to prepare coupler 9 but using an equivalent amount of 4-sulfamylphenol sodium salt in place of 4-nitrophenol sodium salt. The coupler had a M.P. of 193.5–197° C.

Coupler 12

This coupler was prepared like coupler 9 but using an equivalent amount of 4-phenylphenol sodium salt.

Coupler 13

This coupler was prepared by the method used to prepare coupler 8 but by using equivalent amounts of 4-(N-methyl-N-octadecylsulfamyl)phenol sodium salt and α-benzoyl-α-chloro-2-ethoxyacetanilide. The coupler product had a M.P. of 73–77° C.

Coupler 14

A mixture of 1.5 g. of 4-methylsulfonylphenol, 1 g. of triethylamine and 5.5 g. of α-(4-methoxybenzoyl)-α-chloro-5-[λ-(2,4-di-tert-amylphenoxy)butyramido]-2 - chloroacetanilide in 40 ml. of acetonitrile was refluxed overnight, cooled and filtered to remove a small quantity of precipitate. The filtrate was concentrated in vacuo and the residue was recrystallized three times from ethanol, yielding 2 g. of product, M.P. 155–160° C.

Coupler 15

A mixture of 4 g. of the intermediate below and 1 g. of succinic anhydride in 25 ml. of acetonitrile was stirred at room temperature overnight. The white solid which had separated from the clear reaction mixture was collected, washed with acetonitrile, and dried to yield 4.6 g. of product, M.P. 196–201° C.

Intermediate

Alpha-(4-aminophenoxy-alpha-pivalyl-4-(N,N-dimethylsulfamyl)acetanilide

A mixture of 14 g. of alpha-(4-nitrophenoxy)-alpha-pivalyl-4-(N,N-dimethylsulfamyl)acetanilide and a small amount of 10% palladium on charcoal catalyst in 150 ml. of p-dioxane was hydrogenated overnight at room temperature in a low pressure Parr apparatus. The reaction mixture was filtered, and the filtrate was concentrated in vacuo to yield a yellow gum. This residue was triturated with methanol, whereupon a white crystalline solid separated, was collected, washed with methanol, and dried to yield 11 g. of product.

Coupler 16

This coupler was prepared by the method used for coupler 1 but using equivalent amounts of 4-nitrophenol sodium salt and alpha - pivalyl-alpha-chloro-4-(N,N-dimethylsulfamyl)acetanilide. The product had a M.P. of 195–197° C.

Coupler 17

This coupler was prepared by the method used for coupler 8 but using an equivalent amount of 4-nitrophenol sodium salt in place of the 4-nitro-3-pentadecylphenol sodium salt. The coupler product had a M.P. of 141–157° C.

Coupler 18

To 20 ml. of dihydropyran was added 3 g. of alpha-benzoyl-alpha-hydroxyacetanilide, Intermediate No. 2, and one drop of concentrated hydrochloric acid with stirring. The resultant solution became hot and reaction was allowed to take place with external heating or cooling. The clear solution was left at room temperature overnight. To the clear reaction mixture was then added hexane, whereupon a solid separated, was filtered, and recrystallized twice from methanol, yielding 1 g. of product, M.P. 130–131° C.

Intermediate No. 1

Alpha-acetoxy-alpha-benzoylacetanilide

A solution of 170 g. of alpha-benzoyl-alpha-chloroacetanilide and 75 g. of anhydrous sodium acetate in 1 liter of glacial acetic acid was refluxed overnight, after which time 500 ml. of water was added. The resultant solution was cooled, whereupon a solid precipitated, was filtered and dried, yielding 150 g. of product.

Intermediate No. 2

Alpha-benzoyl-alpha-hydroxyacetanilide

A solution of 30 g. of Intermediate No. 1 in 1 liter of ethanol, to which had been added 30 drops of concentrated sulfuric acid was refluxed for forty-eight hours, after which time the clear solution was cooled to room temperature. To this solution was added 7 g. of sodium acetate to neutralize the sulfuric acid. The solution was then poured into 2 liters of water and the white solid which separated was filtered and dried, yielding 15 g. of product.

Coupler 19

A mixture of 10.5 g. of 4-carbomethoxyphenol sodium salt and 15 g. of alpha-benzoyl-alpha-chloro-2-methoxyacetanilide in 150 ml. of acetonitrile was refluxed overnight, after which time it was filtered and concentrated in vacuo. The residual oil was triturated with diethyl ether, whereupon it solidified. The solid was recrystallized several times from acetonitrile, yielding 3 g. of product, M.P. 146–156° C.

Coupler 20

This coupler was prepared as Coupler 19, but using an equivalent amount of 4-sulfamylphenol sodium salt. The coupler had a M.P. of 191.5–196° C.

Coupler 21

A mixture of 14 g. of alpha-benzoyl-alpha-(4-nitrophenoxy)-2-methoxyacetanilide and a small amount of 10% palladium on charcoal catalyst in 200 ml. of p-dioxane was hydrogenated overnight at room temperature in a low pressure Parr apparatus. After this time, the reaction mixture was filtered and the filtrate was concentrated to dryness in vacuo. The solid residue was dissolved in diethyl ether at reflux. This ether solution was saturated with anhydrous hydrogen chloride gas, whereupon a solid separated. This solid was collected, washed with additional anhydrous ether, and dried to yield 15 g. of product, M.P. 122–124° C.

Coupler 22

A mixture of 14 g. of 4-nitro-3-pentadecylphenol, 4.3 g. of diethylamine, 13.5 g. of alpha-pivalyl-alpha-chloro-4-fluorosulfonylacetanilide in 160 ml. of acetonitrile was refluxed overnight, after which time the clear solution was concentrated in vacuo. The residual oil was dissolved in 100 ml. of acetone. To this solution was added a solution of 8 g. of potassium hydroxide in 150 ml. of water. The resultant solution was refluxed for 30 minutes, after which time a solution of 10 ml. of acetic acid in 20 ml. of acetone was added, whereupon oil separated. This oil was triturated with ethanol and the solution which formed was collected and recrystallized several times from ethanol, yielding 2.3 g. of product.

Coupler 23

This coupler was prepared by reacting 4-(N-methyl-N-octadecylsulfamyl)phenol sodium salt and alpha-pivalyl-alpha-chloro-4-sulfoacetanilide, according to the procedure used for Coupler 4.

Coupler 24

A mixture of 6.7 g. of the intermediate below and 1 g. of succinic anhydride in 25 ml. of acetonitrile was stirred at room temperature overnight. An additional 50 ml. of acetonitrile was added and the mixture was warmed on a steam bath, whereupon a complete solution resulted. This solution was allowed to stir and cool to room temperature, during which time a solid separated. This solid was collected and recrystallized once from acetonitrile to yield 7.4 g. of product, M.P. 133–134° C.

Intermediate

Alpha-(4-aminophenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)-acetanilide

A mixture of 12 g. of alpha-(4-nitrophenoxy)-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide and a small amount of 10% palladium on charcoal catalyst in 200 ml. of p-dioxane was hydrogenated at room temperature in a low pressure Parr apparatus for a period of 18 hours. The catalyst was removed by filtration and the filtrate was concentrated to dryness in vacuo. The solid residue was recrystallized twice from acetonitrile and once from methanol to yield 18 g. of product, M.P. 98–100° C.

Coupler 25

This was prepared by reacting 4-sulfophenol sodium salt and alpha-pivalyl-alpha-chloro-4-(N-methyl-N-octadecylsulfamyl)acetanilide, according to the procedure used for Coupler 4.

Coupler 26

A mixture of 24 g. of alpha-chloro-alpha-pivalyl-(N-methyl-N-octadecylsulfamyl)acetanilide, 6 g. of methyl p-hydroxybenzoate, and 4 g. of triethylamine in 150 ml. of acetonitrile was refluxed overnight with stirring, after which time it was concentrated in vacuo. The residue was recrystallized twice from methyl alcohol to yield the product, M.P. 69–70° C.

Coupler 27

To a solution of 10 g. of alpha-(4-carbomethoxyphenoxy) - alpha - pivalyl-4-(N-methyl-N-octadecylsulfamyl)-acetanilide in 45 ml. of acetone was added 20 ml. of 2 N potassium hydroxide. The resultant mixture was stirred and refluxed for 15 minutes, after which time 21 ml. of water were added. The mixture was stirred for an additional 15 minutes in an ice bath and acidified with 3.7 ml. of concentrated hydrochloric acid, whereupon a solid separated, was collected, washed with a 1:1 mixture of acetone-water, and dried. This solid was recrystallized twice from methyl alcohol to yield the product, M.P. 79–80° C.

Coupler 28

A mixture of 12 g. of alpha-chloro-alpha-pivalyl-4-acetylacetanilide, 18 g. of 4-(N-methyl-N-octadecylsulfamyl)-phenol, and 4 g. of triethylamine in 120 ml. of acetonitrile was refluxed with stirring overnight, after which time the mixture was concentrated in vacuo. The residue was recrystallized several times from methyl alcohol to yield the product, M.P. 79–81° C.

Coupler 29

A mixture of 12 g. of alpha-chloro-alpha-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide, 10 g. of 4,4'-sulfonyldiphenol, and 9 g. of triethylamine in 100 ml. of acetonitrile was refluxed with stirring overnight, after which time the solution was concentrated in vacuo. The residue was recrystallized several times from methyl alcohol to yield the product.

Coupler 30

A mixture of 12 g. of alpha-chloro-alpha-pivalyl-2-chloro - 5 - [γ - (2,4-di-t-amylphenoxy)butyramido]acetanilide, 4 g. of 4-hydroxy benzenesulfonic acid sodium salt, and 2 g. of triethylamine in 150 ml. of acetonitrile was refluxed with stirring overnight, after which time it was concentrated in vacuo. The residue was dissolved in 70 ml. of absolute ethyl alcohol and to this solution was added a solution of 6 g. of potassium acetate in 70 ml. of absolute ethyl alcohol. A small amount of solid which separated was removed by filtration and the filtrate was again concentrated in vacuo. The residue was dissolved with a mixture of 120 ml. of ethyl alcohol and 40 ml. of water. A small amount of insoluble material was removed by filtration and the filtrate again concentrated in vacuo. The residue was then recrystallized from acetonitrile to yield the product.

Coupler 31

A solution of 30 g. of alpha-chloro-alpha-pivalyl-2-chloro -5- [γ - (2,4 - di-t-amylphenoxy)butyramido]acetanilide, 25 g. of 4,4'-sulfonyldiphenol, and 20 g. of triethylamine in 250 ml. of acetonitrile was refluxed with stirring overnight, after which time it was concentrated in vacuo. The residue was dissolved in 300 ml. of methyl alcohol. The solution was poured with stirring into 1 liter of ice and water. The solid which separate was collected, dried, and triturated several times with boiling hexane to yield the product, M.P. 99–101° C.

Coupler 32

A solution of 10 g. of alpha - (4 - carbobenzyloxyphenoxy) - alpha - pivalyl - 3-(N-methyl-N-octadecylsulfamyl)acetanilide in 100 ml. of dioxane was reduced on the low pressure Par hydrogenation apparatus using about ½ g. of palladium on charcoal as the catalyst at 45° C. After the reduction was complete the catalyst was removed by filtration and the filtrate was concentrated in vacuo. The residue was recrystallized once from methanol and again from acetonitrile to yield the product, M.P. 93–95° C.

Coupler 33

A solution of 180 g. of alpha-chloro-alpha-pivalyl-4-(N - methyl - N - octadecylsulfamyl)acetanilide, 69, g. of benzyl 4-hydroxybenzoate, and 32 g. of triethylamine in 1 liter of acetonitrile was refluxed with stirring overnight, after which time it was concentrated in vacuo. The residue was slurried in diethyl ether and the insoluble triethylamine chloride was removed by filtration. The filtrate was chilled in an ice bath, whereupon a white solid separated, was collected and recrystallized from hexane to yield the product, M.P. 89–91° C.

Coupler 34

A solution of 87 g. of α-(4-carbobenzyloxyphenoxy)-α - pivalyl - 2 - chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide in 400 ml. of absolute ethyl alcohol was reduced at room temperature on the low pressure Parr hydrogenation apparatus using 10% palladium on charcoal catalyst. After the reduction was complete, the catalyst was removed by filtration and the filtrate concentrated in vacuo. The residue was recrystallized from acetonitrile to yield the product, M.P. 193–194° C.

Coupler 35

A solution of 18 g. of α-chloro-α-pivalyl-4-(N-methyl-N-octadecylsulfamyl)acetanilide, 5.5 g. of pentafluorophenol, and 4.6 g. of triethylamine in 150 ml. of acetonitrile was refluxed with stirring overnight, after which time it was concentrated in vacuo. The residue was recrystallized 3 times from methyl alcohol to yield the product, M.P. 66–68° C.

Coupler 36

A solution of 25 g. of α-chloro-α-pivalyl-2-chloro-5-[γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide, 5 g. of 4,4'-sulfonyldiphenol, and 5 g. of triethylamine was refluxed with stirring for 6 hours, after which time the reaction mixture was concentrated in vacuo. The residue was recrystallized from cyclohexane to yield the product, M.P. 109–111° C.

Coupler 37

This coupler was prepared in accordance with the procedure used for the preparation of Coupler 36 except that alpha-benzoxyl-alpha-chloroacetanilide was used in place of the coupler intermediate used in the preparation of Coupler 36.

Coupler 38

This coupler was prepared in accordance with the procedure used to prepare Coupler 36 except that alpha-chloro-alpha-pivalylacetanilide was used in place of the coupler intermediate of Example 36 and hydroquinone was used in place of the phenol used in preparing Coupler 36.

Couplers 39, 40, 41 and 43

Each of these couplers were prepared by reacting the alpha-chloro coupler intermediate with the respective phenols, using a procedure similar to that given for the preparation of Coupler 1. The intermediates used in prepraing these couplers are given in the following Table 3.

TABLE 3

Coupler No.	Coupler Intermediate	Phenol Used
39	2-(alpha-chloro-alpha-cyanoacetyl)-coumarone.	4-sulfamylphenol.
40	2-(alpha-chloro-alpha-cyanoacetyl)-5-[4-(N-octadecylcarbamyl)phenylsulfamyl]coumarone.	4-nitrophenol.
41	Alpha-chloro-alpha-(2-naphthoyl)-acetanilide.	Phenol.
43	Alpha-benzoyl-alpha-chloroacetanilide.	4-hydroxypyridine.

Coupler 42

To a solution of 2 g. of acetyl H-acid in 100 ml. of methyl alcohol and about 50 ml. of crushed ice was added a methanolic solution of the intermediate prepared below, together with a slight excess of sodium acetate, with stirring. The red solid which separated was collected and an additional second crop was obtained by partial evaporation of the reaction solution. The total solids were combined and slurried in water, triturated with dry petroleum ether, collected and dried to yield the product, M.P. decompose at 250° C.

Intermediate

To a solution of 3.35 g. of alpha-(4-aminophenoxy)-alpha - pivalyl - 4 - (N - methyl - N - octadecylsulfamyl)-acetanilide in 150 ml. of n-propyl alcohol was added a mixture of 3 g. of p-toluene sulfonic acid and 5 ml. of acetic acid. To the resultant solution was added 3 g. of isopentylnitrile. The reaction mixture was then stirred at room temperature overnight, after which time it was heated to 45° C. and then cooled to room temperature. The solvent was removed in vacuo and the gummy residue (i.e., the diazotized amine coupler) was used as such, without further purification, in the above reaction.

Coupler 43

This coupler was prepared by a method similar to that used to make Coupler 19 but using as the intermediates equimolar amounts of 4-(N,N-dimethylsulfamyl)phenol sodium salt and alpha-benzoyl-alpha-chloro-2-decyloxyacetanilide. The coupler had a M.P. of 89° C.

The chloroacetanilides used in the coupler syntheses were prepared as described by McCrossen et al., U.S. Patents 2,728,658, issued Dec. 27, 1955, and 2,875,057, issued Feb. 24, 1959, respectively, Loria, U.S. Ser. No. 247,302, filed Dec. 26, 1962, and Kibler and Weissberger, U.S. Ser. No. 364,450, filed May 4, 1964.

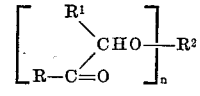
My two-equivalent dye-forming couplers are characterized from other couplers by having a cyclooxy or a heterocyclooxy group attached to the active carbon atom of the coupler molecule. My couplers are valuable for use in color photography because of their relatively low printout, and yellowing in processed elements containing them, and because of the desirable characteristics of the dyes produced from them, for example low heat fade, low light fade, good λ_{max}, D_{max}, etc.

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:

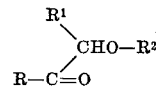
1. An image-forming layer containing silver halide emulsion and a coupler which is capable of forming a dye on coupling with the oxidation product of an aromatic amino developing agent, said coupler containing from one to two open-chain reactive methylene groups, said methylene group being joined directly to two activating groups, at least one of said activating groups being a carbonyl group, said active methylene group also being joined directly to a cyclooxy group selected from the class consisting of a phenoxy group, a phenylenedioxy group, a naphthoxy group, a naphthylenedioxy group, a pyridinyloxy group, a pyridyldioxy group, a tetrahydropyranyloxy group, a tetrahydropyranylenedioxy group, a tetrahydroquinolyloxy group, and a tetrahydroquinolylenedioxy group, such that when the said coupler contains one open-chain reactive methylene group the said cyclooxy group is monovalent and when the said coupler contains two reactive methylene groups the said cyclooxy group is divalent, which cyclooxy group is eliminated on the coupling of said coupler with said oxidation products.

2. An image-forming layer containing silver halide emulsion and a coupler of the formula:



wherein n represents an integer of from 1 to 2; R represents a group selected from the class consisting of an alkyl radical, an aryl radical, and a heterocyclic radical; R^1 represents a group selected from the class consisting of a carbamyl radical and a cyano radical; and R^2 represents a cyclo group selected from the class consisting of a phenyl group, a phenylene group, a naphthyl group, a naphthylene group, a pyridinyl group, a pyridyl group, a tetrahydropyranyl group, a tetrahydropyranylene group, a tetrahydroquinolinyl group and a tetrahydroquinolylene group, such that when n represents the integer 1, R^2 represents a monovalent cyclo group and when n represents the integer 2, R^2 represents a divalent cyclo group.

3. An image-forming layer containing silver halide emulsion and a coupler of the formula:



wherein R represents a group selected from the class consisting of an alkyl radical, an aryl radical, and a heterocyclic radical; R^1 represents a group selected from the class consisting of a carbamyl radical and a cyano radical; R^2 represents a cyclo group selected from the class consisting of a phenyl group, a naphthyl group, a pyridinyl group, a tetrahydropyranyl group and a tertahydroquinolyl group.

4. A light-sensitive hydrophilic colloid-silver halide emulsion layer containing the coupler, alpha-{3-[γ-(2,4-di - t - amylphenoxy)butyramido]benzoyl} - alpha - (4-nitrophenoxy-2-methoxyacetanilide.

5. A light-sensitive hydrophilic colloid-silver halide emulsion layer containing the coupler, alpha-[4-(N-methyl - N - octadecylsulfamyl)phenoxy] - alpha - pivalyl-4-sulfoacetanilide potassium salt.

6. A light-sensitive hydrophilic colloid-silver halide emulsion layer containing the coupler, alpha-pivalyl-alpha - (4 - sulfophenoxy) - 4 - (N - methyl - N - octadecylsulfamyl)acetanilide potassium salt.

7. A light sensitive hydrophilic colloid-silver halide emulsion layer containing the coupler, alpha-[4-(4-hydroxyphenylsulfonyl)phenoxy] - alpha-pivalyl-2-chloro-5-[γ(2,4-di-t-amylphenoxy)butyramido]acetanilide.

8. A light-sensitive hydrophilic colloid-silver halide emulsion layer containing the coupler, alpha-(4-carboxyphenoxy) - alpha - pivalyl - 2 - chloro - 5 - [γ-(2,4-di-t-amylphenoxy)butyramido]acetanilide.

9. A light-sensitive hydrophilic colloid-silver halide emulsion layer containing the coupler, 4,4'-bis[alpha-pivalyl - alpha - {2 - chloro-5-[γ-(2,4-di-t-amylphenoxy)-butyramido]-phenylcarbamyl}methoxy]diphenylsulfone.

References Cited

UNITED STATES PATENTS

3,227,550	1/1966	Whitmore et al.	96—3
3,227,551	1/1966	Barr et al.	96—3

J. TRAVIS BROWN, *Primary Examiner.*

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,408,194 Dated October 29, 1968

Inventor(s) Anthony Loria

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 19, line 51, delete "43", and substitute in its place --44--.

Column 20, line 58, delete the term "terta-", and substitute in its place --tetra- --.

SIGNED AND
SEALED
JAN 27 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents