Jan. 4, 1966 C. R. BARR ET AL **3,227,551**

PHOTOGRAPHIC COLOR REPRODUCTION PROCESS AND ELEMENT

Filed Dec. 14, 1962 2 Sheets-Sheet 1

Fig. 1

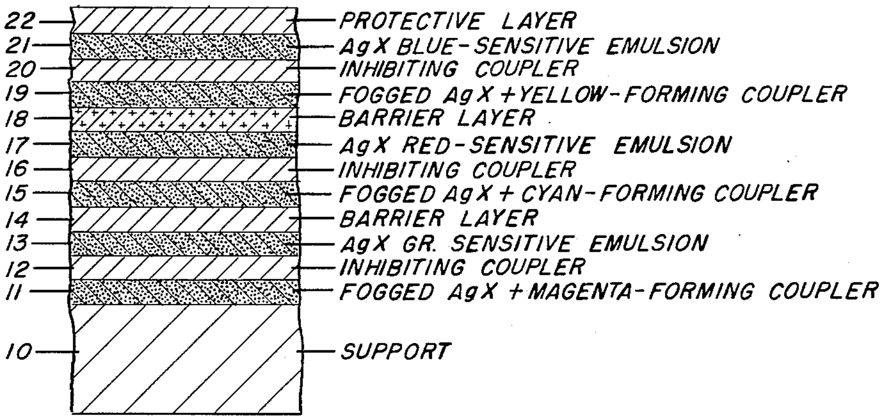


Fig. 2

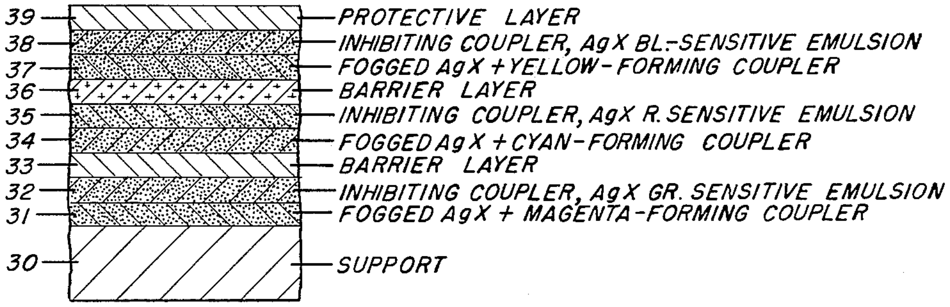
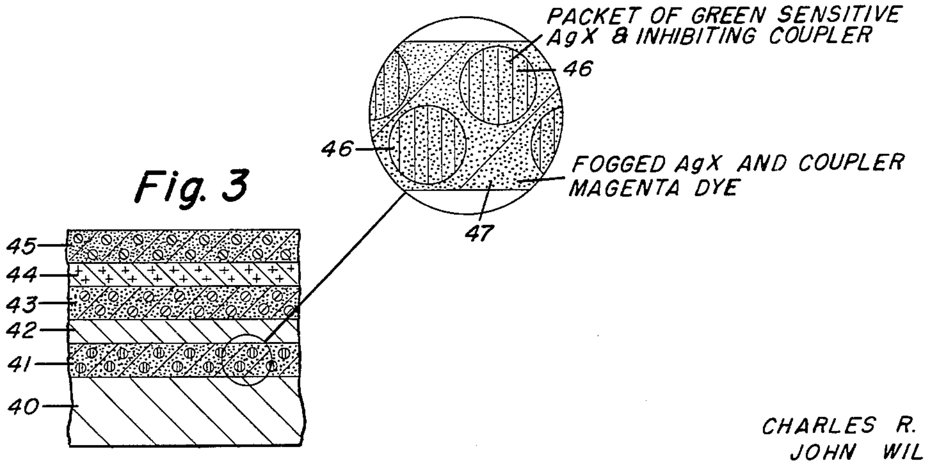


Fig. 3



CHARLES R. BARR
JOHN WILLIAMS
KEITH E. WHITMORE
INVENTORS

BY R. Frank Smith
James B. Frederick
ATTORNEYS

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Fig. 4

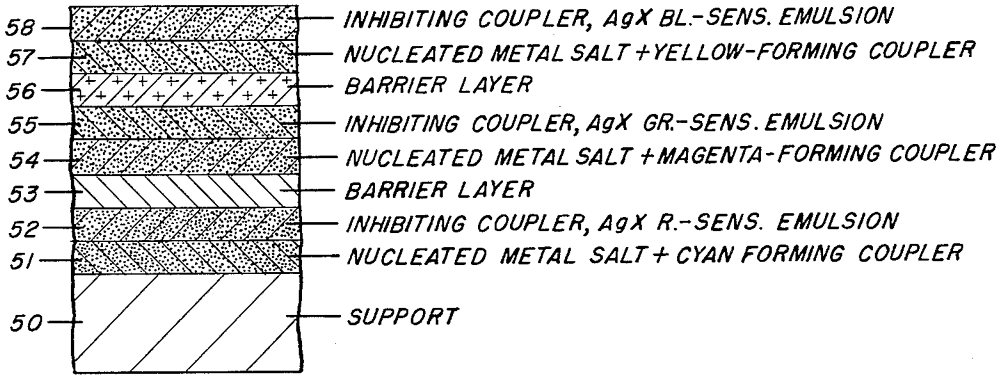
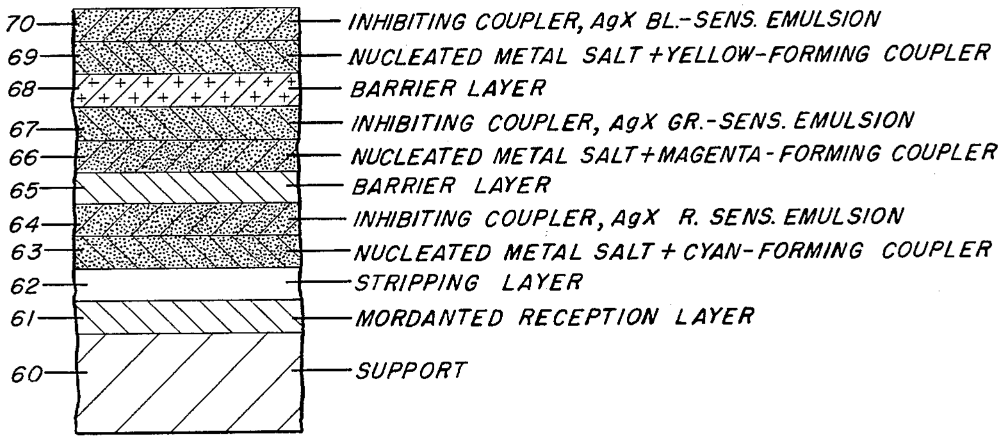


Fig. 5



CHARLES R. BARR
JOHN WILLIAMS
KEITH E. WHITMORE
INVENTORS

BY R. Frank Smith
James R.

ATTORNEYS

3,227,551

PHOTOGRAPHIC COLOR REPRODUCTION PROCESS AND ELEMENT

Charles R. Barr, John Williams, and Keith Whitmore, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Filed Dec. 14, 1962, Ser. No. 244,774
21 Claims. (Cl. 96—3)

This application is a continuation-in-part application of co-pending U.S. Serial No. 817,860 filed June 3, 1959 (now abandoned); U.S. Serial No. 126,782 filed June 29, 1961 (now abandoned); and U.S. Serial No. 126,783 filed June 29, 1961 (now abandoned).

This invention relates to color photography, and more particularly, to photographic direct positive color diffusion transfer processes and photographic elements suitable for use in such processes.

Direct positive photographic color processes are well known in the art, and generally comprise a number of steps. A typical color process comprises such steps as a black-and-white development to form a negative image, a reversal exposure, development with an aromatic primary amino color developing agent to form insoluble image dyes in the areas of development, and a bleach step to remove developed silver. Color proceses are also known whereby color images are transferred to receiving elements, and which have the advantage of producing color images free of residual color couplers and other products of development. However, many of such processes of the latter type involve several complex steps, require several processing baths with large volumes of processing solutions, and produce poor quality color images due to lateral diffusion of dye-forming components.

It is an object of the present invention to provide a new color process in the photographic art.

It is another object of this invention to provide a new photographic process for producing sharp color images.

It is another object of this invention to provide a novel photographic diffusion transfer process wherein a dye image is transferred to a receiving layer.

It is another object of this invention to provide a novel color diffusion transfer process that can be effected in one wet processing step.

It is another object of this invention to provide a novel color diffusion transfer process wherein the color development is carried out in the presence of a predominant proportion of the products of oxidation of the color developing agent.

It is still another object of this invention to provide a novel process for preparing direct positive color images.

It is also an object of this invention to provide a novel color diffusion transfer process for producing direct positive full-color images.

It is likewise an object of this invention to provide a novel photographic element suitable for use in preparing direct positive color images by a photographic diffusion transfer process.

These and other objects are attained by means of this invention as described hereinafter with reference to preferred embodiments thereof.

The present invention concerns light-sensitive photographic elements having coated thereon at least two Color-Forming Units as described herein, and which elements can be processed in the presence of alkaline color developing solutions containing aromatic primary amino color developing agents to prepare direct positive color images.

The Color-Forming Units of the invention comprise:

Component A.—A hydrophilic colloid-silver halide emulsion capable of recording latent images on exposure to light;

Component B.—A photographic color coupler capable of forming a diffusible mercaptan development inhibitor on development with an alkaline color developing solution containing an aromatic primary amino color developing agent, such development inhibitor-releasing couplers being referred to herein as "DIR" couplers (this component can be either in the Color-Forming Unit or the color developing solution);

Component C.—An emulsion of a hydrophilic colloid and a water-insoluble metal salt developable to substantial density without exposure to light, and which is referred to herein as a " 'spontaneously' developable" emulsion; and

Component D.—A nondiffusible photographic color coupler capable of forming a diffusible acid dye on development with an alkaline color developing solution containing an aromatic primary amino color developing agent, and which diffusible dye-releasing coupler is referred to herein as a "DDR" coupler.

When such Color-Forming Units are exposed, a latent image (negative image) pattern of developable silver halide is formed in the light-sensitive emulsion (Component A). When this exposed emulsion is developed in an alkaline color developing solution containing an aromatic primary amino color developing agent in the presence of a DIR coupler (Component B), the DIR coupler reacts with color development oxidation product to form a diffusible mercaptan development inhibitor. The resulting diffusible developement inhibitor diffuses imagewise to the "spontaneously" developable emulsion (Component C) inhibiting development in regions corresponding to the latent image pattern (negative image area) formed in the light-sensitive emulsion. A DDR coupler (Component D) is contiguous to the developable metal salt of the "spontaneously" developable emulsion. The developable metal salt of the "spontaneously" developable emulsion in regions not inhibited against development by the diffusible development inhibitor (positive image area) develops and a diffusible acid dye is formed in such regions when the DDR coupler reacts with color development oxidation product. The resulting acid dye diffuses imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes to produce a positive color reproduction.

The Color-Forming Units are prepared so that the light-sensitive emulsion develops and a development inhibitor is released a finite time prior to the development of the "spontaneously" developable emulsion and the subsequent release of the diffusible dye. Such can be accomplished by physically disposing the light-sensitive emulsion (Component A) and the contiguous DIR coupler (Component B) further from the support than the "spontaneously" developable emulsion, by utilizing a silver halide emulsion having a shorter development induction period for the light-sensitive emulsion than the developable metal salt in the "spontaneously" developable emulsion, and/or by utilizing DIR couplers that react at a faster rate than the DDR couplers.

The DDR couplers are integral components of the present elements while the DIR couplers can be either integral components or used in the alkaline color developing solution. As integral components of the elements, the DIR coupler can either be incorporated in, or in a layer contiguous to, the light-sensitive emulsion, and the DDR coupler can be either incorporated in, or in a layer contiguous to, the "spontaneously" developable emulsion.

Photographic elements suitable for preparing correct full-color positive renditions can be prepared by utilizing three of the present Color-Forming Units wherein the light-sensitive emulsions are sensitive to red, green and blue light respectively, and the DDR couplers are couplers capable of forming diffusible acid dyes complementary to the color of the spectral sensitivity of the respective Color-Forming Units. However, false sensitization can also be utilized in preparing the present photographic elements.

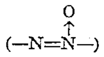
The DDR or diffusible dye-releasing couplers used in the photographic elements of the invention are initially nondiffusing in the layers of the element but form dyes diffusible in the layers of the element on reaction with oxidation product of aromatic primary amino silver halide photographic color developing agents. Such DDR couplers include those having the formulas:

DYE-LINK-(COUP-BALL)$_n$ and
BALL-LINK-(COUP-SOL)$_n$

wherein:

(1) DYE is a dye radical containing an acidic solubilizing radical;

(2) LINK is a connecting or linkage radical such as azo (—N=N—), azoxy



$$(-N=\overset{\overset{O}{\uparrow}}{N}-)$$

mercuri (—Hg—), oxy (—O—), alkylidene (includes both >CH— and =CH—), monothio (—S—), or dithio (—S—S—);

(3) COUP is a photographic color coupler radical such as a 5-pyrazolone coupler radical, a phenolic coupler radical or an open-chain ketomethylene coupler radical, the coupler radical being substituted in the coupling position with the connecting or linkage radical;

(4) BALL is a photographically inert organic radical of such molecular size and configuration as to render the coupler nondiffusing in the element in the alkaline color developing solution;

(5) SOL is either a hydrogen atom or an acidic solubilizing group when the color developing agent contains an acidic solubilizing radical, SOL always being an acidic solubilizing radical when the color developing agent is free of an acidic solubilizing group; and

(6) *n* is an integer of 1 or 2 when LINK is an alkylidene radical, and *n* is always 1 when LINK is one of the other aforementioned connecting radicals, namely, azo, azoxy, mercuri, oxy, thio, or dithio.

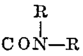
The acidic solubilizing radicals attached to the diffusible dye-releasing (DDR) couplers described above can be solubilizing radicals which when attached to the coupler or developer moieties of the dies, render the dyes diffusible in the element in alkaline processing solutions. Typical of such radicals are carboxylic, sulfonic, ionizable sulfonamido, and hydroxy-substituted groups that lend to dyes negative charges.

Typical dye radical substituents (DYE) of the DDR couplers include azo, azomethine, indoaniline, indophenol, anthraquinone and related dye radicals well known in the art that exhibit selective absorption in the visible spectrum. The dye radicals contain acidic solubilizing moieties.

When DDR couplers having the formula DYE-LINK-(COUP-BALL)$_n$ as described above are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a diffusible preformed acid dye (DYE) is released which diffuses imagewise to a reception layer. An acidic solubilizing group on the preformed dye lends diffusibility and mordantability to the dye molecule. The coupling portion of the DDR coupler (COUP) couples with color developing agent oxidation product to form a dye that is nondiffusible in the element because of the attached ballasting group (BALL) in a noncoupling position. In this type of DDR coupler, the color of the diffusible dye is determined by the color of the preformed dye moiety (DYE), the color of the reaction product of color developer oxidation product and the coupler moiety (COUP) being unimportant to the color of the diffusible image.

When DDR couplers having the formula BALL-LINK-(COUP-SOL)$_n$ as described above are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a diffusible dye is formed with the color developing agent oxidation product and the coupling portion (COUP) of the DDR coupler which diffuses imagewise to a reception layer. Diffusibility is imparted to the dye by an acidic solubilizing group attached to a noncoupling position of the coupling portion (COUP) of the DDR coupler or to the color developing agent. The ballast portion of the DDR coupler remains immobile. In this type of DDR coupler, the color of the diffusible dye is determined by the color of the reaction product of color developer oxidation product and the coupler moiety (COUP).

When the coupler radical (COUP) in the DDR couplers is a 5-pyrazolone radical, we prefer to have substituted in the 3-position of the pyrazolone moiety an analino group or an alkoxy group. When the coupler radical (COUP) in the DDR couplers is a cyan-forming phenolic coupler radical, we prefer to have substituted in the ortho or 2-position of the phenolic moiety a fully substituted amido group (e.g.,



$$-CO\overset{\overset{R}{|}}{N}-R$$

wherein R is an alkyl group or a phenyl group). Also, when the connecting radical (LINK) in the DDR couplers having the formula, BALL-LINK-(COUP-SOL)$_n$, is an azo radical, we prefer that the ballasting radical (BALL) be a phenyl radical containing either a hydroxy group or an amino group (—NH$_2$) substituted in the ortho or 2-position of the phenyl moiety.

The DIR or development inhibitor-releasing couplers used in the photographic elements of the invention release or form development inhibitors that are diffusible in the layers of the Color-Forming Unit on reaction with oxidation product of aromatic primary amino silver halide photographic color developing agents. When the DIR couplers are utilized integral with the present photographic elements, ballasting groups are used to make the coupler nondiffusible in the layers of the Color-Forming Unit in alkaline color developing solutions. Such ballasted DIR couplers are preferred. When the DIR couplers are utilized in the color developing solution, the DIR couplers are free of ballasting groups and are diffusible in the layers of the element in alkaline color developing solutions. DIR couplers of the invention include those having the formulas:

(BALL-COUP)$_n$-LINK-MERC and
(BALL)$_m$-COUP-S-RAD

wherein:

(1) BALL is a ballast group as described above for the DDR couplers;

(2) LINK is a connecting or linkage radical as described above for the DDR couplers;

(3) *m* is an integer of 0 or 1;

(4) *n* is an integer of 1 or 2 as described above for the DDR couplers;

(5) COUP is a photographic color coupler radical as described above for the DDR couplers;

(6) MERC is a diffusible radical containing a mercapto radical (—SH); and

(7) RAD is a photographically inert, diffusible radical that forms a mercaptan with the monothio connecting or linkage radical (—S—).

A wide variety of photographically inert radicals that are diffusible in the layers of the Color-Forming Unit and form mercaptans with the monothio connecting or linkage radical when the connecting radical is split on development can be used for the RAD substituent of the DIR couplers. Typical of such radicals are aryl, alkaryl and carbon-containing heterocyclic radicals. The aryl moiety of such radicals is preferably phenyl, and includes such substituents as nitro, lower alkyl, lower alkylamido, lower alkoxy, lower alkylsulfoamido, lower alkylcarbamyl, carbon-containing heterocyclic radicals and the like. The carbon-containing heterocyclic radicals, which can be attached directly to the monothio linkage radical or as a substituent on the described aryl moieties, generally contain at least one hetero nitrogen, oxygen or sulfur atom, and preferably, 1 to 4 hetero nitrogen atoms. The hetero nitrogen atoms in the heterocyclic radicals have no hydrogen atom attached thereto as the RAD radical is photographically inert. Illustrative carbon-containing heterocyclic radicals include 1-phenyltetrazolyls, oxazolyls, oxadiazolyls, diazolyls, thiadiazolyls, benzoxazolyls, benzothiazolyls, pyrimidyls, pyridinyls, quinolinyls and the like.

MERC is a preformed mercapto development inhibiting moiety. A wide variety of diffusible radicals containing a mercapto radical (—SH) can be used for the MERC substituent of the DIR couplers. The mercapto radical can be suitably attached to an aryl, alkaryl or a carbon-containing heterocyclic radical such as RAD described above except that it is not necessary that the hetero nitrogen atoms on the heterocyclic radicals be free of hydrogen atoms.

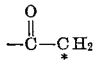
When the DIR couplers are used integral with the photographic element, a ballast group (BALL) is utilized and *m* is 1; and when the DIR couplers are used in the processing solution, such a ballast group is not utilized and *m* is 0. The DIR couplers containing preformed development-inhibiting moieties (MERC) are ballasted and always utilized integral with the photographic element. When DIR couplers are utilized in the processing solution, the "spontaneously" developable emulsions (Component C) are prepared to have longer development induction periods than the light-sensitive silver halide emulsions.

When DIR couplers having the formula $(\text{BALL-COUP})_n$-LINK-MERC are reacted with oxidized color developing agent, the connecting radical (LINK) is split and a mercaptan development inhibitor (MERC) is released that is diffusible in the Color-Forming Unit. A ballasted or immobile dye is formed by reacting the coupler moiety (COUP) at the coupling position with oxidized color developing agent. The connecting radical (LINK) is preferably an azo (—N=N—) or a monothio (—S—) radical in this type of DIR coupler. As such DIR couplers are preformed development inhibitors, they are utilized in a layer adjacent to the light-sensitive silver halide emulsion layer of the present Color-Forming Units.

When DIR couplers having the formula $(\text{BALL})_m$-COUP-S-RAD are reacted with oxidized color developing agent, the connecting thio connecting or linkage radical (S) is split from the coupling position of the coupler moiety (COUP) and a mercaptan development inhibitor is formed that is diffusible in the Color-Forming Unit. When *m* is one, a ballasted or immobile dye is formed by reacting the coupler moiety (COUP) at the coupling position with oxidized color developing agent. When *m* is zero, a nondiffusible or a nonmordantable dye is formed by reacting the coupler moiety (COUP) at the coupling position with oxidized color developing agent, both the DIR coupler and the color developing agent being free of acidic solubilizing groups when *m* is zero and the dye formed is diffusible. The substituent, *m*, is preferably one, and such DIR couplers can be utilized either in the light-sensitive emulsion or in a layer adjacent thereto in the present Color-Forming Units.

The nature of the ballast groups (BALL) in the DIR and DDR coupler compounds described above is not critical as long as they confer nondiffusibility to the coupler compounds. Typical ballast groups exemplified hereinafter in the specific couplers disclosed include long chain alkyl radicals or several short chain alkyl radicals having e.g., 8–22 carbon atoms, linked directly or indirectly to the coupler molecules, as well as aromatic radicals of the benzene and naphthalene series, etc., linked directly or indirectly to the coupler molecules by a splittable linkage, or by a removable or irremovable but otherwise nonfunctional linkage depending upon the nature of the coupler compound. Useful ballast groups generally have at least 8 carbon atoms.

Wtih regard to the above-described coupler radicals (COUP) in the DIR and DDR couplers, the "coupling position" is well known to those skilled in the photographic art. The 5-pyrazolone coupler radicals couple at the carbon atom in the 4-position, the phenolic coupler radicals, including α-napthols, couple at the carbon atom in the 4-position and the open-chain ketomethylene coupler radicals couple at the carbon atom forming the methylene moiety (e.g.,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{*}{C}H_2-$$

* denoting the coupling position).

The term "nondiffusing" used herein as applied to the couplers and coupler reaction products, has the meaning commonly applied to the term in color photography and denotes materials which for all practical purposes do not migrate or wander through organic colloid layers, such as gelatin, comprising the sensitive elements of the invention. The term "diffusible" as applied to the mercaptan development inhibitors released from the DIR couplers and the dyes released from the DDR couplers in the present processes has the converse meaning and denotes materials having the property of diffusing effectively through the colloid layers of the sensitive elements in the presence of the "nondiffusing" materials from which they are derived in alkaline color developing solutions.

The silver halide emulsions of the present photographic elements are conventional developing-out photographic silver halide emulsions including silver chloride, silver bromide, silver bromoiodide, silver chlorobromide and silver chlorobromoiodide emulsions. There can be employed as the dispersing agent or substrate for the silver halide in its preparation, gelatin or some other commonly employed photographic hydrophilic colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, although gelatin is preferred. Such hydrophilic colloidal materials can also be used in the non-light-sensitive layers in the subject elements in accordance with usual practice. Such hydrophilic collids are well known in the art.

The subject photographic emulsions can contain the addenda generally utilized in such products including optical sensitizers, speed-increasing materials, antifoggants, coating aids, gelatin hardeners, plasticizers, ultraviolet, absorbers and the like.

As described above, each Color-Forming Unit in the photographic elements of the invention contains, in addition to a light-sensitive silver halide emulsion (Component A), an emulsion of a water-insoluble metal salt that is developable (i.e., reducible to metal) with alkaline color developing solutions containing aromatic primary amino color developing agents to a substantial density without light exposure of the element (Component C). Such metal salts are preferably such water-insoluble light-sensitive silver salts such as silver chloride, silver bromide, silver iodide, silver bromoiodide, silver chlorobromoiodide, silver citrate, silver oxalate, silver phosphate, silver stearate, silver ferrocyanide, silver cyanide, silver thiocyanate and the like. Other useful salts include palladium bromide, palladium cyanide and related heavy metal salts, as well as cuprous bromide and the like. Such metal salts can be made "spontaneously" developable by incorporating in the emulsion a wide variety of well-known physical development nuclei. Typical development nuclei include colloidal noble metals such as silver and gold; colloidal metal sulfides, selenides and tellurides such as lead sulfide, nickel sulfide, cadmium sulfide, silver sulfide, silver selenide, silver telluride, copper sulfide, zinc sulfide and mercury sulfide; metal proteinates such as silver proteinates; sodium sulfide; colloidal sulfur; and such organic sulfur compounds as thiourea, and xanthates. Conventional developer solvents for the metal salts are utilized in the developing compositions when the physical development nuclei are employed to make the emulsions "spontaneously" developable, including ammonium and alkali metal thiosulfates, thiocyanates, sulfites and the like. Another method that can be utilized to make the light-sensitive, water-insoluble salts "spontaneously" developable is by prefogging the emulsion with light or with chemical reducing agents such as alkali metal borohydrides and the like in accordance with well-known photographic fogging techniques.

A wide variety of alkaline color developing solutions containing aromatic primary amino color developing agents can be utilized to process the present photographic elements. Such developing solutions are utilized to develop or reduce to silver the exposed silver halide in the light-sensitive emulsions (Component A) to form a negative image, and to develop or reduce to a metal the metal salt in the "spontaneously" developable emulsion (Component C) to form a positive image. Particularly useful developing agents are the well-known p-phenylenediamine color developing agents. The color developing agent can be either incorporated in an alkaline photographic developing solution that is topically applied to the present photographic elements on processing, or the color developing agent can be incorporated in the element.

When the color developing agent is used in the present photographic elements it is advantageous to use forms that have substantial stability in emulsions such as Schiff base derivatives of primary amino developing agents. Such Schiff bases are prepared by reacting primary amino developing agents with sulfonated, hydroxylated or carboxylated aromatic aldehydes of the benzene or naphthalene series. Such Schiff bases typically have the formula $R—N=CH—R'$ wherein R is an aryl radical such as a phenyl radical substituted in the ortho or para position with a hydroxyl group or an amino group (e.g., $—OH$, $—NH_2$, $—NHR''$ or $—N(R'')_2$ wherein R″ is a lower alkyl radical having 1 to 6 carbon atoms); and R′ is an aryl radical such as phenyl or naphthyl substituted with an acidic group such as carboxyl, sulfo, and hydroxy lower alkyl groups. A typical Schiff base color developing agent can be prepared by reacting 2-amino-5-diethylaminotoluene and o-sulfobenzaldehyde. Other Schiff base developers that are useful as such, as salts or as sulfur dioxide complexes include:

(1) N - ethyl-N-(β-hydroxyethyl)-4-(o-sulfobenzylideneamino)aniline sodium salt,
(2) N,N - diethyl-4-(2,4-dihydroxybenzylideneamino)-3-methylaniline, and
(3) N - ethyl-3-methyl-N-(β-methylsulfonamidoethyl)-4-(2-sulfobenzylideneamino)aniline sodium salt.

Such incorporated developing agents can be activated by immersing the photographic element in an aqueous alkaline solution or by spreading an aqueous alkaline solution on the surface of the element. Such incorporated developing agents can be positioned in any layer of the present photographic elements from which the developing agents can be readily made available for development on activation with aqueous alkaline solutions. Generally, such incorporated developing agents are either incorporated in the light-sensitive silver halide emulsion layers or in layers contiguous thereto.

Typical supports comprising the photographic elements of the invention 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.

In preparing the photographic elements of the invention, the above-described emulsion layers are coated on the photographic supports in the form of multilayer color photographic elements having at least two and preferably three Color-Forming Units sensitive to different regions of the visible spectrum. The uppermost Color-Forming Unit is preferably selectively sensitive to blue light. Between the blue light-sensitive Color-Forming Unit and the other Color-Forming Units there is typically disposed a yellow dye layer or Carey Lea silver layer for absorbing or filtering blue radiation that may be transmitted through the uppermost blue sensitive layer. However, the physical disposition of the red, green and blue light-sensitive Color-Forming Units within the present photographic elements can be widely varied in accordance with usual practice. Such multilayer photographic elements can also have other interlayers or sublayers for specialized purposes in accordance with usual practice.

In another embodiment of the invention, each Color-Forming Unit can be a single layer. The DIR coupler and the light-sensitive silver halide emulsion (Component A) can be substantially uniformly dispersed in packets in the "spontaneously" developable emulsion containing the DDR coupler. Alternatively, the DDR coupler and the "spontaneously" developable emulsions can be substantially uniformly dispersed in packets in the light-sensitive silver halide emulsion containing the DIR coupler. Reference is made to Godowsky, U.S. Patent 2,698,794 and Van Campen et al., U.S. Patent 2,763,552 for suitable methods for preparing silver halide-color coupler packets and dispersing couplers. In such Color-Forming Units, the "spontaneously" developable emulsions are more generally prepared to have longer development induction periods than the light-sensitive silver halide emulsions. Alternatively, DIR couplers having faster reaction rates than the DDR couplers can be utilized in light-sensitive emulsion packets containing the DIR couplers.

Barrier layers are used between each Color-Forming Unit to ensure that the activity of the development inhibiting mercapto compounds released by the DIR couplers are confined to a single Color-Forming Unit. Hence, the barrier layers contain a water-insoluble salt or metal capable of forming a water-insoluble salt with mercaptans, silver halides such as silver chloride, silver bromide, silver iodide, silver bromoiodide, silver chlorobromoiodide, etc., being preferably used. Other compounds suitable for use in the present barrier layers that react with mercaptans include colloidal metals such as silver and gold; and colloidal metal sulfides, selenides and tellurides such as lead sulfide, nickel sulfide, cadmium sulfide, silver sulfide, copper sulfide, zinc sulfide, mercury sulfide, silver selenide, silver telluride and the like. The barrier layers containing light-sensitive silver salts are prepared to be substantially less sensitive to light than the light-sensitive emulsions in the Color-Forming Units. Such barrier layers also serve to prevent oxidized color developing agent from wandering from one Color-Forming Unit to another where it could cause color contamination. Antioxidants such as n-octadecyl hydroquinone and the like phenolic antioxidants, and nondiffusible photographic color couplers that form nondiffusible dyes on coupling with oxidized aromatic amino color developing agents can be utilized in the barrier layers to prevent wandering of such oxidized color developing agent.

The reception layer used to receive the diffused dye images on color development of the photoelements of the invention can be either a separate sheet pressed in contact with the photoelement or a layer integral with the photoelement.

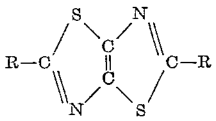
When the reception layer is a separate reception sheet, the development and transfer operations can be effected by bathing either or both the exposed photographic element and the mordanted reception sheet in the developing solution before rolling into contact with each other.

Alternatively, a viscous developing composition can be placed between the elements for spreading in a predetermined amount across and in contact with the exposed surface of the sensitive element so as to provide all of the solution required for the picture area. The viscous developing composition is desirably utilized in one or more pods integral with the photoelement or the reception sheet that can be readily ruptured when development is desired, suitable viscous developer utilization techniques being disclosed in U.S. Patents 2,543,181; 2,559,643; 2,647,049; 2,647,056; 2,661,293; 2,698,244; 2,698,798; and 2,774,668.

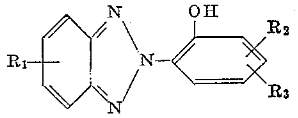
When the reception layer for receiving the diffusible dye is an integral part of the photosensitive assembly it is also useful. A typical element of this type can comprise a support, a mordanted colloid layer thereon and the various emulsion layers described above coated thereover. When easily dissolved emulsions are used such as those containing polyvinyl alcohol or an alkali-soluble cellulose ether phthalate vehicles, or a wet or dry stripping layer containing such vehicles is provided between the emulsions and reception layer, the developed emulsion layers can then be readily separated from the reception layer leaving the dye image thereon. Similarly, the reception layer can be initially bonded to the outer emulsion surface. In this case, it is preferred to expose through the support of the sensitive element unless the reception layer itself is transparent. Such photoelements can be processed in the same manner as those not containing integral reception layers.

The reception layers in the photoelements of the invention can contain any of the conventional mordant materials for acid dyes. The reception layer can contain mordants such as polymers of amino guanidine derivatives of vinyl methyl ketone described in the Minsk U.S. Patent 2,882,156 granted April 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 October 11, 1949 and cetyl trimethylammonium bromide, etc. Particularly effective mordanting compositions are described in copending applications of Knechel et al., U.S. Serial No. 211,095 filed July 19, 1962, and Bush, U.S. Serial No. 211,094 filed July 19, 1962. The mordanting compositions described in the Knechel et al. application comprise at least one hydrophilic organic colloid containing a finely-divided, uniform dispersion of droplets or globules of a high-boiling, water-immiscible organic solvent in which is dissolved a high concentration of a cationic, nonpolymeric, organic dye-mordanting compound for acid dyes. The mordanting compositions described in the Bush application comprise at least one hydrophilic organic colloid containing a finely-divided, uniform dispersion of particles of a salt of an organic acidic composition containing free acid moieties and a cationic, nonpolymeric, organic dye-mordanting compound for acid dyes. Useful cationic or basic organic dye-mordanting compounds for acid dyes include quaternary ammonium and phosphonium, and ternary sulfonium compounds in which there is linked to the N, P, or S onium atom at least one hydrophobic ballast group such as long-chain alkyl or substituted alkyl groups. Furthermore, the reception layer or sheet can be sufficient by itself to mordant the dye as in the case of the use of a sheet or layer of a polyamide or related polymeric material.

Reception sheets for the dye images, as well as the photoelements of the invention can contain ultraviolet absorbing materials. In the reception sheets, ultraviolet absorbers protect the mordanted dye images from fading and print-out due to ultraviolet light. In the photoelements, ultraviolet absorbers can serve as taking filters to reduce ultraviolet sensitivity. Typical ultraviolet absorbing materials are described in copending applications of Sawdey, U.S. Serial Nos. 144,228 filed October 10, 1961 and 183,417 filed March 29, 1962. Illustrative useful ultraviolet absorbing materials disclosed by Sawdey have the formulas



and



wherein: R is a phenyl radical including such substituents as hydrogen atoms, halogen atoms, alkyl radicals, alkoxy radicals or hydroxy radicals; and R_1, R_2 and R_3 are hydrogen atoms, halogen atoms, nitro radicals, alkyl radicals, alkoxy radicals, aryl radicals or aryloxy radicals. Other ultraviolet absorbing materials well known in the photographic art can also be utilized.

If desired, a "keep-negative" as well as a positive color transfer print can be prepared. In preparing such a color negative, a conventional photographic color coupler of the type that forms a nondiffusible dye when reacted with oxidized color coupler is utilized with the DIR coupler. In this embodiment, DDR couplers are chosen that do not form colored nondiffusible dyes during the present process. Further, the DIR couplers are chosen so that the dyes which are formed are either diffusible or have absorptions similar to those of the respective "keep-negative" nondiffusible couplers. Also, the reception layer used to receive the diffused positive dye image is a separate receiving sheet not integral with the element. After the positive image is transferred to the receiving sheet, the remaining negative element is fixed in hypo to remove unexposed silver halide and bleached (i.e., with an alkali metal ferricyanide) to remove silver. Suitable photographic color couplers that form nondiffusible dyes are of the phenolic, 5-pyrazolone and open-chain ketomethylene type such as those disclosed in Spence et al., U.S. Patent 2,640,776; Weissberger et al., U.S. Patent 2,407,210; and Weissberger et al., U.S. Patent 2,474,293.

The drawings illustrate in section and in elevation typical photographic elements of the invention.

FIG. 1 illustrates a typical photographic element of the invention wherein the DIR or development inhibitor-releasing coupler is positioned in a layer contiguous to the light-sensitive silver halide emulsion and the "spontaneously" developable emulsion comprises a fogged silver halide emulsion in each Color-Forming Unit.

FIG. 2 illustrates a typical photographic element of the invention wherein the DIR coupler is positioned in the light-sensitive silver halide emulsion and the "spontaneously" developable emulsion comprises a fogged silver halide emulsion in each Color-Forming Unit.

FIG. 3 illustrates a typical photographic element of the invention in which each Color-Forming Unit is a single layer wherein packets of silver halide and the DIR coupler are dispersed in a fogged silver halide emulsion containing the DDR or diffusible dye-releasing couplers. FIG 3 includes an enlarged section of one Color-Forming Unit.

FIG. 4 illustrates a typical photographic element of the invention wherein the DIR coupler is positioned in the light-sensitive silver halide emulsion and the "spontaneously" developable emulsion comprises a nucleated metal salt in each Color-Forming Unit.

FIG. 5 illustrates a typical photographic element of the invention similar to that of FIG. 4 except that an integral mordanted reception layer is present as well as a stripping layer to facilitate the removal of the Color-Forming Units after processing.

With respect to FIG. 1, on photographic support **10** are coated three Color-Forming Units of the invention that are sensitive to a different region of the visible spectrum. On support **10** is coated fogged silver halide emulsion layer **11** containing a magenta-forming DDR coupler. Over layer **11** is coated development-inhibiting layer **12** containing a DIR coupler. To complete the Color-Forming Unit nearest the support, silver halide emulsion layer **13** that is sensitive to green light is coated over layer **12**. Over the green-sensitive layer **13** is coated barrier layer **14** that contains a compound capable of forming an insoluble salt with mercaptans such as a silver halide. As described above, such barrier layers can contain antioxidants or nondiffusible color couplers that form insoluble dyes on reaction with oxidized color developing agent, such addenda serving to minimize wandering of oxidized color developer and thus reducing color fog. Over barrier layer **14** is coated fogged silver halide emulsion layer **15** containing a cyan-forming DDR coupler. Over layer **15** is coated development inhibitor layer **16** containing a DIR coupler. To complete the second Color-Forming Unit, silver halide emulsion layer **17** that is sensitive to red light is coated over layer **16**. Barrier layer **18** containing a compound capable of forming an insoluble salt with mercaptans and a filter for blue light such as a yellow coupler, a yellow dye or Carey Lea silver is coated over layer **17**. Over barrier layer **18** is coated fogged silver halide emulsion layer **19** containing a yellow-forming DDR coupler. Over layer **19** is coated development inhibiting layer **20** containing a DIR coupler. To complete the third Color-Forming Unit, silver halide emulsion layer **21** that is sensitive to blue light is coated over layer **20**. A layer of a hydrophilic colloid such as protective layer **22** is coated on layer **21**.

With respect to FIG. 2, on photographic support **30** are coated three Color-Forming Units of the invention that are sensitive to different regions of the visible spectrum. On support **30** is coated fogged silver halide emulsion layer **31** containing a magenta-forming DDR coupler. Over layer **31** is coated silver halide emulsion layer **32** that is sensitive to green light and contains a DIR coupler. Over layer **32** is coated barrier layer **33** containing a compound capable of forming an insoluble salt with mercaptans. Over layer **33** is coated fogged silver halide emulsion layer **34** containing a cyan-forming DDR coupler. Over layer **34** is coated silver halide emulsion layer **35** that is sensitive to red light and contains a DIR coupler. Next, barrier layer **36** containing a compound capable of forming an insoluble salt with mercaptans and a yellow filter material is coated. Over layer **36** is coated fogged silver halide emulsion layer **37** containing a yellow-forming DDR coupler. Over layer **37** is coated silver halide emulsion layer **38** that is sensitive to blue light and contains a DIR coupler. Over layer **38** is coated protective layer **39**.

In FIG. 3, each Color-Forming Unit comprises a single layer, namely layers **41**, **43** and **45** that are sensitive to different regions of the visible spectrum. On support **40** is coated Color-Forming Unit **41** which comprises fogged silver halide emulsion **47** containing a magenta-forming DDR coupler and dispersed therein packets **46** comprising a silver halide emulsion that is sensitive to green light and contains a DIR coupler. Over layer **41** is coated barrier layer **42** containing a compound capable of forming an insoluble salt with mercaptans. Over layer **42** is coated a Color-Forming Unit, layer **43**, that is sensitive to red light similar to that described for layer **41** except the fogged silver halide emulsion contains a cyan-forming DDR coupler and the packets comprise a silver halide emulsion sensitive to red light and a DIR coupler. Over layer **43** is coated barrier layer **44** containing a compound capable of forming an insoluble salt with mercaptans and a yellow filter-material. Over layer **44** is coated layer **45** which is a Color-Forming Unit sensitive to blue light similar to that described for layer **41** except that the fogged silver halide emulsion contains a yellow-forming DDR coupler and the packets comprise a silver halide emulsion sensitive to blue light and a DIR coupler.

In FIG. 4, over photographic support **50** are coated three Color-Forming Units of the invention that are sensitive to different regions of the spectrum. Over support **50** is coated nucleated metal salt layer **51** containing a cyan-forming DDR coupler. Over layer **51** is coated a silver halide emulsion that is sensitive to red light and a DIR coupler. Over layer **52** is coated barrier layer **53** containing a compound capable of forming an insoluble salt with mercaptans. Over layer **53** is coated nucleated metal salt layer **54** containing a magenta-forming DDR coupler. Over layer **54** is coated silver halide emulsion layer **55** that is sensitive to green light and DIR coupler. Over layer **55** is coated barrier layer **56** containing a compound capable of forming an insoluble salt with mercaptans and a yellow filter material. Over layer **56** is coated nucleated metal salt layer **57** containing a yellow-forming DDR coupler. Over layer **57** is coated a silver halide emulsion layer **58** that is sensitive to blue light and a DIR coupler.

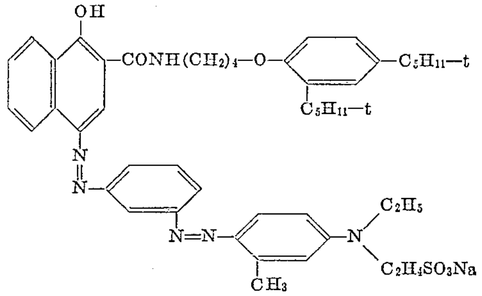
With respect to FIG. 5, on photographic support **60** is coated mordanted reception layer **61** containing a mordant for acid dyes. Over layer **61** is coated stripping layer **62** that serves to separate mordanted reception layer **61** from the light-sensitive and coupler-containing layers. On color development, the diffusible acid dyes produced on reacting oxidized color developing agent with DDR couplers diffuse imagewise in register to mordanted reception layer **61**. Thereafter, stripping layer **22**, along with all layers coated thereover, can be readily removed leaving a positive color image on supported reception layer **61**. Over stripping layer **62** are coated layers **63** to **70** which correspond to layers **51** to **58** of FIG. 4, respectively described above.

The following are representative DDR couplers of the invention, to wit, nondiffusible coupler compounds that release or form diffusible acid dyes on coupling with the oxidation products of color developing agents.

Couplers I to X below are substituted in the coupling position with preformed yellow dyes that are split from the ballasted couplers and become diffusible when said couplers react with oxidized color developers.

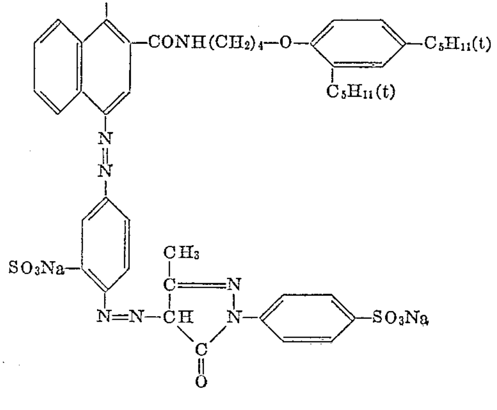
1-hydroxy-4-{3-[4-(N-ethyl-N - β - sulfoethylamino)2-methylphenylazo]phenylazo}-N-[δ-(2,4-di - tert - amylphenoxy)butyl]-2-naphthamide sodium salt.

I.



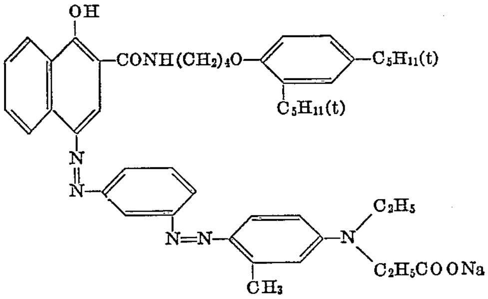
1-hydroxy-4-{4-[1-(4-sulfophenyl) - 3 - methyl-4-pyrazol-5-onylazo]-3-sulfophenylazo}-N-[δ-(2,4 - di - tert-amylphenoxy)butyl]-2-naphthamide disodium salt.

II.



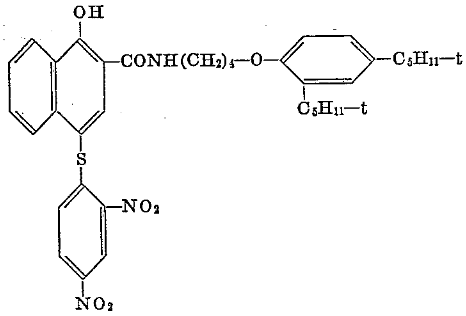
1-hydroxy-4-{3-[4-(N-ethyl - N - β - carboxyethylamino)-2-methylphenylazo]phenylazo} - N - [δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide sodium salt.

III.



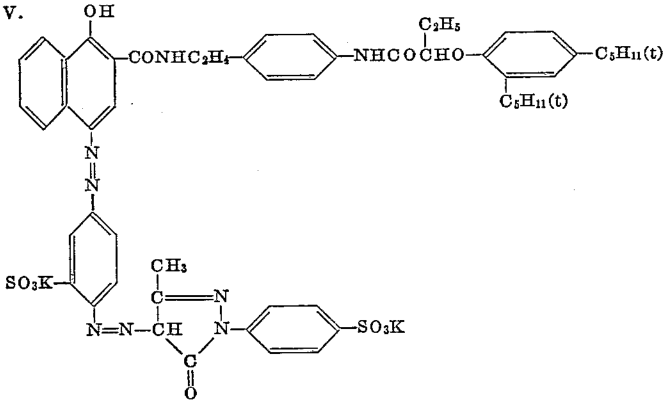
1-hydroxy-4-(2,4-dinitrophenylthio) - N - [δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide.

IV.



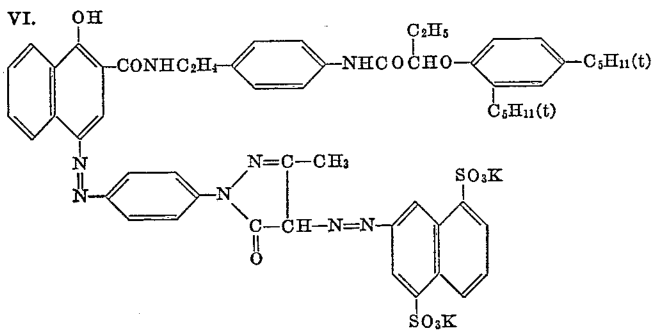
1-hydroxy-4-{4-[1-(4-sulfophenyl) - 3 - methyl-4-pyrazol-5-onylazo]-3 - sulfophenylazo} - N - {4-[α-(2,4-di-tert - amylphenoxy)butyramido]phenethyl} - 2 - naphthamide dipotassium salt.

V.



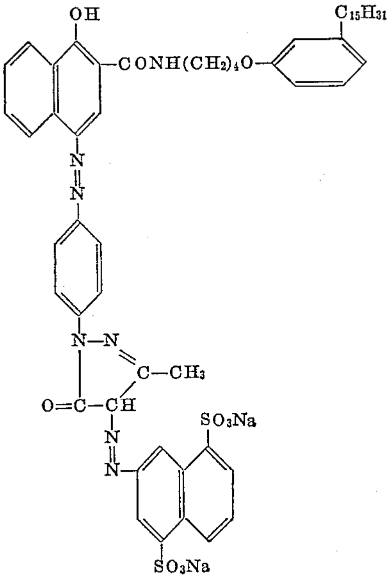
1-hydroxy-4-{4-[3 - methyl - 4 - (1,5-disulfo-3-naphthylazo)-1-pyrazol - 5 - onyl]phenylazo}-N-{4-[α-(2,4-di-tert-amylphenoxy)butyramido]phenethyl} - 2 - naphthamide dipotassium salt.

VI.



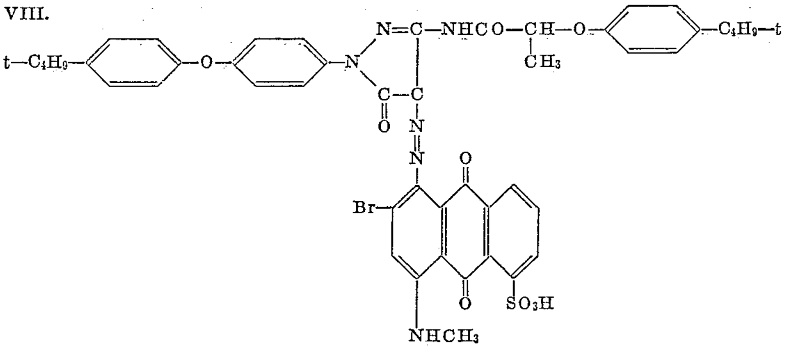
1 - hydroxy - 4 - {4 - [3-methyl - 4 - (1, 5 - disulfo-3 - naphthylazo) - 1 - pyrazol - 5 - onyl]phenylazo}-N-[δ - (3 - pentadecylphenoxy)butyl] - 2 - naphthamide disodium salt.

VII.



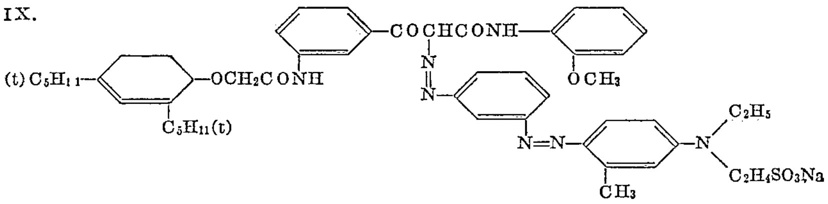
1 - (p - t - butylphenoxyphenyl) - 3 - [α - (4 - t - butylphenoxy)propionamido] - 4 - (2 - bromo - 4 - methylamino - 5 - sulfo - 1 - anthra - 9, 10 - quinonylazo) - 5 - pyrazolone.

VIII.



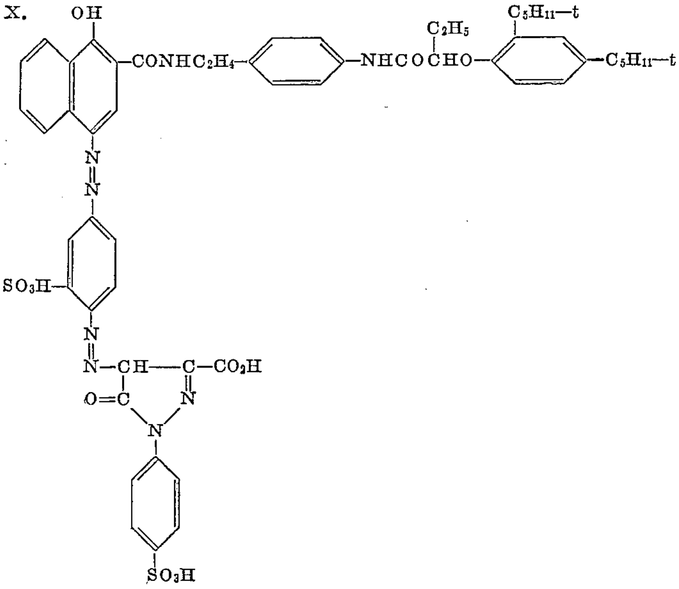
α - {3 - [α - (2, 4 - di - tert - amylphenoxy)acetamido] benzoyl} - α - {3[4 - (N - ethyl - N - β - sulfoethylamino) - 2 - methylphenylazo]phenylazo} - 2 - methoxyacetanilide sodium salt.

IX.



1 - hydroxy - 4 - {4 - [1 - (4 - sulfophenyl) - 3 - carboxy - 4 - pyrazol - 5 - onyl - azo] - 3 - sulfophenylazo}- N - {4 - [α - (2, 4 - di - tert - amylphenoxy) butyramido] phenethyl} - 2 - naphthamide.

X.

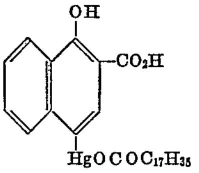


Each of the Couplers XI to XLVI below contain an acid solubilizing group in a noncoupling position and on coupling with oxidized color developer forms a diffusible dye by the elimination of a ballasting group from the coupling position as a direct result of said coupling reaction.

Couplers XI to XXIX below form diffusible cyan dyes.

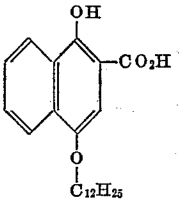
1 - hydroxy - 4 - stearoyloxymercuri - 2 - naphthoic acid.

XI.



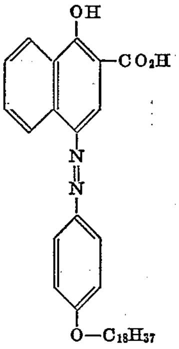
1 - hydroxy - 4 - dodecyloxy - 2 - naphthoic acid.

XII.



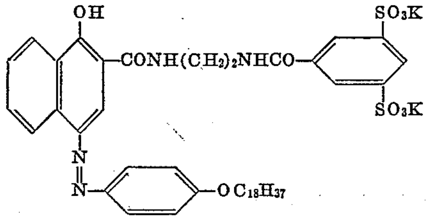
1 - hydroxy - 4 - (4 - octadecyloxyphenylazo) - 2-naphthoic acid.

XIII.



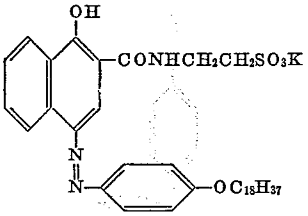
1 - hydroxy - 4 - (4 - octadecyloxyphenylazo) - N - [β-(3,5 - disulfobenzamido)ethyl] - 2 - naphthamide dipotassium salt.

XIV.



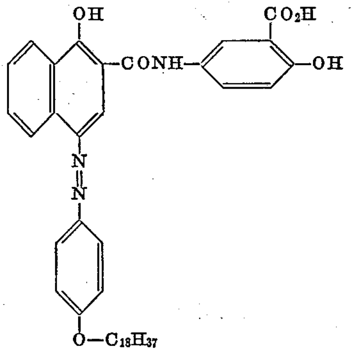
1 - hydroxy - N - (β - sulfoethyl) - 4 - (4 - octadecyloxyphenylazo)-2-naphthamide potassium salt.

XV.



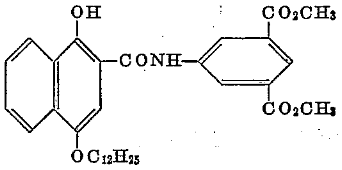
1 - hydroxy - 4 - (4 - octadecyloxyphenylazo) - 3′-carboxy-4′-hydroxy-2-naphthanilide.

XVI.



1 - hydroxy - 3′,5′ - dicarbomethoxy - 4 - dodecyloxy-2-naphthanilide.

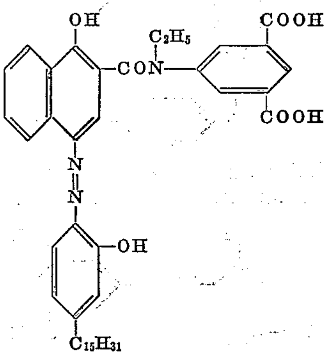
XVII.



(Hydrolize to acid while dispersing)

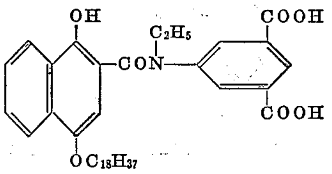
1 - hydroxy - 4 - (2 - hydroxy - 4 - pentadecyl phenylazo)-N-ethyl-3′,5′-dicarboxy-2-naphthanilide.

XVIII.



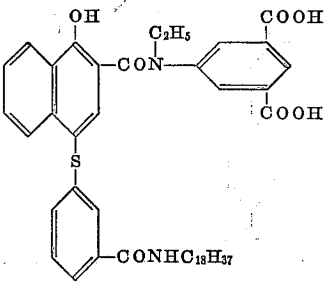
1 - hydroxy - 4 - octadecyloxy - N - ethyl - 3′,5′ - dicarboxy-2-naphthanilide.

XIX.



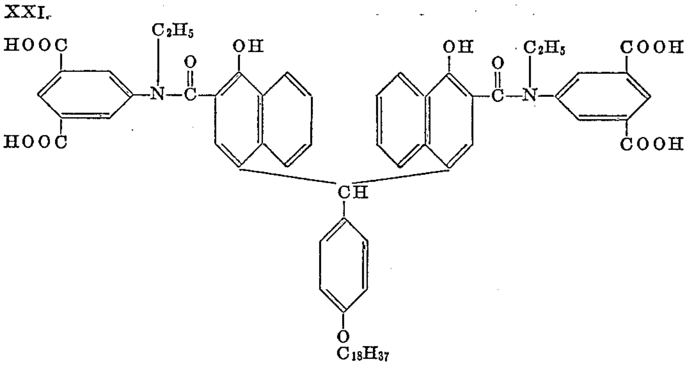
1 - hydroxy - 4 - (3 - octadecylcarbamylphenylthio)-N-ethyl-3′,5′-dicarboxy-2-naphthanilide.

XX.



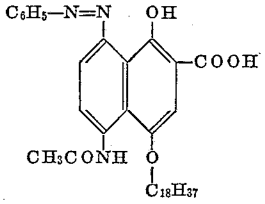
4,4′ - p - octadecyloxybenzylidenebis(1 - hydroxy - N-ethyl-3′,5′-dicarboxy-2-naphthanilide).

XXI.



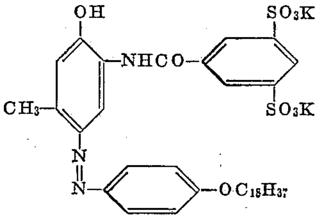
1-hydroxy-5-acetamido-4-octadecyloxy-8-phenylazo-2-naphthoic acid.

XXII.



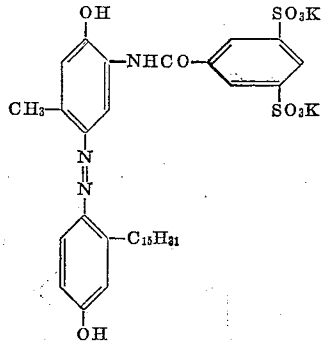
2-(3,5-disulfobenzamido)-5-methyl-4-(4-octadecyloxyphenylazo)phenol dipotassium salt.

XXIII.



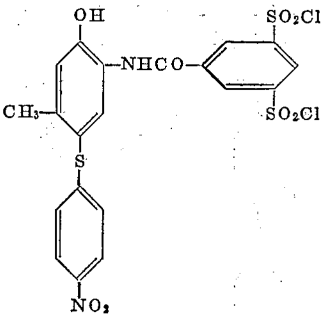
2-(3,5-disulfobenzamido)-4-(4-hydroxy-2-pentadecylphenylazo)-5-methylphenol dipotassium salt.

XXIV.



2-(3,5-dichlorosulfonylbenzamido)-5-methyl-4-(4-nitrophenylthio)phenol.

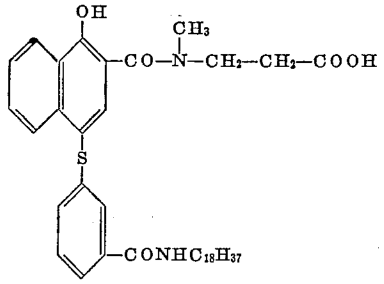
XXV.



(Hydrolyze to acid while dispersing)

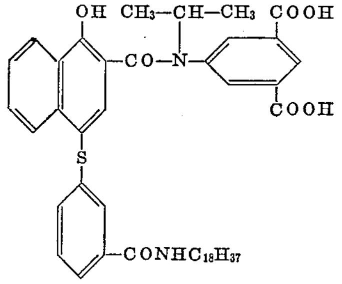
1-hydroxy-4-(3-octadecylcarbamylphenylthio)-N-methyl-N-(β-carboxyethyl)-2-naphthamide.

XXVI.



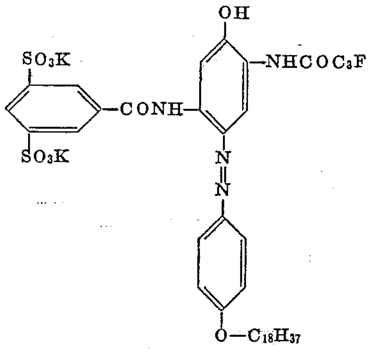
1-hydroxy-4-(3-octadecylcarbamylphenylthio)-N-isopropyl-3′,5′-dicarboxy-2-naphthanilide.

XXVII.



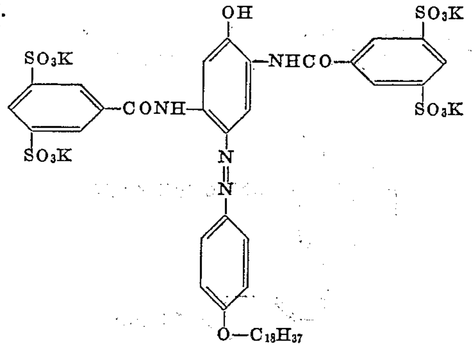
5-(3,5-disulfobenzamido)-4-(4-octadecyloxyphenylazo)-2-heptafluorobutyramidophenol dipotassium salt.

XXVIII.



2,5-bis(3,5-disulfobenzamido)-4-(4-octadecyloxyphenylazo)phenol tetra potassium salt.

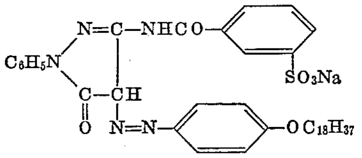
XXIX.



Couplers XXX to XLI below form diffusible magenta dyes.

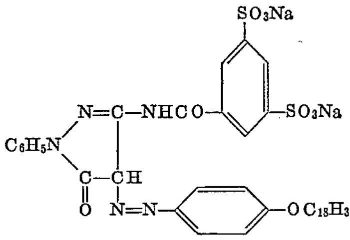
1 - phenyl - 3 - (3-sulfobenzamido)-4-(4-octadecyloxyphenylazo)-5-pyrazolone sodium salt.

XXX.



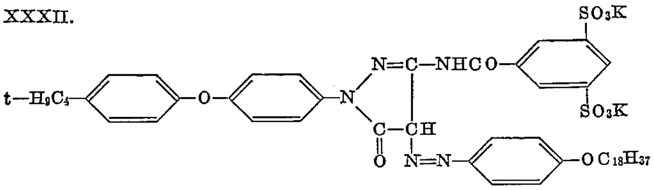
1 - phenyl-3-(3,5-disulfobenzamido)-4-(4-octadecyloxyphenylazo)-5-pyrazolone disodium salt.

XXXI.



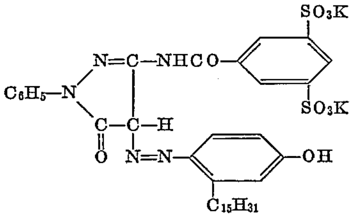
1 - [4 - (4-t-butylphenoxy)phenyl]-3-(3,5-di-sulfobenzamido) - 4-(4-octadecyloxyphenylazo)-5-pyrazolone dipotassium salt.

XXXII.



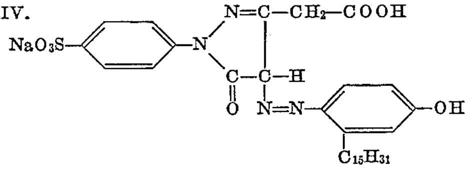
1 - phenyl - 3-(3,5-disulfobenzamido)-4-(4-hydroxy-2-pentadecylphenylazo)-5-pyrazolone dipotassium salt.

XXXIII.



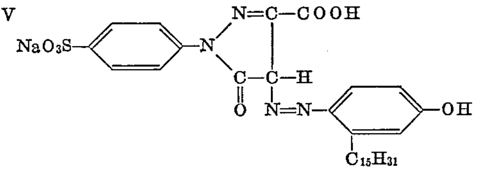
1 - (p - sulfophenyl)-3-carboxymethyl-4-(4-hydroxy-2-pentadecylphenylazo)-5-pyrazolone sodium salt.

XXXIV.



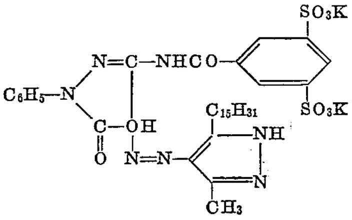
1 - (4 - sulfophenyl)-3-carboxy-4-(4-hydroxy-2-pentadecylphenylazo)-5-pyrazolone sodium salt.

XXXV



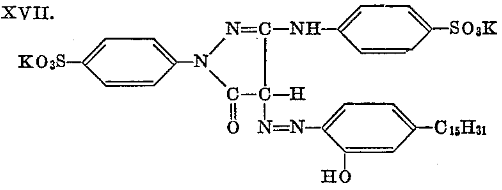
1 - phenyl - 3-(3,5-disulfobenzamido)-4-[4-(3-methyl-5-pentadecyl)pyrazolylazo]-5-pyrazolone dipotassium salt.

XXXVI.



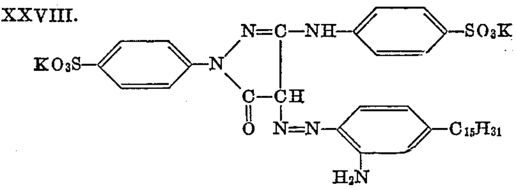
1 - (4 - sulfophenyl)-3-(4-sulfoanilino)-4-(2-hydroxy-4-pentadecylphenylazo)-5-pyrazolone dipotassium salt.

XXXVII.



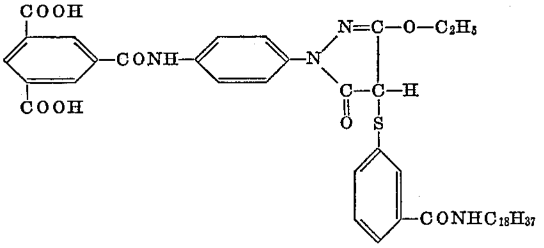
1 - (4 - sulfophenyl)-3-(4-sulfoanilino)-4-(2-amino-4-pentadecylphenylazo)-5-pyrazolone dipotassium salt.

XXXVIII.



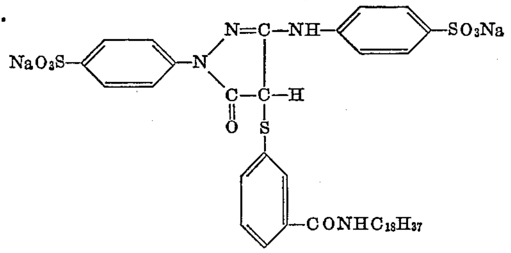
1-[4-(3,5-dicarboxybenzamido)phenyl] - 3 - ethoxy-4-(3-octadecylcarbamylphenylthio)-5-pyrazolone.

XXXIX.



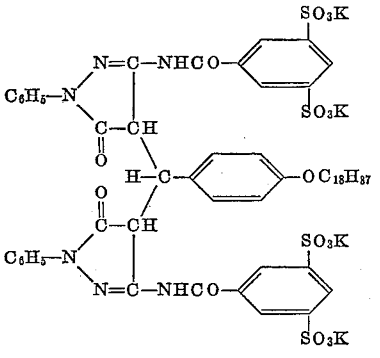
1-(4-sulfophenyl)-3-(4-sulfoanilino) - 4 - (3-octadecylcarbamylphenylthio)-5-pyrazolone disodium salt.

XL.



4,4′-(4-octadecyloxybenzylidene)bis[1 - phenyl - 3-(3,5-disulfobenzamido)-5-pyrazolone]tetra potassium salt.

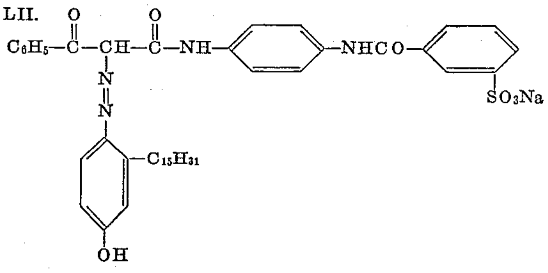
XLI.



Couplers XLII to XLVI below form diffusible yellow dyes.

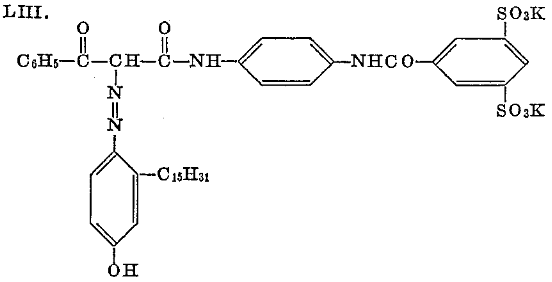
α-Benzoyl-α-(4-hydroxy - 2-pentadecylphenylazo) - 4 - (3-sulfobenzamido)acetanilide sodium salt.

XLII.



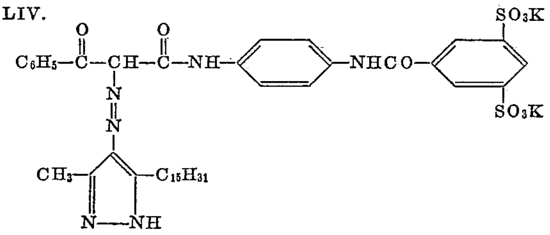
α-Benzoyl-α-(4 - hydroxy-2 - pentadecylphenylazo) - 4-(3,5-disulfobenzamido)acetanilide dipotassium salt.

XLIII.



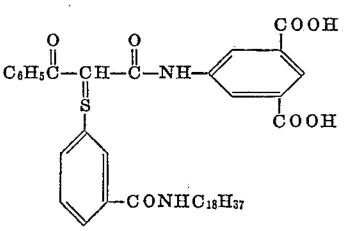
α-Benzoyl-α-[4 - (3-methyl - 5 - pentadecyl)pyrazolylazo]-4 - (3,5 - disulfobenzamido)acetanilide dipotassium salt.

XLIV.



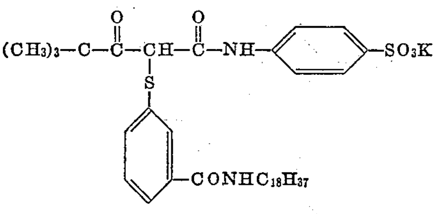
α-Benzoyl-α-(3 - octadecylcarbamylphenylthio) - 3,5 - dicarboxyacetanilide.

XLV.



α-Pivalyl-α-(3 - octadecylcarbamylphenylthio) - 4-sulfoacetanilide potassium salt.

XLVI.



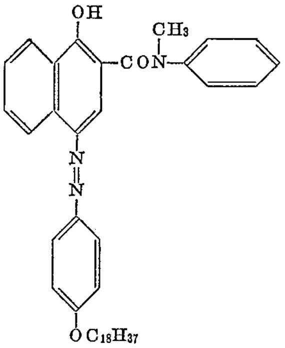
Diffusible dyes are formed when the above listed (i.e., I to XLVI) non-diffusing couplers are employed in the process of the invention with well-known p-phenylenediamine, developing agents, e.g., N,N-diethyl-p-phenylenediamine, 2 - amino - 5 - diethylamino toluene, N-ethyl-β-methanesulfonamidoethyl - 3 - methyl-4-aminoaniline, and other N,N-dialkyl-p-phenylenediamine developing agents described by Bent et al., J.A.C.S. 73, 3100–3125 (1951).

Couplers XLVII to LV are nondiffusible couplers which can also be used in the process of our invention when the color developing agent is supplied with the alkali solubilizing function.

Couplers XLVII to L below form diffusible cyan dyes.

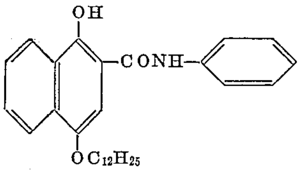
1-hydroxy-4-(4-octadecyloxyphenylazo)-N-methyl - 2-naphthanilide.

XLVII.



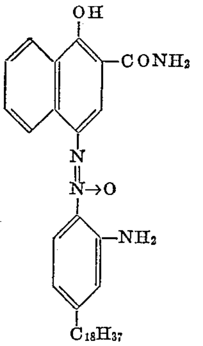
1-hydroxy-4-dodecyloxy-2-naphthanilide.

XLVIII.



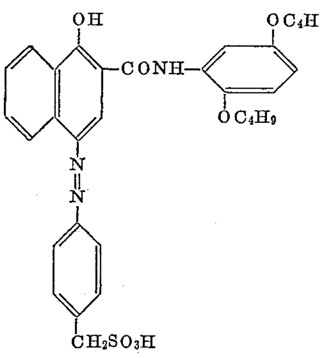
1-hydroxy-4-(2-amino - 4 - octadecylphenylazoxy) - 2-naphthamide.

XLIX.



1-hydroxy-2′,5′-dibutoxy-4 - [4 - (sulfomethyl)phenylazo]-2-naphthanilide.

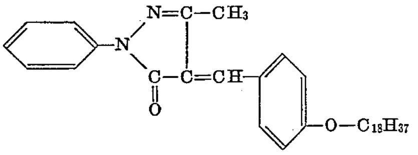
L.



Couplers LI to LIII below form diffusible magenta dyes.

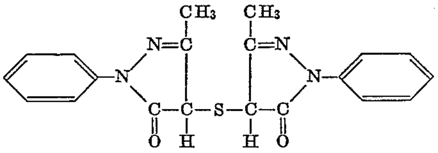
1-phenyl-3-methyl-4-(4-octadecyloxybenzylidene)-5-pyrazolone.

LI.



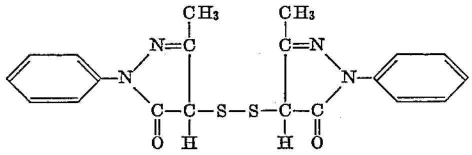
4,4'-thiobis(1-phenyl-3-methyl-5-pyrazolone).

LII.



4,4'-dithiobis(1-phenyl-3-methyl-5-pyrazolone).

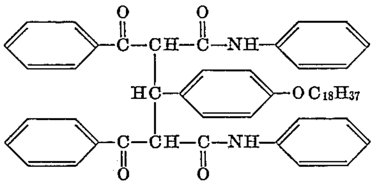
LIII.



Couplers LIV and LV below form diffusible yellow dyes.

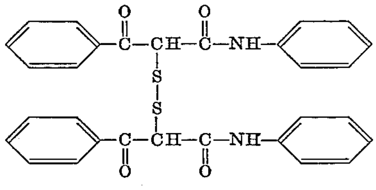
α,α'-(4-octadecyloxybenzylidene)bis[α-benzoylacetanilide].

LIV.



α,α'-Dithiobisbenzoylacetanilide.

LV.



Representative color developing agents possessing the solubilizing functions useful with the nondiffusing couplers above are as follows:

4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline
4-amino-N-ethyl-3-methoxy-N-(β-sulfoethyl)aniline
4-amino-N-ethyl-N-(β-hydroxyethyl)aniline
4-amino-N,N-diethyl-3-hydroxymethyl aniline
4-amino-N-methyl-N-(β-carboxyethyl)aniline
4-amino-N,N-bis(β-hydroxyethyl)aniline
4-amino-N,N-bis(β-hydroxyethyl)-3-methyl aniline
3-acetamido-4-amino-N,N-bis(β-hydroxyethyl)aniline
4-amino-N-ethyl-N-(2,3-dihydroxypropyl)-3-methyl aniline sulfate salt
4-amino-N,N-diethyl-3-(3-hydroxypropoxy)aniline

When the DDR couplers given above were incorporated into exposed silver halide emulsions that were developed in contact with a mordanted reception layer using an alkaline color developing composition containing the developing agent 4-amino-N-ethyl-N-(β-hydroxyethyl)aniline, the following colors of dye images were obtained on the reception layer from the respective couplers:

Coupler:	
I	Yellow.
II	Do.
III	Do.
IV	Orange-yellow.
V	Yellow.
VI	Do.
VII	Do.
VIII	Do.
IX	Do.
X	Do.
XI	Cyan.
XII	Do.
XIII	Do.
XIV	Do.
XV	Do.
XVI	Do.
XVII	Do.
XVIII	Do.
XIX	Do.
XX	Do.
XXI	Do.
XXII	Do.
XXIII	Do.
XXIV	Do.
XXV	Do.
XXVI	Do.
XXVII	Do.
XXVIII	Do.
XXIX	Do.
XXX	Magenta.
XXXI	Do.
XXXII	Do.
XXXIII	Do.
XXXIV	Do.
XXXV	Do.
XXXVI	Do.
XXXVII	Do.
XXXVIII	Do.
XXXIX	Do.
XL	Do.
XLI	Do.
XLII	Yellow.
XLIII	Do.
XLIV	Do.
XLV	Do.
XLVI	Do.

The following syntheses illustrate the methods for preparations of representative DDR couplers of our invention.

COUPLER I

1-hydroxy-4-{3-[4-(N-ethyl-N-β-sulfoethylamino)-2-methylphenylazo]phenylazo}-N-[δ(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide sodium salt

To 200 ml. of concentrated sulfuric acid at 10° C. was added with stirring 17 g. of Intermediate C below. To the resultant solution was added dropwise over a period of 30 minutes at —5° C. with stirring a solution of 3.5 g. of sodium nitrite in 35 ml. of concentrated sulfuric acid (i.e. nitrosylsulfuric acid solution). This solution was stirred for a total of two hours after which time it was poured onto crushed ice. This solution was then added to a solution of 21 g. of 1-hydroxy-N-[δ(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide (U.S. Patent 2,474,293), in two liters of pyridine over a 30-minute period with stirring at 0–5° C. After 12 hours at room temperature the reaction mixture was mixed with 1.5 kg. of crushed ice and acidified with concentrated hydrochloric acid. The red solid which separated was collected, washed with water and recrystallized twice from glacial acetic acid, yielding the product.

COUPLER I, INTERMEDIATE A

N-ethyl-3-methyl-N-(β-sulfoethyl)aniline sodium salt

A mixture of 675 g. of N-ethyl-toluidine and 528 g. of sodium 2-bromoethane sulfonate was heated at 160–190° C. for 3½ hours, after which time mixture was cooled and 1200 ml. of water was added. The solution was made alkaline with sodium hydroxide and the solid which separated was collected, washed with acetone and ether and recrystallized from 2.5 liters of ethyl alcohol, yielding 420 g. of product.

COUPLER I, INTERMEDIATE B

β - {N - ethyl - N - [3 - methyl - 4 - (3 - nitrophenylazo) phenyl]amino}-ethylsulfonic acid sodium salt

To a solution of 27 g. of Intermediate A above in 250 ml. of water at 0° C. was added a chilled diazonium solution consisting of 14 g. of m-nitroaniline and 7.5 g. of sodium nitrite in 200 ml. of 6 N hydrochloric acid. The resultant mixture was neutralized to Congo red paper by the addition of sodium acetate. This mixture was chilled for 2 hours after which time the solid which separated was collected, washed with cold water, and recrystalized from 360 ml. of water, yielding a green product.

COUPLER I, INTERMEDIATE C

β - {N - [4 - (3 - aminophenylazo) - 3 - methylphenyl] - N-ethylamino}ethyl sulfonic acid sodium salt

To a solution of 41 g. of Intermediate B above in 2 liters of water at 90° C. was added over a period of 30 minutes a solution of 40 g. of 60% sodium sulfide in 150 ml. of water. The mixture was refluxed for an additional 2½ hours during which time approximately ½ of the water was distilled off. This mixture was filtered and refrigerated over night during which time a solid separated. The solid was collected and recrystallized from 200 ml. of ethyl alcohol, yielding the product.

COUPLER VII

1-hydroxy-4-{4-[3 - methyl - 4 - (1,5-disulfo-3-naphthylazo) - 1 - pyrazol - 5 - onyl]phenylazo} - N - [δ - (3 - pentadecylphenoxy)butyl] - 2 - naphthamide disodium salt

A solution of 6.5 g. of sodium nitrite in 93 ml. of water was added to a solution of 49.5 g. of Intermediate E below in 300 ml. of five percent sodium carbonate solution. This mixture was cooled to 10° C. and added to a well-stirred mixture of 75 ml. concentrated hydrochloric acid and 150 g. of ice. After 1½ hours, the diazonium suspension was added in portions with vigorous stirring to a solution of 44.4 g. of Intermediate C below in a mixture of 1500 ml. of ethyl alcohol and 55 g. of potassium carbonate in 360 ml. water. After two hours, the crude product was filtered, triturated in boiling ethyl alcohol, then dissolved in 1500 ml. ethyl alcohol and 1500 ml. of 3% potassium carbonate solution. The dark orange solution was filtered and acidified with acetic acid. The solid which separated was filtered, triturated in acetone and benzene, extracted twice with hot water, and recrystallized from a 1:1 n-propyl alcohol-water mixture, yielding 40 g. of product, M.P.>270° C.

COUPLER VII, INTERMEDIATE A

γ-(3-pentadecylphenoxy)butyronitrile

A mixture of 4 g. of sodium hydroxide and 31 g. of 3-pentadecylphenol (Minn. Mining and Mfg. Co.) in 100 ml. of xylene was refluxed for 6 hours during which time 1.8 ml. of water was distilled off. To the mixture was added 11 g. of γ-chlorobutyronitrile dropwise over 1 hour after which time the mixture was refluxed for 7 hours. The xylene was then distilled off over a 12 hour period and the residual oil was poured into 25 ml. of dilute hydrochloric acid. The waxy solid which separated was collected and recrystallized from 100 ml. of acetonitrile, yielding 23 g. of product, M.P. 46–47° C.

COUPLER VII, INTERMEDIATE B

δ(3-pentadecylphenoxy)butylamine

A mixture of 5 g. of Intermediate A above, 3 ml. of ethyl-alcohol, 5 ml. of liquid anhydrous ammonia and 0.1 g. of Raney nickel was heated for 12 hours at 100° C. under a hydrogen atmosphere at a pressure of 2200 p.s.i. The cooled solution was filtered and concentrated in vacuo. The residual oil was distilled at 165° C. at 9 microns, yielding the product.

COUPLER VII, INTERMEDIATE C

1-hydroxy-N-[δ(3-pentadecylphenoxy)butyl]-2-naphthamide

A mixture of 5 g. of phenyl 1-hydroxy-2-naphthoate and 7 g. of Intermediate B above was heated at 150° C. for ½ hour in vacuo during which time phenol was collected from the mixture. The residual oil was poured into 100 ml. of petroleum ether whereupon a crystalline solid separated. This solid was collected and recrystallized from 90 ml. of ethyl alcohol, yielding 8 g. of product, M.P. 64–66° C.

COUPLER VII, INTERMEDIATE D

1-(4-nitrophenyl)-3-methyl-4-(1,5-disulfo-3-naphthylazo)-5-pyrazolone disodium salt

To a solution of 2.8 g. of 1-(4-nitrophenyl)-3-methyl-5-pyrazolone, 0.5 g. of sodium hydroxide and 7 g. of sodium acetate in 40 ml. of water was added at 20° C. over a period of 20 minutes a diazonium mixture consisting of 1.1 g. of 2-amino-1,5-naphthalenedisulfonic acid disodium salt, 1.4 g. of sodium nitrite, 2 ml. of concentrated sulfuric acid and 10 ml. of water. The mixture was stirred for 1 hour at room temperature and heated over steam until all solids dissolved. The solution was cooled to 5° C. whereupon a red solid separated and was collected, yielding 4.5 g. of product.

COUPLER VII, INTERMEDIATE E

1-(4-aminophenyl)-3-methyl-4-(1,5-disulfo-3-naphthylazo)-5-pyrazolone disodium salt

To a mixture of 31 g. of Intermediate D above in 32 ml. of water at 90° C. was added over a period of 20 minutes a solution of 18 g. of 60% sodium sulfide in 40 ml. of water. The mixture was heated at reflux for an additional 2 hours after which time it was cooled to 50° C. and acidified with acetic acid. The solid which separated was collected and recrystallized from 250 ml. of 10% brine solution, yielding 15 g. of product, M.P.>250° C.

COUPLER XI

1-hydroxy-4-stearoyloxymercuri-2-naphthoic acid

To a solution of 9.4 g. of 1-hydroxy-2-naphthoic acid (J.A.C.S. 64, 799 (1942)) in 200 ml. of dioxane was added a solution of 38 g. of mercuric stearate in 500 ml. of dioxane. The mixture was heated over steam for 5 hours during which time a white solid separated. This solid was collected, washed with hot methyl alcohol and dried, yielding 30 g. of product.

COUPLER XII

1-hydroxy-4-dodecyloxy-2-naphthoic acid

To a suspension of 2 g. of 1,4-dihydroxy-2-naphthoic acid (J.A.C.S. 64, 799 (1942)) in 40 g. of lauryl alcohol was added dry hydrogen chloride gas at 90° C. over a period of 11 hours while stirring. The clear reaction mixture was left at room temperature over night during which time a white solid separated. This solid was filtered, slurried in 50 volumes of petroleum ether, refiltered and dried, yielding 1.25 g. of product, M.P. 135–136° C.

COUPLER XV

1-hydroxy-N-(β-sulfoethyl)-4-(4-octadecyloxyphenylazo)-2-naphthamide potassium salt

To a solution of 51 g. of potassium hydroxide and 63 g. of Intermediate A below in 350 ml. of water and 1700 ml. of ethyl alcohol was added at 5° C. over a period of 1 hour, a diazonium solution consisting of 72 g. of Intermediate B below, 120 g. of p-toluene sulfonic acid, and 30 g. of isoamylnitrite in 2 liters of n-propyl alcohol. The mixture was stirred at room temperature for 5 hours after which time 3 liters of water were added and the mixture brought to reflux. The hot solution was filtered, acidified with glacial acetic acid and cooled whereupon a solid separated. The solid was collected, recrystallized from 1.5 liters of n-butyl alcohol, yielding 80 g. of product, M.P. 228–30° C.

COUPLER XV, INTERMEDIATE A

1-hydroxy-N-(β-sulfoethyl)-2-naphthamide potassium salt

A mixture of 132 g. of phenyl 1-hydroxy-2-naphthoate, 1 liter of ethyl alcohol, 57.5 g. of taurine, 300 ml. of water and 28 g. of potassium hydroxide was refluxed for 15 hours after which time the solution was cooled and the solid which separated was collected, washed with ethyl alcohol, recrystallized from H_2O and dried, yielding 71 g. of product, M.P. 284–286° C.

COUPLER XV, INTERMEDIATE B

4-octadecyloxyaniline

A mixture of 39 g. of 4-nitrophenyloctadecyl ether (J.A.C.S. 73, 458 (1951)) and 0.5 g. of 10% palladium on charcoal in 300 ml. of ethyl alcohol was heated at 50° C. for ½ hour under a hydrogen atmosphere at a pressure of 50 p.s.i.

The catalyst was filtered from the hot solution which was then chilled whereupon a solid separated. This solid was collected, and dried, yielding 32 g. of product, M.P. 78–81° C.

The preparations for couplers XVIII, XIX, XX, and XXI are given in copending application U.S. Serial No. 154,841, filed Nov. 24, 1961.

COUPLER XXIV

2-(3,5-disulfobenzamido)-4-(4-hydroxy-2-pentadecylphenylazo)-5-methylphenol dipotassium salt

To a solution of 21 g. of 2-(3,5-dichlorosulfonylbenzamido)-5-methylphenol in 50 ml. of pyridine and 10 ml. of water was added a diazonium solution consisting of 16 g. of 4-amino-3-pentadecylphenol, 7 g. of isoamylnitrite, and 10 ml. of concentrated hydrochloric acid in 100 ml. of n-propyl alcohol. The mixture was stirred at room temperature for 12 hours after which time it was poured into 400 ml. of saturated potassuim chloride solution. The gummy solid which separated was collected, triturated twice in methyl alcohol and dried, yielding 11 g. of product.

COUPLER XXX

1-phenyl-3-(3-sulfobenzamido)-4-(4-octadecyloxyphenylazo)-5-pyrazolone sodium salt

To a solution of 3.6 g. of Intermediate B below and 2 g. of sodium hydroxide in 55 ml. of 90% ethyl alcohol at 0° C. was added with stirring a diazonium solution consisting of 3.6 g. of 4-octadecyloxyaniline (Intermediate B of Coupler XV above), 5.7 g. of p-toluenesulfonic acid monohydrate and 1.5 g. of isoamylnitrite in 100 ml. of n-propyl alcohol at 20° C. The mixture was stirred at room temperature for 3 hours after which time 25 ml. of water was added and the mixture was acidified with acetic acid. To this solution at 90° C. was added 100 g. of sodium chloride and the resultant solution was filtered and cooled. The solid which separated was collected, washed with water and dried, yielding 6 g. of product, M.P. 198–200° C.

COUPLER XXX, INTERMEDIATE A

1-phenyl-3-(3-chlorosulfonylbenzamido)-5-pyrazolone

To a solution of 88 g. of 1-phenyl-3-amino-5-pyrazolone in 400 ml. of diethyl oxalate at 90° C. was added with stirring 120 g. of m-chlorosulfonylbenzoyl chloride. The mixture was heated for ½ hour, cooled to 20° C. and the solid which separated was collected, triturated in water, ethyl acetate and dried, yielding 98 g. of product, M.P. 176–177° C.

COUPLER XXX, INTERMEDIATE B

1-phenyl-3-(3-sulfobenzamido)-5-pyrazolone

A mixture of 58 g. of Intermediate A above in 250 ml. of 10% sodium hydroxide was stirred at room temperature for 2 hours after which time the solution was acidified with concentrated hydrochloric acid whereupon a solid separated. This solid was collected, washed with water and dried, yielding 23 g. of product, M.P. dec. 292° C.

Couplers XXXI and XXXII were each prepared according to the procedure given for coupler XXX above using the appropriate intermediates.

COUPLER XXXIII

1-phenyl-3-(3,5-disulfobenzamido)-4-(4-hydroxy-2-pentadecylphenylazo)-5-pyrazolone dipotassium salt

To a solution of 5 g. of 1-phenyl-3-(3,5-disulfobenzamido)-5-pyrazolone dipotassium salt (prepared according to the procedure given for Intermediate B, coupler XXX above using the appropriate intermediates) in 20 ml. of 50% pyridine was added at 20° C. a diazonium solution consisting of 3 g. of 4-amino-3-pentadecylphenol, 1.5 g. of isoamylnitrite and 2 g. of concentrated hydrochloric acid in 20 ml. of n-propyl alcohol. The resultant mixture was stirred at room temperature for 12 hours after which time it was poured into 100 ml. of saturated potassium chloride solution. The solid which separated was collected, and recrystallized from 50 ml. of 60% ethyl alcohol, yielding the product.

Couplers XXXIV, XXXV, XXXVI, XXXVII, and XXXVIII were each prepared according to the procedure given for coupler XXXIII above using the appropriate intermediates.

COUPLER XXXIX

1-[4-(3,5-dicarboxybenzamido)phenyl]-3-ethoxy-4-(3-octadecylcarbamylphenylthio)-5-pyrazolone

A mixture of 7.8 g. of Intermediate H below, 25 ml. of ethyl alcohol, 15 ml. of 2 N aqueous NaOH, and 35 ml. of water was stirred at 85° C. for 15 minutes. The solution was cooled to room temperature and acidified with 1:2 concentrated HCl-water.

The solid which separated was filtered off, washed with water, acetonitrile, and recrystallized from methanol, yielding 4 g. of product, M.P. 200–202° C.

COUPLER XXXIX, INTERMEDIATE A

1-(4-nitrophenyl)-3-ethoxy-5-pyrazolone

A mixture of 31 g. of 4-nitrophenylhydrazine, 100 ml. of ethyl alcohol, and 38 g. of ethyl-β,β-diethoxyacrylate was refluxed for ½ hour. A solution of sodium ethoxide (prepared from 4.6 g. of sodium and 100 ml. of ethyl alcohol) was added and refluxed for another 20 minutes. This solution was acidified with glacial acetic acid and the solid which separated was filtered off, and recrystallized from 250 ml. of n-butyl alcohol, yielding 31 g. of product, M.P. 153–4° C.

COUPLER XXXIX, INTERMEDIATE B

1-(4-aminophenyl)-3-ethoxy-5-pyrazolone

A mixture of 15 g. of Intermediate A above in 150 ml. of ethyl alcohol was reduced using Pd/Charcoal at 50 p.s.i., hydrogen pressure.

The catalyst was filtered off and the solution poured into 500 ml. of water.

The product was filtered off and air dried, yielding 8.2 g. of product, M.P. 121–122° C.

COUPLER XXXIX, INTERMEDIATE C

Triethyltrimesate

A mixture of 37 g. of trimesic acid (proc. N. Dak. Acad. SC: 8, 54 (1954); CA (1955) 8898b), 100 ml. of ethyl alcohol, 50 ml. of benzene, and 1 ml. of concentrated H_2SO_4 was refluxed through a 6" packed column surmounted by a Dean Stark water spouter for 24 hours after which time the residue was cooled and the solid which crystallized was filtered and dried.

The yield of the triester was 38 g., M.P. 133–5° C.

COUPLER XXXIX, INTERMEDIATE D

Diethyl ester of trimesic acid (3,5-dicarbethoxybenzoic acid)

To a solution of 147 g. of the Intermediate C above in 2 liters of ethyl alcohol was added with stirring 250 ml. of 2 N NaOH in 500 ml. of ethyl alcohol. This mixture was refluxed for 30 minutes and stirred at room temperature for 12 hours, during which time a solid separated. This solid was filtered off and recrystallized from a mixture of 500 ml. of ethyl alcohol and 500 ml. of water, yielding 80 g. of product, M.P. 153–5° C.

COUPLER XXXIX, INTERMEDIATE E

3,5-dicarbethoxybenzoyl chloride

A mixture of 300 g. of Intermediate D above and 2 liters of thionyl chloride was refluxed for 2 hours, after which time it was concentrated in vacuo.

To the residue was added 250 ml. of dry benzene and again concentrated in vacuo.

The acid chloride thus formed was used as such in preparing Intermediate F below.

COUPLER XXXIX, INTERMEDIATE F

1-[4-(3,5-dicarbethoxybenzamido)phenyl]-3-ethoxy-5-pyrazolone

A mixture of 6.6 g. of Intermediate B above and 8.5 g. of Intermediate E above and 100 ml. of dry acetonitrile was refluxed for 5 hours. The mixture was cooled to room temperature and the solid was filtered off, dried, and recrystallized from glacial acetic acid, yielding 10 g. of product, M.P. 200–201° C.

COUPLER XXXIX, INTERMEDIATE G

3-octadecylcarbamylphenylsulfenyl chloride

Into a suspension of 8 g. of 3,3'-dioctadecylcarbamyldiphenyldisulfide (Loria et al. U.S. patent application Ser. No. 154,841, filed Nov. 24, 1961) in 120 ml. of anhydrous carbon tetrachloride was bubbled dry chlorine gas for 1½ hours at room temperature, during which time all of the solid dissolved and a clear light yellow solution was formed. The solution was concentrated in vacuo to a volume of 50 ml. to remove excess chlorine.

This solution of the sulfenyl chloride was used as such in the following reaction (i.e., Intermediate H below).

COUPLER XXXIX, INTERMEDIATE H

1-[4-(3,5-dicarbethoxybenzamido)phenyl]-3-ethoxy-4-(3-octadecylcarbamylphenylthio)-5-pyrazolone

A mixture of Intermediate G above and 9.35 g. of Intermediate F above in 200 ml. of dry dioxane was stirred at room temperature for 2 hours, heated to reflux for 1 hour, and concentrated in vacuo.

The residue was recrystallized from ethyl alcohol, yielding 8.5 g. of product, M.P. 156–8° C.

COUPLER XL

1-(4-sulfophenyl)-3-(4-sulfoanilino)-4-(3-octadecylcarbamylphenylthio)-5-pyrazolone disodium salt

A suspension of 25 g. of Intermediate B below in 100 ml. of ethyl alcohol and 200 ml. of 2% aqueous NaOH was stirred at room temperature for ½ hour, during which time all solid dissolved. The solution was cooled and acidified with 5 ml. of acetic acid and concentrated in vacuo.

The crude solid residue was recrystallized from methyl alcohol, yielding 10 g. of product, M.P. >250° C.

COUPLER XL, INTERMEDIATE A

1-(4-fluosulfonylphenyl)-3-(4-fluosulfonylanilino)-5-pyrazolone

To 450 ml. of fluosulfonic acid at 5° C. was added with stirring 80 g. of 1-phenyl-3-anilino-5-pyrazolone.

The resultant solution was stirred at 50° C. for 4½ hours, then poured onto 2 kg. of crushed ice. The solid was collected, washed with water, filtered, and dissolved in 2 liters of ethyl acetate. This solution was washed with 5% sodium bicarbonate solution, water, and saturated brine.

It was concentrated in vacuo and the residue was recrystallized from acetonitrile, yielding 36 g. of product, M.P. 290° C. decomp.

COUPLER XL, INTERMEDIATE B

1-(4-fluosulfonylphenyl)-3-(4-fluosulfonylanilino)-4-(3-octadecylcarbamylphenylthio)-5-pyrazolone

A mixture of Intermediate G of Coupler XXXIX above (prepared from 24.5 g. of the disulfide) and 25 g. of Intermediate A above in 320 ml. of dry carbon tetrachloride was stirred at 55° C. for 12 hours.

The solution was then concentrated in vacuo and the residue was recrystallized from 300 ml. of ethyl acetate yielding 25 g. of product, M.P. 209–11° C.

COUPLER XLI

4,4'-(4-octadecyloxybenzylidene)bis[1-phenyl-3-(3,5-disulfobenzamido)-5-pyrazolone]tetrapotassium salt

To a refluxing solution of 5.2 g. of 1-phenyl-3-(3,5-disulfobenzamido)-5-pyrazolone dipotassium salt in 45 ml. of ethyl alcohol and 20 ml. of water was added a solution of 1.9 g. of Intermediate A below and 0.5 g. of piperidine in 35 ml. of ethyl alcohol. The solution was refluxed for ½ hour and cooled to room temperature. The solid which separated was collected, recrystallized from 90% ethyl alcohol, yielding 5 g. of product.

COUPLER XLI, INTERMEDIATE A

4-octadecyloxybenzaldehyde

To a solution of 23 g. of sodium metal and 122 g. of 4-hydroxybenzaldehyde in 500 ml. of ethyl alcohol was added 333 g. of 1-bromooctadecane. The mixture was refluxed with stirring for 20 hours during which time a solid separated. This solid was filtered and the filtrate was concentrated in vacuo. The residual material was then distilled at 253° C. at 1 mm. pressure, yielding 250 g. of product.

COUPLER XLII

α-Benzoyl-α-(4-hydroxy-2-pentadecylphenylazo)-4-(3-sulfobenzamido) acetanilide sodium salt

To a solution of 4.5 g. of α-benzoyl-4-(3-chlorosulfonylbenzamido) acetanilide in 12 ml. of 90% pyridine was added at 20° C. a diazonium mixture consisting of 3.2 g. of 4-amino-3-pentadecylphenol, 1.4 g. of isoamylnitrite and 2 ml. of conc. hydrochloric acid in 20 ml. of n-propyl alcohol. The resultant solution was stirred at room temperature for 12 hours after which time it was poured into 50 ml. of saturated sodium chloride solution. The yellow solid which separated was collected, and recrystallized twice from ethyl alcohol, yielding 2.2 g. of product.

Coupler XLIII was prepared according to the procedure given for coupler XLII above using the appropriate intermediates.

COUPLER XLV

α-Benzoyl-α-(3-octadecylcarbamylphenylthio)-3,5-dicarboxyacetanilide

To a mixture of 7 g. of Intermediate A below in 100 ml. of dioxane at 50° C. was added a solution of 3-octadecylcarbamylphenylsulfenyl chloride (Intermediate G of coupler XXXIX above, prepared from 8.1 g. of disulfide), in 100 ml. of dioxane. This mixture was stirred for 12 hours after which time the solution was concentrated in vacuo. A solution of the gummy residue in 100 ml. of ethyl alcohol and 13 ml. of 2 N aqueous sodium hydroxide was heated at 40° C. for 1 hour after which time it was acidified with concentrated hydrochloric acid. The solid which separated was collected and recrystallized twice from ethyl alcohol, yielding 2 g. of product, M.P. 140–142° C.

COUPLER XLV, INTERMEDIATE A

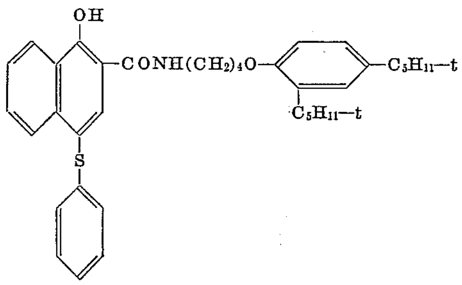
α-Benzoyl-3,5-dicarbomethoxyacetanilide

To a refluxing mixture of 102 g. of ethyl α-benzoylacetate and 5 g. of sodium acetate in 100 ml. of xylene was added 105 g. of dimethyl 5-aminoisophthalate. The resulting solution was refluxed under a steam condenser for 3 hours after which time it was concentrated to ½ the original volume and cooled to room temperature. The solid which separated was collected and recrystallized from methyl alcohol, yielding 40 g. of product, M.P. 165–167° C.

The following are representative development inhibitor releasing (DIR) coupler compounds of the invention that form or release development inhibitors when reacted with oxidized color developing agents.

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

LVI.



1 - hydroxy - 4 - (2 - nitrophenylthio) - N - [δ - (2,4-di-tert-amylphenoxy)butyl]-2-naphthamide. LVII.

1 - hydroxy - 4 - (4 - nitrophenylthio) - N - [δ - (2,4-di-tert-amylphenoxy)butyl]-2-naphthamide. LVIII.

1 - hydroxy - 4 - (2 - aminophenylthio) - N - [δ - (2,4-di-tert-amylphenoxy)butyl]-2-naphthamide. LIX.

1 - hydroxy - 4 - (4 - aminophenylthio) - N - [δ - (2,4-di-tert-amylphenoxy)butyl]-2-naphthamide. LX.

1 - hydroxy - 4 - (4 - acetamidophenylthio) - N - [δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide. LXI.

1 - hydroxy - 4 - [2 - (diethylcarbamyl)phenylthio] - N-[δ - (2,4 - di - tert - amylphenoxy)butyl] - 2 - naphthamide. LXII.

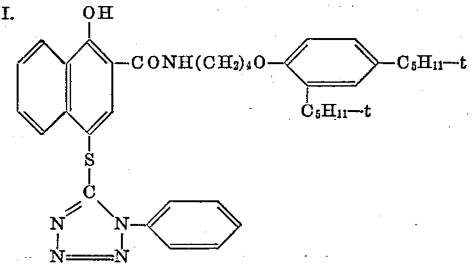
1 - hydroxy - 4 - (2 - methylsulfonamidophenylthio)-N - [δ - (2,4 - di - tert - amylphenoxy)butyl] - 2 - naphthamide. LXIII.

1 - hydroxy - 4 - (4 - methylsulfonamidophenylthio)-N - [δ - (2,4 - di - tert - amylphenoxy)butyl] - 2 - naphthamide. LXIV.

1 - hydroxy - 4 - (2 - benzothiazolylthio) - N - [δ - (2,4-di-tert-amylphenoxy)butyl]-2-naphthamide. LXV.

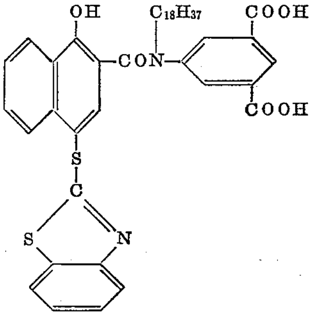
1 - hydroxy - 4 - (1 - phenyl - 5 - tetrazolylthio) - N-[δ - 2,4 - di - tert - amylphenoxy)butyl] - 2 - naphthamide.

LXVI.



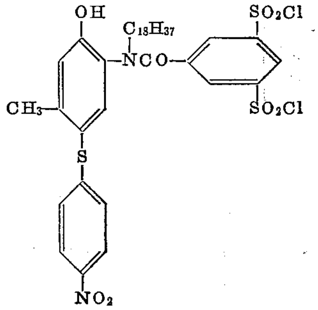
1 - hydroxy - 4 - (2 - benzothiazolylthio) - N - octadecyl-3′,5′-di-carboxy-2-naphthanilide.

LXVII.



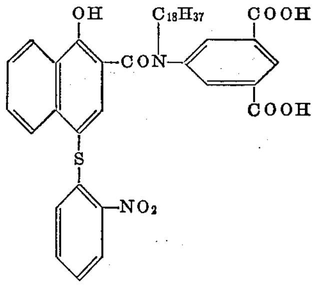
2 - (3,5 - dichlorosulfonyl - N - octadecylbenzamido)-5-methyl-4-(4-nitrophenylthio)phenol.

LXVIII.



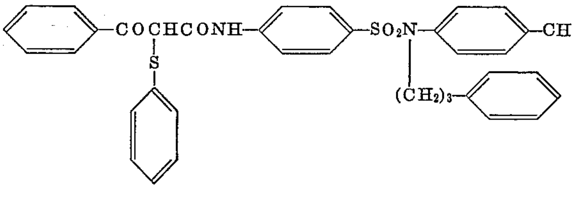
1 - hydroxy - 4 - (2 - nitrophenylthio) - N - octadecyl-3′,5′-dicarboxy-2-naphthanilide.

LXIX.



α - Benzoyl-α-phenylthio-4-[N-(γ-phenylpropyl)-N-(p-tolyl) sulfamyl]acetanilide.

LXX

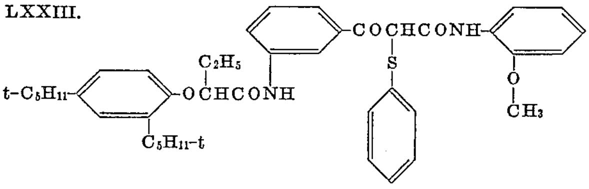


α-Benzoyl-α-(4-nitrophenylthio)-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide. LXXI.

α-Benzoyl-α-[3-(butylcarbamyl)phenylthio]-4-[N-(γ-phenylpropyl)-N-p-tolyl)sulfamyl]acetanilide. LXXII.

α-Benzoyl-α-[3-(butylcarbamyl)phenylthio]-4-[N-benzoyl}-α-phenylthio-2-methoxyacetanilide.

LXXIII.

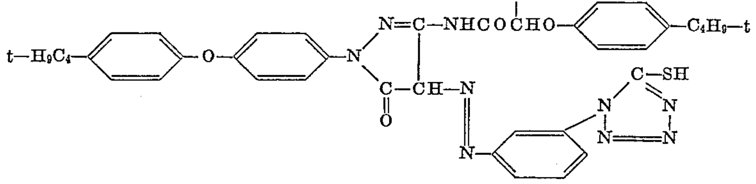


α-[3-(butylcarbamyl)phenylthio]-α{3-[α-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide. LXXIV.

The above coupler (LXXVI) is suitable for use in alkaline color developing solutions in which case the sensitive element used can contain the non-diffusing coupler (DDR) providing the diffusible dye in the spontaneously developable emulsion layer overcoated with the negative or light-sensitive silver halide emulsion layer. During development coupler LXXVI forms a non-diffusible dye in the region of negative development and the mercaptotetrazole compound splits off and inhibits development of the underlying emulsion in the negative region, the emulsion in the positive region develops and a diffusable dye is formed from the more reactive image forming coupler which dye transfers to the reception layer thus forming a transferred positive dye image.

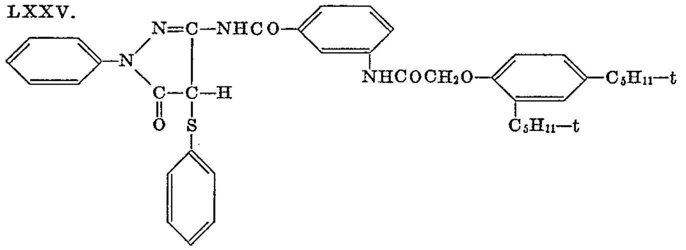
1-[4-A4-t-butylphenoxy)phenyl]-3-[α-(4-t-butylphenoxy)propionamido]-4-[3-(5-mercapto-1-tetrazolyl)-phenylazo]-5-pyrazolone.

LXXVII.



1-phenyl-3-{3-[α-(2,4-di-tert-amylphenoxy)acetamido]benzamido}-4-phenylthio-5-pyrazolone.

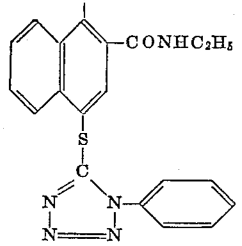
LXXV.



In other 5-pyrazolone compounds having the —S—R group in the 4-position, R can be any of the moieties given immediately above such as 2-nitrophenyl, aminophenyl, acylamidophenyl, etc.

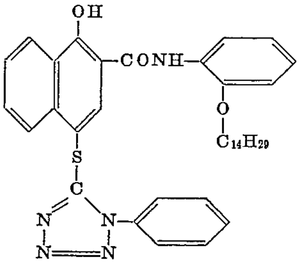
1-hydroxy-4-(1-phenyl-5-tetrazolythio)-N-ethyl-2-naphthamide.

LXXVI.



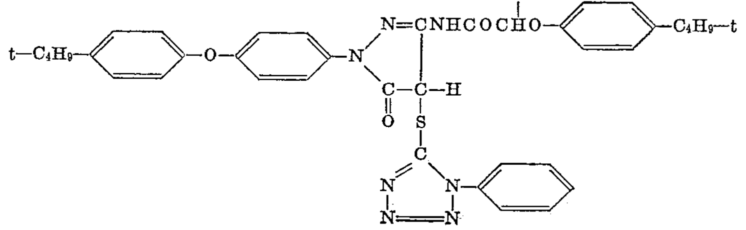
1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecycloxy-2-naphthanilide.

LXXVIII.



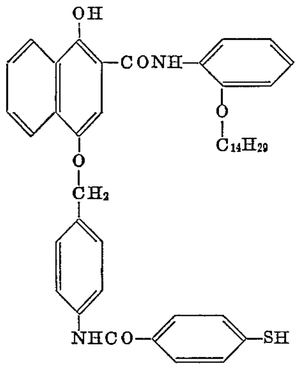
1-[4-(4-tert-butylphenoxy)phenyl]-3-[α-(4-tert-butylphenoxy)propionamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone.

LXXIX.



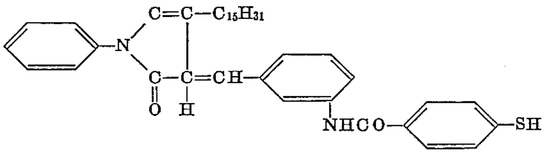
1-hydroxy-4-[4-(4-mercaptobenzamido)benzyloxy]-2′-tetradecyloxy-2-naphthanilide.

XXC.



1 - phenyl - 3 - pentadecyl-4-[3-(4-mercaptobenzamido)benzylidene]-5-pyrazolone.

XXCI.



The following syntheses illustrate the methods for preparing representative development inhibitor releasing (DIR) couplers utilized in our invention.

COUPLER LVII

1-hydroxy-4-(2-nitrophenylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

To a solution of 47.5 g. of 1-hydroxy-N-[α-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide in 1000 ml. of toluene was added over a period of 20 minutes a solution of 19 g. of o-nitrophenyl-sulfur chloride in 250 ml. of toluene. This solution was refluxed for 25 hours and concentrated in vacuo. The solid residue was recrystallized from 500 ml. of cyclohexane, yielding 30 g. of yellow product which melted at 109–10° C.

COUPLER LVIII

1-hydroxy-4-(4-nitrophenylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

To a solution of 47.5 g. of 1-hydroxy-N-[δ-(2-4,-di-tert-amylphenoxyl)butyl]-2-naphthamide in 750 ml. of diethyl ether was added over a period of 20 minutes, with stirring at 5° C., a solution of 19 g. of p-nitrophenylsulfur chloride (J.A.C.S., 56, 1978 (1934)) in 200 ml. of chloroform. The clear solution was refluxed for 6 hours and concentrated in vacuo. The solid residue was recrystallized from 1500 ml. of acetonitrile, yielding 40 g. of product, M.P. 156–57° C.

COUPLER LIX

1-hydroxy-4-(2-aminophenylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

A solution of 12.6 g. of 1-hydroxy-4-(2-nitrophenylthio)-N-[δ-(2,4 - di-tert-amylphenoxy)butyl] - 2 - naphthamide (LVII) in 200 ml. of dioxane was reduced at 50 p.s.i. hydrogen pressure and 60° C. on the Parr Hydrogenation apparatus using palladium on charcoal as a catalyst. The product was isolated by concentrating the filtered reduction solution in vacuo.

COUPLER LX

1-hydroxy-4-(4-aminophenylthio)-N-[δ-2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

A solution of 12.6 g. of 1-hydroxy-4-(4-nitrophenylthio)-N-[δ-(2,4 - di-tert-amylphenoxy)butyl] - 2 - naphthamide (LVIII) in 200 ml. of dioxane was reduced on the Parr Hydrogenation apparatus at 50 p.s.i. hydrogen pressure and 600° C. using palladium on charcoal as a catalyst. The product was isolated by drowning the filtered reduction solution in 1000 ml. of water.

COUPLER LXIV

1-hydroxy-4-(4-methylsulfonamidophenylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

To a solution of 6 g. of 1-hydroxy-4-(4-aminophenylthio)-N-[δ-(2,4 - di-tert-amylphenoxy)butyl] - 2 - naphthamide (LX) and 2.6 g. of quinoline in 150 ml. of dioxane was added with stirring at 25° C., 1.15 g. of methane sulfonyl chloride. The clear reaction mixture was left at room temperature overnight. It was poured into 1000 ml. of 5% hydrochloric acid and the solid product was filtered and dried.

COUPLER LXV

1-hydroxy-4-(2-benzothiazolylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

To a solution of 47.5 g. of 1-hydroxy-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide in 300 ml. of carbon tetrachloride was added at the reflux a solution of 20 g. of 2-benzothiazolylsulfur chloride (U.S.P. 2,257,974) in 300 ml. of hot carbon tetrachloride. This solution was refluxed overnight and concentrated in vacuo. The solid residue was recrystallized from 250 ml. of ethanol, yielding 43 g. of product which melted at 150° C.

COUPLER LXVI

1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-N-[δ-(2,4-di-tert-amylphenoxy)butyl-2-naphthamide

To a solution of 47.6 g. of 1-hydroxy-N-[δ-(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide in 500 ml. of carbon tetrachloride was added a solution of 21 g. of 1-phenyl-5-tetrazolylsulfur chloride, Org. Syn. Coll. vol. II, p. 455, in 200 ml. of carbon tetrachloride. The mixture was refluxed overnight and concentrated in vacuo. The solid was recrystallized from 500 ml. of acetonitrile, yielding 50 g. of product which melted at 148° C.

COUPLER LXVII

1-hydroxy-4-(2-benzothiazolylthio)-N-octadecyl-3′,5′-dicarboxy-2-naphthanilide

To a solution of 60 g. of 1-hydroxy-N-octadecyl-3′,5′-dicarboxy-3-naphthanilide in 100 ml. of dioxane and 500 ml. of carbon tetrachloride was added at the reflux a solution of 20 g. of 2-benzothiazolylsulfur chloride in 100 ml. of carbon tetrachloride. This solution was refluxed overnight. It was concentrated in vacuo. The solid residue was slurried in 1000 ml. of methanol, filtered and the filtrate concentrated again in vacuo. The residue was recrystallized from a mixture of 500 ml. of acetic acid and 500 ml. of acetonitrile, yielding 40 g. of product.

COUPLER LXVIII

2-(3,5-dichlorosulfonyl-N-octadecylbenzamido)-5-methyl-4-(4-nitrophenylthio)phenol

To a solution of 42 g. of 2-(3,5-dichlorosulfonyl-N-octadecylbenzamido-5-methylphenol in 3000 ml. of diethyl ether was added a solution of 20 g. of p-nitrophenyl sulfur chloride in 200 ml. of chloroform. The mixture was refluxed overnight and concentrated in vacuo. The residual solid was collected and air dried.

COUPLER LXIX

1-hydroxy-4-(2-nitrophenylthio)-N-octadecyl-3′,5′-dicarboxy-2-naphthanilide

A mixture of 6 g. of 1-hydroxy-N-octadecyl-3′,5′-dicarboxy-2-naphthanilide and 1.9 g. of 2-nitrophenylsulfur chloride in 50 ml. of acetic acid containing 8 g. of sodium acetate was refluxed for 2 hours. The mixture was then concentrated to dryness and the residue was stirred with ligroin and recrystallized from acetic acid, yielding 4 g. of product, M.P. 172–74° C.

COUPLER LXX

α-Benzoyl-α-phenylthio-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulmamyl]acetanilide

To a solution of 15.8 g. of α-benzoyl-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide (M.P. 128–130° C.) in 200 ml. dry dioxane was added 4.4 g. of benzenesulfur chloride in 10 ml. of dry dioxane at room temperature. The mixture was stirred at room temperature for 1½ hours and then heated on a steam bath for 30 minutes. It was concentrated to an amber glass. 300 ml. absolute ethanol was added and the product solidified. The slurry was heated to reflux, and stirred vigorously. The solid which separated was collected and recrystallized from 300 ml. of glacial acetic acid, followed by a second recrystallization from 250 ml. of acetonitrile, yielding 10 g. of product, M.P. 155–57° C.

COUPLER LXXI

α-Benzoyl-α-(4-nitrophenylthio)-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide

13.5 g. of the 4,4′-dinitrodiphenyldisulfide was suspended in 300 ml. of dry carbon tetrachloride. The mixture was stirred and cooled to 5–10° C. and chlorine gas was slowly passed through the mixture. After 45 minutes the chlorine was stopped and the temperature was raised to 30° C. and held for an additional 30 minutes. The small amount of insoluble material was filtered off and the filtrate was concentrated to an orange oil under aspirator pressure. This was taken up in 100 ml. dry dioxane. One half of the above solution was added to a solution of 15.8 g. of α-benzoyl-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide in 150 ml. dioxane. The mixture was stirred at room temperature for 1½ hours and then heated on a steam bath for ¾ hour. The resulting amber colored solution was concentrated to a syrup and this syrup was take up in 250 ml. boiling methanol. The solid which separated when the solution was cooled was collected and recrystallized from 100 ml. of acetic acid and twice from benzene, yielding 4 g. of product, M.P. 142–44° C.

COUPLER LXXII

α-Benzoyl-α-[3-(butylcarbamyl)phenylthio]-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide

To a solution of 3-(butylcarbamyl)phenylsulfur chloride (prepared from 6 g. of 3,3′-di(butylcarbamyl)diphenyldisulfide) in 250 ml. of dry dioxane was added 10.5 g. of α-benzoyl-4-[N-(γ-phenylpropyl)-N-(p-tolyl)sulfamyl]acetanilide. The resulting almost colorless solution was stirred gently overnight at room temperature. It was concentrated to a viscous yellow syrup. This was taken up in 250 ml. boiling acetonitrile and cooled. The product separated as a somewhat gelatinous white solid. It was recrystallized from 400 ml. of acetonitrile.

COUPLER LXXIII

α{3-[α(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-α-phenylthio-2-methoxyacetanilide

A solution of 14.5 g. of benzenesulfur chloride in 50 ml. of dry carbon tetrachloride was added dropwise to a solution of 59 g. of α-{3-[α-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide in 500 ml. of dry carbon tetrachloride which was cooled and stirred in an ice bath. The addition required about 30 minutes (hydrogen chloride was evolved). On completion of the addition, the mixture was stirred and allowed to warm to room temperature over a period of 3½ hours. It was then heated to reflux for 30 minutes and concentrated to a viscous amber syrup. To this syrup 100 ml. of ligroin was added and the solution was again concentrated down. To this was added 200 ml. ligroin. The solution was stirred gently at room temperature for 4 days. The solid which separated was filtered off and recrystallized from ligroin, yielding 25 g. of product, M.P. 92–93° C.

COUPLER LXXIV

α-[3-(butylcarbamyl)phenylthio]-α-{3-[α-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide

To a solution of 3-(butylcarbamyl)phenylsulfur chloride (prepared from 3 g. of 3,3′-di(butylcarbamyl)diphenylsulfide) in 150 ml. of dry dioxane was added 12 g. of α-{3-[α-(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide in 100 ml. of dry dioxane. The mixture immediately became homogeneous and lighter in color. It was stirred at room temperature overnight and then concentrated to a viscous syrup. This residue was taken up in 150 ml. absolute ethanol and cooled. A white solid was obtained. A second crop was obtained by adding 50 ml. methanol to the filtrate and cooling.

COUPLER LXXVII

1-[4-(4-tert-butylphenoxy)phenyl]-3-[α-(4-tert-butylphenoxy)propionamido]-4-[3-(5-mercapto-1-tetrazolyl)phenylazo]-5-pyrazolone

To a stirred slurry of 1.4 g. of 1-(3-aminophenyl)-5-mercaptotetrazole in a mixture of 15 ml. of water and 8 ml. of concentrated hydrochloric acid at −5° C. was added a solution of 0.44 g. of sodium nitrite in 4 ml. of water.

This diazonium solution was then added to a solution of 2.5 g. of 1-[4-(4-tert-butylphenoxy)phenyl]-3-[α-(4-tert-butylphenoxy)propionamido]-5-pyrazolone (U.S.P. 2,369,489) in 100 ml. of pyridine. The resultant red solution was stirred at room temperature for one hour, then poured into 500 ml. of water. The gummy solid which separated was collected and recrystallized from ligroin, yielding 1 g. of product, M.P. 185–86° C.

COUPLER LXXVIII

1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecyloxy-2-naphthanilide

Into a solution of 1.6 g. of 1-phenyl-5-mercaptotetrazole in 100 ml. of acetonitrile, chlorine gas was bubbled for one hour. The excess chlorine gas was removed at room temperature by means of reduced pressure. This solution was added to a solution of 4.1 g. of 1-hydroxy-2′-tetradecyloxy-2-naphthanilide in 300 ml. of acetonitrile at 50° C. This solution was stirred at room temperature for 15 hours. The solid which separated was filtered off and dried, M.P. 99–100° C.

COUPLER LXXIX

1-[4-(4-tert-butylphenoxy)phenyl]-3-[α-(4-tert-butylphenoxy)propionamido]-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone

7.08 g. of 5,5′-bis(1-phenyltetrazolyl)disulfide (Ber. 28, 77–81) was suspended in 50 ml. dry carbon tetrachloride. A stream of dry chlorine gas was passed into the suspension for 45 minutes, and a pale yellow solution resulted. The solution was filtered and concentrated in vacuo to a yellow solid. This solid was then taken up in 5 ml. dry carbon tetrachloride and added all at once to a solution of 21 g. of 1-[4-(p-tert-butylphenoxy)phenyl]-3-[α-(p-tert-butylphenoxy)propionamido]-5-pyrazolone in 200 ml. dry carbon tetrachloride. This yellowish solution was refluxed for 3 hours. The solvent was removed in vacuo. The residue was taken up in boiling cyclohexane, and after cooling to room temperature, a white solid separated. This solid was filtered and recrystallized twice from acetonitrile, M.P. 130–32° C.

The following examples illustrate typical embodiments of the invention.

EXAMPLE 1

A color film having the structure substantially as shown in FIG. 4 was prepared by coating a subbed cellulose acetate film support successively with the following layers which correspond to the numbered layers in FIG. 4:

Layer 51.—A gelatino silver chloride emulsion coated at 0.040 gram silver per square foot and 100 mg. gelatin per square foot and containing 2.7×10^{-7} gm. zinc sulfide (nuclei) per square foot, 50 mg. 1-hydroxy-4-(3-octadecylcarbamylphenylthio)-N-ethyl-3′,5′-dicarboxy-2-naphthanilide per square foot and 15 mg. 2-octadecyl-5-sulfohydroquinone potassium salt per square foot. The phenolic DDR coupler of this layer yields a diffusible indoaniline cyan dye image upon reaction with oxidized color developing agent in the uninhibited areas of layer **51**.

Layer 52.—A red-sensitive gelatino-silver bromoiodide emulsion coated at 0.075 gram silver per square foot and 100 mg. gelatin per square foot and containing 30 mg. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecyloxy-2-naphthanilide, per square foot. The phenolic DIR coupler of this layer, and of layers **55** and **58**, reacts at its coupling position with oxidized color developing agent, in the region of exposure, to form a nondiffusing cyan dye and replace the tetrazolylthio radical to yield the corresponding mercaptan which is effective to inhibit the development of the adjacent nucleated silver halide of layers **51**, **54** and **57**, respectively.

Layer 53.—A gelatino-silver iodide emulsion coated at 0.050 gram silver per square foot and 100 mg. gelatin per square foot and containing 30 mg. of the nondiffusing magenta colored filter dye, 1-hydroxy-4′-(4-tert.-butylphenoxy)-4-phenylazo-2-naphthamide, per square foot and 30 mg. 2-octadecyl-5-sulfo-hydroquinone potassium salt per square foot. The silver iodide of this layer and of layer **56** serves to prevent upward diffusion of the mercaptan layers **52** and **55**.

Layer 54.—A gelatino-silver chloride emulsion coated at 0.040 gram silver per square foot and 100 mg. gelatin per square foot and containing 5.5×10^{-6} gm. zinc sulfide (nuclei) per square foot, 50 mg. of 1-phenyl-3(3,5-disulfobenzamido)-4-(2-hydroxy-4-n - pentadecylphenylazo) - 5-pyrazolone dipotassium salt per square foot and 15 mg. 2-octadecyl - 5 - sulfo - hydroquinone potassium salt per square foot. This 5-pyrazolone DDR coupler yields a diffusible magenta azomethine dye image in the process.

Layer 55.—A green-sensitive gelatino-silver bromoiodide emulsion coated at 0.075 gram silver per square foot, 100 mg. gelatin per square foot, and 30 mg. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio - 2′-tetradecyloxy-2-naphthanilide, per square foot.

Layer 56.—A gelatino-silver iodide emulsion containing 0.05 gram silver per square foot and 100 mg. gelatin per square foot and also 66 mg. 1-(2,4,6-trichlorophenyl)-3 - {3 - [α - (2,4-di - tert. - amylphenoxy)acetamido]benzamido}-4-(p-methoxyphenylazo)-5-pyrazolone per square foot and 30 mg. 2-octadecyl-5-sulfo-hydroquinone potassium salt per square foot. The yellow pyrazolone coupler of this layer serves as a light filter to confine the blue image exposure to layer **58**.

Layer 57.—A gelatino-silver chloride emulsion coated at 0.05 gram silver per square foot and 100 mg. gelatin per square foot and containing also 1.1×10^{-6} gm. zinc sulfide (nuclei) per square foot, 100 mg. α-benzoyl-α-(3-octadecylcarbamylphenylthio) - 3,5 - dicarboxyacetanilide per square foot and 15 mg. 2-octadecyl-5-sulfo-hydroquinone potassium salt per square foot. The DDR coupler of this layer yields a diffusible yellow azo methine dye image in the process.

Layer 58.—A blue-sensitive gelatino-silver bromoiodide emulsion coated at 0.075 gram silver per square foot and 100 mg. gelatin per square foot and containing in addition, 30 mg. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecyloxy-2 - napthanilide, per square foot.

The resulting element was exposed to a colored subject and immersed with a paper receiving sheet having a gelatin layer containing a mordant such as cetyl trimethyl ammonium bromide in the following color developing solution and pressed for about 5 minutes at 85° F. into contact with the paper reception sheet.

Ascorbic acid	mg	200.0
4-amino-N-ethyl-N - β - hydroxyethyl aniline sulfate	g	4.0
4-amino-N-ethyl-N-β - methylsulfonamido - ethyl-2-methyl aniline sulfate	g	1.0
$Na_2CO_3\cdot H_2O$	g	40.0
Aminoethanol	ml	2.2
Potassium bromide	mg	500.0
Sodium thiosulfate (pentahydrate)	mg	200.0
6-nitrobenzimidazole nitrate	mg	5.0

H_2O to 1 liter
pH 11.0 (adjusted)

As a result, the exposed silver halide in layers **52**, **55** and **58** develops and the DIR couplers therein react with oxidized color developing agent obtained in the reaction thereby forming a development inhibiting mercaptan that inhibits development of adjacent areas of the nucleated emulsion layers **51**, **54** and **57**, respectively. The residual developer solution migrates to the positive areas of layers **51**, **54** and **57**, causing physical development to proceed and diffusible cyan, magenta and yellow dyes to be produced which transfer by diffusion imagewise and in register to the mordanted receiving sheet to provide a multicolor positive reproduction of the original subject. Similar results are obtained if the DIR coupler were eliminated from layers **52**, **55** and **58** and the diffusible DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio) - N-ethyl-2-naphthamide, utilized in the developing solution, 4 g. of this DIR coupler and 2 cc. of isopropanol being suitable per liter of color developing solution.

EXAMPLE 2

A color film having the structure substantially as shown in FIG. 4 was prepared by coating on a cellulose acetate film support successively with the following layers which correspond to the numbered layers in FIG. 4:

Layer 51.—A gelatino - silver thiocyanate emulsion coated at 0.030 gram silver per square foot and 100 mg. gelatin per square foot and containing 2.7×10^{-7} grams zinc sulfide (nuclei) per square foot, 50 mg. 1-hydroxy-4-(3-n-octadecylcarbamylphenylthio)-N-ethyl - 3′,5′ - dicarboxy-2-naphthamide per square foot and 15 mg. 2-octadecyl-5-sulfohydroquinone potassium salt per square foot. The phenolic DDR coupler of this layer yields a diffusible indoaniline cyan dye image upon reaction with the oxidized color developing agent in the uninhibited areas of layer **51**.

Layer 52.—A red-sensitive gelatino-silver bromoiodide emulsion coated at 0.112 gram silver per square foot and 160 mg. gelatin per square foot and containing 45 mg. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecyloxy - 2 - naphthanilide, per square foot. The phenolic DIR coupler of this layer, and of layers **55** and **58**, reacts at its coupling position with oxidized color developing agent, in the region of exposure, to form a nondiffusing cyan dye and replace the tetrazolylthio radical to yield the corresponding mercaptan which is effective to inhibit the development of the adjacent nucleated silver salt of layers **51**, **54** and **57**, respectively.

Layer 53.—A gelatino-silver iodide emulsion coated at 0.050 gram silver per square foot and 80 mg. gelatin per square foot and containing 22.5 mg. of the nondiffusing magenta colored filter dye, 1-hydroxy-4′-(4-tert.-butylphenoxy)-4-phenylazo-2-naphthamide, per square foot and 30 mg. 2-octadecyl-5-sulfohydroquinone potassium salt per square foot. The silver iodide of this layer and of layer **56** serves to prevent upward diffusion of the mercaptan from layers **52** and **55**.

Layer 54.—A gelatino-silver thiocyanate emulsion coated at 0.049 gram silver per square foot and 100 mg. gelatin per square foot and containing 5.4×10^{-6} gm. zinc sulfide (nuclei) per square foot, 50 mg. of 1-phenyl-3-(3,5-disulfobenzamido)-4-(2-hydroxy-4-n-pentadecylphenylazo)-5-pyrazolone dipotassium salt per square foot and 15 mg. 2-octadecyl-5-sulfohydroquinone potassium salt per square foot. This 5-pyrazolone DDR coupler yields a diffusible magenta azomethine dye image in the process.

Layer 55.—A green-sensitive gelatino-silver bromoiodide emulsion coated at 0.075 gram silver per square foot, 100 mg. gelatin per square foot, and 30 mg. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecyloxy-2-naphthanilide, per square foot.

Layer 56.—A gelatino-silver iodide emulsion containing 0.05 gram silver per square foot and 100 mg. gelatin per square foot and also 66 mg. 1-(2,4,6-trichlorophenyl)-3-{3-[α-(2,4-di-tert.-amylphenoxy)acetamido]-benzamido}-4-(p-methoxyphenylazo)-5-pyrazolone per square foot and 30 mg. 2-octadecyl-5-sulfohydroquinone potassium salt per square foot. The yellow pyrazolone coupler of this layer serves as a light filter to confine the blue image exposure to layer **58**.

Layer 75.—A gelatino silver thiocyanate emulsion coated at 0.04 gram silver per square foot and 100 mg. gelatin per square foot and containing also 7.2×10^{-7} grams zinc sulfide (nuclei) per square foot, 100 mg. α-benzoyl-α-(3-octadecylcarbamylphenylthio)-3,5-dicarboxyacetanilide per square foot and 15 mg. 2-octadecyl-5-sulfohydroquinone potassium salt per square foot. The DDR coupler of this layer yields a diffusible yellow azomethine dye image in the process.

Layer 58.—A blue-sensitive gelatino-silver bromoiodide emulsion coated at 0.075 gram silver per square foot and 100 mg. gelatin per square foot and containing, in addition, 30 mg. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5-tetrazolylthio)-2′-tetradecyloxy-2-naphthanilide, per square foot.

The resulting element was exposed to a colored subject and immersed with a paper receiving sheet having a gelatin layer containing a mordant such as cetyl trimethyl ammonium bromide in the following color developing solution and placed for about 5 minutes at 85° F. into contact with the paper reception sheet.

Ascorbic acid	mg..	200
4-amino-N-ethyl-N-β-hydroxyethyl aniline sulfate	g..	5
$Na_2CO_3\cdot H_2O$	g..	40
N,N-diethyl-1,3-propanediamine	ml..	1
Sodium thiosulfate (pentahydrate)	mg..	100
H_2O to 1 liter.		
pH 11.0 (adjusted).		

As a result the exposed silver halide in layers **52**, **55** and **58** develops and the DIR couplers therein react with the oxidized color developing agent obtained in the reaction thereby forming a development inhibiting mercaptan that inhibits development of adjacent areas of the nucleated silver thiocyanate emulsion layers **51**, **54** and **57**, respectively. The residual developer solution migrates to the positive areas of layers **51**, **54** and **57** causing physical development to proceed and diffusible cyan, magneta and yellow dyes to be produced which transfer by diffusion imagewise and in register to the mordanted receiving sheet to provide a multicolor positive reproduction of the original subject thereon.

EXAMPLE 3

The process described in Example 2 was carried out except that the silver thiocyanate of layers **51**, **54** and **57** was substituted with a silver cyanide emulsion in equal molar amount and development was carried out using the following developer solution instead of that of Example 2.

Ascorbic acid	mg..	200
4-amino-N-ethyl-N-β-hydroxyethyl aniline sulfate	g..	4
$Na_2CO_3\cdot H_2O$	g..	40
Potassium chloride	g..	10
Sodium thiosulfate (pentahydrate)	mg..	500
H_2O to 1 liter.		
pH (unadjusted).		

The resulting element was then exposed to a colored subject and treated with the developer solution and placed for about 5 minutes at 85° F. into contact with the paper reception sheet containing a dye mordant as described in Example 2. The exposed silver halide in layers **52**, **55** and **58** develops, and the DIR couplers therein react with oxidizer color developing agent obtained in the reaction thereby forming a development inhibiting mercaptan that inhibits development of adjacent areas of the nucleated emulsion layers **51**, **54** and **57** respectively. The residual developer solution migrates to the positive areas of layers **51**, **54** and **57** causing physical development to proceed and diffusible cyan, magenta and yellow dyes to be produced which transfer by diffusion imagewise and in register to the mordanted receiving sheet to provide a multicolor positive reproduction of the original subject thereon.

EXAMPLE 4

A color film having the structure substantially as shown in FIG. 1 was prepared by coating a subbed cellulose acetate film support successively with the following layers which correspond to the numbered layers in FIG. 1:

Layer 11.—A fogged gelatino-silver chlorobromoiodide emulsion containing one mole of the silver halide, 12,600 cc. of a 1% solution of the magenta-forming DDR coupler, 1-phenyl-3-(3,5-disulfobenzamino)-4-(4-octadecyloxyphenylazo)5-pyrazolone disodium salt, in aqueous gelatin solution, 740 cc. of 7.5% saponin solution, 134 cc. of 2.7% mucochloric acid solution made up to 22,100 cc. with water was coated on the film support at a coverage of 6,150 cc. per 1,000 square feet. The coating contained 30 mg. of silver, 30 mg. of the DDR coupler per square foot and 184 mg. of gelatin per square foot.

Layer 12.—A dispersion in gelatin solution of 1 g. of the DIR coupler, 1-[4-(4-t-butylphenoxy)phenyl]-3-[α(4-t-butylphenoxy)-propionamido]-4-[3-(5-mercapto-1-tetrazolyl)phenylazo]-5-pyrazolone, 3 g. of tricresyl phosphate, 3 g. of diethyl lauramide, 512 cc. of 7.5% saponin solution, 90 cc. of 2.7% mucochloric acid and water to 16,800 g. was coated at a coverage of 8,575 cc. per 1,000 square feet. The coating containing 92 mg. of the DIR coupler, 267 mg. of the phosphate and lauramide, and 230 mg. of gelatin per square foot.

Layer 13.—A gelatino-silver bromide emulsion that was sensitized to green light and contained one mole of the silver halide, 400 cc. of 7.5% saponin solution, 108 cc. of 2.7% mucochloric acid solution and water to 1,200 g. was coated at a coverage of 462 cc. per 100 square feet. The coating contained 415 mg. of silver and 210 mg. of gelatin per square foot.

Layer 14.—A gelatino-silver chloride emulsion containing one mole of silver, 216 cc. of 7.5% saponin, 43 cc. of 2.7% of mucochloric acid and water to make 6,480 g. was coated over 10,080 square feet. The resulting layer contained 100 mg. of silver per square foot and 200 mg. of gelatin per square foot.

Layer 15.—This layer is substantially identical to layer **11** except that the cyan-forming DDR coupler, 2-(3,5-disulfobenzamido)-5-methyl-4-(4-octadecyloxyphenylazo)phenol dipotassium salt, is used in lieu of the magenta-forming coupler.

Layer 16.—This layer is substantially the same as layer **12**.

Layer 17.—This layer is substantially the same as layer **13** except that the silver halide is sensitized to red light rather than green light.

Layer 18.—This layer is substantially the same as layer **14** except that sufficient Carey Lea silver is added to obtain a coverage of 4.6 mg. per square foot.

Layer 19.—This layer is substantially the same as layer **11** except that the yellow-forming DDR coupler, 2-(3,5-disulfobenzamido) - 5 - methyl - 4-(4-octadecyloxyphenylazo)phenol dipotassium salt, is used in lieu of the magenta-forming DDR coupler.

Layer 20.—This layer is substantially the same as layer **12.**

Layer 21.—This layer is substantially the same as layer **13** except that it is sensitive to blue light only.

Layer 22.—This is a protective gelatin layer at a coverage of 50 mg. of gelatin per square foot.

The fogged silver halide emulsions were prepared by exposing the emulsions to a 40-watt bulb at 60 inches for 30 seconds. The resulting photographic element was exposed to a colored subject and immersed with a paper receiving sheet having a gelatin layer containing a mordant such as dimethyl - β - hydroxyethyl-α-(octadecylamido)-propyl ammonium dihydrogen phosphate in the following color developing solution and squeegeed together for about 5 minutes at 85° F.

Sodium carbonate	g	20
Sodium hexametaphosphate	g	20
Benzyl alcohol	cc	10
3-acetamido-4-amino-N,N-diethylaniline	g	2

Water to one liter.
pH adjusted to 11.

As a result, the exposed silver halide in layers **13**, **17** and **21** develops and the DIR couplers in layers **12**, **16** and **20** contiguous thereto react with oxidized color developing agent obtained in the reaction thereby releasing a diffusible mercaptan that inhibits development in adjacent negative areas in the fogged emulsion layers **11**, **15** and **19**. The residual developer solution migrates to the positive areas of layers **11**, **15** and **19**, and proceeds to develop these fogged layers to form diffusible magenta, cyan and yellow dyes which transfer by diffusion imagewise and in register to the mordanted receiving sheet to provide a multi-color positive reproduction of the original subject.

EXAMPLE 5

A color film having the structure substantially as shown in FIG. 2 was prepared by coating a subbed cellulose acetate film support successively with the following layers which correspond to the numbered layers of FIG. 2:

Layer 31.—A fogged gelatino-silver chlorobromoiodide emulsion containing one mole of silver, 8,400 cc. of 1% aqueous solution of the magenta-forming DDR coupler, 1 - phenyl - 3-(3,5-disulfobenzamido)-4-(4-octadecyloxyphenylazo)-5-pyrazolone disodium salt, 740 cc. of 7.5% saponin in water, 134 cc. of 2.7% mucochloric acid in water and water to make 22,100 g. was coated on the support so that the resulting layer contained 30 mg. of silver per square foot, 30 mg. of the DDR coupler per square foot and 184 mg. of gelatin per square foot.

Layer 32.—A gelatino-silver chlorobromoiodide emulsion sensitized to green light and containing one mole of the silver halide, the DIR coupler, 1-hydroxy-4-(2-nitrophenylthio) - 2 - [δ-(2,4-di-tert.-amylphenoxy)butyl]naphthamide in 159 cc. of 2,4-di-n-amylphenol dispersed in aqueous gelatin solution, 400 cc. of 7.5% saponin, 73 cc. of 2.7% mucochloric acid and water to make 12,000 g. was coated to give 62 mg. of silver per square foot, 91 mg. of the DIR coupler and coupler solvent per square foot and 214 mg. of gelatin per square foot.

Layer 33.—A gelatino-silver chloride emulsion containing one mole of silver, 2.6 cc. of 7.5% saponin, 43 cc. of 2.7% mucochloric acid and water to make 6,480 g. was coated in a layer having 100 mg. of silver per square foot and 200 mg. of gelatin per square foot.

Layer 34.—This layer is substantially the same as layer **31** except that the fogged silver halide emulsion contained the cyan-forming DDR coupler, 2-(3,5-disulfobenzamido)-5-methyl-4-(4-octadecyloxyphenylazo)phenol dipotassium salt, in lieu of the magenta-forming DDR coupler, the coupler being coated to obtain a layer having 87 mg. of the coupler per square foot.

Layer 35.—This layer is substantially the same as layer **32** except that one mole of a gelatino-silver chlorobromide emulsion sensitive to red light was utilized in lieu of the green-sensitive silver halide emulsion.

Layer 36.—This layer is substantially the same as layer **33** except that sufficient Carey Lea Silver is added to obtain a coverage of 4.6 mg. per square foot.

Layer 37.—This layer is substantially the same as layer **31** except that the fogged silver halide emulsion containing the yellow-forming DDR coupler, 1-hydroxy-4-(2,4-dinitrophenylthio) - N-[δ-(2,4-di-tert.-amylphenoxy)butyl]-2-naphthamide, was used in lieu of the magenta-forming DDR coupler.

Layer 38.—This layer is substantially the same as layer **32** except that one mole of gelatino-silver chlorobromide emulsion sensitive to blue light was used in lieu of the green-sensitive silver halide emulsion.

Layer 39.—This is a protective gelatin layer at a coverage of 50 mg. of gelatin per square foot.

The fogged gelatino-silver halide emulsions were prepared as described in Example 4. The resulting film was exposed and processed as described in Example 4 to yield a multi-colored positive reproduction on the receiving sheet.

EXAMPLE 6

A color film having the structure substantially as shown in FIG. 3 is prepared by coating a subbed cellulose acetate film support successively with the following layers which correspond to the numbered layers of FIG. 3:

Layer 41.—50 g. of the DIR coupler, 1-hydroxy-4-(1-phenyl-5 - tetrazolylthio) - N - [δ-(2,4-di-tert.-amylphenoxy)butyl]-2-naphthamide, are dissolved in 200 ml. of ethyl acetate at 40° C. and the resulting solution mixed with 500 ml. of 10% phthaloylated gelatin containing 30 ml. of 5% Alkanol B at 40° C. The resulting composition is then dispersed by passing it through a colloid mill. The dispersion is then set on a chilled plate, noodled, and air-dried to constant weight. 1.45 g. of the resulting dried DIR coupler dispersion containing 0.71 g. of coupler is soaked in 8 ml. of 2.5% sodium citrate solution for about 30 minutes, and then dispersed by heating at 40° C. with stirring. To this dispersion is added 17.5 g. of 20% phthaloylated gelatin and the mixture stirred for about 5 minutes. Thereafter, 2.8 ml. of 5% styrene-maleamic polymeric solution is added, followed one minute later by 25.9 g. (containing 0.01 M of silver) of melted green-sensitized gelatino-silver chlorobromide emulsion. Packets form with continued stirring at 40° C. which are hardened after 10 minutes with 3 ml. of 10% calcium acetate solution. Following the procedure disclosed in U.S. Patent 2,787,544, the packets are dispersed at the time of coating in a coupler solvent in an amount such that about twice the weight of the coupler solvent to the DIR coupler is contained in the coating mixture. The coupler solvent is prepared by mixing 20 g. of 2,4-di-n-amyl phenol with a solution of 75 ml. of 20% phthalolylated gelatin and 5 ml. of 10% Alkanol B at 40° C., followed by a dispersing of the mixture in a colloid mill. A gelatin dispersion of silver bromoiodide light-fogged as described in Example 4 and containing the magenta-forming DDR coupler, 1-phenyl-3-(3,5 - disulfobenzamido)-4-(4-n-pentadecyl-2-hydroxyphenylazo)-5-pyrazolone disodium salt, and the antioxidant, n-octadecyl hydroquinone monosulfonate potassium salt, is prepared. The resulting emulsion is coated to form a Color-Forming Unit, layer **41.**

Layer 42.—A gelatino-silver chloride emulsion containing one mole of silver, 2.6 cc. of 7.5% saponin, 43 cc. of 2.7% mucochloric acid and water to make 6,480 g. is coated in a layer having 100 mg. of silver per square foot and 200 mg. of gelatin per square foot.

Layer 43.—This red-sensitive Color-Forming Unit is prepared substantially the same as described above for layer **41** except that a red-sensitized gelatino-silver chlorobromide emulsion is utilized in the packet in lieu of the green-sensitized emulsion and the cyan-forming DDR coupler, 2-(3,5-disulfobenzamido)-5-methyl-4-(4 - octadecyloxyphenylazo)phenol dipotassium salt, is utilized in lieu of the magenta-forming DDR coupler of layer **41**.

Layer 44.—This layer is substantially the same as layer **42** except that sufficient Carey Lea silver is added to obtain a coverage of 4.6 mg. per square foot.

Layer 45.—This blue-sensitive Color-Forming Unit is prepared substantially the same as layer **41** described above, except that the gelatino-silver chlorobromide emulsion is a blue-sensitive emulsion rather than a green-sensitive emulsion and the yellow-forming DDR coupler, 1-hydroxy-4-{4-[4-(1-sulfophenyl-3-methyl pyrazolyl)azo]-3-sulfophenylazo}-N-[δ-(2,4-di-tert. - amylphenoxy)butyl]-2-naphthamide disodium salt, is utilized in lieu of the magenta-forming coupler of layer **41**.

Each Color-Forming Unit is coated to have substantially the same coverage with respect to couplers, silver and gelatin as described in Example 4. The resulting film is exposed and processed as described in Example 4 to yield a multicolored positive reproduction on the receiving sheet.

In the above examples, the barrier layers were prepared with silver chloride or iodide salts having substantially less sensitivity to light than the light-sensitive latent image-recording silver halide emulsions. Further, in the above examples, the transfer dye images obtained were full color positive images having good "clean out" (low D_{min}), such not being obtained if the development inhibitor-releasing (DIR) couplers were not present in the photographic elements or in the processing solutions as described.

The present invention thus provides new and useful photographic elements as well as new diffusion transfer processes for preparing color images from such photographic elements.

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

We claim:

1. A color photographic diffusion transfer process for treating an exposed photographic element containing latent negative image regions and having at least two Color-Forming Units in layers sensitive to different regions of the visible spectrum, and a barrier layer separating each of said Color-Forming Units comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt of mercaptans; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion of a hydrophilic colloid and a silver halide,

(2) a developable emulsion of a hydrophilic colloid and a water-insoluble metal salt developable to substantial density without exposure to light with a color developing agent, and

(3) a nondiffusible acid dye-releasing coupler contiguous to said water-insoluble metal salt of said developable emulsion that releases a diffusible acid dye on reaction with an oxidized color developing agent;

which comprises treating said exposed photographic element with a photographic alkaline color developing solution containing an aromatic primary amino developing agent so that in each of said Color-Forming Units said silver halide in said negative image regions of said light-sensitive emulsion is developed with said developing agent in the presence of a development inhibitor-releasing coupler that reacts with oxidized color developing agent to form a diffusible mercaptan development inhibitor in said negative image regions, reacting said development inhibitor-releasing coupler with resulting oxidized developing agent and forming a diffusible mercaptan development inhibitor, said diffusible mercaptan development inhibitor thereafter diffusing to said developable emulsion and inhibiting development in regions corresponding to said negative image regions, said barrier layer preventing said diffusible mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble salt with mercaptans diffusing to said barrier layer, said developable emulsion thereafter being developed with said developing agent in the presence of said acid dye-releasing coupler that reacts with resulting oxidized developing agent to form a diffusible acid dye in regions not inhibited against development by said mercaptan development inhibitor, and said diffusible acid dye diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes.

2. A photographic element comprising at least two Color-Forming Units in layers sensitive to different regions of the visible spectrum, and a barrier layer separating each of said Color-Forming Units comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion of a hydrophilic colloid and a silver halide,

(2) a nondiffusible development inhibitor-releasing coupler contiguous to said silver halide of said light-sensitive emulsion that releases a diffusible marcaptan development inhibitor on reaction with oxidized developing agent of a photographic alkaline color developing solution containing an aromatic primary amino developing agent,

(3) a developable emulsion of a hydrophilic colloid and a water-insoluble metal salt developable to substantial density without exposure to light with said color developing solution, and

(4) a nondiffusible acid dye-releasing coupler contiguous to said water-insoluble metal salt of said developable emulsion that releases a diffusible acid dye on reaction with said oxidized developing agent.

3. A color photographic diffusion transfer process for treating an exposed photographic element containing latent negative image regions and having at least two Color-Forming Units in layers sensitive to different regions of the visible spectrum, and a barrier layer separating each of said Color-Forming Units comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion of a hydrophilic colloid and a silver halide,

(2) a developable emulsion of a hydrophilic colloid and a water-insoluble metal salt developable to substantial density without exposure to light with a color developing agent,

(3) a nondiffusible acid dye-releasing coupler contiguous to said water-insoluble metal salt of said developable emulsion that releases a diffusible acid dye on reaction with an oxidized color developing agent;

which comprises treating said exposed photographic element with a photographic alkaline color developing solution containing an aromatic primary amino developing agent so that in each of said Color-Forming Units said silver halide in said negative image regions of said light-sensitive emulsion is developed with said developing agent in the presence of a development inhibitor-releasing coupler that reacts with oxidized color developing agent to form a diffusible mercaptan development inhibitor in said negative image regions, reacting said development inhibitor-releasing coupler with resulting oxidized developing agent and forming a diffusible mercaptan development inhibitor, said diffusible mercaptan development inhibitor thereafter diffusing to said developable emulsion and inhibiting development in regions corresponding to said negative image regions, said barrier layer preventing said diffusible mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble salt with mercaptans diffusing to said barrier layer, said developable emulsion thereafter being developed with said developing agent in the presence of said acid dye-releasing coupler that reacts with resulting oxidized developing agent to form a diffusible acid dye in regions not inhibited against development by said mercaptan development inhibitor, and said diffusible acid dye diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes; said acid dye-releasing coupler having a formula selected from the group consisting of

DYE-LINK-(COUP-BALL)$_n$ and
BALL-LINK-(COUP-SOL)$_n$

and said development inhibitor-releasing coupler having a formula selected from the group consisting of

(BALL-COUP)$_n$-LINK-MERC and
(BALL)$_m$-COUP-S-RAD

wherein

(1) DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group,

(2) LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, and alkylidene radical, a monothio radical, a dithio radical and an azoxy radical,

(3) —S— is a monothio connecting radical,

(4) COUP is a photographic coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with one of said connecting radicals,

(5) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible,

(6) SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said developing agent is free of an acidic solubilizing group,

(7) *m* in an integer of 0 to 1,

(8) n is an integer of 1 to 2 when said LINK is an alkylidene radical, and *n* is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a monothio radical, a dithio radical and an azoxy radical,

(9) MERC is a diffusible radical containing a mercapto group, and

(10) RAD is a photographically inert diffusible radical that forms a mercaptan with said monothio connecting radical.

4. The process as described in claim 3 wherein the developable emulsion is an emulsion of a hydrophilic colloid and a silver halide that is fogged so that it can be developed to substantial density without exposure to light with a photographic alkaline color developing solution containing an aromatic primary amino developing agent.

5. The process as described in claim 3 wherein the developable emulsion is an emulsion of a hydrophilic colloid and a silver halide containing physical development nuclei.

6. A color photographic diffusion transfer process for treating an exposed photographic element containing latent negative image regions and having superposed on a photographic support three Color-Forming Units in layers sensitive to red, green and blue light respectively, and a barrier layer separating each of said Color-Forming Units comprising a hydrophilic colloid containing a silver halide; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion layer of a hydrophilic colloid and a silver halide,

(2) a nondiffusible development inhibitor-releasing coupler contiguous to said silver halide of said light-sensitive emulsion layer that releases a diffusible mercaptan development inhibitor on reaction with an oxidized color developing agent,

(3) a developable emulsion layer of a hydrophilic colloid and a water-insoluble silver salt developable to substantial density without exposure to light with a color developing agent, and

(4) a nondiffusible acid dye-releasing coupler capable of forming a diffusible acid dye contiguous to said water-insoluble silver salt of said developable emulsion layer on reaction with an oxidized color developing agent, said acid dye-releasing coupler releasing a diffusible yellow acid dye when said light-sensitive emulsion layer is sensitive to blue light, a diffusible magenta dye when said light-sensitive emulsion layer is sensitive to green light and a diffusible cyan dye when said light-sensitive emulsion layer is sensitive to red light;

which comprises treating said exposed photographic element with a photographic alkaline color developing solution containing an aromatic primary amino developing agent so that in each of said Color-Forming Units, silver halide in said negative image regions of said light-sensitive emulsion layer is developed with said developing agent and said development inhibitor-releasing coupler contiguous to the silver halide reacts with resulting oxidized developing agent to form a diffusible mercaptan development inhibitor in said negative image regions, said diffusible mercaptan development inhibitor thereafter diffusing to said developable emulsion layer and inhibiting development in regions corresponding to said negative image regions, said barrier layers preventing said diffusible mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble silver salt with mercaptans diffusing to said barrier layers, said developable emulsion layer thereafter being developed with said developing agent and said acid dye-releasing coupler contiguous to said water-insoluble silver salt in said developable emulsion layer reacting with resulting oxidized developing agent to form a diffusible acid dye in regions not inhibited against development by said mercaptan development inhibitor, and said diffusible acid dye diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes; said acid dye-releasing coupler having a formula selected from the group consisting of

DYE-LINK-(COUP-BALL)$_n$ and
BALL-LINK-(COUP-SOL)$_n$

and said development inhibitor-releasing coupler having a formula selected from the group consisting of

(BALL-COUP)$_n$-LINK-MERC and
BALL-COUP-S-RAD

wherein

(1) DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group,

(2) LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a monothio radical, a dithio radical and an azoxy radical,

(3) —S— is monothio connecting radical;

(4) COUP is a photographic coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with one of said connecting radicals,

(5) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible,

(6) SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said developing agent is free of an acidic solubilizing group,

(7) *n* is an integer of 1 to 2 when said LINK is an alkylidene radical, and *n* is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a monothio radical, a dithio radical and an azoxy radical,

(8) MERC is a diffusible radical containing a mercapto group, and

(9) RAD is a photographically inert diffusible radical that forms a mercaptan with said monothio connecting radical.

7. The process as described in claim 6 wherein the reception layer is a receiving sheet separate from the photographic element and wherein said receiving sheet is wetted with the developing solution substantially concurrently with the photographic element, pressed in superposed relation to the emulsion side of the photographic element, and after the diffusible acid dyes have diffused imagewise thereto, stripped from the photographic element.

8. A color photographic diffusion transfer process for treating an exposed photographic element containing latent negative image regions and having superposed on a photographic support three Color-Forming Units in layers sensitive to red, green and blue light respectively, the said Color-Forming Unit sensitive to blue light being furthest from said support and being separated from the other of said Color-Forming Units by a barrier layer comprising in a hydrophilic colloidal substrate containing a yellow filter material and a silver halide less sensitive to light than said Color-Forming Units, and the said Color-Forming Units sensitive to red and green light respectively being separated by a barrier layer comprising a hydrophilic colloidal substrate containing a silver halide less sensitive to light than said Color-Forming Units; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion layer of a hydrophilic colloid and a silver halide,

(2) a nondiffusible development inhibitor-releasing coupler contiguous to said silver halide of said light-sensitive emulsion layer that releases a diffusible mercaptan development inhibitor on reaction with an oxidized color developing agent,

(3) a developable emulsion layer of a hydrophilic colloid and a water-insoluble silver salt developable to substantial density without exposure to light with a color developing agent and positioned closer to said support than said light-sensitive layer, and

(4) a nondiffusible acid dye-releasing coupler capable of forming a diffusible acid dye complementary to the color of the spectral sensitivity of the light-sensitive emulsion layer on reaction with an oxidized color developing agent contiguous to said water-insoluble silver salt of said developable emulsion;

which comprises treating said exposed photographic element with a photographic alkaline color developing solution containing an aromatic primary amino developing agent so that in each of said Color-Forming Units silver halide in said negative image regions of said light-sensitive emulsion layer is developed with said developing agent and said development inhibitor-releasing coupler continguous to the silver halide reacts with resulting oxidized developing agent to form a diffusible mercaptan development inhibitor in said negative image regions, said diffusible mercaptan development inhibitor thereafter diffusing to said developable emulsion layer and inhibiting development in regions corresponding to said negative image regions, said barrier layers preventing said diffusible mercaptan development inhibitor formed in one Color-Forming Unit from diffusing to another Color-Forming Unit by forming an insoluble silver salt with mercaptans diffusing to said barrier layers, said developable emulsion layer thereafter being developed with said developing agent and said acid dye-releasing coupler contiguous to said water-insoluble silver salt in said developable emulsion layer reacting with resulting oxidized developing agent to form a diffusible acid dye in regions not inhibited against development by said mercaptan development inhibitor, and said diffusible acid dye diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes; said acid dye-releasing coupler having the formula

BALL-LINK-COUP-SOL

and said development inhibitor-releasing coupler having the formula

BALL-COUP-S-RAD

wherein

(1) LINK is a connecting radical selected from the group consisting of an azo radical, an oxy radical and a monothio radical,

(2) —S— is a monothio connecting radical,

(3) COUP is a photographic coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with one of said connecting radicals,

(4) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible,

(5) SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing agent when said developing agent is free of an acidic solubilizing group, and

(6) RAD is a photographically inert diffusible radical that forms a mercaptan with said monothio connecting radical.

9. The process as described in claim 8 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and silver thiocyanate containing physical development nuclei.

10. The process as described in claim 8 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and silver cyanide containing physical development nuclei.

11. The process as described in claim 8 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and a silver halide fogged so that it can be developed to substantial density without exposure to light with a photographic alkaline color developing solution containing an aromatic primary amino developing agent.

12. The process as described in claim 8 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and a silver halide containing zinc sulfide physical development nuclei.

13. A photographic element comprising at least two Color-Forming Units in layers sensitive to different regions of the visible spectrum, and a barrier layer separating each of said Color-Forming Units comprising a hydrophilic colloid containing a water-insoluble reactant capable of forming a water-insoluble salt with mercaptans; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion of a hydrophilic colloid and a silver halide,

(2) a nondiffusible development inhibitor-releasing coupler contiguous to said silver halide of said light-sensitive emulsion that releases a diffusible mercaptan development inhibitor on reaction with oxidized developing agent of a photographic alkaline color developing solution containing an aromatic primary amino developing agent,

(3) a developable emulsion of a hydrophilic colloid and a water-insoluble metal salt developable to substantial density without exposure to light with said color developing solution,

(4) a nondiffusible acid dye-releasing coupler contiguous to said water-insoluble metal salt of said developable emulsion that releases a diffusible acid dye on reaction with said oxidized developing agent;

said acid dye-releasing coupler having a formula selected from the group consisting of

$$\text{DYE-LINK-(COUP-BALL)}_n \text{ and}$$
$$\text{BALL-LINK-(COUP-SOL)}_n$$

and said development inhibitor-releasing coupler having a formula selected from the group consisting of

$$\text{(BALL-COUP)}_n\text{-LINK-MERC and}$$
$$\text{(BALL)}_m\text{-COUP-S-RAD}$$

wherein

(1) DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group,

(2) LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a monothio radical, a dithio radical and an azoxy radical,

(3) —S— is a monothio connecting radical,

(4) COUP is a photographic coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with one of said connecting radicals,

(5) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible,

(6) SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said developing agent is free of an acidic solubilizing group,

(7) *m* is an integer of 0 to 1,

(8) *n* is an integer of 1 to 2 when said LINK is an alkylidene radical, and *n* is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a monothio radical, a dithio radical and an azoxy radical,

(9) MERC is a diffusible radical containing a mercapto group, and

(10) RAD is a photographically inert diffusible radical that forms a mercaptan with said monothio connecting radical.

14. A photographic element as described in claim **13** wherein the developable emulsion is an emulsion of a hydrophilic colloid and a silver halide that is fogged so that it can be developed to substantial density without exposure to light with a photographic alkaline color developing solution containing an aromatic primary amino developing agent.

15. A photographic element as described in claim **13** wherein the developable emulsion is an emulsion of a hydrophilic colloid and a silver halide containing physical development nuclei.

16. A photographic element comprising a photographic support, three Color-Forming Units in layers sensitive to red, green and blue light respectively superposed on said support, and a barrier layer separating each of said Color-Forming Units comprising a hydrophilic colloid containing a silver halide; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion layer of a hydrophilic colloid and a silver halide,

(2) a nondiffusible development inhibitor-releasing coupler contiguous to said silver halide of said light-sensitive emulsion layer that releases a diffusible mercaptan development inhibitor on reaction with oxidized color developing agent of a photographic alkaline color developing solution containing an aromatic primary amino developing agent,

(3) a developable emulsion layer of a hydrophilic colloid and a water-insoluble silver salt developable to substantial density without exposure to light with said color developing solution, and

(4) a nondiffusible acid dye-releasing coupler capable of forming a diffusible acid dye contiguous to said water-insoluble silver salt of said developable emulsion layer on reaction with said oxidized developing agent, said acid dye-releasing coupler releasing a diffusible yellow acid dye when said light-sensitive emulsion layer is sensitive to blue light, a diffusible magenta dye when said light-sensitive emulsion layer is sensitive to green light and a diffusible cyan dye when said light-sensitive emulsion layer is sensitive to red light;

said acid dye-releasing coupler having a formula selected from the group consisting of

$$\text{DYE-LINK-(COUP-BALL)}_n \text{ and}$$
$$\text{BALL-LINK-(COUP-SOL)}_n$$

and said development inhibitor-releasing coupler having a formula selected from the group consisting of

$$\text{(BALL-COUP)}_n\text{-LINK-MERC and}$$
$$\text{BALL-COUP-S-RAD}$$

wherein

(1) DYE is a dye radical exhibiting selective absorption in the visible spectrum and containing an acidic solubilizing group,

(2) LINK is a connecting radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, an alkylidene radical, a monothio radical, a dithio radical and an azoxy radical,

(3) —S— is a monothio connecting radical,

(4) COUP is a photographic coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with one of said connecting radicals,

(5) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible,

(6) SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing group when said developing agent is free of an acidic solubilizing group,

(7) *n* is an integer of 1 to 2 when said LINK is an alkylidene radical, and *n* is 1 when said LINK is a radical selected from the group consisting of an azo radical, a mercuri radical, an oxy radical, a monothio radical, a dithio radical and an azoxy radical,

(8) MERC is a diffusible radical containing a mercapto group, and

(9) RAD is a photographically inert diffusible radical that forms a mercaptan with said monothio connecting radical.

17. A photographic element comprising superposed on a photographic support three Color-Forming Units in layers sensitive to red, green and blue light respectively, the said Color-Forming Unit sensitive to blue light being furthest from said support and being separated from the other of said Color-Forming Units by a barrier layer comprising in a hydrophilic colloidal substrate containing a yellow filter material and a silver halide less sensitive to light than said Color-Forming Units, and the said Color-Forming Units sensitive to red and green light respectively being separated by a barrier layer comprising a hydrophilic colloidal substrate containing a silver halide less sensitive to light than said Color-Forming Units; each of said Color-Forming Units comprising

(1) a light-sensitive emulsion layer of a hydrophilic colloid and a silver halide,

(2) a nondiffusible development inhibitor-releasing coupler contiguous to said silver halide of said light-sensitive emulsion layer that releases a diffusible mercaptan development inhibitor on reaction with oxidized color developing agent of a photographic alkaline color developing solution containing an aromatic primary amino developing agent,

(3) a developable emulsion layer of a hydrophilic colloid and a water-insoluble silver salt developable to substantial density without exposure to light with said developing agent and positioned closer to said support than said light-sensitive layer, and

(4) a nondiffusible acid dye-releasing coupler capable of forming a diffusible acid dye complementary to the color of the spectral sensitivity of the light-sensitive emulsion layer on reaction with said oxidized developing agent contiguous to said water-insoluble silver salt of said developable emulsion;

said acid dye-releasing coupler having the formula

BALL-LINK-COUP-SOL

and said development inhibitor-releasing coupler having the formula

BALL-COUP-S-RAD

wherein

(1) LINK is a connecting radical selected from the group consisting of an azo radical, an oxy radical and a monothio radical,

(2) —S— is a monothio connecting radical,

(3) COUP is a photographic coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with one of said connecting radicals,

(4) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible,

(5) SOL is selected from the group consisting of a hydrogen atom and an acidic solubilizing group when said developing agent contains an acidic solubilizing group, and SOL is an acidic solubilizing agent when said developing agent is free of an acidic solubilizing group, and

(6) RAD is a photographically inert diffusable radical that forms a mercaptan with said monothio connecting radical.

18. A photographic element as described in claim 17 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and silver thiocyanate containing physical development nuclei.

19. A photographic element as described in claim 17 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and silver cyanide containing physical development nuclei.

20. A photographic element as described in claim 17 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and a silver halide fogged so that it can be developed to substantial density without exposure to light with a photographic alkaline color developing solution containing an aromatic primary amino developing agent.

21. A photographic element as described in claim 17 wherein the developable emulsion layer is an emulsion of a hydrophilic colloid and a silver halide containing zinc sulfide physical development nuclei.

References Cited by the Examiner

UNITED STATES PATENTS

2,455,170	11/1948	Glass et al.	96—100
2,543,181	2/1951	Land	96—29
2,661,293	12/1953	Land	96—29
2,673,800	3/1954	Meenssen et al.	96—74
2,688,539	9/1954	Heimbach et al.	96—100
2,694,008	11/1954	Berger et al.	96—100
2,712,995	7/1955	Weyde	96—29
2,756,142	7/1956	Yutzy	96—3
2,774,668	12/1956	Rogers	96—29
2,808,329	10/1957	Whitmore	96—100
2,860,974	11/1958	Williams	96—9
3,148,062	9/1964	Whitmore et al.	96—3

NORMAN G. TORCHIN, *Primary Examiner.*