July 11, 1967 W. M. SALMINEN 3,330,655

PREPARATION OF PHOTOGRAPHIC DIRECT POSITIVE COLOR IMAGES

Filed Sept. 20, 1963

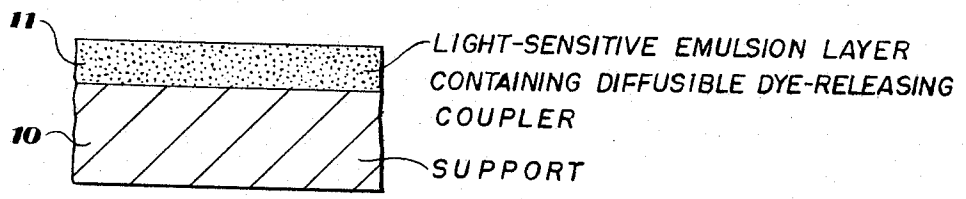


Fig. 1

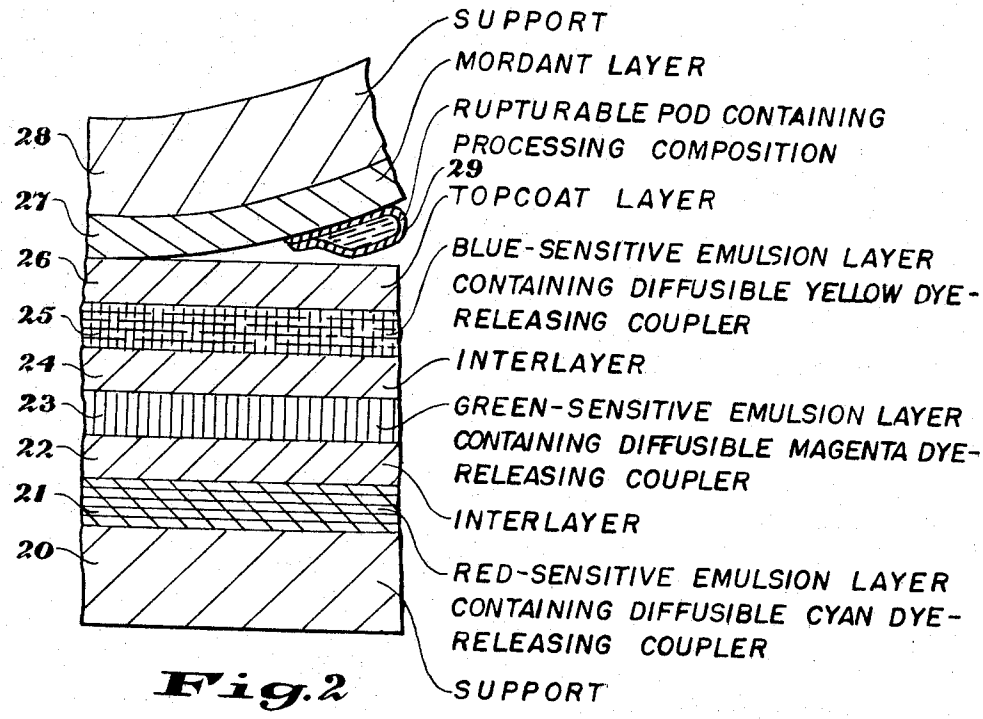


Fig. 2

Wilho M. Salminen
INVENTOR.
BY R. Frank Smith
James R. Lucas
ATTORNEYS

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PREPARATION OF PHOTOGRAPHIC DIRECT POSITIVE COLOR IMAGES

Wilho M. Salminen, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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14 Claims. (Cl. 96—3)

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

Useful photographic color diffusion transfer processes for preparing direct positive color images are described in British Patents 840,731 and 904,364. In such processes, direct positive silver halide emulsions having silver halide grains with substantial internal sensitivity of the type described in Davey et al., U.S. Patent 2,592,250 are desirably utilized. In such processes, the photographic element containing a Davel et al. internal latent image silver halide emulsion and a nondiffusible coupler that releases a diffusible dye on coupling with oxidized aromatic primary amino color developing agent is processed by treating the element in an alkaline processing medium in the presence of a color developing agent. Development occurs in the unexposed or positive image areas of the emulsions, resulting oxidized developing agent reacting with the color coupler in such areas to produce a positive dye image which thereafter is allowed to diffuse to a dye image reception layer. Fogging agents or nucleating agents are used to facilitate the reversal effect obtained with internal latent image silver halide emulsions used in such color processes.

A good color saturation or dye density is desired in diffusion transfer processes. It is particularly desirable in color diffusion transfer processes that the emulsion layers be relatively thin to aid in the reduction of the image transfer time. However, the emulsion layers must be of sufficient thickness to contain enough color coupling material to form transfer images having high color density. Hence, it is desirable to have a method for obtaining maximum of dye densities with the thinnest possible thickness of emulsion layers in color diffusion transfer processes.

It is an object of this invention to provide a new fogging agent for use in conjunction with the color development of silver halide emulsion that form latent images predominantly inside the silver halide grains when such emulsions are utilized in color diffusion transfer processes.

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

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

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

The present invention concerns the processing of photographic elements having superposed thereon at least one silver halide emulsion having substantial proportions of silver halide that form latent images predominantly inside the silver halide grains and a nondiffusible coupler that forms a diffusible dye on reaction with oxidized aromatic primary amino developing agent contiguous to the silver halide of the emulsion, said processing being carried out in the presence of an ethylene bis(pyridinium) salt as described below.

The silver halide emulsions utilized in the photographic or light-sensitive elements of the invention are prepared with silver halide grains wherein a substantial amount, and preferably a predominant amount, of the sensitivity to light is internal to the grain. Such emulsions are to be distinguished from emulsions containing silver halide grains that form latent images on the surface thereof. Suitable silver halides include silver chloride, silver bromide, silver bromoiodide, silver chloroiodide, and silver chlorobromoiodide. For a description of suitable emulsions that form latent images internal to the silver halide grains, reference is made to Davey et al., U.S. Patent 2,592,250; and Glafkides, Photographic Chemistry, vol. 1, pages 31–2, Fountain Press, London. Typically, such emulsions are those which, when measured according to normal photographic techniques by coating a test portion of the emulsion on a transparent support, exposing to a light intensity scale having a fixed time between 1×10^{-6} and 1 second, bleaching 5 minutes in a 0.3% potassium ferricyanide solution at 65° F. and developing for about 5 minutes at 65° F. in Developer B below (an "internal-type" developer), have a sensitivity, measured at a density of 0.1 above fog, greater than the sensitivity of an identical test portion which has been exposed in the same way and developed for 6 minutes at 68° F. in Developer A below (a "surface-type" developer).

Developer A

	Grams
N-methyl-p-aminophenol sulfate	0.31
Sodium sulfite, desiccated	39.6
Hydroquinone	6.0
Sodium carbonate, desiccated	18.7
Potassium bromide	0.86
Citric acid	0.68
Potassium metabisulfite	1.5
Water to make 1 liter.	

Developer B

	Grams
N-methyl-p-aminophenol sulfate	2.0
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrate	52.5
Potassium bromide	5.0
Sodium thiosulfate	10.0
Water to make 1 liter.	

A wide variety of hydrophilic, water-permeable organic colloids can be suitably utilized in preparing the silver halide emulsions or dispersions of the invention. Gelatin is preferably utilized although other colloidal material such as colloidal albumin, cellulose derivatives, synthetic resins or the like can be utilized. Suitable colloids that can be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe, U.S. Patent 2,286,215 issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19 to 26% as described in U.S. Patent 2,327,808 of Lowe and Clark issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy, U.S. Patent 2,322,085 issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30 to 60% and a specific viscosity of 0.25 to 1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon, U.S. Patent 2,541,474 issued Feb. 13, 1951; zein as described in Lowe, U.S. Patent 2,563,791 issued Aug. 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith, U.S. Patent 2,768,154 issued Oct. 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest, U.S. Patent 2,808,331 issued Oct. 1, 1957; or a polymeric material which

results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth, Dann and Gates, U.S. Patent 2,852,382 issued Sept. 19, 1958.

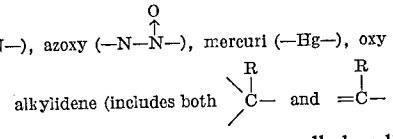
The subject photographic silver halide emulsions of the invention can contain the addenda generally utilized in such products including gelatin hardeners, gelatin plasticizers, coating aids, chemical sensitizers, optical sensitizers and the like.

The color couplers used in the photographic elements of the invention are ballasted and initially nondiffusing in photographic silver halide emulsions but form diffusible dyes on development with aromatic primary amino silver halide photographic color developing agents such as p-phenylenediamine color developing agents. The color couplers utilized in the invention possess a substituent in the coupling position which is displaceable upon coupling with oxidation products of color developing agents. Such color couplers can be referred to as "DDR" or diffusible dye releasing couplers and 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—N—), mercuri (—Hg—), oxy (—O—) alkylidene (includes both $\diagdown\!\overset{R}{\underset{|}{C}}\!-$ and $=\!\overset{R}{\underset{|}{C}}\!-$

wherein R is a hydrogen atom or an alkyl radical generally having 1 to 4 carbon atoms), thio (—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 LINK;

(4) BALL is a photographically inert organic radical of such molecular size and configuration as to render the coupler nondiffusing 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

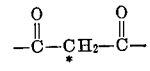
(6) *n* is an integer of 1 to 2 when LINK is an alkylidene radical, and *n* is always 1 when LINK is one of the other aforementioned connecting radicals, namely, azo, azoxy, mercuri, oxy, thio, or dithio.

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

The nature of the ballast groups in the diffusible dye-producing coupler compounds described above (BALL-) 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 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 have at least 8 carbon atoms.

Typical dye radical substituents (DYE-) 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.

With regard to the above-described coupler radicals (COUP-), 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-naphthols, couple at the carbon atom in the 4-position and the open-chain ketomethylene coupler radicals couple to the carbon atom forming the methylene moiety (e.g.,



*denoting the coupling position).

The term "nondiffusing" used herein as applied to the couplers, 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 in the presence of aqueous alkaline processing solution. The same meaning is to be attached to the term "immobile." The term "diffusible" as applied to the dyes formed from the "nondiffusing" couplers in the 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 aqueous alkaline processing solution. "Mobile" has the same meaning.

When 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 dye (DYE) is released which diffuses imagewise to a reception layer. An acidic solubilizing group on the preformed dye lends diffusibility to the dye molecule. The coupling portion of the coupler (COUP) couples with the color developing agent oxidation product to form a dye that is nondiffusible because of the attached ballasting group (BALL) in a noncoupling position. In this type of 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 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 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 coupler or to the color developing agent. The ballast portion of the coupler remains immobile. In this type of 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).

The following are representative DDR couplers used in the present 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.

(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.

(II) 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.

(III) 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.

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

(V) 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.

(VI) 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.

(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.

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

(IX) 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.

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

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.

(XI) 1-hydroxy-4-stearoyloxymercuri-2-naphthoic acid.

(XII) 1-hydroxy-4-dodecyloxy-2-naphthoic acid.

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

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

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

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

(XVII) 1-hydroxy-3',5'-dicarbomethoxy-4-dodecyloxy-2-naphthanilide.

(XVIII) 1-hydroxy-4-(2-hydroxy-4-pentadecylphenylazo)-N-ethyl-3',5'-dicarboxy-2-naphthanilide.

(XIX) 1-hydroxy-4-octadecyloxy-N-ethyl-3',5'-dicarboxy-2-naphthanilide.

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

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

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

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

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

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

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

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

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

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

Couplers XXX to XLI below form diffusible magneta dyes.

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

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

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

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

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

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

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

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

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

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

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

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

Couplers XLII to XLVI below form diffusible yellow dyes.

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

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

(XLIV) α-benzoyl-α-[4-(3-methyl-5-pentadecyl)pyrazoylazo]-4-(3,5-disulfobenzamido)acetanilide dipotassium salt.

(XLV) α-benzoyl-α-(3-octadecylcarbamylphenylthio)-3,5-dicarboxyacetanilide.

(XLVI) α-pivalyl-α-(3-actadecylcarbamylphenylthio)-4-sulfoacetanilide potassium salt.

Diffusible dyes are formed when the above listed (i.e., I to XLVI) nondiffusing 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 our invention when the color developing agent is supplied with the alkali solubilizing function.

Couplers XLVII to L below form diffusible cyan dyes.

(XLVII) 1-hydroxy-4-(4-octadecylphenylazo)-N-methyl-2-naphthanilide.

(XLVIII) 1-hydroxy-4-dodecyloxy-2-naphthanilide.
(XLIX) 1-hydroxy-4-(2-amino-4-octadecylphenylazoxy)-2-naphthamide.
(L) 1-hydroxy-2',5'-dibutoxy-4-[4-(sulfomethyl)phenylazo]-2-naphthanilide.

Couplers LI to LIII below form diffusible magenta dyes.

(LI) 1-phenyl-3-methyl-4-(4-octadecyloxybenzylidene)-5-pyrazolone.
(LII) 4,4'-thiobis(1-phenyl-3-methyl-5-pyrazolone).
(LIII) 4,4'-dithiobis(1-phenyl-3-methyl-5-pyrazolone).

Couplers LIV and LV below form diffusible yellow dyes.

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

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 or diffusible dye-releasing 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 aromatic primary amino color 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:

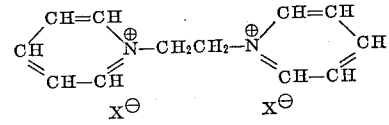
Coupler:	Color
I	Yellow.
II	Do.
III	Do.
IV	Orange-yellow.
V	Yellow.
VI	Do.
VII	Do.
VIII	Do.
IX	Do.
X	Do.
XI	Cyan.
XII	Do.
XIII	Do.
XIV	Do.
XV	Do.
XVI	Do.
XVII	Do.
XVIII	Do.
XIX	Do.
XX	Do.
XXI	Do.
XXII	Do.
XXIII	Do.
XXIV	Do.
XXV	Do.
XXVI	Do.
XXVII	Do.
XXVIII	Do.
XXIX	Do.
XXX	Magenta.
XXXI	Do.

Coupler:	Color
XXXII	Magenta.
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.
XLVII	Cyan.
XVLIII	Do.
XLIX	Do.
L	Do.
LI	Magenta.
LII	Do.
LIII	Do.
LIV	Yellow
LV	Do.

The above-identified couplers have been described in the patent literature. Typical methods for preparing such couplers and related suitable couplers are described in the following patents:

Canada, 602,606, granted Aug. 2, 1960
Canada, 602,607, granted Aug. 2, 1960
Great Britain, 840,731, published July 7, 1960
Great Britain, 904,364, published Aug. 29, 1962
France, 1,224,012, délivré June 19, 1961
France, 1,291,110, délivré Mar. 12, 1962
France, 1,293,709, délivré Apr. 9, 1962
Belgium, 578,470, granted Nov. 6, 1959
Belgium, 591,444, granted June 30, 1960
Belgium, 603,213, granted May 15, 1961
Belgium, 603,747, granted May 31, 1961
Belgium, 625,137, granted Dec. 14, 1962.

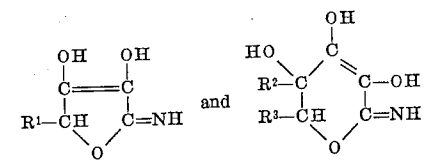
The ethylene bis(pyridinium) salts utilized as fogging or nucleating agents in the process of the invention can be represented by the formula



wherein X is an anion such as sulfonate, methane sulfonate, perchlorate, chloride, bromide and the like.

Other fogging or nucleating agents are desirably utilized in combination with the subject ethylene bis(pyridinium) salts such as 3-hydroxy tetronimides, 3,4,5-trihydroxy-dihydro-pyronimides, and hydrazines.

Typical suitable tetronimides and pyronimides that can be used in combination with ethylene bis(pyridinium) salts can be represented by the following formulas

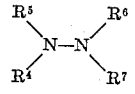


wherein R^1, R^2 and R^3 can each be an aryl radical of the phenyl or naphthyl series, an alkyl radical suitably having 1 to 18 and preferably 1 to 8 carbon atoms, or a

heterocyclic radical desirably having 5 to 6 atoms such as pyridino, morpholino and pyrrolino. R^1, R^2 and R^3 are preferably phenyl radicals, and including phenyl radicals containing such substituents as lower alkyl and alkoxy having 1 to 8 carbon atoms, sulfo, carboxy and the like. I also contemplate the use of acyl esters including benzoate and lower alkanoic esters such as acetate, butyrate and the like esters, as well as ammonium and alkali metal salts such as sodium and potassium, of such tetronimides and pyronimides. Illustrative suitable tetronimides and pyronimides include:

5-(4-ethoxyphenyl)-3-hydroxy tetronimide,
5-phenyl-3-hydroxy tetronimide,
5-(4-carboxyphenyl)-3-hydroxy tetronimide acetate,
5-(3,4-dimethoxyphenyl)-3-hydroxy tetronimide,
5-(p-tolyl)-3-hydroxy tetronimide acetate,
5-(4-pyridyl)-3-hydroxy tetronimide,
5-(2-sulfophenyl)-3-hydroxy tetronimide sodium salt,
5-(phenyl)-3-hydroxy tetronimide benzoate,
5-(n-butyl)-3-hydroxy tetronimide,
5,6-diphenyl-3,4,5-trihydroxy-5,6-dihydro-pyronimide,
5,6-di-n-butyl-3,4,5-trihydroxy-5,6-dihydro-pyronimide,
5,6-di-morpholino-3,4,5-trihydroxy-5,6-dihydro-pyronimide,
5,6-di(p-tolyl)-3,4,5-trihydroxy-5,6-dihydro-pyronimide ammonium salt,
5,6-(2-sulfophenyl)-3,4,5-trihydroxy-5,6-dihydro-pyronimide, and the like.

Typical suitable hydrazines that can be used in combination with ethylene bis(pyridinium) salts are disclosed in Ives, U.S. Patents 2,563,785 and 2,588,982. Such hydrazines can be represented by the following formula



wherein at least two of R^4, R^5, R^6 and R^7 are hydrogen atoms, and when less than all of R^4, R^5, R^6 and R^7 are hydrogen atoms, the remaining can be aryl radicals of the phenyl or naphthyl series, acyl radicals such as those having the formula



wherein R^8 is an aryl or alkyl, aralkyl radicals, or carboxylic acid amide radicals. Preferably the hydrazine compound does not contain more than one aralkyl radical, acyl radical or carboxylic acid amide radical, although it can contain either one or two aryl radicals. Illustrative suitable hydrazines include:

hydrazine dihydrochloride,
p[β-(methylsulfoamido)ethyhl]phenyl hydrazine,
α-naphthylhydrazine,
n-amyl succinyl dihydrazide,
hydrazobenzene,
phenyl hydrazine hydrochloride,
p-actylphenylhydrazine,
p-phenylene disemicarbazide,
sodium sulfosuccinyl dihydrazide,
and the like.

In accordance with the invention, the above-described fogging or nucleating agents can be either incorporated in the processing composition or in hydrophilic colloid layers on dye image receiving sheets that are used in conjunction with the light-sensitive elements during color development. The amount of such addenda can be widely varied. When the ethylene bis(pyridinium) salts are utilized in the processing compositions, amounts ranging from about .1 to 10 grams per liter of processing composition are used. When the ethylene bis(pyridinium) salts are utilized in the dye image receiving sheets, about 1 to 100 mg. per mole of silver halide in the light-sensitive element being processed are typically used. Similar concentrations of the tetronimides, pyronimides and hydrazines that can be used in combination with the ethylene bis(pyridinium) salts can be utilized.

The photographic elements of the invention are processed with aqueous alkaline compositions in the presence of an aromatic primary amino color developing agent, p-phenylenediamine developing agents being particularly useful. The color developing agent can be either incorporated in an aqueous alkaline composition that is applied to the present photographic elements on processing or the color developing agent can be incorporated in the light-sensitive element. During processing, the color developer is oxidized in positive image regions of the emulsion being developed, resulting oxidized color developer reacting with a non-diffusible DDR coupler to form a diffusible dye which diffuses imagewise in register to a reception layer for dye images.

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 emulsion layer and a mordanted reception sheet in the aqueous alkaline processing composition before rolling into contact with each other. Alternately, a viscous processing 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 processing 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 processing composition utilization techniques being disclosed in Land U.S. Patents 2,559,643, 2,647,049, 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 hydrophilic colloid layer thereon and emulsion layers coated thereover. When easily dissolved emulsions are used such as those containing polyvinyl alcohol or an alkali-soluble cellulose ether phthalate vehicle, 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 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 dyes. The recepiton layer can contain mordants such as polymers of amino guanidine derivatives of vinyl methyl ketone such as described in the Minsk U.S. Patent 2,882,156 granted Apr. 14, 1959. Other mordants include the 2-vinyl pyridine polymer metho-p-toluene sulfonate and similar compounds described in Sprague et al. U.S. Patent 2,484,430 granted Oct. 11, 1959 and cetyl trimethylammonium bromide, etc. Particularly effective mordanting compositions are described in copending ap-

plications of Knechel et al. U.S. Ser. No. 211,095 filed July 19, 1962, and Bush U.S. Ser. 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 use of a sheet or layer of a polyamide or related polymeric material.

The emulsions comprising the photographic elements processed in accordance with the invention can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include paper, polyethylene-coated paper, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene-terephthalate film and related films of resinous materials and others. Similar supports can be used for the dye image receiving sheets.

In preparing the photographic elements of the invention, silver halide emulsions are preferably coated on photographic supports in the form of multilayer color photographic elements wherein at least three emulsion layers sensitive to defferent regions of the visible spectrum are coated on the support. For example, the uppermost light-sensitive emulsion layer is generally selectively sensitive to blue light, the next light-sensitive emulsion layer is generally selectively sensitive to green light, and the light-sensitive emulsion layer nearest the support is generally selectively sensitive to red light. Between the blue and green sensitive emulsion layers there is typically disposed a Carey Lea filter layer for absorbing blue radiation that may be transmitted through the uppermost blue sensitive layer. The red, green and blue light-sensitive silver halide layers have contiguous to the silver halide (e.g., incorporated in the emulsion or in adjacent layers) a cyan-forming, a magenta-forming and a yellow-forming coupler respectively so that dyes substantially complementary to the color sensitivities of the emulsions are formed on color development. However, the physical disposition of the red, green and blue light-sensitive silver halide layers 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, a single layer light-sensitive element could be utilized to prepare diffusion transfer full-color images. Three types of packets of differently sensitized silver halide emulsions and their corresponding couplers for subtractive color photography can be incorporated into a single emulsion layer on a photographic support. Reference is made to Godowsky, U.S. Patent 2,698,794, for suitable methods for preparing silver halide-color coupler packets.

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

FIG. 1 of the drawings illustrates a typical photographic element of the invention wherein the diffusible dye releasing or DDR coupler is positioned in light-sensitive emulsion layer **11** coated on support **10**. Such an element is a single color element and can be processed after exposure to prepare a direct positive color image by wetting the exposed element with an aqueous processing solution containing an aromatic primary amino developing agent and a fogging agent of the invention. A receiving sheet having a reception layer which desirably contains a mordant is juxtaposed on light-sensitive emulsion layer **11** and the positive image formed when the diffusible dye releasing coupler reacts with oxidized color developing agent is allowed to diffuse and be transferred to the receiving sheet. The fogging addenda of the invention could also be incorporated in the receiving sheet.

FIG. 2 illustrates a typical multicolor photographic element of the invention as well as a typical mordanted receiving sheet and a rupturable pod containing a processing composition that can be suitably utilized in conjunction with such photographic element. Coated on support **20** is red-sensitive emulsion layer **21** which contains a nondiffusible coupler that forms a diffusible cyan dye when reacted with oxidized color developing agent. Over red-sensitive emulsion layer **21** is coated interlayer **22** that serves to separate green-sensitive emulsion layer **23** and red-sensitive emulsion layer **21**. Interlayer **22** can contain such addenda as antioxidants, couplers to form nondiffusible dyes with oxidized color developing agent from adjacent layers, filter dyes such as magenta filter dye or the like. Green-sensitive emulsion layer **23** contains a nondiffusible coupler that forms a diffusible magenta dye on color development. Over green-sensitive emulsion layer **23** is coated interlayer **24** that serves to separate green-sensitive emulsion layer **23** and blue-sensitive emulsion layer **25**. Interlayer **24**, like interlayer **22**, can contain antioxidants, couplers that react to form nondiffusible dyes with oxidized color developing agent from adjacent layers, filter dyes and the like. Interlayer **24** typically contains yellow Carey Lea silver to serve as a filter for blue light. Blue-sensitive emulsion layer **25** contains a nondiffusible coupler that forms a diffusible yellow dye on reaction with oxidized color developing agent. Over blue-sensitive emulsion layer **25** is coated topcoat layer **26** that typically contains such addenda as antioxidants, ultraviolet absorbers and the like. In FIG. 2 is also illustrated a receiving sheet comprising support **28** having coated thereon mordant layer **27** and affixed thereto rupturable pod **29** containing processing solution. Such processing solution is an aqueous alkaline material and can contain the fogging addenda of the invention. Light-sensitive layers **21**, **23** and **25** are direct positive silver halide emulsion layers wherein the silver halide grains have a substantial amount of sensitivity internal to the grains. When such emulsions are processed in the presence of a fogging agent such as those described hereinabove, they develop in positive image areas or unexposed areas. Accordingly, in the processing of an exposed photographic element of the type described in FIG. 2 of the drawings, development occurs in the unexposed areas and resulting oxidized color developing agent reacts with the nondiffusible DDR color couplers in the respective red, green, and blue-sensitive layers to form diffusible cyan, magenta, and yellow dyes respectively. Such dyes diffuse imagewise to the surface of the photographic element and can be transferred in register to juxtaposed mordant layer **27** as positive color images.

The invention is illustrated by the following examples of preferred embodiments thereof. In the examples, DDR couplers are identified by the same Roman numerals used above.

EXAMPLE 1

A multilayer photographic element suitable for use in preparing three-color diffusion transfer images of the type illustrated by FIG. 2 of the drawings was prepared by coating on a cellulose acetate film support the following layers numbered in sequence from the support:

(1) *Red-sensitive layer (e.g., layer No. 21, FIG. 2).*—To one mole of a melted direct positive silver bromoiodide emulsion that had been red-sensitized, was added 108 g. of cyan coupler XX in 2500 ml. of water and enough photographic gelatin to make a total of 139 g. per mole of silver halide. This solution was then coated so as to obtain 193 mg. per square foot of gelatin, 150 mg. per square foot of coupler, and 150 mg. per square foot of silver.

(2) *Interlayer (e.g., layer No. 22, FIG. 2).*—To 4540 g. of a 10% photographic gelatin solution was added 250 g. of the antioxidant, 2-octadecyl-4-sulfohydroquinone potassium salt, in 5000 ml. of hot water. This was coated to obtain 91 mg. per square foot of gelatin and 50 mg. per square foot of the antioxidant.

(3) *Green-sensitive layer (e.g., layer No. 23, FIG. 2).*—To one mole of a melted direct positive silver bromoiodide emulsion that had been green-sensitized, was added 81 g. of magenda coupler XXXVII in 3000 ml. of water and enough photographic gelatin to have a total of 162 g. per mole of silver halide. This solution was coated so as to obtain 180 mg. per square foot of gelatin, 90 mg. per square foot of coupler, and 120 mg. per square foot of silver.

(4) *Interlayer (e.g., layer No. 24, FIG. 2).*—To 4540 g. of 10% photographic gelatin solution was added 250 g. of the antioxidant used in layer **2** in 5000 ml. of hot water and 4.0 g. of yellow Carey Lea silver as a dispersion. This solution was then coated to obtain 91 mg. per square foot of gelatin, 50 mg. per square foot of antioxidant, and 8 mg. per square foot of Carey Lea silver.

(5) *Blue-sensitive layer (e.g., layer No. 25, FIG. 2).*—To one mole of a melted direct positive silver bromoiodide emulsion that was inherently blue light-sensitive, was added 144 g. of coupler XLVI that had been dissolved in 750 ml. of ethyl alcohol and 3000 ml. of water and enough photographic gelatin to have a total of 118 g. per mole of silver halide. This solution was coated so as to obtain 161 mg. per square foot of gelatin, 200 mg. per square foot of coupler, and 150 mg. per square foot of silver.

(6) *Topcoat layer (e.g., layer No. 26, FIG. 2).*—To 4540 g. of a 10% photographic gelatin solution was added 250 g. of ultraviolet absorbing compound, 5-(4-methoxy-3-sulfo)-benzylidene-2-phenylimino-3-octylthiazolidone sodium salt in 5000 ml. of water. This solution was coated to obtain 91 mg. per square foot of gelatin and 50 mg. per square foot of the ultraviolet absorbing compound.

The silver bromoiodide emulsions utilized in layers **1**, **3** and **5** (layers **21**, **23** and **25** of FIG. 2) were of the type described in Davey et al., U.S. Patent 2,592,250 wherein the silver halide grains have high internal sensitivity and low surface sensitivity. Test samples of the prepared photographic element were then exposed for 1/10 second with a 500-watt positive lamp and a 4.08 Corning filter on an Eastman Type IB intensity scale sensitometer, thereafter immersed in a color developing composition for 30 seconds at 75° F. and then pressed in contact with receiving sheets for 3 minutes at 75° F. The receiving sheets utilized were white pigmented cellulose acetate sheets having coated thereon a dimethyl-β-hydroxyethyl-α-(octadecylamido)-propyl ammonium dihydrogen phosphate mordant in gelatin. Thereafter, the receiving sheets were removed and the dye densities of the positive images on the receiving sheets determined. The color developing composition had the following basic formulation, to which was added ethylene bis(pyridinium) perchlorate and other closely-related alkylene bis(pyridinium) perchlorates at concentrations of 1.0 gram per liter of color developing composition.

Color developing composition

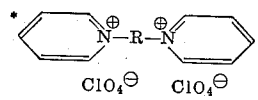
4-amino-N-ethyl-N-(β-hydroxyethyl)-aniline	g.	20.0
Sodium hydroxide	g.	15.0
Dihydroxylamine oxalate	g.	1.0
Benzotriazole	g.	0.16
Dimethyl sulfoxide	cc.	25.0
p-[β-(Methylsulfonamido)ethyl]phenyl hydrazine	g.	0.3

Water to make one liter.

The results are summarized in Table I below.

TABLE I

	Feature Alkylene Derivative (—R—)*	$D_{max.}$ Red	$D_{max.}$ Green	$D_{max.}$ Blue	$D_{min.}$ Red	$D_{min.}$ Green	$D_{min.}$ Blue
(1)	None	.85	1.30	1.36	.28	.38	.32
(2)	$-(CH_2)-$	.70	1.32	1.36	.28	.34	.32
(3)	$-(CH_2)_2-$**	1.65	2.46	1.56	.30	.40	.36
(4)	$-(CH_2)_3-$	.48	.76	1.30	.28	.34	.32
(5)	$-(CH_2)_4-$	.48	.75	1.18	.28	.34	.34
(6)	$-(CH_2)_5-$	.48	.76	.92	.30	.34	.36



**Feature addendum of the invention.

As can be observed from the data set out in Table I above, the ethylene bis(pyridinium) salt facilitated the reversal effect, substantially higher dye densities in the $D_{max.}$ areas for all colors being obtained when the color development was effected in the presence of this addendum than those obtained with closely related homologous compounds.

EXAMPLE 2

Samples of three-color photographic elements of the type described in Example 1 were exposed, developed in the developing compositions described below in the presence of various fogging agents of the invention and positive dye images transferred to receiving sheets as described in Example 1 except that the exposed photographic element was soaked for 10 seconds at 72° F. in the developing compositions and then pressed in contact with receiving sheets for 5 minutes at 75° F. The color developing composition utilized had the following formulation:

Color developing composition

4-amino-N-ethyl-N-(β-hydroxyethyl)-aniline	g.	10.0
Sodium sulfite, desiccated	g.	0.25
Sodium hydroxide	g.	7.5
Benzotriazole	g.	0.1

Fogging agent (see Table II).

Water to make one liter.

The $D_{max.}$ and $D_{min.}$ values of the transferred positive dye images resulting when the various feature fogging or nucleating agents of the invention were utilized in the color developing composition are summarized by the data in Table II below. Each of the feature fogging addenda identified in Table II were utilized at concentrations of .5

gram per liter of developing composition. In Table II, ethylene bis(pyridinium) perchlorate is denominated "Q-salt."

TABLE II

Feature Fogging Agent		$D_{max.}$			$D_{min.}$		
		Red	Green	Blue	Red	Green	Blue
(1)	Q-salt	.39	.42	.69	.24	.18	.19
(2)	5-phenyl-3-hydroxy tetronimide	.34	.50	.83	.26	.28	.26
(3)	Q-salt plus 5-phenyl-3-hydroxy tetronimide.	1.00	.85	1.12	.39	.23	.22
(4)	Q-salt plus 5-(4-carboxy phenyl)-3-hydroxy-tetronimide acetate.	1.10	.89	1.26	.28	.20	.19
(5)	Q-salt plus 5-(3, 4-dimethoxy phenyl)-3-hydroxy tetronimide.	1.18	.97	1.13	.34	.22	.22
(6)	Q-salt plus 5-(p-tolyl)-3-hydroxy-tetronimide acetate.	1.27	.95	1.16	.40	.23	.22
(7)	Q-salt plus 5, 6-diphenyl-3, 4, 5-trihydroxy-5, 6-dihydro-2-pyronimide.	1.17	1.66	1.65	.34	.27	.23
(8)	Q-salt plus p[β-(methyl-sulfonamido)ethyl]-phenyl hydrazine.	1.34	1.02	1.14	.28	.23	.22

As can be observed from the data set out in Table II above, substantially increased densities of the transferred positive dye images resulted with the fogging agents of the invention. It is also to be observed that there is a coaction or synergism between ethylene bis(pyridinium) salts and the other fogging agents set out in Table II.

The tetronimides and pyronimides utilized in the present invention can be prepared by the methods described in British Patent 782,304 and Helvetica Chimica Acta 39, 1780 (1956), respectively.

Ethylene bis(pyridinium) salts can be prepared by reacting ethylene dibromide and pyridine at elevated temperatures. If a perchlorate salt is desired, the resulting ethylene bis(pyridinium) bromide is reacted with sodium perchlorate. More specifically, 47.0 g. of ethylene dibromide and 47.5 g. of pyridine were stirred and placed in a reaction vessel at 95° C. Over a 20-minute period, the temperature of the reaction mixture increased to 130° C. and the reaction mixture became almost solid. The heat was removed and 1800 ml. of hot methanol added to the reaction mixture. The resulting mixture was filtered and the filtrate concentrated to about 900 ml. A solution of 84.3 g. of sodium perchlorate in 300 ml. of methanol was added to the concentrated filtrate with the immediate formation of a precipitate. The resulting mixture was chilled and filtered to separate out ethylene bis(pyradinium) perchlorate crystals.

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.

I claim:

1. A color photographic diffusion transfer process which comprises exposing to a visible subject a photographic element comprising a support with superposed red, green and blue light-sensitive direct positive hydrophilic colloid silver halide emulsion layers wherein the silver halide forms latent images predominantly inside the silver halide grains and having disposed integral with said element and contiguous to said emulsions a cyan-forming coupler, a magenta-forming coupler and a yellow-forming coupler, said couplers being nondiffusible during development in the presence of an alkaline color developing composition containing an aromatic primary amino color developing agent, capable of forming diffusible acid dyes substantially complementary to the color of the spectral sensitivity of the respective contiguous light-sensitive layers in said alkaline color developing composition by reaction with color development oxidation product of said color developing agent and having a formula selected from the group consisting of

DYE-LINK-(COUP-BALL)$_n$ and BALL-LINK-(COUP-SOL)$_n$ 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 thio radical, a dithio radical and an azoxy radical;

(3) COUP is a 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 said LINK;

(4) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible during development in said alkaline color developing solution;

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

(6) 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 thio radical, a dithio radical and an azoxy radical;

wetting said element with said alkaline color developing composition and reversal developing said emulsions in the presence of a fogging composition, said couplers coupling with oxidation product of said color developing agent during said color development and thereby cleaving said LINK in said couplers releasing diffusible acid dye images in areas of the said development, during the course of said color development said dye images diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes and thereby producing a positive color reproduction of said subject, said fogging composition comprising an ethylene bis(pyridinium) salt and a nitrogen-containing compound selected from the group consisting of a hydrazine, a 3-hydroxy tetronimide and a 3,4,5-trihydroxy-5,6-dihydro-2-pyronimide.

2. The process of claim 1 wherein the fogging composition is incorporated in the developing composition.

3. A color photographic diffusion transfer process which comprises exposing to a visible subject a photographic element comprising a support with superposed red, green and blue light-sensitive direct positive gelatino-silver halide emulsion layers wherein the silver halide forms latent images predominantly inside the silver halide grains and having disposed integral with said element and contiguous to said emulsions a cyan-forming coupler, a magenta-forming coupler and a yellow-forming coupler, said

couplers being nondiffusible during development in the presence of an alkaline color developing composition containing an aromatic primary amino color developing agent, capable of forming diffusible acid dyes substantially complementary to the color of the spectral sensitivity of the respective contiguous light-sensitive layers in said alkaline color developing solution by reaction with color development oxidation product of said color developing agent and having a formula selected from the group consisting of

DYE-LINK-(COUP-BALL)$_n$ and BALL-LINK-COUP-SOL)$_n$ 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 thio radical, a dithio radical and an azoxy radical;

(3) COUP is a 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 said LINK;

(4) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible during development in said alkaline color developing solution;

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

(6) *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 thio radical, a dithio radical and an azoxy radical;

wetting said element with said alkaline color developing composition containing about .1 to 10 grams per liter of developing composition of each of an ethylene bis(pyridinium) salt and a 5-phenyl-3-hydroxy tetronimide, and reversal developing said emulsions, said couplers coupling with oxidation product of said color developing agent during said color development and thereby cleaving said LINK in said couplers releasing diffusible acid dye images in areas of the said development, during the course of said color development said dye images diffusing imagewise in register to a juxtaposted reception layer containing a mordant for acid dyes and thereby producing a positive color reproduction of said subject.

4. A color photographic diffusion transfer process which comprises exposing to a visible subject a photographic element comprising a support with superposed red, green and blue light-sensitive direct positive gelatino-silver halide emulsion layers wherein the silver halide forms latent images predominantly inside the silver halide grains and having disposed integral with said element and contiguous to said emulsions a cyan-forming coupler, a magenta-forming coupler and a yellow-forming coupler, said couplers being nondiffusible during development in the presence of an alkaline color developing composition containing an aromatic primary amino color developing agent, capable of forming diffusible acid dyes substantially complementary to the color of the spectral sensitivity of the respective contiguous light-sensitive layers in said alkaline color developing solution by reaction with color development oxidation product of said color developing agent and having a formula selected from the group consisting of

DYE-LINK-(COUP-BALL)$_n$ and BALL-LINK-(COUP-SOL)$_n$ 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 thio radical, a dithio radical and an azoxy radical;

(3) COUP is a 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 said LINK;

(4) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible during development in said alkaline color developing solution;

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

(6) *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 thio radical, a dithio radical and an azoxy radical;

wetting said element with said alkaline color developing composition containing about .1 to 10 grams per liter of developing composition of each of an ethylene bis(pyridinium) salt and a 5,6-diphenyl-3,4,5-trihydroxy-5,6-dihydro-2-pyronimide, and reversal developing said emulsions, said couplers coupling with oxidation product of said color developing agent during said color development and thereby cleaving said LINK in said couplers releasing diffusible acid dye images in areas of the said development, during the course of said color development said dye images diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes and thereby producing a positive color reproduction of said subject.

5. A color photographic diffusion transfer process which comprises exposing to a visible subject a photographic element comprising a support with superposed red, green and blue light-sensitive direct positive gelatino-silver halide emulsion layers wherein the silver halide forms latent images predominantly inside the silver halide grains and having disposed integral with said element and contiguous to said emulsions a cyan-forming coupler, a magenta-forming coupler and a yellow-forming coupler, said couplers bein nondiffusible during development in the presence of an alkaline color developing composition containing an aromatic primary amino color developing agent, capable for forming diffusible acid dyes substantially complementary to the color of the spectral sensitivity of the respective contiguous light-sensitive layers in said alkaline color developing solution by reaction with color development oxidation product of said color developing agent and having a formula selected from the group consisting of

DYE-LINK-(COUP-BALL)$_n$ and BALL-LINK-(COUP-SOL)$_n$ 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 thio radical, a dithio radical and an azoxy radical;

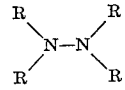
(3) COUP is a coupler radical selected from the group consisting of a 5-pyrazolone coupler radical, a phenolic coupler radical and an open-chain ketomethylene coupler radical, said COUP being substituted in the coupling position with said LINK;

(4) BALL is a photographically inert organic ballasting radical of such molecular size and configuration as to render said couplers nondiffusible during development in said alkaline color developing solution;

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

(6) *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 thio radical, a dithio radical and an azoxy radical;

wetting said element with said alkaline color developing composition containing about .1 to 10 grams per liter of developing composition of each of an ethylene bis(pyridinium) salt and a hydrazine having the formula



wherein at least 2 R's are hydrogen atoms, and when less than 4 R's are hydrogen atoms, the remaining R's being selected from the group consisting of aryl, aralkyl, acyl and carboxylic acid amide radicals, and reversal developing said emulsions, said couplers coupling with oxidation product of said color developing agent during said color development and thereby cleaving said LINK in said couplers releasing diffusible acid dye images in areas of the said development, during the course of said color development said dye images diffusing imagewise in register to a juxtaposed reception layer containing a mordant for acid dyes and thereby producing a positive color reproduction of said subject.

6. The process of claim **3** wherein the pyridinium salt is ethylene bis(pyridinium) perchlorate and the tetronimide is 5-phenyl-3-hydroxy tetronimide.

7. The process of claim **3** wherein the pyridinium salt is ethylene bis(pyridinium) perchlorate and the tetronimide is 5-(4-carboxyphenyl)-3-hydroxy tetronimide acetate.

8. The process of claim **3** wherein the pyridinium salt is ethylene bis(pyridinium) perchlorate and the tetronimide is 5-(3,4-dimethoxyphenyl)-3-hydroxy tetronimide.

9. The process of claim **3** wherein the pyridinium salt is ethylene bis(pyridinium) perchlorate and the tetronimide is 5-(p-toyl)-3-hydroxy tetronimide acetate.

10. The process of claim **4** wherein the pyridinium salt is ethylene bis(pyridinium) perchlorate and the pyronimide is 5,6-diphenyl-3,4,5-trihydroxy-5,6-dihydro-2-pyronimide.

11. The process of claim **5** wherein the pyridinium salt is ethylene bis(pyridinium) perchlorate and the hydrazine is p-[p-methylsulfoamido)ethyl]phenyl hydrazine.

12. In the color developing with an alkaline developing composition containing an aromatic primary amino color developing agent of a photographic element comprising a support and a direct positive silver halide emulsion layer having substantial proportions of silver halide that form latent images inside the silver halide grains, and having disposed integral with said element and contiguous ot said emulsion a nondiffusible photographic color coupler that reacts with oxidized aromatic primary amino color developing agent to form a diffusible dye, forming a diffusible dye in positive image areas, and transferring said diffusible dye to a reception layer, the improvement which comprises carrying out said color developing in the presence of an ethylene bis(pyridinium) salt and a hydrazine as fogging agents to facilitate reversal development.

13. In the color developing with an alkaline developing composition containing an aromatic primary amino color deveolping agent of a photographic element comprising a support and a direct positive silver halide emulsion layer having substantial proportions of silver halide that form latent images inside the silver halide grains, and having disposed integral with said element and contiguous to said emulsion a nondiffusible photographic color coupler that reacts with oxidized aromatic primary amino color developing agent to form a diffusible dye, forming a diffusible dye in positive image areas, and transferring said diffusible dye to a reception layer, the improvement which comprises carrying out said color developing in the presence of an ethylene bis(pyridinium) salt and a 3-hydroxy tetronimide as fogging agents to facilitate reversal development.

14. In the color developing with an alkaline developing composition containing an aromatic primary amino color developing agent of a photographic element comprising a support and a direct positive silver halide emulsion layer having substantial proportions of silver halide that form latent images inside the silver halide grains, and having disposed integral with said element and contiguous to said emulsion a nondiffusible photographic color coupler that reacts with oxidized aromatic primary amino color developing agent to form a diffusible dye, forming a diffusible dye in positive image areas, and transferring said diffusible dye to a reception layer, the improvement which comprises carrying out said color developing in the presence of an ethylene bis(pyridinium) salt and a 3,4,5-trihydroxy-5,6-dihydro-2-pyronimide as fogging agents to facilitate reversal development.

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NORMAN G. TORCHIN, *Primary Examiner.*

J. T. BROWN, *Examiner.*