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O. W. MURRAY

2,386,167

PHOTOGRAPHIC ARTICLE OF MANUFACTURE

Filed Aug. 28, 1943

Fig. 1.

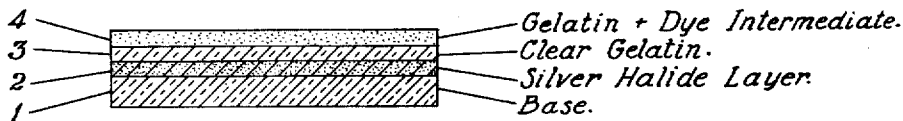


Fig. 2.

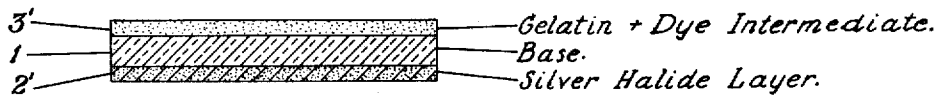


Fig. 3.

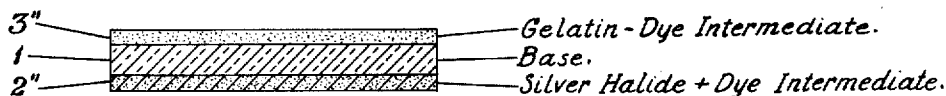


Fig. 4.

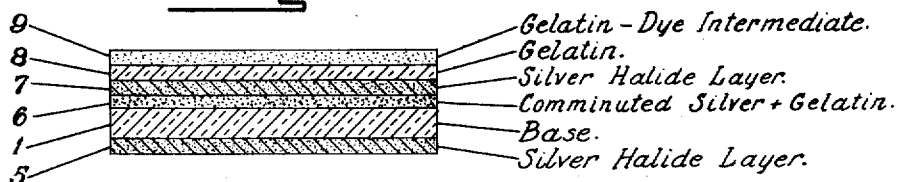
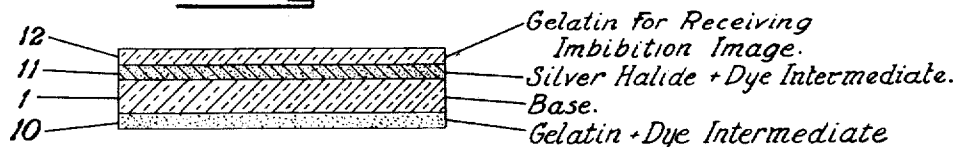


Fig. 5.



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2,386,167

PHOTOGRAPHIC ARTICLE OF
MANUFACTURE

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Application August 28, 1943, Serial No. 500,346

11 Claims. (Cl. 95—2)

This invention relates to photography. More particularly, it relates to methods for producing colored images and to novel elements therefor. Still more particularly, it relates to the production of dye image records in layers free from reducible silver salts and to novel elements therefor, and to the preparation of such elements. The invention further relates to a method of making two and three or multicolor reflection prints and transparencies, especially paper prints.

This invention has for an object the provisions of a new method of making color prints. A further object is to provide a simple and economical method of making color prints. A further object is to provide a method of making a plurality of color prints from single image records. A still further object is to provide a method of making color prints free from silver images in situ therewith. Another object is to provide an element which can be used for the preparation of a two, three or multicolor print. A further object is to provide an element which can be used to produce a color print in toned and color developed images. Still other objects are to provide methods and elements for making color transparencies or reflection prints which require a minimum of equipment and processing steps and to make a general advance in the art.

The above objects are accomplished by the hereinafter described invention which in its broader aspects comprises producing—

- (1) A colored image record in an inner layer by exposing and color forming development or color tuning, and
- (2) Producing a dye image color record in an outer layer of a color yielding element by contact development.

Colored image records can be produced in the inner layer by forming a latent image in the inner light sensitive silver salt layer and then coloring the developed image record. In color forming development procedures this can be accomplished in several ways—

- (1) By having the two components necessary for forming color, e. g. the color former and the development agent in the developer solution
- (2) By using an immobile color former and having it uniformly distributed throughout the original light sensitive silver salt layer and a developer solution containing a color forming developing agent

- (3) By placing an immobile color developing agent in the original silver salt layer and using a solution containing a color former and other remaining necessary developer components

- (4) Placing both immobile color former and developer in the original light sensitive silver salt layer and using a solution containing the necessary developer components.

Toned images can be produced in the inner layer by printing a color separation record onto the light sensitive inner layer, developing and fixing, and then treating the silver image with a toning bath or baths.

The outer partial color record is produced in quinoneimine dyes including indophenol, indoaniline and indoamine dyes or azomethine or azo dyes by imbibition contact with a separate photographic element bearing a color record comprised of a reducible silver salt which is preferably a bleached silver image with the outer layer of a color yielding element containing a dye intermediate capable of forming the aforementioned dyes in the presence of a color forming developing solution. The respective color yielding elements and photographic elements contain aqueous solutions of one or more developer components prior to contact with each other. The color element is preferably impregnated with an aqueous alkaline solution and the photographic element containing the reducible silver salt image is preferably treated with an aqueous solution of an aromatic amino color developing agent containing a color coupling developing agent prior to contact with the color element.

Various types of elements can be used in carrying out the above-described processes. In general, they comprise

- (a) A base
- (b) One light sensitive silver salt layer on the base, which may contain immobile dye components and
- (c) A color yielding layer comprising an immobile dye component free from silver or reducible silver salts which is spaced from said silver salt layer so that development of the latter will not produce color coupling or dye formation in the former.

In one modification, the color yielding layer is spaced from the silver salt layer by means of a water permeable layer of sufficient thickness to prevent color coupling. In another modification, the developer oxidation products couple with dye

intermediates in a separation layer which are chosen to form colorless or extremely weakly colored dyes. Suitable intermediates include 1-phenyl-4,6-diketotetrahydro pyridazine, perinaphthindone, etc. In still another embodiment an unstable color forming compound which can be destroyed with weak acids, e. g. phenol, after processing, can be used in a separatory layer, e. g. of gelatin. In a preferred embodiment, however, the light sensitive silver salt layer and the color yielding layers are placed on opposite sides of the transparent water impermeable base.

The water permeable layers may be thin membranes or composed of water permeable materials, e. g. cellulose derivatives such as lower alkyl ethers and highly esterified partially hydrolyzed esters of cellulose, e. g. methyl cellulose, ethyl cellulose, cellulose acetate, cellulose acetate propionate, regenerated cellulose, etc., or composed of film forming colloids, e. g. gelatin, agar-agar, polyglucuronic acid, deacetylated chitin, amino celluloses, zein derivatives, polyvinyl alcohol, etc., which have been hardened if necessary so that they are cold water insoluble, but are water permeable.

The film base may be made of various materials, including cellulose derivatives, e. g. nitrocellulose, cellulose acetate, cellulose acetate propionate, synthetic resins, e. g. polyvinyl chloride, polyvinyl alcohol and polyvinyl acetal, and super polymers such as ethylene and isobutylene polymers and superpolyamines, e. g. nylon.

Color yielding layers of two general types constitute useful aspects of the invention. They may thus be

- (1) Composed of an immobile dye intermediate uniformly distributed or dispersed in a water-permeable binding or supporting agent, and
- (2) Composed of film forming synthetic resins containing nuclei capable of forming a quinoneimine or azomethine or azo dye on color forming development.

The aforementioned reversible colloids are useful binding agents.

In the accompanying drawing which will make the invention more easily understood, similar reference numerals refer to similar parts throughout the several views.

Fig. 1 is a schematic cross-sectional view of a film element useful for contact development and toning or color development procedures.

Fig. 2 is a schematic cross-sectional view of a modified film element useful for contact development and toning or color development procedures.

Fig. 3 is a schematic cross-sectional view of a photographic element for contact development with an element similar to that of Fig. 2, but containing a color former in the silver salt layer.

Fig. 4 is a schematic cross-sectional view of a photographic element containing two radiation sensitive layers and a color yielding layer free from radiation sensitive materials.

Fig. 5 is a schematic cross-sectional view of a photographic element containing a gelatin layer, a silver halide dye intermediate layer and a color yielding layer free from radiation sensitive materials.

Referring now to the drawing, a base 1 which may be composed of a sized white paper or a cellulosic or resin material containing a white pigment is coated first with a sub-stratum layer and then with a gelatino-silver-halide emulsion

to form a layer 2. On layer 2 is coated an aqueous gelatin dispersion to form a clear separation layer 3 which is substantially thicker than layer 2. On layer 3 is coated a gelatin dispersion containing at least one immobile dye intermediate or color-former to form layer 4, which layer yields a dye image by the procedure described below or composite dye image. The gelatin dispersion can be made by dissolving the dye intermediate in 5 to 10% caustic alkali to form a soluble paste. This may be diluted with about 5 parts of water and 1 part of alcohol, added to 5% aqueous gelatin and the excess alkali neutralized with a mineral acid such as hydrochloric. The concentration of the coating compositions, temperatures and coating speeds are adjusted to yield the desired thickness.

In Fig. 2, a subbed, transparent cellulose acetate film base 1 is coated on one side with a gelatin silver halide emulsion to form a thin layer 2'. On the other side of the base is coated a gelatin dispersion to form a layer 3' which contains at least one immobile color former so that said layer will yield a dye image or mixed dye images.

In Fig. 3 a thin transparent film base 1, e. g. composed of a fusible superpolymer of the type set forth in U. S. Patents 2,216,735 and 2,216,736, was coated on one side with an aqueous alkaline gelatin dispersion containing a blue-green immobile dyestuff component and a light sensitive silver halide, e. g., silver bromide to form a thin layer 2''. On the other side was coated thin layer 3'' comprising an aqueous alkaline dispersion of gelatin containing a mixture of immobile dyestuff components yielding an orange-red dye, and a variable-gamma, mixed emulsion layer as described in U. S. Patent 2,202,026.

Example I

A color yielding element of the type shown in Fig. 1 having layer 4 composed of gelatin containing 0.25 part of the o-sulfobenzaldehyde dimer of 1-(m-octadecylaminophenyl)-3-methyl-5-pyrazolone was exposed to a printing light passing through the red separation negative of a tri-pack color film combination. The color yielding element was then developed in a solution of the following composition:

	Parts
4-chloro-n-phenyl-phenol	2
N-diethyl-p-phenylenediamine hydrochloride	2
Na ₂ CO ₃	20
Sodium sulfite	1
H ₂ O to	1000

then treated with Farmer's reducer and washed.

A positive film was printed from the green negative record of the tri-pack combination, developed, fixed and washed. It was bleached in an aqueous solution of alkaline potassium ferricyanide to form silver ferrocyanide images, washed thoroughly and soaked in 10% Na₂CO₃. The color yielding element was soaked in a solution of the following composition:

N-diethyl-p-phenylene diamine hydrochloride	grams	10
Na ₂ SO ₃	do	2
"Metol"	do	0.6
Water to	cc	1000

The bleached positive was then squeegeed in register contact with the color yielding element,

with the emulsion surface in contact with layer 4 and contact was maintained until a dye image formed in layer 4, then removed. On this blue-green-magenta transparency is imbibed a yellow dye image from a matrix representing the minus blue record, thus giving a color print transparency.

Example II

A color yielding element of the type shown in Fig. 1 containing as the blue-green color former in layer 4 a salicylaldehyde-o-sulfobenzaldehyde polyvinyl acetal was exposed to a printing light from the blue-green record of bi-pack color separation negatives, developed, fixed and washed. The element was then treated in a toning bath of the following composition:

Uranium nitrate	grams	5
Potassium oxalate	do	5
Potassium ferricyanide	do	2
Ammonium alum	do	12
HCl (100 cc. conc./liter H ₂ O)	cc	10
Water to	cc	2000

whereby an orange-red color image record was formed in layer 2. The element was washed and soaked in a bath of the type set forth in Example I.

The orange-red bi-pack record was printed onto positive film stock. The latter was developed, fixed, bleached to silver ferrocyanide, washed, soaked in 10% aqueous sodium carbonate, and the emulsion surface pressed into contact with layer 4 with the images in register until a blue-green image formed in layer 4. Upon removal of the positive film, a 2-color print was formed.

Example III

A film element as shown in Fig. 3 was made by using as the color formers for layer 3' a mixture of the reaction product of diacetoacetolindine sulfone with ortho sulfobenzaldehyde and an ortho sulfobenzaldehyde dimer of 1-(m-stearoylamino-phenyl)-3-methyl-5-pyrazolone and adding to layer 2', 1-dodecoylamino-5-naphthol. The element was exposed to a printing light from the orange-red record of bi-pack separation negatives. The color yielding element was then developed in a solution of the following composition:

N-diethyl-p-phenylene diamine hydrochloride	grams	10
Sodium sulfite	do	2
Metol	do	0.6
Water to	liter	1
Na ₂ CO ₃	grams	30

fixed, washed, and soaked in 10% sodium carbonate. A positive from the blue-green bi-pack combination was bleached to form silver ferrocyanide images, washed, soaked in alkali solution and squeegeed with the color yielding element after the manner set forth in Example I, yielding a color transparency having particularly good color rendition.

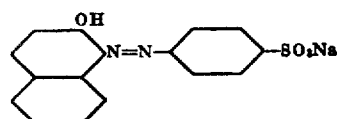
Example IV

A color yielding element of the type shown in Fig. 2 containing layer 3' as a blue-green color former the arylide of 1-hydroxy-2-naphthol acid with p-dodecylanilide was exposed to printing light from an orange-red bi-pack color separation negative, developed and fixed. The

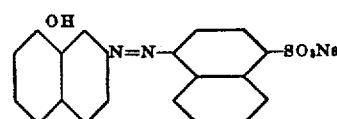
silver image record was then bleached by floating on a bath of the composition:

Potassium dichromate	grams	2.25
Potassium bromide	do	20
Copper sulfate	do	18
Chrom alum	do	3
Acetic acid	cc	3.5
Water to	liters	2

The element was bathed in hypo, washed and immersed in a dye bath containing 2.13 grams of Wool Orange A (C. I. #151) of the formula



and 1.54 grams of Serichrome Blue R. (C. I. #180) of the formula



per liter of solution to form orange-red dye images which were washed thoroughly. The layer on the opposite side of the support from that which has just been processed was then treated by contact development after the manner of Example III to form a blue-green dye record therein from the red bi-pack color separation negative.

Example V

A color yielding element of the type shown in Fig. 3 containing in layer 2' resorcinol-monooctadecylether as a blue-green dye intermediate and in layer 3' a mixture of the dye intermediates of Example III as orange-red dye intermediates. An orange-red color separation negative was printed onto layer 2' which was developed in an ordinary positive type metol-hydroquinone developer, fixed, washed, bleached with alkaline ferricyanide, washed and treated with a dye-generating reducer such as bath "C" (hereinafter described) for 3 minutes, then bleached, fixed and washed. The blue-green color separation negative was printed onto a positive film stock which was developed and fixed and then bleached to silver ferrocyanide images, soaked in a 2% aqueous solution of NaOH and the emulsion pressed into contact with layer 3' which had previously been soaked in an aqueous solution of the following formula:

	Parts
Monophenylhydrazine	2
2% aqueous sodium oleate	5
Sodium carbonate	2

The elements were squeegeed in register until a dye image formed in the outer layer, whereupon the elements were separated, washed and mounted on a paper base. A two-color print of good strength, color rendition and improved resistance to fading was obtained by the above combination of film element and process.

Example VI

An element of the type set forth in Example IV was prepared which contains in addition to the dye intermediate in layer 3', p-amino-diethylaniline. The layer corresponding to 2' was processed after the manner set forth in Example IV except that all stages of this process were conducted by floatation so as to exclude aqueous solu-

tions from contact with layer 3' on the opposite side of the support. A bleached positive was made in a similar manner to that described in Example IV and after soaking in an aqueous bath containing 30 cc. of hexamethylene diamine-1.6 per liter, was placed in contact with the dry surface of layer 3' and allowed to remain until a color image appeared in said layer.

Example VII

A color yielding element of the type shown in Fig. 4 comprises a transparent support 1 coated on one side with an ordinary positive type silver bromide emulsion 5. On the other side of the transparent support is a thin layer 6 of comminuted silver dispersed in gelatin so as to form a light barrier layer of metallic silver having a density such that less than 1% of the light is transmitted by the layer. On the light barrier layer is coated a silver halide emulsion layer 7. On the silver halide layer is coated a layer 8 of clear gelatin and over this a layer 9 of gelatin containing 25 parts of diacetoacet-tolidine sulfone per 100 parts of gelatin. A positive type silver bromide emulsion coated on an aluminum foil support prepared as described in Mason 2,115,339 was printed from the blue separation negative, developed in an ordinary black and white developer, fixed, washed and bleached with alkaline ferricyanide. The green separation negative was printed onto the inner silver halide layer and, at the same time and in register, the red separation negative was printed onto the rear silver halide emulsion layer. The entire color yielding unit was then immersed in an ordinary black and white positive type of developer to develop the latent images in both of the exposed silver halide layers. After development, the film unit was washed. The inner silver image in layer 7 was then toned magenta by treating it first with a solution comprised of 1 liter of a solution containing 5% nickel nitrate and 15% of potassium citrate with 50 cc. of a 4% solution of potassium ferricyanide and 5 cc. of 10% nitric acid. The bleaching was done by floating the side of the film carrying the gelatin and dye intermediate and silver halide layers on the surface of the bleaching solution for approximately 6 minutes and then washing the entire film and then floating the same side in a solution comprising:

	Parts by volume
Saturated solution of dimethylglyoxime----	50
0.4% sodium hydroxide-----	50
Water-----	400

after which the film was rinsed for two minutes. The rear side was then floated on an alkaline ferricyanide bleach bath, washed and redeveloped in a blue-green color forming developer similar to that described under Example I. After the final development, the blue-green layer was floated on an alkaline ferricyanide bleach bath, washed and the entire film was then immersed in a 5% plain hypo solution and given the final washing. After washing, the color element was immersed in a color developer as described under Example III and squeegeed into contact with the bleached positive image on the metallic foil base which had first been saturated with a 10% sodium carbonate solution, and left in contact until the yellow dye image was produced in the outer layer, after which it was given the final washing and drying.

Example VIII

A color yielding element of the type shown in Fig. 5 comprises a transparent support 1 coated on the one side with a gelatin layer 10 containing approximately 1 gram of 2-hydroxy-3-methyl benzaldehyde phthalaldehydic acetal of polyvinyl alcohol per 4 grams of gelatin. On the other side of the transparent support is coated a silver halide emulsion layer 11 containing approximately 6 grams of 1-(m-octadecoyl-amino-phenyl-3-methyl-5-pyrazolone) per 1000 grams of emulsion. Over the magenta yielding layer is coated a layer 12 of plain gelatin from an 8% aqueous dispersion. Using 3-color separation negatives, the green record was printed onto the silver halide layer and the entire film was then developed in a p-amino-N-diethylaniline-"Metol" developer as described under Example I. The element was then treated with Farmer's reducer to remove the metallic silver and undeveloped silver halides from the inner layer. The red color separation negative was printed onto a positive silver halide emulsion on the aluminum oxide surface of aluminum foil prepared as described in Mason, U. S. Patent 2,115,339. The red record positive was developed in an ordinary metol-hydroquinone developer, fixed, washed and bleached with alkaline ferricyanide solution. A positive matrix was prepared from the blue separation negative by printing through the base of a film coated with a positive type silver bromide emulsion, developing it in a pyro developer containing a minimum of sulfite (to harden the gelatin in situ with the silver image), fixing and washing in warm water to remove the unhardened gelatin. Of course, any of the other well-known methods for forming matrices can also be used (for example, see "History of Three Color Photography," by E. J. Wall). The silver image was then removed by treatment with alkaline ferricyanide and sodium thiosulfate. A yellow imbibition image and a blue-green color developed dye image were then formed respectively in the two outside layers of this element in the following manner: The bleached positive from the red separation negative was saturated with 10% sodium carbonate solution and the blue-green dye component layer was floated on a developer comprising:

	grams--	10
p-Amino-N-diethylaniline hydrochloride,		
Na ₂ SO ₃ -----	do----	2
Metol-----	do----	6
Water to-----	liter--	1

and then squeegeed into contact with the bleached image on the aluminum foil support. While this contact development was in progress, the upper clear gelatin layer was saturated with a 1% aqueous solution of silver nitrate and the matrix on the transparent base was soaked in a 10% potassium iodide solution and then squeegeed into registered contact with the clear gelatin layer forming therein a silver iodide image which is an excellent mordant for basic dyes. The matrix was then removed and a yellow dye fixed on the mordant image by floating on or swabbing on the surface with a solution of Auramine (C. I. #655) or Chrysoidine (C. I. #20) in a 0.5% solution. Both foil matrix and the film positive squeegeed onto the two outer layers are then removed, the film is cleared in plain hypo, and washed, yielding a brilliant three color transparency comprised of a metallo-organic image,

a color developed image and a mordanted dye image.

The invention is not limited to the exact procedures and materials, compounds or elements set forth in the above examples. On the contrary, a wide variety of color yielding elements, dye components or color formers, developing agents and solutions, toning baths, dye mordants, coupling baths, can be substituted with similar results.

The color yielding elements may contain light sensitive layers composed of simple or mixed silver halides which may contain the usual sensitizers, desensitizers, stabilizers, fog inhibitors, emulsion hardeners, etc. Suitable types include silver chloride, silver bromide, silver chlorobromide, silver chloride-bromide-iodide, silver bromide-iodide, etc., which may contain cyanine, carbocyanine, polymethine cyanine, cyazine, carbocyanine, pseudocyanine, kryptocyanine, merocyanine, rhodanine, etc. salts and bases. The silver halide layers are anchored to the supports by means of the usual subbing solutions. Such solutions are also useful for anchoring dye component layers to bases.

While the above description has been restricted for the most part to the formation of dye images in non-photographic layers by bringing a separate element containing reducible silver salt images into contact with the dye yielding layer in the presence of the constituents of a color coupling developer, it is also possible to form such dye images by separate elements containing images other than silver salt images. For instance, one may employ the reducing action of chromium oxides formed by exposing bichromated gelatin layers. For preparing such images, a film support is coated with a thin gelatin layer, sensitized, for example, by bathing in an alkaline bichromate solution, dried and exposed under a negative to a printing light containing some ultra-violet radiations. The exposed film element is then soaked in alkali and pressed into contact with the color yielding element which has been saturated with a color coupling developing solution. In fact, each of the above described procedures for imbibition or contact development can be used with the elements containing other types of developable images.

The procedures and compositions for forming colored or dye images set forth in a copending application of O. W. Murray and V. B. Sease, entitled "Photographic elements and processes," Serial No. 370,194, filed December 14, 1940, now United States Patent 2,328,034, can be used in the procedures hereof.

The dye components or color formers are in general selected so that they together form a composite dye image which reproduces a color scene or object. Thus, the dye components used in the layer which is treated by contact development in general should form dyes complementary in color to that which exposed the color separation negative record employed therewith. Likewise, the dye components or color formers used in the inner layer or the developing solution used for processing thereof should form a dye which is complementary in color to that which exposed the color separation record. However, the above general considerations are not true when it is desirable to print a negative color record from a negative color record or a positive color record from a positive color record. When reproduction of an original color object field is not a desired

eratum, a dye which forms any desired color can be used.

As examples of suitable yellow to orange-red color formers which can be used in emulsion layers or in developing solutions upon being dispersed therein if necessary by means of alkali and/or alcohol are the diacetylacetamino-1,2,4,5-benzobisthiazoles of U. S. Patent 2,140,540 of which difuroylacetamino-1,2,4,5-benzobisthiazole and diacetoacetamino-1,2,4,5-benzobisthiazole are especially useful. Additional yellow color formers include 2-hydroxy-3-naphthoylamino-benzoyl-acetanilide, sodium stearylaminobenzoyl-acetanilide-p-carboxylate, p-caproylamino, benzoyl-amino salicylic acid, furoylacet-p-amino phenylamyl ether (described in Jennings and Middleton U. S. Patent 2,184,303, issued December 26, 1939, and di-picolinoylacet benzidine.

Suitable non-migratory magenta color formers which are especially useful are 1-(3'-sulfo-phenyl)-3-(4''-stearylaminophenyl)-3-(4''-dodecoylamino-phenyl)-5-pyrazolone, 4,4'-bis-(3''-methyl pyrazolonyl-1'')-diphenyl (described in Jennings and Middleton U. S. P. 2,200,924, issued May 14, 1940), 4,4'-methylene-bis-(m-stearylaminophenyl)-methyl pyrazolone (described in Jennings U. S. P. 2,294,909, issued September 8, 1942), and 4,4'-o-sulfobenzylidene-bis (phenyl methyl pyrazolone) (described in Jennings U. S. P. 2,294,909).

Suitable non-migratory blue-green color formers of especial utility include 4,4'-di-(1-hydroxy-2-naphthoyl-amino) diphenyl, 1-hydroxy-2-carboxy-5-dodecoylamino naphthalene, 1-N-stearyl-4-N-(1'-oxy-2'-naphthoyl)-phenylenediamine sodium sulfonate, resorcinol mono-n-dodecyl ether (described in Salzberg and White U. S. P. 2,166,181, issued July 18, 1939), product of p-hydroxybenzoic acid and formaldehyde (described in McQueen U. S. P. 2,323,481, issued July 6, 1943), product of polyvinyl alcohol and salicyl-aldehyde (described in Dorough and McQueen U. S. P. 2,310,943, issued February 16, 1943).

Additional color formers which are useful not only with arylene diamino developing agents, but also the aryl-hydrazines, are described in U. S. Patents 2,154,918, 2,166,181, 2,178,612, 2,179,228, 2,179,238, 2,179,239, 2,213,986, 2,179,244, 2,186,045, 2,186,719, 2,186,734, 2,186,735, 2,186,736, 2,186,849, 2,140,540, 2,133,937, and 2,200,924, etc. Others are set forth in Sease and Murray application Serial No. 370,194, filed December 14, 1940, and may be substituted for the dye intermediates of the above examples in accordance with the teachings hereof.

The preferred developing agents which may be used in the dye coupling development steps hereof are derivatives of p-phenylenediamine and particularly the asymmetric dialkyl p-phenylenediamines of 1 to 4 carbon atoms, e. g., p-amino-dimethylaniline, p-aminodiethylaniline, p-aminodibutylaniline, etc. Other developing agents which may be used include p-phenylenediamine itself, p-methylaminoaniline, p-ethylaminoaniline, p-aminophenol, N,N-diethyl-o-phenylenediamine, chloro-p-phenylenediamine, 1,2,5-toluylenediamine, 2-amino-5-diethyl-amino-toluene, p-amino-N-phenylmorpholine, N-p-aminophenyl-piperidine, N-methyl-N-hydroxyethyl-p-phenylenediamine, N-butyl-N-hydroxyethyl-p-phenylene-diamine, 2-amino-5-(N-butyl-N-hydroxyethyl) aminotoluene, beta-gamma-dihydroxypropyl-p-phenylenediamine, etc. These aromatic amino developing agents in the form of their or-

ganic or inorganic acid salts may be used in the preparation of the developing solutions. The salts are in general more stable than the free bases. As examples of suitable salts, mention is made of the hydrochloride, sulfates, acetates, etc.

In addition to the developing agents as afore-described, the developing solutions may contain from about 3 to 30 parts of an organic nitrogen base having an association exponent of at least 5.0 to about 11.40 including aliphatic amines, primary, secondary and tertiary alkyl mono- and polyamines, cycloaliphatic amines, ammonium hydroxides, ammonia, N-heterocyclic amines, etc. per 1000 parts of solution. Suitable bases are described in the following solutions which can be used as described above. The bases can be used in water alone as described in Example V.

Bath A

p-Amino - N - diethylaniline	grams	2
Ammonium hydroxide, conc	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

Bath B

p-Aminodiethylaniline	grams	2
Hexamethylenediamine (55% in methanol)	cc	15
Sodium sulfite, anhy	grams	3
Water to	liter	1

Bath C

p-Aminodiethylaniline	grams	3
Ammonium hydroxide, conc	cc	30
Sodium carbonate, anhy	grams	2
Water to	liter	1

Bath D

p-Aminodiethylaniline	grams	3
β -dimethylaminoethylamine	cc	20
Sodium sulfite, anhy	grams	3
Water to	liter	1

Bath E

p-Aminodiethylaniline	grams	2
Piperidine	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

Bath F

2-amino-5-diethylamino-toluene	grams	5
Trimethyl-benzyl-ammonium hydroxide	cc	20
Sodium sulfite, anhy	grams	5
Water to	liter	1

Bath G

4:4-diaminodiphenylamine	grams	4
Hexamethylenediamine	cc	10
Sodium sulfite, anhy	grams	2
Water to	liter	1

Bath H

1:4-diaminonaphthalene	grams	3
Dimethylcyclohexylamine	cc	30
Sodium sulfite, anhy	grams	3
Water to	liter	1

Bath I

4-diethylamino-1-naphthylamine	grams	5
β -Dimethylaminoethylamine	cc	20
Sodium sulfite, anhy	grams	5
Water to	liter	1

Bath J

p-Aminodibutylaniline	grams	3
Hexamethylenediamine (55% solution in methanol)	cc	20
Sodium sulfite, anhy	grams	2
Water to	liter	1

Bath K

p-Aminodiethylaniline	grams	3
Trimethyl-benzyl-ammonium hydroxide	cc	25
Sodium sulfite, anhy	grams	3
Water to	liter	1

15 In place of the specific hydrazines set forth in Example IV may be substituted other hydrazines such as o-, m- or p-tolyl-hydrazine, p-nitrophenylhydrazine, p-hydrazino-diphenyl, p-bromo-phenylhydrazine, chlorophenyl hydrazines, chloronaphthyl hydrazines, bromonaphthylhydrazines, p-diphenylhydrazines, p,p'-diphenyldihydrazines, alpha-naphthylhydrazines, betanaphthylhydrazines which may be employed in the form of their salts, e. g., hydrochloride, acetate, chloroacetate, sulfates, etc. The hydrazines may be solubilized by means of long chain aliphatic carboxylic acid salts and long chain aliphatic sulfonic acid salts as set forth in Kirby U. S. P. 2,220,929.

30 In the case of elements which contain film forming color formers as the outer layers, no additional binding agents such as gelatin need be present. Color formers of this type which are especially suitable are (1) polyvinyl acetals of aromatic aldehydes which are capable of reacting with diazo compounds and the oxidation products of photographic color developers. The acetals are formed from polyvinyl alcohol or partially hydrolyzed polyvinyl esters and aromatic aldehydes which contain a phenolic hydroxyl, amino, alkyl-, cycloalkyl-, or aryl-substituted amino group including mixed groups of this type which are further characterized in that they have a reactive position, but not necessarily unoccupied position, ortho or para to the mentioned groups or the aromatic aldehydes having an active methylenegroup. The preparation of suitable compounds of this type is set forth in Dorough and McQueen U. S. P. 2,310,943; and (2) condensation products of phenols and naphthols or hydroxy aromatic carboxylic or sulfonic acids with difunctional resin-forming reagents such as aldehydes and ketones, dimethylol derivatives of phenols, amides and amines and equivalent compounds. The preparation of suitable color formers of this type is described in McQueen U. S. P. 2,323,481.

Various other toning baths and procedures may be substituted for the specific one set forth in Example II. Additional ones include:

Toning bath A (red)

Potassium ferricyanide	grams	12.5
Uranium nitrate	do	12.5
Rose Bengal	do	0.013
Naphthol yellow	do	0.013
Iodine	do	0.013
Glacial acetic acid	cc	12.5
Water to	cc	1000

Toning bath B (minus blue)

Vanadium oxalate solution	cc	50
Oxalic acid (set)	cc	50
Glycerin	cc	50
Water to	cc	1000

For use add 1 part 5% KFe (CN)₆ to 100 parts of above solution and bathe silver image in it.

Toning bath C (blue)

Oxalic acid	grams	1.75
Iron ammonium oxalate	do	4.75
Potassium ferricyanide	do	1.75
Water to	cc	1000

Toning bath D (blue-green)

Solution A:

Oxalic acid	grams	20
Ferric ammonium oxalate	do	50
Potassium ferricyanide	do	20
Water to	liter	1

Solution B:

Ammonium vanadate	grams	2.5
Oxalic acid	do	4.5
Water to	cc	40

For use mix solutions A and B and add water to make 4 liters.

A number of different bleaching procedures can be used for the elements which are used for contact development. Films or plates containing a positive or negative silver image can be bleached to redevelopable silver salts, as for example, with potassium ferricyanide, copper chloride, or copper bromide in the presence of an oxidizing agent such as chromic acid, potassium ferricyanide in the presence of alkali carbonate or ammonia, etc.

In place of the sodium carbonate solutions may be used potassium carbonate, potassium hydroxide, lithium carbonate, and other aqueous solutions for soaking the bleached photographic elements. The concentrations may range somewhat depending on the pH of the particular agent, the bleaching agent used, the dye intermediate used and the concentration of the developing agent, and amount of sulfite present. In general, amounts of 2 to 15% are practical.

In making the above color yielding elements, the color formers may be made into a paste with alkali and brought into solution with water or alcohol and then mixed with an aqueous dispersion of a reversible colloid, e. g., gelatin, preferably containing a dispersing agent and coated onto a base having a substratum of the type suitable for anchoring silver halide layers. The same types of coating procedures used for silver halide emulsion layers have been found satisfactory. In the case of film forming color formers, the alkaline aqueous or alcoholic solutions may be cast in a similar manner.

For the production of color prints and transparencies from strip or continuous film, e. g., colored cine prints or transparencies, the dye images can be prepared in the same general manner as previously described. The color yielding should in general have the same shape as the photographic element. Intimate contact may be maintained between the color element and the bleached element by running the elements in intimate contact after they have been suitably treated for color coupling through pressure rolls or down a belt until color coupling and the formation of dye images has been completed.

The pressure rolls and belts are preferably provided with sprockets which fit into perforations in the color yielding elements and photographic elements to insure accurate registration of images if they are mounted in registration with other color component records, e. g., from color separation negatives. However, even in

the case of single color elements, the sprockets and perforations insure against slipping with the resultant production of fuzzy dye image records.

It will be apparent from the above that this invention is of wide utility and has a number of decided advantages.

A major advantage resides in the fact that two-color prints can be made in a simple and economical manner. A further advantage resides in the fact that a number of tedious steps are eliminated from prior processes of making two color prints. A still further advantage resides in the fact that the color development of one layer can be conducted under ordinary illumination which permits accurate registration of color records to be made.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof it is to be understood that I do not limit myself to the specific embodiments herein except as defined by the appended claims.

This application is a continuation-in-part of application Serial No. 370,195, now United States Patent 2,369,171.

I claim:

1. A photographic element consisting of a transparent base, a light sensitive silver halide layer imposed on said base, a water permeable layer of appreciable thickness imposed on said layer and a water-permeable layer embodying a color-former which is free from silver and silver salts imposed on the last mentioned layer, said second layer being of such thickness that no coupling co-action takes place between the silver halide layer and said color-former.

2. A photographic element consisting of a transparent base, a light sensitive silver halide layer imposed on said base, a water permeable layer of appreciable thickness imposed on said layer and a water-permeable layer embodying an immobile color-former which is free from silver and silver salts imposed on the last mentioned layer, said second layer being of such thickness that no coupling co-action takes place between the silver halide layer and said color-former.

3. A photographic element consisting of a transparent base, a light sensitive silver halide layer imposed on one side of said base and on the other side of said base a water-permeable colloid layer embodying an immobile color-former which is free from silver and silver salts.

4. A photographic element consisting of a transparent base, a water-permeable colloid layer containing light-sensitive silver halides and an immobile color-former on one side of said base and on the other side of said base a water-permeable colloid layer embodying an immobile color-former of a different type which is free from silver and silver salts.

5. An element as set forth in claim 4 wherein said color-formers are capable of forming dyes taken from the group consisting of quinoneimine, asomethine and azo dyes.

6. An element as defined in claim 4 wherein blue-green color-formers are in one of said layers and orange-red in the other.

7. A photographic element consisting of a transparent base, a light sensitive silver halide layer on one side thereof and in order on the other side thereof a comminuted silver colloid layer, a silver halide color-former layer, a water-permeable colloid layer free from developer responsive materials and a color yielding layer comprising essentially an immobile color-former

which is free from silver and silver salts, said fourth layer being of such thickness that no coupling co-action takes place between said third layer and said fifth layer.

8. A photographic element consisting of a transparent base, a water-permeable colloid layer on one side thereof embodying a color-former which is free from silver and silver salts and on the other side thereof in order a water-permeable silver halide layer containing an immobile color-former and a water-permeable colloid layer free from developer responsive materials taken from the group consisting of dye intermediates and reducible silver salts.

9. A photographic element having a support and at least one light-sensitive silver halide layer, an outer-most water-permeable colloid layer free from silver and silver salts embodying a color former, said layer being physically separated from all silver halide layers by a layer which prevents

color coupling co-action with any silver halide layer thereof.

10. A photographic element having a support and at least one light-sensitive silver halide layer, an outer-most water-permeable colloid layer free from silver and silver salts embodying an immobile color former, said layer being physically separated from all silver halide layers by a layer which prevents color coupling coaction with any silver halide layer thereof.

11. A photographic element having a transparent support and at least one light-sensitive silver halide layer, an outer-most water-permeable colloid layer free from silver and silver salts embodying an immobile color former, said layer being physically separated from all silver halide layers by a layer which prevents color coupling coaction with any silver halide layer thereof.

OTIS WILLARD MURRAY.

CERTIFICATE OF CORRECTION.

Patent No. 2,386,167.

October 2, 1945.

OTIS WILLARD MURRAY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 52, for "4-chloro-n-phenyl-phenol" read --4-chloro-o-phenyl-phenol--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of January, A. D. 1946.

Leslie Frazer

(Seal)

First Assistant Commissioner of Patents.

which is free from silver and silver salts, said fourth layer being of such thickness that no coupling co-action takes place between said third layer and said fifth layer.

8. A photographic element consisting of a transparent base, a water-permeable colloid layer on one side thereof embodying a color-former which is free from silver and silver salts and on the other side thereof in order a water-permeable silver halide layer containing an immobile color-former and a water-permeable colloid layer free from developer responsive materials taken from the group consisting of dye intermediates and reducible silver salts.

9. A photographic element having a support and at least one light-sensitive silver halide layer, an outer-most water-permeable colloid layer free from silver and silver salts embodying a color former, said layer being physically separated from all silver halide layers by a layer which prevents

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