

May 21, 1968

R. W. BECKER

3,384,483

MULTICOLOR DYE DEVELOPER IMAGE TRANSFER SYSTEMS

Filed March 23, 1964

2 Sheets-Sheet 1

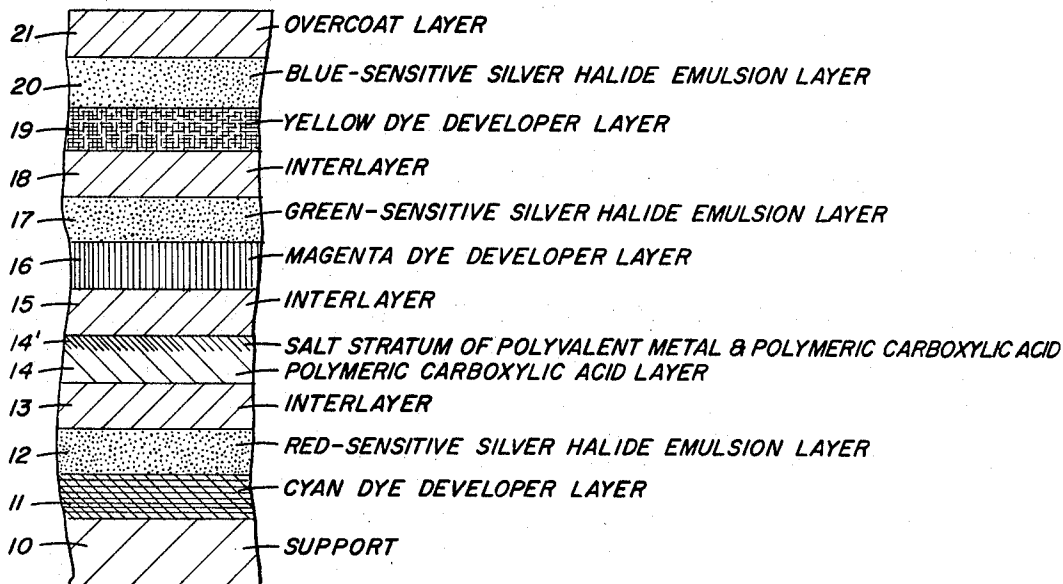


FIG. 1

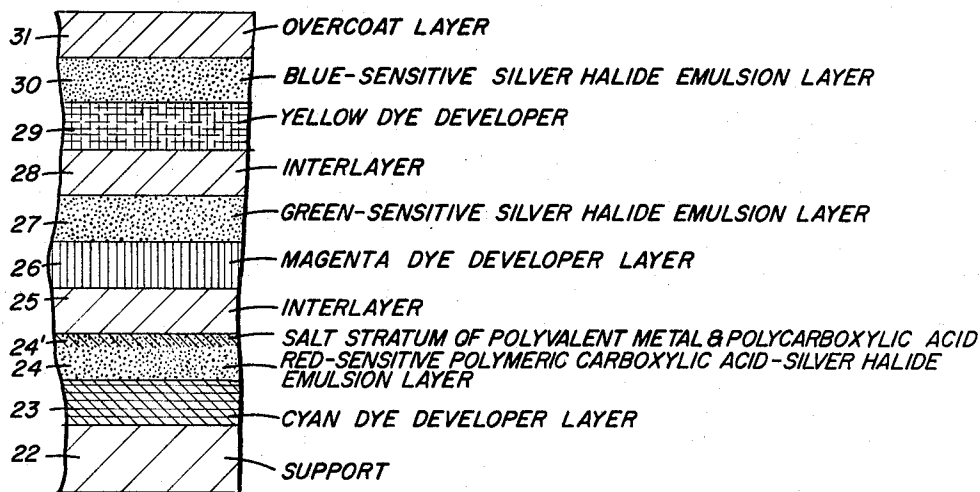


FIG. 2

RICHARD W. BECKER
INVENTOR.

BY *R. Frank Smith*
James R. Ludwig

ATTORNEYS

May 21, 1968

R. W. BECKER

3,384,483

MULTICOLOR DYE DEVELOPER IMAGE TRANSFER SYSTEMS

Filed March 23, 1964

2 Sheets-Sheet 2

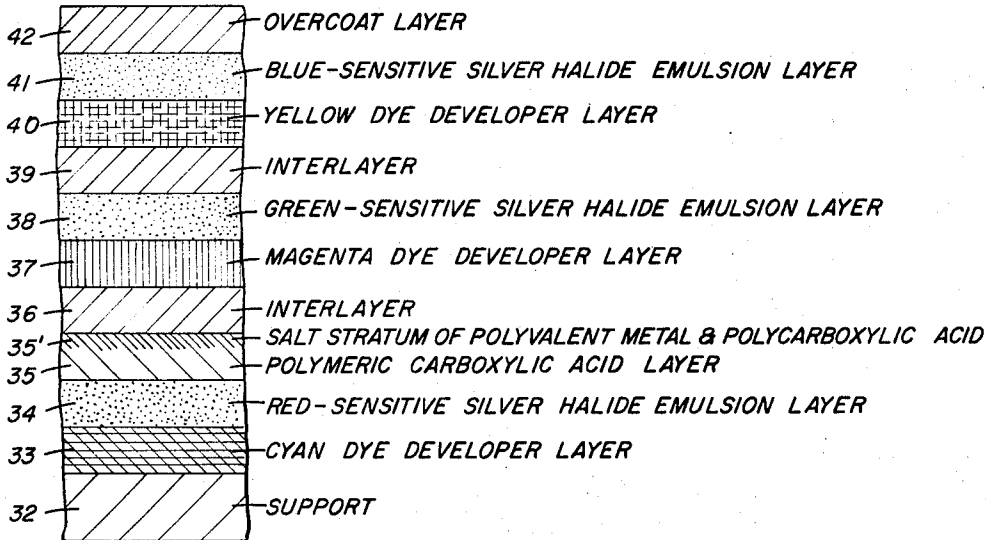


FIG. 3

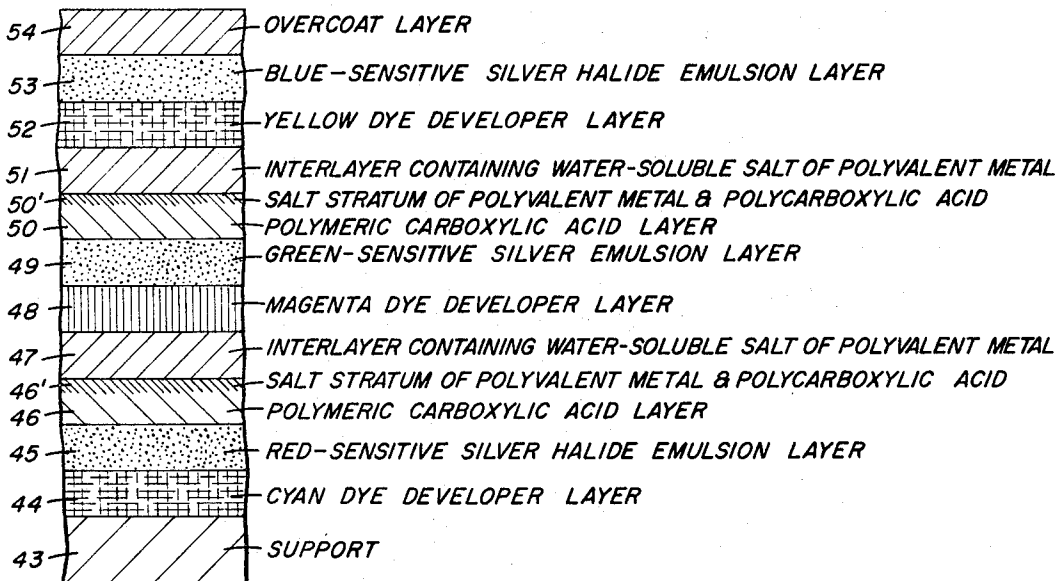


FIG. 4

RICHARD W. BECKER
INVENTOR.

BY *R. Frank Smith*
James R. Fredrick

ATTORNEYS

1

3,384,483

MULTICOLOR DYE DEVELOPER IMAGE TRANSFER SYSTEMS

Richard W. Becker, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

Filed Mar. 23, 1964, Ser. No. 353,706

17 Claims. (Cl. 96—29)

ABSTRACT OF THE DISCLOSURE

Photographic elements having at least two adjacent dye image forming units, each of which comprise silver halide emulsion and dye developer contiguous to the silver halide of the emulsion, separated by an alkali-permeable, water-insoluble stratum of a polyvalent metal salt and a film forming, alkali-permeable, water-soluble polymer having free carboxylic acid groups, the stratum being less permeable to dye developer in aqueous alkaline solution than the polymeric carboxylic acid used to prepare the salt stratum.

The present invention relates to the art of photography, and more particularly, to multicolor dye diffusion transfer systems utilizing dye developers.

Compounds which contain in the same molecule both the chromophoric system of a dye and a photographic silver halide developing moiety have been described in the photographic art as useful compounds in photographic elements for preparing color images by diffusion transfer processes. Such compounds are commonly called "dye developers." Photographic elements containing such dye developers generally comprise a plurality of photosensitive silver halide emulsions wherein each of the emulsions is selectively sensitized to a different region of the spectrum. A dye developer is positioned contiguous to the silver halide in each of such emulsions, the dye developer being substantially complementary in color to the color of light recorded in the contiguous silver halide. Such a photoelement is processed with an alkaline composition. The latent image is developed in the negative image areas with the dye developers, this development immobilizing the dye developers in such negative image areas. The dye developers in the unexposed areas diffuse to the surface imagewise and are transferred to a reception layer or receiving sheet to form a positive multicolor image. Such color diffusion transfer processes are disclosed in U.S. Patent 2,983,606, British Patent 804,971, and French Patent 1,313,767, as well as elsewhere in the literature.

Ideally, each dye developer should develop only contiguous silver halide, to wit, the cyan dye developer should develop only the red-sensitive silver halide emulsion layer, the magenta dye developer should develop only the green-sensitive silver halide emulsion layer, and the yellow dye developer should develop only the blue-sensitive silver halide emulsion layer in a conventional three-color system. However, in practice, each dye developer has been found to develop to an undesirable extent each silver halide emulsion layer. The result of this effect is to produce color contamination and desaturation of colors in the transfer prints, red in particular being a color of relatively poor quality. Conventional interlayers or barrier layers between each of the color-forming units of such materials as gelatin have been utilized, such layers, however, only being effective to a limited degree in improving

2

the interimage characteristics in multicolor dye developer diffusion transfer systems.

It is accordingly an object of this invention to provide a novel photographic element useful for preparing multicolor dye developer images having improved saturation and reduced color contamination.

It is another object of this invention to provide a photographic element for use in preparing positive multicolor dye developer transfer images having at least one novel stratum to improve the interimage characteristics of the system.

It is still another object of the invention to provide a novel process for preparing multicolor dye developer images of high color saturation and low color contamination.

It is likewise an object of this invention to provide a novel photographic process for preparing multicolor diffusion transfer dye developer images having improved red purity and saturation.

These and other objects of the invention are accomplished with photographic elements comprising a support having coated thereon (1) at least two dye image-forming units composed of a light-sensitive silver halide emulsion and a dye developer contiguous to silver halide of the emulsion, and (2) an alkali-permeable and water-insoluble stratum of a polyvalent metal salt of a film-forming, alkali-permeable, water-soluble polymeric carboxylic acid positioned between at least two of the dye image-forming units, such stratum being less permeable to dye developers in aqueous alkaline solution than the polymeric carboxylic acid used to prepare the salt stratum.

The feature salt strata utilized in the subject dye developer diffusion transfer system can be prepared with a variety of polyvalent metal salts and polymeric carboxylic acids. The subject salt strata can be formed on the element by coating a solution, or a water-permeable substrate, containing the polyvalent metal in water-soluble form on a polymeric carboxylic acid layer previously coated on the element to form a thin layer of a water-insoluble salt. The polyvalent metal in water-soluble form can be coated directly on silver halide emulsion layers if the vehicle for the silver halide is a polymeric carboxylic acid that forms a water-insoluble salt with the polyvalent metal moiety. Interlayers of water-permeable materials can be utilized on either side of the subject water-insoluble salt strata. Such salt strata are preferably utilized between the magenta and cyan dye image-forming units to particularly improve red purity and saturation of the transferred dye developer images. Similarly, the subject salt strata can be utilized between the yellow and the magenta dye image-forming units as well as between both the magenta and the cyan dye image-forming units to improve color purity and saturation of the transfer dye developer images.

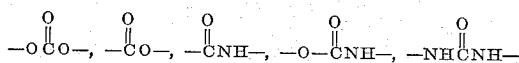
A wide variety of film-forming, alkali-permeable, water-soluble polymeric compositions containing free carboxylic acid groups, and including water-soluble salts thereof, can be utilized to form the subject salt strata with polyvalent metal moieties. Typically, such polymers contain about 5% to 60% by weight of polymer of free carboxylic acid groups (i.e., available for reaction with the subject polyvalent metal moieties in aqueous alkaline solutions) or the equivalent weight of water-soluble salts thereof. Typical of such suitable acid polymers include:

(1) Natural occurring carboxylic acid group-contain-

ing polymers and derivatives thereof including such proteins as gelatin, casein and the like,

(2) Natural occurring high molecular weight carboxylic acid group-containing polysaccharides and derivatives thereof such as alginic acid, pectic acid, tragacanthic acid, carboxymethyl cellulose, cellulose sulfate and the like, and

(3) Synthetic linear polymers containing carboxylic acid groups such as addition vinyl polymers and condensation polymers wherein the monomeric repeating units are connected with such groups as $-\text{O}-$,



and the like, illustrative of such synthetic polymers are disclosed in U.S. Patent 2,565,418, U.S. Patent 3,062,674, U.S. Patent 3,007,901 and British Patent 886,882 and include succinoylated polyvinyl alcohol, maleic acid-styrene polymers, alkylacrylate-acrylic acid polymers, formaldehyde-salicylic acid polymers, acidic polyesters, acid polyamides and the like.

Polyvalent metal moieties are utilized to form the present salts as such moieties can be used to cross-link carboxylic acid moieties of the polymeric carboxylic acid to form the present strata which have the proper degree of alkali permeability and water-insolubility to serve as barrier layers to prevent color contamination and interdevelopment between dye image-forming units. A wide variety of polyvalent metal moieties can be utilized in preparing the subject salt strata. Suitable polyvalent metals with which suitable salt strata of the invention can be prepared include alkaline earth metals such as calcium, barium and strontium, zirconium, thorium, magnesium, manganese, lead, tin, cobalt, nickel, cadmium, iron, chromium and the like polyvalent metals that form alkali-permeable, water-insoluble salts with the above-described polymeric materials containing carboxylic acid groups.

The amount of polymeric salt utilized in the subject salt strata can be widely varied, the amount varying with the effect desired and the nature of the polyvalent metal and the polymeric carboxylic acid. More generally, the amount or coverage of the polyvalent metal-polymeric carboxylic acid salt stratum utilized is that which is substantially equivalent in permeability to dye developers in aqueous alkaline solution to the calcium alginate formed when a stratum consisting essentially of sodium alginate is reacted with calcium chloride coated thereover at a coverage of about 5 to 100 mg. per square foot.

Typical alkali-permeable water-insoluble salts of the invention include:

zirconium gelatinate,
thorium gelatinate,
calcium pectinate,
calcium alginate,
zirconium alginate,
lead-carboxymethyl cellulose,
manganese alginate,
chromium alginate,
calcium-succinoylated polyvinyl alcohol,
calcium-polyacrylic acid,
barium alginate,
tin alginate,
magnesium alginate,
strontium alginate,
cobalt alginate,
nickel alginate,
iron alginate,
cadmium alginate,
lead alginate,

calcium-condensation of formaldehyde and salicylic acid, and the like, and including mixtures thereof.

The dye developers used in the invention are widely described in the literature. Such compounds function

as a silver halide developing agent and as a dye in photographic diffusion transfer systems. Dye developers are characterized as being relatively nondiffusible in colloid layers such as the hydrophilic organic colloids used in photographic emulsions at neutral pH, but diffusible in such emulsions in the presence of alkaline processing solutions. Useful dye developers are described in the patent literature, including: Australian 220,279; German 1,036,640; British 804,971 and 804,973-5; Belgian 554,935; French 1,168,292 and 1,313,765; Canadian 577,021 and 579,038 and elsewhere in the literature. In general, dye developers are characterized as having both a chromophoric or dye moiety and at least one moiety having a silver halide developing function. Typical of the useful dye developers are those wherein the chromophoric moiety is an azo or anthraquinone dye moiety and the silver halide developing moiety is a benzenoid moiety such as hydroquinonyl moiety.

In the photographic elements of the invention, the dye developers are preferably incorporated in hydrophilic organic colloidal vehicles or carriers comprising the layers of the photographic element dissolved in high-boiling or crystalloidal solvents and dispersed in finely-divided droplets. In preparing such dispersions of dye developers, high-boiling or substantially water-immiscible organic liquids having boiling points above about 175° C. are utilized. The high-boiling solvent can be used alone in dissolving the dye developer and in forming the dispersion or it can be mixed with a low-boiling organic solvent (e.g., boiling at least 25° C. below the boiling point of the higher boiling solvent), or a water-soluble organic solvent, as an auxiliary solvent to facilitate solution of the dye developer. A preferred range of proportions of high-boiling solvent to auxiliary is 1/0 to 1/10 on a weight basis. Such auxiliary solvents can be readily removed from the high-boiling solvent, for example, by air-drying a chilled, noddled dispersion or by continuous water washing. Several of such high-boiling solvents and auxiliary solvents utilized for incorporating dye developers are described in French Patent 1,313,765. The dye developers can also be incorporated into vehicles soluble in organic solvents which are also solvents for the dye developer. Likewise, other incorporating techniques for the dye developer such as ball-milling can be utilized.

The photographic elements of the invention desirably contain auxiliary developing agents such as colorless substantially water-insoluble hydroquinone derivatives such as are disclosed in French Patent 1,313,086. Such auxiliary developing agents can be incorporated in the silver halide emulsion layers, in overcoat layers, in interlayers or in other layers of the element.

The silver halide emulsions utilized in preparing the photographic elements of the invention can be any of the conventional negative-type, developing-out emulsions. Typical suitable silver halides include silver chloride, silver bromide, silver bromiodide, silver chloriodide, silver chlorobromiodide and the like. Mixtures of more than one of such silver halides can also be utilized. In preparing such silver halide emulsions, a wide variety of hydrophilic organic colloids can be utilized as the vehicle or carrier. I prefer to utilize gelatin as the hydrophilic colloid or carrier material although such material as polyvinyl alcohol and its water-soluble derivatives and copolymers, water-soluble copolymers such as polyacrylamide, imidized polyacrylamide, etc., and other water-soluble film-forming materials that form water-permeable coats such as colloidal albumin, water-soluble cellulose derivatives, etc., can be utilized in preparing the present photographic elements. Compatible mixtures of two or more of such colloids can also be utilized.

In the present photographic elements, the dye developers are disposed integral with the element and contiguous to silver halide of each of the light-sensitive silver halide emulsion layers. Such dye developers can be incorporated directly in the light-sensitive silver halide emulsion layers

5

or in separate layers contiguous to the layers containing the silver halide. The present photographic elements contain at least two dye image-forming units, each unit comprising a light-sensitive silver halide emulsion and a dye developer contiguous to silver halide in the unit. Each dye image-forming unit is preferably spectrally sensitized to record light that is substantially complementary to the color of the dye developer in the unit.

The various layers utilized in preparing the present photographic elements can be coated on a wide variety of photographic supports. Typical supports include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, polyethylene film, polypropylene film, paper, polyethylene-coated paper, glass and the like.

A wide variety of receiving sheets can be utilized to receive the dye developer images from the present light-sensitive photographic elements. Typical reception layers for dye developer receiving sheets include such materials as linear polyamides, proteins such as gelatin, polyvinyl pyrrolidones, poly-4-vinyl pyridine, polyvinyl alcohol, polyvinyl salicylal, partially hydrolyzed polyvinyl acetate, methyl cellulose, regenerated cellulose, carboxymethyl cellulose and hydroxyethyl cellulose, or mixtures of such. These reception layers can be coated on a suitable support of the type described above for the light-sensitive elements of the invention and including transparent as well as opaque supports. Also, receiving sheets that release acidic material such as that derived from an acidic polymer or other acidic compound at a controlled rate as are described in U.S. Patent 2,584,030 are particularly useful. Such acidic materials are typically positioned in layers on the receiving sheet below the dye developer reception layer, there suitably being a spacer layer between the acid layer and the mordanting layer to control the release of acidic material. Such acidic materials serve to neutralize residual portions of the alkaline activator on the receiving sheet. A wide variety of nondiffusible cationic or basic dye-mordanting compounds can be used in liquid permeable reception layers including amines such as polymeric amines, quaternary ammonium compounds, quaternary phosphonium compounds and tertiary sulfonium compounds. Such mordants are nondiffusible in the alkaline processing composition and contain at least one hydrophobic ballast group.

Light-sensitive elements containing integral reception layers for dye developer images can also be utilized. Such integral reception layers can be coated beneath the emulsion and dye developer layers near the support. A stripping layer coated over the integral reception layer can be used to facilitate the removal of the overcoated layers after the diffusion of the dye developer images to the reception layer.

The processing compositions or activators used to initiate development of the exposed light-sensitive elements of the invention are strongly alkaline. Such processing compositions generally have a pH of at least about 12 or contain at least .01 N hydroxyl ion. Alkali metal hydroxides, such as sodium hydroxide, and sodium carbonate, are advantageously used in the composition for imparting such high alkalinity. However, volatile amines such as diethyl amine can also be used, such amines having the advantage of being volatilized from the prints to leave no residue of alkali. Such processing compositions are generally aqueous liquids or solutions, and when utilized in rupturable pods for in-camera processing, generally contain thickening agents such as hydroxyethyl cellulose or carboxymethyl cellulose. Onium compounds such as are disclosed in French Patent 1,313,767 and British Patent 938,865 are preferably utilized in the alkaline processing composition.

Camera apparatus of the type useful for exposing and processing the sensitive elements of the invention have been described, for example, in U.S. Patent 2,435,717. The processing of the subject photographic elements can also be effected outside of camera apparatus by imbibing

6

either the receiving element or the negative element or both in the alkaline processing composition, and thereafter sandwiching together the two elements to allow the dye developer images to diffuse to the receiving element.

In accordance with usual practice, the positioning of the dye image-forming units of the photographic elements of the invention can be varied. In three-color systems, it is preferred to utilize the cyan dye image-forming unit most proximate to the support, the yellow dye-forming unit furthest from the support, and the magenta dye image-forming unit between the cyan and yellow dye image-forming units. It is also preferred to utilize the dye developers in the respective dye image-forming units in a separate underlying layer contiguous to the silver halide emulsion layer. Likewise, it is preferred to utilize in each dye image-forming unit a dye developer that is substantially complementary in color to the color of light recorded by the silver halide in the unit.

FIGS. 1, 2, 3 and 4 of the drawings are enlarged fragmentary sectional views illustrating typical light-sensitive photographic elements or color films of the invention utilizing various strata of salts of polyvalent metals and polymeric carboxylic acids.

FIG. 1 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing a salt stratum of a polyvalent metal and a polymeric carboxylic acid positioned between the magenta dye image-forming unit and the cyan dye image-forming unit. On support 10 is coated layer 11 containing a cyan dye developer. Over layer 11 is coated layer 12 which is a red-sensitive silver halide emulsion layer. Over layer 12 is coated interlayer 13. Over layer 13 is coated polymeric carboxylic acid layer 14, a portion of layer 14 comprising salt stratum 14' which comprises a salt of a polyvalent metal and the polymeric carboxylic acid of layer 14. Layer 14' can be prepared, for example, by coating a water solution of a water-soluble salt of a polyvalent metal over layer 14, the polyvalent metal moiety reacting with the carboxylic acid of polymeric layer 14 to form water-insoluble salt stratum 14'. Over salt stratum 14' is coated interlayer 15. Over interlayer 15 is coated layer 16 containing a magenta dye developer. Over layer 16 is coated green-sensitive silver halide emulsion layer 17. Over layer 17 is coated interlayer 18. Over layer 18 is coated layer 19 which contains a yellow dye developer. Over layer 19 is coated layer 20 which is a blue-sensitive silver halide emulsion layer. Over layer 20 is coated overcoat layer 21.

FIG. 2 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing a salt stratum of a polyvalent metal and a polymeric carboxylic acid positioned between the magenta dye image-forming unit and the cyan dye image-forming unit wherein the salt stratum is formed with a portion of the polymeric carboxylic acid serving as the carrier for the red-sensitive silver halide. On support 22 is coated layer 23 containing a cyan dye developer. Over layer 23 is coated layer 24 which can comprise one or more red-sensitive silver halide emulsion layers. Over emulsion layer 24 is coated interlayer 25 which contains a water-soluble salt of a polyvalent metal, that on coating over layer 24, forms a water-insoluble salt with silver halide polymeric carboxylic acid carrier material in a layer 24 at the interface of layers 24 and 25, to wit, salt stratum 24'. Over layer 25 is coated layer 26 containing a magenta dye developer. Over layer 26 is coated green-sensitive silver halide emulsion layer 27. Over layer 27 is coated interlayer 28. Over layer 28 is coated layer 29 which contains a yellow dye developer. Over layer 29 is coated layer 30 which is a blue-sensitive silver halide emulsion layer. Over layer 30 is coated overcoat layer 31.

FIG. 3 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing a salt stratum of a polyvalent metal and a polymeric carboxylic acid positioned between a magenta dye image-forming unit and a cyan dye image-forming unit. On support 32 is

coated layer 33 containing a cyan dye developer. Over layer 33 is coated layer 34 which is a red-sensitive silver halide emulsion layer. Over layer 34 is coated polymeric carboxylic acid layer 35, a portion of layer 35 comprising salt stratum 35' which comprises a salt of a polyvalent metal and the polymeric carboxylic acid of layer 35. Layer 35' can be prepared, for example, by coating a water solution of a water-soluble salt of the polyvalent metal over layer 35, the polyvalent metal reacting with the carboxylic acid of polymeric layer 35 to form water-insoluble salt stratum 35'. Over salt stratum 35' is coated interlayer 36. Salt stratum 35' can also be formed by incorporating in interlayer 36 a water-soluble salt of the polyvalent metal. On coating such a composition over layer 35, a water-insoluble salt stratum is formed, e.g., layer 35'. Over layer 36 is coated layer 37 containing a magenta dye developer. Over layer 37 is coated green-sensitive silver halide emulsion layer 38. Over layer 38 is coated interlayer 39. Over layer 39 is coated layer 40 which contains a yellow dye developer. Over layer 40 is coated layer 41 which is a blue-sensitive silver halide emulsion layer. Over layer 41 is coated overcoat layer 42.

FIG. 4 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing salt strata of a polyvalent metal and a polymeric carboxylic acid positioned between the yellow dye image-forming unit and the magenta dye image-forming unit as well as between the magenta dye image-forming unit and the cyan dye image-forming unit. On support 43 is coated layer 44 containing a cyan dye developer. Over layer 44 is coated layer 45 which is a red-sensitive silver halide emulsion layer. Over layer 45 is coated polymeric carboxylic acid layer 46, a portion of layer 46 comprising water-insoluble salt stratum 46' which comprises a salt of a polyvalent metal and the polymeric carboxylic acid of layer 46. Interlayer 47 contains a water-soluble salt of a polyvalent metal, which on coating over layer 46, forms salt stratum 46' at the interface of layers 46 and 47. Over layer 47 is coated layer 48 containing a magenta dye developer. Over layer 48 is coated green-sensitive silver halide emulsion layer 49. Over layer 49 is coated polymeric carboxylic layer 50, a portion of layer 50 comprising water-insoluble salt stratum 50' which comprises a salt of a polyvalent metal and the polymeric carboxylic acid of layer 50. Interlayer 51 contains a water-soluble salt of a polyvalent metal, which on coating over layer 50, forms salt stratum 51' at the interface of layers 50 and 51. Over layer 51 is coated layer 52 which contains a yellow dye developer. Over layer 52 is coated layer 53 which is a blue-sensitive silver halide emulsion layer. Over layer 53 is coated overcoat layer 54.

The following examples will serve to further illustrate the present invention.

Example I

A photographic element having the structure substantially as shown in FIG. 3 of the drawings was prepared by coating successively the following layers on a subbed cellulose acetate film support:

(1) Cyan dye developer layer (a.g., layer No. 33 of FIG. 3).—A coating of the cyan dye developer, 5,8-dihydroxy - 1,4 - bis[(β - hydroquinonyl- α -methyl)ethyl-amino]-anthraquinone, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 120 mg. of the cyan dye developer per square foot and 158 mg. of gelatin per square foot.

(2) Red-sensitive emulsion layer (e.g., layer No. 34 of FIG. 3).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion sensitized to red light coated at a coverage of 180 mg. of silver per square foot and 117 mg. of gelatin per square foot.

(3) Interlayer (e.g., layer No. 35 of FIG. 3).—A coating of gelatin at a coverage of 95 mg. per square foot overcoated with a zirconium-gelatin salt (e.g., layer No. 35' of FIG. 3), the overcoat prepared by overcoating

the gelatin with a one percent aqueous solution of zirconium sulfate coated at a coverage of 3 grams of zirconium sulfate per square foot.

(4) Interlayer (e.g., layer No. 36 of FIG. 3).—A coating of gelatin at a coverage of 95 mg. per square foot.

(5) Magenta Dye Developer Layer (e.g., layer No. 37 of FIG. 3).—A coating of the magenta dye developer, 4-isopropoxy - 2 - [p-(β -hydroquinonyl)ethyl]-phenylazo]-1-naphthol, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 60 mg. of the dye developer per square foot and 73 mg. of gelatin per square foot.

(6) Green-sensitive emulsion layer (e.g., layer No. 38 of FIG. 3).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion sensitized to green light coated at a coverage of 75 mg. of silver per square foot and 60 mg. of gelatin per square foot.

(7) Interlayer (e.g., layer No. 39 of FIG. 3).—A coating of gelatin at a coverage of 140 mg. per square foot.

(8) Yellow dye developer layer (e.g., layer No. 40 of FIG. 3).—A coating of the yellow dye developer, 1-phenyl-3-N-n-hexylcarboxamido - 4 - [p-(2',5' - hydroxyphenethyl)phenylazo]-5-pyrazolone, dissolved in diethyldrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 60 mg. of the dye developer per square foot and 50 mg. of gelatin per square foot.

(9) Blue-sensitive emulsion layer (e.g., layer No. 41 of FIG. 3).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion that is inherently sensitive to blue light was coated at a coverage of 65 mg. of silver per square foot and 41 mg. of gelatin per square foot.

(10) Overcoat layer (e.g., layer No. 42 of FIG. 3).—A gelatin coating containing dispersed therein the colorless auxiliary developed, 4'-methylphenylhydroquinone, at a coverage of 32 mg. of gelatin per square foot and 40 mg. of the auxiliary developer per square foot.

Other photographic elements as described above were prepared except that in lieu of zirconium sulfate being coated on interlayer 3, 2 percent solutions of zirconium nitrate and thorium nitrate were utilized at coverages of 3 grams per square foot to form zirconium-gelatin and thorium-gelatin salt strata. Also, for purposes of comparison, a photographic element was prepared wherein the zirconium and thorium salt treatments of interlayer 3 were omitted. The resulting photographic elements were exposed in an intensity scale sensitometer. Each of the exposed elements were thereafter processed by applying an alkaline activator solution to the emulsion surfaces thereof and receiving sheets superposing thereover. The receiving sheets were composed of a white pigmented cellulose acetate support having a dye developer receiving layer containing a mixture of gelatin at a coverage of 300 mg. per square foot, poly-4-vinylpyridine mordant at a coverage of 300 mg. per square foot and 1-phenyl-5-mercaptotetrazole at a coverage of 15 mg. per square foot. The receiving sheets and the exposed photographic elements were left in contact with the alkaline activator material therebetween for a period of about 2 minutes at about 70° F., and thereafter stripped apart. The alkaline activator material comprised an aqueous solution containing, on a weight basis, 3.9% high viscosity hydroxyethyl cellulose, 4.5% sodium hydroxide, 2% benzotriazole, 2% 1-benzyl-2-picolinium bromide, and 1% sodium thiosulfate pentahydrate. The resulting prints were washed in 2% boric acid, rinsed in water and dried. The reflection densities of the graduated scales of the transferred dye developer images on the receiving sheets were determined. Summarized in Table A below are data illustrating the increased magenta $D_{\max}$ (i.e., improved magenta dye developer image saturation) and the reduced magenta "drop-off" (i.e., decreased desaturation of the magenta dye developer image resulting from the magenta dye developer developing in the red-sensitive emulsion layer) that resulted from the salt strata of the invention.

TABLE A

Feature Interlayer Coating Addenda	Magenta Density		Magenta Drop-Off
	D _{max.}	1st Step in Red Scale	
None (Control).....	1.98	1.15	.83
Zr(SO ₄) ₂	2.28	2.28	0
None (Control).....	2.12	1.34	.78
Zr(NO ₃) ₄	2.60	2.06	.54
Th(NO ₃) ₄	2.58	2.43	.15

The data in Table A indicates that the zirconium and thorium gelatinates formed effective strata to reduce the wandering of magenta dye developer. The dye developer transfer images prepared with photographic elements having the feature interlayers of the invention had substantially improved reds with respect to saturation and purity.

Example II

A photographic element having the structure substantially as shown in FIG. 1 of the drawings was prepared by coating successively the following layers on a subbed cellulose acetate film support:

- (1) Cyan dye developer layer (e.g., layer No. 11 of FIG. 1).—A coating of the cyan dye developer, 5,8-dihydroxy-1,4-bis[(β - hydroquinonyl - 2 - methyl)ethylamino]-anthraquinone, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 186 mg. of the cyan dye developer per square foot and 214 mg. of gelatin per square foot.
- (2) Red-sensitive emulsion layer (e.g., layer No. 12 of FIG. 1).—A coating of developing-out negative gelatino-silver bromiodide (6% iodide) emulsion sensitized to red light was coated at a coverage of 210 mg. of silver per square foot and 117 mg. of gelatin per square foot.
- (3) Interlayer (e.g., layer No. 13 of FIG. 1).—A coating of gelatin at a coverage of 45 mg. per square foot.
- (4) Interlayer (e.g., layer No. 14 of FIG. 1).—A coating of sodium alginate coated at a coverage of 27 mg. per square foot overcoated with a calcium alginate salt (e.g., Layer No. 14' of FIG. 1), the overcoat of calcium alginate prepared by overcoating the sodium alginate with an aqueous solution of calcium chloride at a coverage of 8 mg. of calcium chloride per square foot.
- (5) Interlayer (e.g., layer No. 15 of FIG. 1).—A coating of gelatin at a coverage of 140 mg. per square foot.
- (6) Magenta dye developer layer (e.g., layer No. 16 of FIG. 1).—A coating of the magenta dye developer, 4-isopropoxy-2-[p - (β - hydroquinonyl) ethyl] phenylazo]-1-naphthol, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 44 mg. of the dye developer per square foot and 45 mg. of gelatin per square foot.
- (7) Green-sensitive emulsion layer (e.g., layer No. 17 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion sensitized to green light, coated at a coverage of 86.5 mg. of silver per square foot and 48 mg. of gelatin per square foot.
- (8) Interlayer (e.g., No. 18 of FIG. 1).—A coating of gelatin at a coverage of 140 mg. per square foot.
- (9) Yellow dye developer layer (e.g., layer No. 19 of FIG. 1).—A coating of the yellow dye developer, 1-phenyl - 3 - (N - n - hexylcarboxamido) - 4 - [p - (2',5'-dihydroxyphenethyl)phenylazo]-5-pyrazolone, dissolved in ditetrahydrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 38 mg. of the dye developer per square foot and 38 mg. of gelatin per square foot.
- (10) Blue-sensitive emulsion layer (e.g., layer No. 20 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion that is inherently sensitive to blue light was coated at a coverage of 55 mg. of silver per square foot and 41 mg. of gelatin per square foot.
- (11) Overcoat layer (e.g., layer No. 21 of FIG. 1).—

A gelatin coating containing dispersed therein the colorless auxiliary developer, 4'-methylphenylhydroquinone, at a coverage of 32 mg. of gelatin per square foot and 32 mg. of the auxiliary developer per square foot.

- The prepared photographic element is referred to as Element B. For purposes of comparison, a photographic element like Element B was prepared except that the interlayer containing the sodium alginate overcoated with calcium chloride (layer No. 4) was omitted, this photographic element being referred to as Element A. Also,
- photographic elements similar to Element B were prepared wherein the amount of sodium alginate in layer No. 4 was varied 18 mg. and 9 mg., per square foot being used, these photographic elements being referred to as Element C and Element D respectively. Another photographic element like Element B was prepared except that the sodium alginate layer was overcoated with the calcium chloride at a coverage of 24 mg. per square foot, this photographic element being referred to as Element E. The resulting photographic elements were exposed in an intensity scale sensitometer. Each of the exposed elements were thereafter processed by applying an alkaline activator solution to the emulsion surfaces thereof and superposing thereover receiving sheets composed of a paper support having a dye developer receiving layer containing a poly-4-vinylpyridine mordant in a polyvinyl alcohol substrate. The receiving sheets and the exposed photographic elements were left in contact with the alkaline activator material therebetween for a period of about one minute at about 70° F., and thereafter stripped apart. The alkaline activator material comprised an aqueous solution containing, on a weight basis, 2.0% high viscosity hydroxyethyl cellulose, 5.7% sodium hydroxide, 2.4% benzotriazole, 2.4% 1-benzyl- α -picolinium bromide and 0.4% sodium thiosulfate pentahydrate. The reflection densities of the graduated scales of the transferred dye developer images on the receiving sheets were determined. Summarized in Table B below are data illustrating the magenta densities, and including the reduced magenta "drop-off," of the transfer prints.

TABLE B

Feature Element	Magenta Density		Magenta Drop-Off
	D _{max.}	1st Step in Red Scale	
Element A (Control).....	1.67	1.05	0.62
Element B.....	1.68	1.47	0.21
Element C.....	1.71	1.37	0.34
Element D.....	1.61	1.21	0.40
Element E.....	1.65	1.24	0.41

As can be observed from the data set out in Table B, the feature salt strata utilized in Elements B, C, D and E of the invention substantially reduced the amount of magenta dye developer that developed silver halide in a silver halide emulsion layer other than in the green-sensitive silver halide emulsion layer. Similar improved results are obtained when zirconium sulfate is substituted for the calcium chloride or when succinoylated polyvinyl alcohol (half ester) of the type described in Example 1 of French Patent 1,335,297 is substituted for the sodium alginate.

Example III

A photographic element having the structure substantially as shown in FIG. 2 of the drawings was prepared by coating successively the following layers on a subbed cellulose acetate film support:

- (1) Cyan dye developer layer (e.g., layer No. 23 of FIG. 2).—A coating of the cyan dye developer, 5,8-dihydroxy - 1,4 - bis[(β - hydroquinonyl - α - methyl)ethylamino] - anthraquinone, dissolved in N - n - butylacetanilide, dispersed in gelatin and coated at a coverage of 174 mg. of the cyan dye developer per square foot and 205 mg. of gelatin per square foot.
- (2) Red-sensitive emulsion layer (e.g., layer No. 24

of FIG. 2).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion sensitized to red light coated at a coverage of 189 mg. of silver per square foot and 70 mg. of gelatin per square foot. An additional red-sensitive portion of the developing-out negative gelatino-silver bromoiodide emulsion containing sodium alginate was then coated thereover at a coverage of 39 mg. of sodium alginate per square foot, 21 mg. of silver per square foot and 8 mg. of gelatin per square foot.

(3) Interlayer (e.g., layer No. 25 of FIG. 2).—A coating of gelatin containing calcium chloride at a coverage of 21 mg. of calcium chloride per square foot and 190 mg. of gelatin per square foot. A water-insoluble salt stratum of calcium alginate (e.g., layer No. 24' of FIG. 2) formed between the red-sensitive silver halide emulsion layer containing the sodium alginate and the overcoated gelatin layer containing the calcium chloride.

(4) Magenta dye developer layer (e.g., layer No. 26 of FIG. 2).—A coating of the magenta dye developer, 4-isopropoxy-2-[p-(β -hydroquinonyl-ethyl)-phenylazo]-1-naphthol, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 45 mg. of gelatin per square foot and 44 mg. of the dye developer per square foot.

(5) Green-sensitive emulsion layer (e.g., layer No. 27 of FIG. 2).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion sensitized to green light was coated at a coverage of 86.5 mg. of gelatin per square foot and 48 mg. of silver per square foot.

(b) Interlayer (e.g., layer No. 28 of FIG. 2).—A coating of gelatin at a coverage of 140 mg. per square foot.

(7) Yellow dye developer layer (e.g., layer No. 29 of FIG. 2).—A coating of the yellow dye developer, 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β -hydroquinonyl-ethyl)-phenylazo]-5-pyrazolone, dissolved in dithetrahydrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 38 mg. of the dye developer per square foot and 38 mg. of gelatin per square foot.

(8) Blue-sensitive emulsion layer (e.g., layer No. 30 of FIG. 2).—A coating of a developing-out gelatino-silver bromoiodide (6% iodide) emulsion that is inherently sensitive to blue light was coated at a coverage of 55 mg. of silver per square foot and 41 mg. of gelatin per square foot.

(9) Overcoat layer (e.g., layer No. 31 of FIG. 2).—A gelatin coating containing dispersed therein the colorless auxiliary developer, 4'-methylphenyl hydroquinone, at a coverage of 32 mg. of gelatin per square foot and 40 mg. of the auxiliary developer per square foot.

For purposes of comparison, a similar photographic element as that described above was prepared except the sodium alginate and the calcium chloride were omitted from their respective layers, 39 mg. of gelatin per square foot being substituted for the sodium alginate. These two photographic elements were thereafter exposed, processed with an alkaline activator material and dye developer images transferred to a receiving sheet as described in Example 1. The reflection densities of the graduated scales of the transferred dye developer images on the receiving sheets were obtained. Summarized in Table C below are data illustrating the improved transfer images that resulted from utilizing the calcium alginate stratum in the photographic element.

TABLE C

Feature Salt Stratum	Magenta Density		Magenta Drop-Off
	D_{max}	1st Step in Red Scale	D_{max} -Density of 1st Step in Red Scale
None (Control).....	1.62	1.12	0.50
Calcium alginate.....	1.69	1.58	0.11

Example IV

A photographic element having the structure substantially shown in FIG. 4 of the drawings was prepared by coating successively the following layers on a subbed cellulose acetate film support:

(1) Cyan dye developer layer (e.g., layer No. 44 of FIG. 4).—A coating of the cyan dye developer, 5,8-dihydroxy-1,4-bis[(β -hydroquinonyl- α -methyl)ethyl-amino]-anthraquinone, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 186 mg. of the dye developer per square foot and 214 mg. of gelatin per square foot.

(2) Red-sensitive emulsion layer (e.g., layer No. 45 of FIG. 4).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion sensitized to red light coated at a coverage of 210 mg. of silver per square foot and 117 mg. of gelatin per square foot.

(3) Polymeric carboxylic acid layer (e.g., layer No. 46 of FIG. 4).—A coating of sodium alginate at a covering of 27 mg. per square foot.

(4) Interlayer (e.g., layer No. 47 of FIG. 4).—A coating of calcium chloride and gelatin at a coverage of 21 mg. of calcium chloride per square foot and 190 mg. of gelatin per square foot. A water-insoluble calcium alginate salt stratum (e.g., layer No. 46' of FIG. 4) formed between the polymeric carboxylic acid layer No. 3 and this interlayer.

(5) Magenta dye developer layer (e.g., layer No. 48 of FIG. 4).—A coating of the magenta dye developer, 4-isopropoxy-2-[p-(β -hydroquinonyl-ethyl)-phenylazo]-1-naphthol, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 45 mg. of the dye developer per square foot and 45 mg. of gelatin per square foot.

(6) Green-sensitive emulsion layer (e.g., layer No. 49 of FIG. 4).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) emulsion sensitized to green light was coated at a coverage of 86.5 mg. of silver per square foot and 48 mg. of gelatin per square foot.

(7) Polymeric carboxylic acid layer (e.g., layer No. 50 of FIG. 4).—A coating of sodium alginate at a coverage of 27 mg. per square foot.

(8) Interlayer (e.g., layer No. 51 of FIG. 4).—A coating of calcium chloride and gelatin at a coverage of 21 mg. of calcium chloride per square foot and 140 mg. of gelatin per square foot. A water-insoluble calcium alginate salt stratum (e.g., layer No. 51' of FIG. 4) formed between the polymeric carboxylic acid layer No. 7 and this interlayer.

(9) Yellow dye developer layer (e.g., layer No. 52 of FIG. 4).—A coating of the yellow dye developer, 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β -hydroquinonyl-ethyl)-phenylazo]-5-pyrazolone, dissolved in dithetrahydrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 38 mg. of the dye developer per square foot and 38 mg. of gelatin per square foot.

(10) Blue-sensitive emulsion layer (e.g., layer No. 53 of FIG. 4).—A coating of a developing-out gelatino-silver bromoiodide (6% iodide) emulsion that is inherently sensitive to blue light, coated at a coverage of 55 mg. of silver per square foot and 41 mg. of gelatin per square foot.

(11) Overcoat layer (e.g., layer No. 54 of FIG. 4).—A gelatin coating containing dispersed therein the colorless auxiliary developer, 4'-methylphenyl hydroquinone, at a coverage of 32 mg. of gelatin per square foot and 32 mg. of the auxiliary developer per square foot.

For purposes of comparison, a similar photographic element was prepared wherein the calcium chloride and the sodium alginate were omitted therefrom. The photographic elements were thereafter exposed, processed with an alkaline activator and dye developer images transferred to a receiving sheet as described in Example 1.

The reflection densities of the graduated scales of the transferred dye developer images on the receiving sheets were determined. Summarized below in Table D are data illustrating the improved results that are obtained with the use of the calcium alginate salt strata positioned between the cyan dye image-forming unit and the magenta dye image-forming unit as well as between the yellow dye image-forming unit and the magenta dye image-forming unit.

TABLE D

Feature Salt Stratum	Yellow Density		Yellow Drop-Off
	D _{max.}	1st Step in Yellow Scale	D _{max.} -Density of 1st Step in Yellow Scale
None (Control).....	1.64	0.91	0.73
Calcium alginate.....	1.53	1.12	0.42

As can be observed from the data set out in Table D, the water-insoluble salt strata of the invention can also be utilized to substantially improve yellows with respect to saturation and purity.

Example V

A photographic element having the structure substantially as shown in FIG. 3 of the drawings was prepared by coating successively the following layers on a subbed cellulose acetate film support:

(1) Cyan dye developer layer (e.g., layer No. 33 of FIG. 3).—A coating of the cyan dye developer, 5,8-dihydroxy-1,4-bis[(β - hydroquinonyl - α - methyl)ethylamino]-anthraquinone, dispersed in gelatin and coated at a coverage of 186 mg. of the dye developer per square foot and 214 mg. of gelatin per square foot.

(2) Red-sensitive emulsion layer (e.g., layer No. 34 of FIG. 3).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion sensitized to red light, coated at a coverage of 210 mg. of silver per square foot and 117 mg. of gelatin per square foot.

(3) Polymeric carboxylic acid layer (e.g., layer No. 35 of FIG. 3).—A coating of gelatin and sodium alginate at a coverage of 45 mg. of gelatin per square foot and 27 mg. of sodium alginate per square foot.

(4) Inteler (e.g., layer No. 36 of FIG. 3).—A coating of gelatin containing calcium chloride at a coverage of 140 mg. of gelatin per square foot and 21 mg. of calcium chloride per square foot. A water-insoluble stratum of calcium alginate (e.g., layer No. 35' of FIG. 3) is formed between the sodium alginate-gelatin layer No. 3 and the calcium chloride-gelatin layer No. 4.

(5) Magenta dye developer layer (e.g., layer No. 37 of FIG. 3).—A coating of the magenta dye developer, 4-isopropoxy-2-[p-(β -hydroquinonyl)ethyl]-phenylazo]-1-naphthol, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 44 mg. of the dye developer per square foot and 45 mg. of gelatin per square foot.

(6) Green-sensitive emulsion layer (e.g., layer No. 38 of FIG. 3).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion sensitized to green light was coated at a coverage of 86.5 mg. of silver per square foot and 48 mg. of gelatin per square foot.

(7) Interlayer (e.g., layer No. 39 of FIG. 3).—A coating of gelatin at a coverage of 140 mg. per square foot.

(8) Yellow dye developer layer (e.g., layer No. 40 of FIG. 3).—A coating of the yellow dye developer, 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β -hydroquinonyl)ethyl]-phenylazo]-5-pyrazolone, dissolved in ditetrahydrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 38 mg. of the dye developer per square foot and 38 mg. of gelatin per square foot.

(9) Blue-sensitive emulsion layer (e.g., layer No. 41 of FIG. 3).—A coating of a developing-out negative gelatino-silver bromiodide (6% iodide) emulsion that is inherently sensitive to blue light, coated at a coverage of

55 mg. of silver per square foot and 41 mg. of gelatin per square foot.

(10) Overcoat layer (e.g., layer No. 42 of FIG. 3).—A gelatin coating containing dispersed therein the colorless auxiliary developer, 4'-methylphenyl hydroquinone, at a coverage of 32 mg. of gelatin per square foot and 32 mg. of the auxiliary developer per square foot.

The above-described element is identified as Element G in Table E below. An element similar to Element G was prepared except that the sodium alginate and the calcium chloride in layers 3 and 4 were omitted, this element being referred to as Element F in Table E below. An element similar to Element G was prepared except that the gelatin was omitted from layer 3 and the gelatin layer 4 was coated at a coverage of 185 mg. per square foot, this element being referred to as Element I in Table E. For purposes of comparison, an element similar to Element I was prepared except that the sodium alginate and the calcium chloride were omitted, this element being referred to as Element H in Table E. An element similar to Element I was prepared except that sodium pectinate was substituted for the sodium alginate in layer 3 at a coverage of 40 mg. per square foot, this element being referred to as Element K in Table E. For purposes of comparison, an element similar to Element K was prepared except that the sodium pectinate and the calcium chloride were omitted, this element being referred to as Element J in Table E. An element similar to Element I was prepared except that carboxymethyl cellulose was substituted for sodium alginate in layer 3 at a coverage of 32 mg. per square foot and lead acetate was substituted for calcium chloride in layer 4 at a coverage of 100 mg. per square foot, the gelatin in layer 4 having a coverage of 70 mg. per square foot, this element being referred to as Element M in Table E. For purposes of comparison, an element similar to Element M was prepared except that the carboxymethyl cellulose was omitted from layer 3, this element being referred to as element L in Table E. An element similar to Element I was prepared except that layer 4 contained manganous chloride at a coverage of 33 mg. per square foot in place of 18 mg. of the calcium chloride per square foot and 70 mg. of the gelatin per square foot, this element being referred to as Element O in Table E. For purposes of comparison, an element similar to Element O was prepared except the manganous chloride and the sodium alginate were omitted, this element being referred to as Element N in Table E. Also, an element similar to Element O was prepared except that lead acetate at a coverage of 62 mg. per square foot was substituted for the manganous chloride in layer 4, this element being referred to as Element P in Table E.

TABLE E

Feature Salt Strata	Magenta Density		Magenta Drop-Off
	D _{max.}	1st Step in Red Scale	D _{max.} -Density of 1st Step in Red Scale
F. None (Control).....	1.72	1.11	0.61
G. Calcium alginate.....	1.59	1.25	0.44
H. None (Control).....	1.63	1.09	0.59
I. Calcium alginate.....	1.67	1.39	0.29
J. None (Control).....	1.80	1.12	0.68
K. Calcium pectinate.....	1.80	1.55	0.25
L. None (Control).....	1.45	0.82	0.63
M. Plumbous carboxymethyl cellulose.....	1.48	1.33	0.15
N. None (Control).....	1.88	1.29	0.57
O. Manganous alginate.....	1.64	1.53	0.11
P. Lead alginate.....	1.66	1.39	0.27

As can be observed from the data set out in Table E, a wide variety of water-insoluble salts of polyvalent metals and polymeric carboxylic acid compositions can be utilized in the multicolor dye developer diffusion transfer systems of the invention to produce increased color saturation and decreased color contamination.

In the above examples, the percentages by weight of carboxylic acid groups on the water-soluble polymer re-

actants were: gelatin, 5% alginic acid, 22%; pectic acid, 10.7%; and carboxymethyl cellulose, 10%.

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 photographic element comprising a support having coated thereon at least two dye image-forming units with an alkali-permeable, water-insoluble salt stratum positioned between at least two of said dye image-forming units which are adjacent, said dye image-forming units comprising a silver halide emulsion layer and a dye developer contiguous to silver halide of said emulsion, and said salt stratum comprising an alkali-permeable, water-insoluble salt of a polyvalent metal and a film-forming, alkali-permeable, water-soluble polymer having free carboxylic acid groups, said salt stratum being less permeable to dye developers comprising said dye image-forming units in aqueous alkaline solution than said water-soluble polymer used to prepare said salt stratum.

2. A photographic element comprising a support having coated thereon three superposed dye image-forming units capable of recording red, green and blue light respectively and an alkali-permeable, water-insoluble salt stratum positioned between at least two of said dye image-forming units which are adjacent, said dye image-forming units comprising a silver halide emulsion layer and a contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer, and said salt stratum comprising an alkali-permeable, water-insoluble salt of a polyvalent metal and a film-forming, alkali-permeable, water soluble polymer having free carboxylic acid groups, said salt stratum being less permeable to dye developers comprising said dye image-forming units in aqueous alkaline solution than said water-soluble polymer used to prepare said salt stratum.

3. A photographic element comprising a support having coated thereon three superposed dye image-forming units capable of recording red, green and blue light respectively and an alkali-permeable, water-insoluble salt stratum positioned between at least two of said dye image-forming units, said dye image-forming units comprising a silver halide emulsion layer and a contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer, and said water-insoluble salt stratum comprising a salt selected from the group consisting of zirconium gelatinate, thorium alginate, calcium alginate, calcium pectinate, lead alginate, manganese alginate, zirconium alginate and lead-carboxymethyl cellulose.

4. A photographic element as described in claim 2 wherein the polyvalent metal-polycarboxylic acid salt stratum is substantially equivalent in permeability to dye developers in aqueous alkaline solution to the calcium alginate formed when a stratum consisting essentially of sodium alginate is reacted with calcium chloride coated thereover at a coverage of about 5 to 100 mg. per square foot.

5. A photographic element as described in claim 2 wherein the water-insoluble salt stratum is positioned between the image-forming units recording red and green light.

6. A photographic element as described in claim 2 wherein a water-insoluble salt stratum is positioned between the image-forming units recording red and green light and between the image-forming units recording green and blue light.

7. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light re-

spectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of zirconium gelatinate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer.

8. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of calcium alginate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer.

9. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of thorium gelatinate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer.

10. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of calcium pectinate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer.

11. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of zirconium alginate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer substantially complementary in color to the color of light recorded in the contiguous silver halide emulsion layer.

12. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of zirconium gelatinate positioned between the

said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer, the dye developer in the image-forming unit recording red light being 5,8-dihydroxy - 1,4 - bis[(β - hydroquinonyl - α - methyl)ethylamino]-anthraquinone, the dye developer in the image-forming unit recording green light being 4-isopropoxy-2-[p - (β - hydroquinonylethyl) - phenylazo] - 1 - naphthol, and the dye developer in the image-forming unit recording blue light being 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β' -hydroquinonylethyl)phenylazo]-5-pyrazolone.

13. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of calcium alginate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer, the dye developer in the image-forming unit recording red light being 5,8-dihydroxy - 1,4 - bis[(β - hydroquinonyl - α - methyl)ethylamino]-anthraquinone, the dye developer in the image-forming unit recording green light being 4-isopropoxy-2-[p - (β - hydroquinonylethyl)phenylazo] - 1 - naphthol, and the dye developer in the image-forming unit recording blue light being 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β' -hydroquinonylethyl)phenylazo]-5-pyrazolone.

14. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of thorium gelatinate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer, the dye developer in the image-forming unit recording red light being 5,8-dihydroxy - 1,4 - bis[(β - hydroquinonyl - α - methyl)ethylamino]-anthraquinone, the dye developer in the image-forming unit recording green light being 4-isopropoxy-2-[p - (β - hydroquinonylethyl) - phenylazo] - 1 - naphthol, and the dye developer in the image-forming unit recording blue light being 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β' -hydroquinonylethyl)phenylazo]-5-pyrazolone.

15. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-

forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of calcium pectinate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer, the dye developer in the image-forming unit recording red light being 5,8-dihydroxy-1,4-bis[(β - hydroquinonyl- α -methyl)ethylamino]-anthraquinone, the dye developer in the image-forming unit recording green light being 4-isopropoxy-2-[p-(β -hydroquinonylethyl)-phenylazo]-1-naphthol, and the dye developer in the image-forming unit recording blue light being 1 - phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β' -hydroquinonylethyl)phenylazo]-5-pyrazolone.

16. A photographic element comprising superposed on a photographic support three dye image-forming units in layers capable of recording red, green and blue light respectively, the dye image-forming unit recording blue light being furthest from the support and the dye image-forming unit recording red light being most proximate to the support, and an alkali-permeable, water-insoluble stratum of zirconium alginate positioned between the said image-forming units recording red and green light, said dye image-forming units comprising a gelatino-silver halide emulsion layer and an underlying contiguous layer containing a dye developer, the dye developer in the image-forming unit recording red light being 5,8-dihydroxy-1,4-bis[(β -hydroquinonyl - α - methyl)ethylamino]-anthraquinone, the dye developer in the image-forming unit recording green light being 4-isopropoxy-2-[p-(β -hydroquinonylethyl)-phenylazo]-1-naphthol, and the dye developer in the image-forming unit recording blue light being 1 - phenyl-3-(N-n-hexylcarboxamido)-4-[p-(β' -hydroquinonylethyl)phenylazo]-5-pyrazolone.

17. A process for preparing multicolor dye developer diffusion transfer images having high color saturation and low color contamination which comprises treating an exposed photographic element as described in claim 1 with an alkaline liquid, developing a latent image in the regions of exposure of the silver halide emulsion layers and thereby immobilizing dye developers in said regions of exposure, dye developers in undeveloped regions diffusing imagewise to the surface of said photographic element, and transferring the resulting diffused images from said undeveloped regions in register to a dye developer receiving sheet superposed on said photographic element.

References Cited

UNITED STATES PATENTS

3,345,163	10/1967	Land et al.	96—3
3,077,400	2/1963	Rogers et al.	96—3
3,192,044	6/1965	Rogers et al.	96—3
3,239,336	3/1966	Rogers et al.	96—3
3,257,208	6/1966	Van Paesschen	96—111

J. TRAVIS BROWN, *Primary Examiner.*