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R. W. BECKER

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MULTI-COLOR DYE DEVELOPER SYSTEMS

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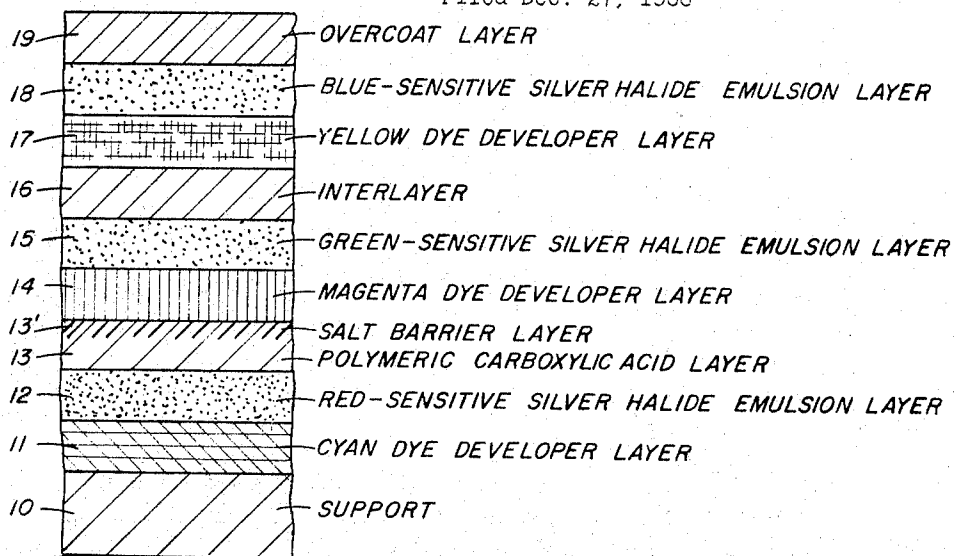


FIG. 1

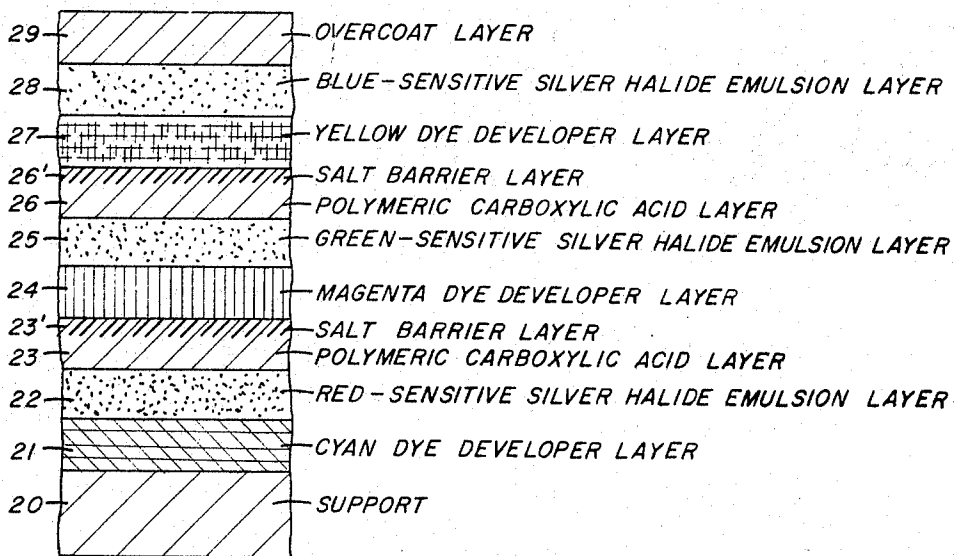


FIG. 2

RICHARD W. BECKER
INVENTOR.

BY *James R. Friedman*

ATTORNEY

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MULTI-COLOR DYE DEVELOPER SYSTEMS

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

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22 Claims

ABSTRACT OF THE DISCLOSURE

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 the 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 between at least two of the dye image-forming units are processed in the presence of a sequestering agent for the polyvalent metal moiety of the insoluble salt stratum. The sequestering agent can be present in the photographic element, the processing composition used to develop the photographic element, or the dye developer image-receiving element.

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 more generally 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. Patents 2,983,606, 3,253,915, 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 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 the inter-image characteristics in multicolor dye developer diffusion transfer systems.

In my copending application, Ser. No. 353,706, filed Mar. 23, 1964, and now U.S. Patent No. 3,384,483, I described photographic elements useful in preparing multicolor dye developer diffusion transfer images containing certain alkali-permeable, water-insoluble salt strata or barrier layers between the silver halide emulsion layers that can be utilized to reduce color contamination of the transferred images. However, such barrier layers tend to prevent some of the soluble image-forming dye developer in underlying layers, particularly cyan dye developer, from diffusing to the receiving sheet for the multicolor dye developer images, thus resulting in lowered $D_{\max}$ in the transferred image for the undercoated dye developer.

It is an object of this invention to provide novel photographic elements useful for preparing multicolor dye developer diffusion transfer images having high color saturation as well as low color contamination.

It is another object of this invention to provide novel photographic elements particularly useful for preparing multicolor dye developer diffusion transfer images having high red saturation as well as low red contamination.

It is still another object of this invention to provide a new method for preparing multicolor dye developer diffusion transfer images having high color saturation as well as low color contamination utilizing photographic elements containing alkali-permeable, water-insoluble strata of a polyvalent metal and a polymeric carboxylic acid positioned between at least two of the dye image-forming units of such elements.

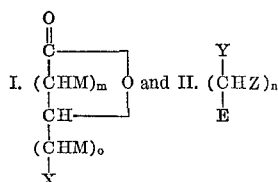
These and other objects of the invention are accomplished with photographic elements comprising a support having coated thereon (1) at least two dye image-forming units composed of a light-sensitive silver halide emulsion and a dye developer contiguous to silver halide of the emulsion, and (2) an alkali-permeable and water-insoluble stratum or barrier layer 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. Such photographic elements are described in my copending application, Serial No. 353,706, filed March 23, 1964. In accordance with the present invention, the processing of such photographic elements is carried out in the presence of an organic alkali-soluble sequestering agent for the polyvalent metal moiety of the barrier layer or salt stratum of a polyvalent metal and a polymeric carboxylic acid comprising the photographic element. The sequestering agent increases the permeability of the barrier layer. Such sequestering agents can be initially present in the light-sensitive photographic element, in the processing composition or in the dye developer image receiving element. The sequestering agents utilized in the present system chelate the polyvalent ions of the barrier strata rendering the barrier permeable to underlying dye-developer after such dye-developer has developed exposed silver halide contiguous thereto.

A wide variety of organic alkali-soluble sequestering agents for polyvalent metal moieties can be utilized in the present invention. Typical useful classes of sequestering agents include such acidic materials as amino carboxylic acids, hydroxyalkylamino acids, sulfhydrylamino acids, aminosulfonic acids, aminophosphonic acids and hydroxy carboxylic acids, including derivatives of such acids that form or release sequestering agents in the

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alkaline processing compositions used in processing the present photographic elements.

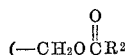
A class of sequestering agents useful in the invention are derivatives of hydroxy carboxylic acids having Formulas I and II,



wherein: M and Z are each hydroxy radicals or acyloxy radicals



wherein R is an alkyl radical or an aryl radical; X is a hydrogen atom, an acyloxymethyl radical



wherein R² is an alkyl radical or an aryl radical) or a carbinol radical ($-\text{CH}_2\text{OH}$); Y is a carboxy radical



a carbamyl radical



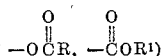
or a radical having the formula



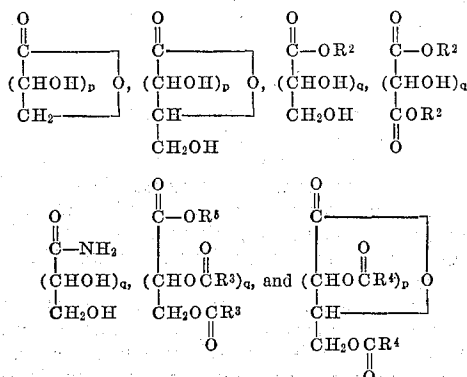
wherein R¹ is an alkyl radical (more generally having 1 to 2 carbons, particularly when Z is a hydroxyl radical); E is a carbinol radical, a radical having the formula



as described for Y, a carboxy radical, an acyloxymethyl radical or a carbamyl radical; m is an integer of 2 to 3; n is an integer of 1 to 5; and o is an integer of 0 to 2. The subject addenda contain at least one carbamyl or ester moiety including γ or δ lactone or inner ester groups (e.g., Formula I) as well as the more conventional ester groups described above (e.g.,



Hence, at least one of E, Y and Z of Formula II forms a carbamyl or an ester radical. Typical useful sequestering agents can be represented by the following more subgeneric formulas:



wherein: R² is an alkyl radical having 1 to 2 carbon atoms; R³ and R⁴ are each an alkyl radical which more generally has 1 to 8 carbon atoms or a phenyl radical, including substituted phenyl radicals; R⁵ is an alkyl radical

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which more generally has 1 to 8 carbon atoms or a hydrogen atom; p is an integer of 2 to 3; and q is an integer of 1 to 5. Other subgeneric formulas defining sequestering addenda of the invention included within generic Formulas I and II can be formulated. The alkyl substituents described above suitably have 1 to 20 carbon atoms, and preferably 1 to 8 carbon atoms, including methyl, ethyl, isopropyl, butyl, heptyl, octyl, decyl, octadecyl, eicosyl and the like. The aryl substituents described above include such radicals as phenyl, tolyl, naphthyl and the like, phenyl being preferred.

Such derivatives of hydroxy carboxylic acids can be prepared by conventional amidation and esterification techniques with such saturated, aldehyde radical-free, hydroxy carboxylic acids as glyceric, erythronic, arabonic, lyxonic, ribonic, xylonic, gluconic, galactonic, mannonic, gulonic, tartaric, glucoguloheptonic and the like hydroxy carboxylic acids. Literature references describing the preparation of such derivatives of hydroxy carboxylic acids include:

- (a) J. Am. Chem. Soc. 37, 345 (1915).
- (b) J. Am. Chem. Soc., 55, 2512 (1933).
- (c) J. Am. Chem. Soc., 62, 1074 (1940).
- (d) J. Am. Chem. Soc., 69, 915 (1947).
- (e) J. Org. Chem., 18, 952 (1953).
- (f) J. Am. Chem. Soc., 78, 2825 (1956).
- (g) Helv. Chim. Acta, 34, 2343.
- (h) J. Am. Pharm. Assoc., 28, 364 (1949).
- (i) U.S. Patent 2,380,444.

Typical sequestering agents useful in the invention are described hereinafter, particular reference being made to Table E. Other examples of useful sequestering agents include:

- 1,2-diamino cyclohexane N,N'-tetraacetic acid,
- N-hydroxyethyl ethylene diamine tetraacetic acid,
- β -mercaptoethyl imino diacetic acid,
- 2-sulfoaniline diacetic acid,
- adenosine triphosphate,
- glycolic acid,
- salicylic acid,
- ethylene diamine tetra(methylene phosphonic)acid,
- N,N-dihydroxyethyl ethylene diamine tetraacetic acid,
- N-methylthioethyl imino diacetic acid.

The amount of sequestering agent utilized in the invention can be widely varied, the amount varying with such variables as the number and type of barrier layers of polyvalent metal-polycarboxylic acid salt in the photographic element, the amount of polyvalent ion present in the system, the type of sequestering agent, the processing time, the particular positioning of the sequestering agent in the system, and related variables. Also, of course, the concentration of sequestering agent is dictated by how much color contamination or purity one is willing to sacrifice in order to get high color saturation in the transferred dye developer images. Optimum amounts can be readily determined by one skilled in the art. Typical useful concentration ranges are about 25 to 150 mg. of sequestering agent per square foot when utilized in the light sensitive element, about 50 to 200 mg. of sequestering agent per square foot when utilized in the dye developer image receiving sheet or layer, and about .1 to 5% by weight of the alkaline processing composition when utilized therein.

The sequestering agents can be coated in combination with other constituents in the present photographic elements and image receiving sheets, or they can be coated in separate layers. The sequestering agent can be coated in an organic hydrophilic colloid as an aqueous coating melt. Likewise, the sequestering agent can be dissolved in a high-boiling (e.g., greater than 175° C.) solvent and dispersed in finely divided droplets in a hydrophilic colloid and the resulting dispersion coated.

The salt strata or barrier layers utilized in the sub-

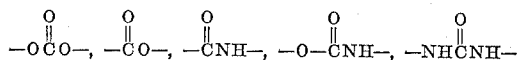
ject dye developer diffusion transfer system can be prepared with a variety of polyvalent metal salts and polymeric carboxylic acids. The subject salt strata can be formed on the element by coating a solution, or a water-permeable substrate, containing the polyvalent metal in water-soluble form on a 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-containing 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 crosslink 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 comprising the barrier layers of the light-sensitive photographic elements used in 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.

Dye developers are well known in the photographic art. Such compounds function both 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 the photographic elements in the presence of alkaline processing solutions. Generally, such dye developers are substantially insoluble in water, which property usually necessitates the use of organic solvents to incorporate the dye developers into the organic colloid layers of the photoelements. The dye developers are particularly characterized as containing both a chromophoric or dye moiety and at least one moiety having a silver halide developing agent function. Particularly 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 a hydroquinonyl moiety.

Representative dye developers of use in the dispersions of the invention have the general formula $\text{M}-\text{N}=\text{N}-\text{D}$ in which M is an aromatic or heterocyclic ring or ring system such as a benzene, naphthylene, tetralin, anthracene, anthraquinone, pyrazole, quinoline, etc., ring which can be substituted with such groups as hydroxyl, amine, keto, nitro, alkoxy, aryloxy, acyl, alkylamino, alkylaryl, carbboxamido, sulfonamide, carboxyl or sulfo groups. D represents a silver halide developing agent moiety imparting the developing agent function to the dye developer such as a hydroquinonyl group which can be substituted with amino, alkylamino, alkyl, hydroxyl, alkoxy or halogen groups.

Typical useful dye developers are described in columns 9-13 of U.S. Patent 3,146,102, as well as elsewhere 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 Canadian 577,021 and 579,038.

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 drop-

lets. 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, noodled 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 are more generally the conventional negative-type, developing-out emulsions, positive transfer images resulting from such emulsions. However, reversal emulsions such as solarized emulsions and emulsions that form latent images predominantly internal to the silver halide grains as described in U.S. Patent 2,592,250, can also be used, negative transfer images, resulting from such emulsions. Typical suitable silver halides include silver chloride, silver bromide, silver bromiodide, silver chloriodide, silver chlorobromiodide, etc. Useful sensitizers are those in Kennard Serial No 337,792, filed January 15, 1964. 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 or in separate layers contiguous to the 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 transparent and opaque 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. The sequestering agents used in the invention can be positioned in any of the layers of the receiving sheet. Typical reception layers for dye developer receiving sheets which are, or include, mordants for dye developers, are 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 are as described in U.S. Patent 2,584,030 are particular 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.

To facilitate a clean stripping away of the receiving sheet from the negative element after the transfer of the dye developer images to the receiving sheet, the receiving sheet can be prepared by superficially hardening with a nondiffusing hardener and a surfactant. For example, a dye developer image receiving layer on a receiving sheet containing poly-4-vinyl pyridine mordant in polyvinyl alcohol can be efficaciously treated with an oxyguar gum hardener solution containing a surfactant such as sodium cetyl sulfate or sodium N-methyl-N-oleoyl taurate.

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, particularly as described in U.S. Patent 3,266,894, or carboxymethyl cellulose. Onium compounds such as are disclosed in U.S. Patent 3,146,102 are preferably utilized in the alkaline processing composition. The described sequestering agents can also be utilized in the alkaline processing compositions used in the processes of the invention.

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 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 and 2 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. A sequestering agent as described herein is preferably incorporated in such a cyan dye developer layer. Over layer 11 is coated layer 12 which is a red-sensitive silver halide emulsion layer. Over layer 12 is coated polymeric carboxylic acid layer 13, a portion of layer 13 comprising salt stratum 13' which comprises a salt of polyvalent metal and the polymeric carboxylic acid of layer 13. Layer 13' can be prepared, for example, by coating a water solution of a water-soluble salt of a polyvalent metal over layer 13, the polyvalent metal moiety reacting with the carboxylic acid of polymeric layer 13 to form water-insoluble barrier layer 13'. Over barrier layer 13' is coated layer 14 containing a magenta dye developer. Barrier 13' can also be formed on coating layer 14 over layer 13 wherein layer 14 contains a polyvalent metal moiety that reacts with the polymeric carboxylic acid. Over layer 14 is coated green-sensitive silver halide emulsion layer 15. Over layer 15 is coated interlayer 16. Over layer 16 is coated layer 17 which contains a yellow dye developer. Over layer 17 is coated layer 18 which is a blue-sensitive silver halide emulsion layer. Over layer 18 is coated overcoat layer 19.

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 as well as between the yellow dye image-forming unit and the cyan dye image-forming unit. On support 20 is coated layer 21 containing a cyan dye developer, and preferably a sequestering agent as described herein. Over layer 21 is coated red-sensitive silver halide emulsion layer 22. Over emulsion layer 22 is coated layer 23 which contains a polymeric carboxylic acid. Over layer 23 is coated layer 24 containing a magenta dye developer and a water-soluble salt of a polyvalent metal which reacts with the polymeric carboxylic acid of layer 23 to form salt barrier layer 23'. Over layer 24 is coated green-sensitive silver halide emulsion layer 25. Over layer 25 is coated polymeric carboxylic acid layer 26. Over layer 26 is coated layer 27 which contains a yellow dye developer and a water-soluble salt of a polyvalent metal which reacts with the polymeric carboxylic acid of layer 26 to form salt barrier layer 26'. Over layer 27 is coated layer 28 which is a blue-sensitive silver halide emulsion layer. Over layer 28 is coated overcoat layer 29.

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

EXAMPLE I

(Sequestering agents in the light-sensitive element)

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- α -methyl)ethyl-amino]-anthraquinone, dissolved in N-n-butylacetanilide, dispersed in gelatin and coated at a coverage of 146 mg. of the cyan dye developer per square foot and 221 mg. of gelatin per square foot, and containing 55 mg. of the sequestering agent, D-gelactono- γ -lactone, per square foot.

(2) Red-sensitive emulsion layer (e.g., layer No. 12 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide emulsion sensitized to red light coated at a coverage of 219 mg. of silver per square foot and 86 mg. of gelatin per square foot.

(3) Sodium alginate layer (e.g., layer No. 13 of FIG. 1).—A coating of sodium alginate at a coverage of 27 mg. per square foot.

(4) Magneta dye developer layer (e.g., layer No. 14 of FIG. 1).—A coating of the magneta 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 64 mg. of the dye developer per square foot and 92.5 mg. of gelatin per square foot, and containing 18 mg. of calcium chloride per square foot. The calcium chloride reacted with the sodium alginate in the adjacent layer to form a calcium alginate salt barrier layer between the two layers (e.g., Layer 13' of FIG. 1).

(5) Green-sensitive emulsion layer (e.g., layer No. 15 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide emulsion sensitized to green light coated at a coverage of 103 mg. of silver per square foot and 43 mg. of gelatin per square foot.

(6) Interlayer (e.g., layer No. 16 of FIG. 1).—A coating of gelatin at a coverage of 140 mg. per square foot and 4'-methylphenylhydroquinone at a coverage of 10.5 mg. per square foot.

(7) Yellow dye developer layer (e.g., layer No. 17 of FIG. 1).—A coating of the yellow dye developer, 1-phenyl-3-N-n-hexylcarboxamide - 4 - [p-(2',5'-dihydroxy-phenethyl)-phenylazo]-5-pyrazolone, dissolved in ditetrahydrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 48 mg. of the dye developer per square foot and 48 mg. of gelatin per square foot.

(8) Blue-sensitive emulsion layer (e.g., layer No. 18 of FIG. 1).—A coating of a developing-out negative gelatino-silver bromiodide emulsion that is inherently sensitive to blue light was coated at a coverage of 69 mg. of silver per square foot and 49.5 mg. of gelatin per square foot.

(9) Overcoat layer (e.g., layer No. 19 of FIG. 1).—A gelatin coating containing dispersed therein 4'-methylphenyl-hydroquinone at a coverage of 10.5 mg. per square foot and gelatin at a coverage of 32 mg. per square foot.

The prepared photographic element is referred to as "Sequest A" in Table A below. Other photographic elements as described above were prepared, except that in lieu of D-galactone- γ -lactone in the cyan dye developer layer, 45 mg. per square foot of D-ara-bono lactone and 55 mg. per square foot of methyl 1-arabonate per square foot respectively were utilized, these photographic elements being identified as "Sequest B" and "Sequest C," respectively. For purposes of comparison, a photographic element was prepared as described wherein the sequestering agent was omitted from the cyan developer layer (referred to as "Control 2" in Table A below). Also for purposes of comparison, a photographic element was pre-

pared as described wherein the sequestering agent, the sodium alginate and the calcium chloride were omitted, a gelatin layer at a coverage of 205 mg. per square foot being substituted for the sodium alginate layer (referred to as "Control 1" in Table A below). The resulting photographic elements were exposed through a .3 density increment color step wedge 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 paper support having coated thereon a plurality of layers including a layer containing a poly-4-vinyl pyridine mordant in polyvinyl alcohol, an undercoated acid-releasing layer containing a polymeric acid such as copoly-(methylvinyl ether-maleic acid), and a polyvinyl alcohol spacer layer between the mordant and acid-releasing layers. 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 or 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-2-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 A below are data illustrating the increased cyan D_{max} (i.e., improved cyan 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 measured as magenta D_{max} minus density of the first .3 density exposure step in the red scale) that resulted from utilizing the described sequestering agents in the undercoated cyan dye developer layer.

TABLE A

Photoelement:	Cyan D_{max}	Magenta D_{max}	Yellow D_{max}	Magenta "Drop-Off"
Control 1.....	1.51	1.91	1.95	0.61
Control 2.....	1.30	2.05	1.85	0.08
Sequest A.....	1.59	2.03	1.90	0.19
Sequest B.....	1.60	2.02	1.87	0.26
Sequest C.....	1.68	1.99	1.85	0.32

As can be observed from the data set out in Table A, the calcium alginate barrier layer in "Control 2" significantly decreased the magenta "drop-off," but also resulted in a loss of cyan dye density. The photographic elements containing the sequestering agents in the cyan dye developer layer, namely, "Sequest A," "Sequest B," and "Sequest C" resulted in increased cyan dye density over both the photographic element containing the calcium alginate barrier layer ("Control 2") and the photographic element containing no calcium alginate ("Control 1") as well as substantially reducing the magenta "drop-off" with respect to the latter.

EXAMPLE II

(Sequestering agents in the alkaline activator)

Photographic elements as described in Example I as "Control 1" and "Control 2" were prepared, "Control 1" being the photographic element without a calcium alginate barrier layer and "Control 2" being the photographic element with such a barrier layer. Such photographic elements were exposed and processed as described in Example I except that the alkaline activator or processing solution contained 1% by weight based on the activator of a sequestering agent as described in Table B below.

TABLE B

Feature	Activator Addendum	Cyan D_{max}	Magenta "Drop-Off"
Photoelement:			
Control 1.....	None.....	1.52	0.53
Control 2.....	do.....	0.63	0.03
Do.....	EDTA ¹	1.18	0.22
Do.....	None.....	0.90	0.07
Do.....	D-galactono- γ -lactone.....	1.38	0.28

¹ Ethylene diamine tetraacetic acid.

As can be observed from the data set out in Table B, sequestering agents can be usefully employed in the alkaline activator solution to effectively produce high cyan density while maintaining magenta "drop-off" to reasonable limits.

EXAMPLE III

(Sequestering agents in the receiving sheet)

Photographic elements as described in Example I as "Control 1" and "Control 2" were prepared, "Control 1" being the photographic element without a calcium alginate barrier layer and "Control 2" being the photographic element with such a barrier layer. Such photographic elements were exposed and processed as described in Example I except that the receiving sheet for the dye developer images in the case of one processing of "Control 2" contained 100 mg. per square foot of tetrasodium ethylene diamine tetraacetic acid in the polyvinyl alcohol spacer layer between the mordant and acid-releasing layers. Table C below summarizes the results.

TABLE C

Photoelement	Feature Receiving Sheet Addendum	Cyan D_{max}	Magenta "Drop-Off"
Control 1.....	None.....	1.41	0.46
Control 2.....	do.....	0.82	0.21
Do.....	EDTA Na ₄ ¹	1.16	0.28

¹ Tetrasodium salt of ethylene diamine tetraacetic acid.

The data in Table C illustrates sequestering agents having utility in the dye developer diffusion transfer processes of the present invention when employed in receiving sheets for the dye developer images.

EXAMPLE IV

(Processing of photoelement with two salt barrier layers)

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. 21 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 146 mg. of the cyan dye developer per square foot and 221 mg. of gelatin per square foot, and containing 60 mg. of D-galactono- γ -lactone sequestering agent per square foot as well as 10.5 mg. of 4'-methylphenyl hydroquinone per square foot.

(2) Red-sensitive emulsion layer (e.g., layer No. 22 of FIG. 2).—A coating of a developing-out negative gelatino-silver bromiodide emulsion sensitized to red light coated at a coverage of 219 mg. of silver per square foot and 86 mg. of gelatin per square foot.

(3) Sodium alginate layer (e.g., layer No. 23 of FIG. 2).—A coating of sodium alginate at a coverage of 27 mg. per square foot.

(4) Magenta dye developer layer (e.g., layer No. 24 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 64 mg. of the dye developer per square foot and 74 mg. of gelatin per square foot, and containing 18 mg. of calcium chloride per square foot. The calcium chloride reacted with the

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sodium alginate in the adjacent undercoated layer to form a calcium alginate salt barrier layer between the two layers (e.g., layer 23' of FIG. 2).

(5) Green-sensitive emulsion layer (e.g., layer No. 25 of FIG. 2).—A coating of a developing-out negative gelatino-silver bromiodide emulsion sensitized to green light was coated at a coverage of 34 mg. of gelatin per square foot and 103 mg. of silver per square foot.

(6) Sodium alginate layer (e.g., layer No. 26 of FIG. 2).—A coating of sodium alginate at a coverage of 27 mg. per square foot.

(7) Yellow dye developer layer (e.g., layer No. 27 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 ditetrahydrofurfuryl adipate, dispersed in gelatin and coated at a coverage of 40 mg. of the dye developer per square foot and 72 mg. of gelatin per square foot, and containing 18 mg. of calcium chloride per square foot. The calcium chloride reacted with the sodium alginate in the adjacent undercoated layer to form a calcium alginate salt barrier layer between the two layers (e.g., layer 26' of FIG. 2).

(8) Blue-sensitive emulsion layer (e.g., layer No. 28 of FIG. 2).—A coating of a developing-out gelatino-silver bromiodide emulsion that is inherently sensitive to blue light was coated at a coverage of 69 mg. of silver per square foot and 40 mg. of gelatin per square foot.

(9) Overcoat layer (e.g., layer No. 29 of FIG. 2).—A gelatin coating containing dispersed therein 4'-methyl-phenyl hydroquinone at a coverage of 10.5 mg. per square foot and gelatin at a coverage of 26 mg. per square foot.

The above described photographic element of the invention is designated "Element A" in Table D below. For purposes of comparison, a photographic element similar to "Element A" was prepared except that the D-galactono- γ -lactone sequestering agent was omitted from the cyan dye developer layer, layer No. 1, this photographic element being designated "Element B" in Table D. Also, a photographic element similar to "Element B" was prepared except the sodium alginate layer between the green sensitive silver halide emulsion layer and the yellow dye developer layer was replaced with a gelatin layer at a coverage of 140 mg. per square foot (i.e., layer No. 6) and the calcium chloride removed from the yellow dye developer layer (i.e., layer No. 7), this photographic element being designated "Element C" in Table D. The photographic elements were thereafter exposed and processed as described in Example I except the receiving sheet and the photographic elements were left in contact for 1¼ minutes to effect the development and transfer of the images. Summarized in Table D are data for the yellow and magenta "drop-off" or desaturation of these colors resulting from the yellow dye developer developing in the green-sensitive emulsion and the magenta dye developer developing in the red-sensitive emulsion respectively. Also set out in Table D are the Cyan D_{max} values for the transfer prints.

TABLE D

	Cyan D_{max}	Magenta "Drop-Off" ¹	Yellow "Drop-Off" ²
Photoelement:			
Element A	1.40	0.07	0.43
Element B	1.00	0.07	0.42
Element C	1.80	0.11	0.80

¹ magenta D_{max} minus density of first .3 density exposure step in red scale.

² Yellow D_{max} minus density of first .3 density exposure step in yellow scale.

EXAMPLE V

A series of photographic elements of the type identified as "Control 2" in Example I were prepared, such photographic elements containing a calcium alginate barrier layer between the red-sensitive silver halide layer and the magenta dye developer layer (see FIG. 1 of the drawing). The photographic elements were exposed and processed

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as described in Example I except that various sequestering materials were added to the alkaline activator as described in Table E below. In Table E the results are summarized in terms of the increase of Cyan D_{max} (ΔD_{max}) resulting from using the respective sequestering material in the alkaline activator. One percent by weight of the sequestering material based on the alkaline activator was used unless otherwise indicated. Likewise, the processing time used was 2 minutes unless otherwise indicated.

TABLE E

Sequestering material in activator:	ΔD_{max}
(1) Gluconic acid (1 min.)	.28
(2) n-Propyl-D-gluconate pentaacetate	.27
(3) Methyl-D-gluco-D-gulo-heptonate hexaacetate	.35
(4) D-gluconamide pentaacetate (1 min.)	.22
(5) Isopropyl D-gluconate pentaacetate (1 min.)	.28
(6) Methyl glycolate D-gluconate pentaacetate	.40
(7) D-gluco-D-gulo-heptonamide hexaacetate (1 min.)	.26
(8) Ethyl-D-gluconate pentaacetate	.32
(9) Methyl-D-gluconate pentaacetate	.36
(10) Gulonic lactone	.74
(11) Sulfosalicylic acid, 2% (1 min.)	.37
(12) Glucono heptonic acid, 1.5% (1 min.)	.71
(13) Sodium guanylate, 1.5% (1 min.)	.51
(14) Adenosine triphosphate sodium salt (1 min.)	.87
(15) Potassium acid saccharate (1 min.)	.86
(16) Dihydroxy benzene disulfonate disodium salt (1 min.)	.58
(17) Methyl L-arabonate	.37
(18) Disodium anthranilic acid, N,N'-diacetate	.65
(19) Pentasodium diethylene triamine pentaacetate	.71
(20) Glycolic acid	.34
(21) D,L-malic acid	.17
(22) Tartaric acid	1.11
(23) Citric acid	1.02
(24) Sulfosalicylic acid	.46
(25) Aminosalicic acid	.77
(26) Salicylic acid	.93
(27) Amino barbituric acid, N,N'-diacetic acid	.83
(28) L-malic acid	.58
(29) D,L-mandelic acid	.28
(30) Methyl L-erythronate (1 min.)	.34
(31) D-lyxonamide	.52
(32) D-arabonamide (1 min.)	.13
(33) Methyl L-arabonate tetraacetate	.39
(34) D-arabono- γ -lactone	.87
(35) D-gluconamide	.45
(36) Glucono- δ -lactone	1.04
(37) Methyl-2,4; 3,5-dimethylene-D-gluconate	1.04
(38) Methyl-D-galactonate	.37
(39) D-galactono- γ -lactone	.71
(40) Ethyl-D-mannate	.78
(41) D-gluco-D-gulo-heptonamide	.75
(42) D-gluco-D-gulo-heptono- γ -lactone	.43

As can be observed from the data in Table E, a wide variety of sequestering agents can be utilized in the present invention.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. In a photographic element comprising a support having coated thereon at least two dye image-forming units with an alkali-permeable, water-insoluble salt barrier 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 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, the improvement which comprises having coated on the salt stratum side of the photographic element an organic alkali-soluble sequestering agent for said polyvalent metal, which sequestering agent renders the barrier layer more permeable to underlying dye developer after the dye developer has developed the silver halide.

2. A photographic element as defined by claim 1 wherein the salt stratum is calcium alginate.

3. A photographic element as defined by claim 1 wherein the sequestering agent is selected from the group consisting of amino carboxylic acids, hydroxyalkylamino acids, sulfhydrylamino acids, aminosulfonic acids, aminophosphonic acids and hydroxy carboxylic acids.

4. A photographic element as defined by claim 1 wherein the sequestering agent is a hydroxy carboxylic acid.

5. A photographic element as defined by claim 1 wherein the sequestering agent is D-galactono-γ-lactone.

6. A photographic element as defined by claim 1 wherein the sequestering agent is D-arabono-lactone.

7. A photographic element as defined by claim 1 wherein the sequestering agent is methyl 1-arabonate.

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 each of the said image-forming units, 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, and an organic, alkali-soluble sequestering agent for calcium ions being positioned between said support and said stratum of calcium alginate at a coverage of about 25 to 150 mg. per square foot of said support.

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 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; and an organic, alkali-soluble sequestering agent for calcium ions being positioned between said support and said stratum of calcium alginate at a coverage of about 25 to 150 mg. per square foot of said support.

10. In the processing of an imagewise exposed 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, 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, which comprises treating the photographic element with an alkaline processing liquid, developing latent images 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 in register to a reception layer for dye developer images, the improvement which comprises carrying out said treating of the photographic element in the presence of an organic alkali-soluble sequestering agent for said polyvalent metal.

11. The process as defined in claim 10 wherein the sequestering agent is coated in a layer on the salt stratum side of the photographic element.

12. The process as defined in claim 10 wherein the sequestering agent is present in the alkaline processing liquid.

13. The process as defined in claim 10 wherein the sequestering agent is present in the reception layer for dye developers.

14. The process as defined in claim 10 wherein the salt stratum is calcium alginate.

15. The process as defined in claim 10 wherein the sequestering agent is selected from the group consisting of amino carboxylic acids, hydroxyalkylamino acids, sulfhydrylamino acids, aminosulfonic acids, aminophosphonic acids and hydroxy carboxylic acids.

16. The process as defined in claim 10 wherein the sequestering agent is a hydroxy carboxylic acid.

17. The process as defined in claim 10 wherein the sequestering agent is ethylene diamine tetraacetic acid.

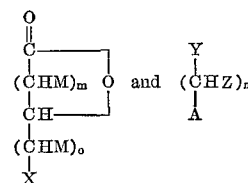
18. The process as defined in claim 10 wherein the sequestering agent is D-arabono-lactone.

19. The process as defined in claim 10 wherein the sequestering agent is D-galactono-γ-lactone.

20. The process as defined in claim 10 wherein the sequestering agent is methyl 1-arabonate.

21. The process defined in claim 10 wherein the sequestering agent is methyl-D-gluconate pentaacetate.

22. The process as defined in claim 10 wherein the sequestering agent has a formula selected from the group consisting of



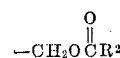
wherein:

(1) M and Z are each selected from the group consisting of a hydroxy radical and an acyloxy radical having the formula



wherein R is selected from the group consisting of an alkyl radical and an aryl radical;

(2) X is selected from the group consisting of a hydrogen atom, a carbinol radical, a radical having the formula



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wherein R² is selected from the group consisting of an alkyl radical and an aryl radical;

- (3) Y is selected from the group consisting of a carboxy radical, a carbamyl radical and a radical having the formula

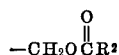


wherein R¹ is an alkyl radical;

- (4) A is selected from the group consisting of a carbinol radical, a carbamyl radical, a carboxy radical, a radical having the formula



wherein R¹ is an alkyl radical and a radical having the formula



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wherein R² is selected from the group consisting of an alkyl radical and an aryl radical;

- (5) *m* is an integer of 2 to 3;
(6) *n* is an integer of 1 to 5; and
(7) *o* is an integer of 0 to 2;

- 5 except that at least one of A, Y and Z forms a radical selected from the group consisting of a carbamyl radical and an ester radical.

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10 NORMAN G. TORCHIN, Primary Examiner

20 ALFONSO T. SURO PICO, Assistant Examiner

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