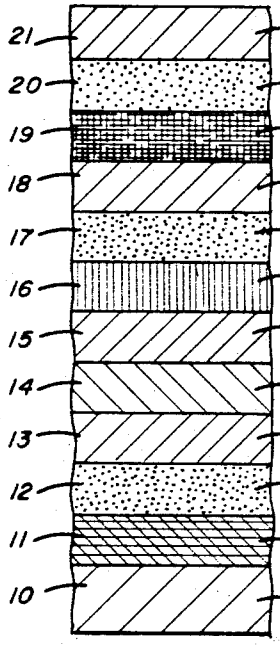
Dec. 24, 1968 R. W. BECKER 3,418,117

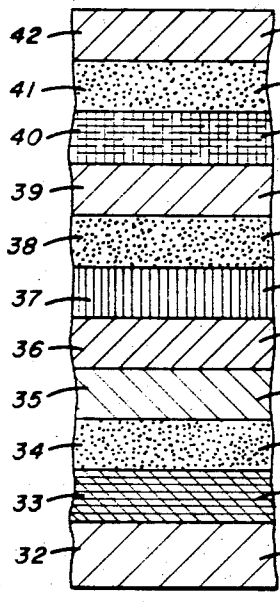
MULTICOLOR DYE DEVELOPER IMAGE TRANSFER SYSTEMS

Filed Aug. 24, 1966 2 Sheets-Sheet 1



21 — OVERCOAT LAYER
20 — BLUE-SENSITIVE SILVER HALIDE EMULSION LAYER
19 — YELLOW DYE DEVELOPER LAYER
18 — INTERLAYER
17 — GREEN-SENSITIVE SILVER HALIDE EMULSION LAYER
16 — MAGENTA DYE DEVELOPER LAYER
15 — INTERLAYER
14 — SALT LAYER OF POLYVALENT METAL & POLYMERIC CARBOXYLIC ACID
13 — INTERLAYER
12 — RED-SENSITIVE SILVER HALIDE EMULSION LAYER
11 — CYAN DYE DEVELOPER LAYER AND FOGGED SILVER HALIDE
10 — SUPPORT

FIG. 1



42 — OVERCOAT LAYER
41 — BLUE-SENSITIVE SILVER HALIDE EMULSION LAYER
40 — YELLOW DYE DEVELOPER LAYER
39 — INTERLAYER
38 — GREEN-SENSITIVE SILVER HALIDE EMULSION LAYER
37 — MAGENTA DYE DEVELOPER LAYER
36 — INTERLAYER
35 — SALT LAYER OF POLYVALENT METAL & POLYCARBOXYLIC ACID AND FOGGED SILVER HALIDE
34 — RED-SENSITIVE SILVER HALIDE EMULSION LAYER
33 — CYAN DYE DEVELOPER LAYER
32 — SUPPORT

FIG. 2

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MULTICOLOR DYE DEVELOPER IMAGE TRANSFER SYSTEMS

Filed Aug. 24, 1966 2 Sheets-Sheet 2

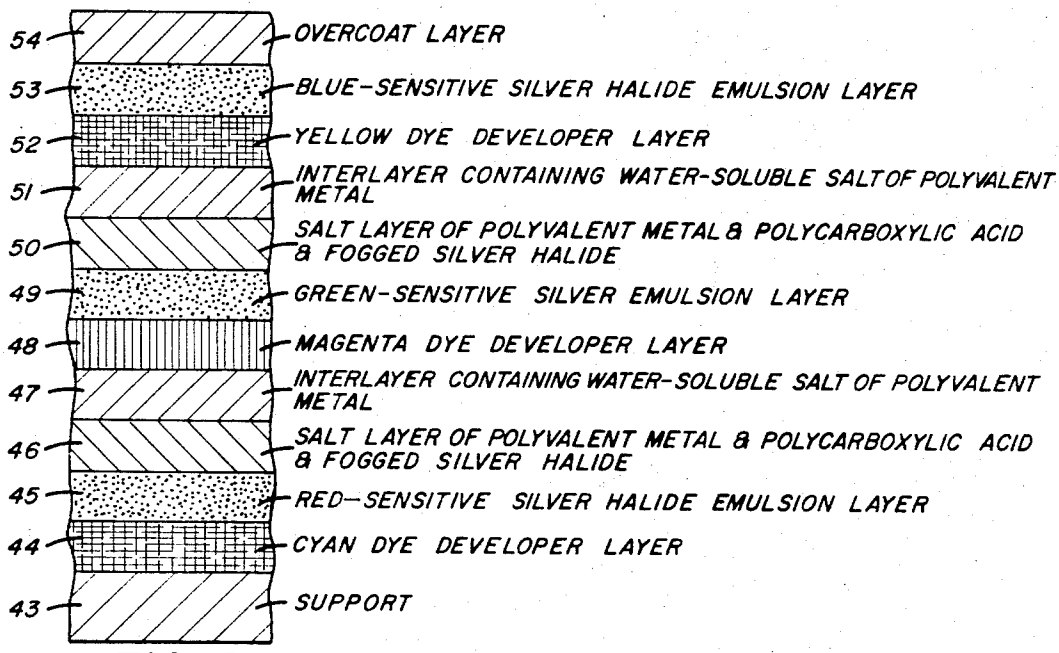


FIG. 3

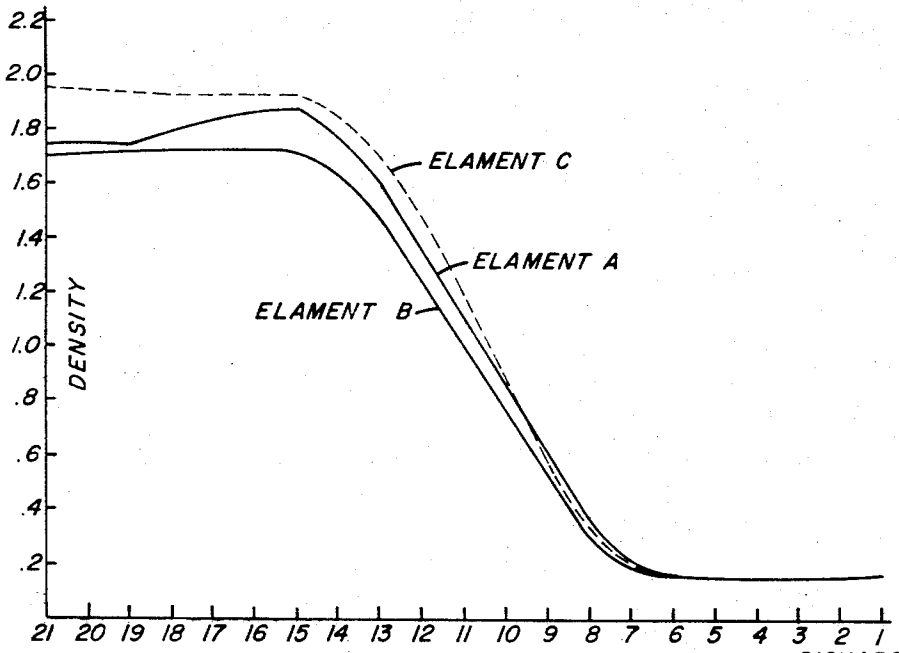


FIG. 4

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MULTICOLOR DYE DEVELOPER IMAGE TRANSFER SYSTEMS

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Filed Aug. 24, 1966, Ser. No. 574,698
17 Claims. (Cl. 96—3)

ABSTRACT OF THE DISCLOSURE

Fog reduction and increase of maximum density are obtained by the use of fogged silver iodide incorporated in any of the non-light sensitive layers of a color diffusion transfer 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 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 the interimage characteristics in multicolor dye developer diffusion transfer systems.

One highly effective technique for increasing color saturation, inhibiting color contamination and improving interimage characteristics is disclosed in Becker U.S. patent application Ser. No. 353,706, filed Mar. 23, 1964 and now U.S. Patent No. 3,384,483. That technique is to provide, between the color-forming units, a barrier layer composed of an alkali-permeable and water-insoluble layer of a polyvalent metal salt of a film-forming, alkalipermeable, water-soluble polymeric carboxylic acid, which layer is less permeable to dye developers in aqueous alkaline solution than the polymeric carboxylic acid used to prepare the salt layer. However, such barrier layers cause an undesirable increase in fog and uneven response in the light sensitive silver halide layer positioned in the color-forming unit below the barrier layer. Means have now been found to inhibit fog and uneven response, while retaining the benefits of the metal salt layers.

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

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 layer to improve the interimage characteristics of the system, and a special additive to inhibit undesirable fogging and uneven response.

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

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.

Other objects of this invention will be apparent from this disclosure and the appended claims.

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, (2) an alkali-permeable and water-insoluble salt layer comprising a polyvalent metal salt of a film-forming, akali-permeable, water-soluble polymeric carboxylic acid positioned between at least two of the dye image-forming units, such salt layer being less permeable to dye developers in aqueous alkaline solution than the polymeric carboxylic acid used to prepare the salt layer, and (3) a fogged silver halide salt, wherein a substantial amount of said halide is iodide, in one layer of said element. In such elements, it has been found that the fogged silver halide effectively inhibits fog and uneven response in that color-forming unit positioned below the metal salt layer.

Advantageously, the fogged silver halide salt is coated uniformly and contains a substantial amount of iodide, for example, at least 5 mole percent iodide. Silver bromoiodide and silver chloroiodide containing at least 5 mole percent iodide provide good results. Best results are obtained with silver bromoiodide or silver chlorobromide containing from 5 to 15, or higher, mole percent iodide. The silver iodide salt is uniformly fogged in any convenient manner, e.g., flashing with light or using chemical fogging agents. Typical chemical fogging agents include thiourea dioxide and stannous compounds, e.g., stannous chloride. The level of fogging should be sufficient so that the silver iodide salt is developed during the development of the element. Thus, the silver iodide salt can be completely fogged, or fogged partially provided that sufficient development will occur to inhibit fog. Advantageously, the silver halide is fogged sufficiently to produce a density of at least 0.5 when developed, without exposure, for 5 minutes at 68° F. in Kodak developer DK–50 when coated in gelatin on a support at a silver coverage of 50 mg. to 500 mg. per square foot.

Surprisingly, the fogged silver iodide salt can be effectively incorporated in any layer (i.e., an alkali-permeable or hydrophilic colloid layer) of the present elements excepting the light-sensitive silver halide emulsion layers thereof. Fog reduction is substantial when fogged silver iodide salt is incorporated, for example, in any dye developer layer, alkali-permeable interlayer, or alkali permeable overcoat layer. Greatest fog reduction is obtained when the fogged silver iodide salt is incorporated in the acid salt layer. When this arrangement is used, there is a greater reduction in fog in the emulsion below the salt layer. Further, there is a substantial increase in the maximum density produced by the emulsion layer below the acid salt layer. In addition, unevenness in response in the layer below the acid salt layer is eliminated with the fogged silver halide.

The effective concentration of fogged silver iodide salt in the elements of the invention varies over a wide range. Good results are obtained with coverages of fogged silver iodide salt at the rate of from about 5 to about 20 mg. per square foot. Especially good results are obtained at a coverage of about 10 mg. per square foot. Preferably, the fogged silver iodide is coated uniformly in the acid salt layer. However, as noted, the silver iodide salt can be present in another layer. Several layers can contain the fogged silver iodide salt. When more than one acid salt layer is used, it is preferred to incorporate fogged silver iodide in each such acid salt layer.

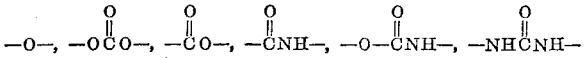
The fogged silver salt additive of the present invention is useful in combination with acid salt barrier layers. The acid salt layer utilized in the subject dye developer diffusion transfer system can be prepared with a variety of polyvalent metal salts and polymeric carboxylic acids. These salt layers 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 layer. Such salt layers 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 layers 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 acid salt layer 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



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 inter-development between dye image-forming units. A wide variety of polyvalent metal moieties can be utilized in preparing the subject salt layers. Suitable polyvalent metals with which suitable salt layers 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 salt with the above-described polymeric materials containing carboxylic acid groups.

The amount of polymeric salt utilized in the salt layers 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 layer 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 salicyclic acid, and the like, and including mixtures thereof.

The use and preparation of the salt layers employed in the elements herein is more fully described in Becker U.S. patent application Ser. No. 353,196, filed Mar. 23, 1964.

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 (or alkali-permeable) organic colloidal vehicles or carriers comprising the layers of the photographic element dissolved in high-boiling or crystalloidal solvents and dispersed of finely-divided droplets. In preparing such disper-

sions 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.

Best results are obtained when the photographic elements of the invention contain auxiliary developing agents such as colorless substantially water-insoluble hydroquinone derivatives such as are disclosed in French Patent 1,313,086. The auxiliary developing agents preferably are highly active, diffusible developers. 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. Preferably, auxiliary developing agent is incorporated in the same layer as the fogged silver halide to assume development thereof.

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 bromoiodide, silver chloroiodide, silver chlorobromoiodide 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 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 terephathalate film, polyethylene film, polypropylene film, paper polyethylenecoated 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 activitators 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 celllose 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 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 furtherest 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, and 3 of the drawings are enlarged fragmentary sectional views illustrative typical light-sensitive photographic elements or color films of the invention utilizing various layers containing fogged silver halide and layers of polyvalent metal salts of polymeric carboxylic acids. FIGURE 4 shows that even response is obtained in the color-forming unit positioned below the acid salt layer when fogged silver halide is incorporated in the elements of the invention.

FIG. 1 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing fogged silver halide and a salt layer 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 die developer and fogged silver halide. 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 layer **14** which comprises a salt of a polyvalent metal and polymeric carboxylic acid. 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 to form water-insoluble salt stratum **14**. If desired, the layer can be prepared by incorporating the water-soluble salt of polyvalent metal in the magenta dye developer layer **16** and coating that layer directly over layer **14** of polymeric carboxylic acid. Over salt layer **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**. Interlayers **13** and **15** are optional when salt layer is used.

FIG. 2 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing fogged silver halide in a salt layer 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 layer **35**, which comprises fogged silver halide and a salt of a polyvalent metal and a polymeric carboxylic acid. Over salt layer **35** is coated interlayer **36**. 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**. Interlayer **36** can be omitted if desired.

FIG. 3 of the drawings illustrates a typical three-color dye developer diffusion transfer system utilizing fogged silver halide in a salt layer 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 layer **46** which comprises fogged silver halide and a polyvalent metal salt of a polymeric carboxylic acid. Interlayer **47** is a hydrophilic colloid. 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 layer **50** which comprises fogged silver halide and a salt of a polyvalent metal and polymeric carboxylic acid. Interlayer **51** is a hydrophilic colloid layer coated over layer **50**. 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 1

A photographic element having the structure substantially as shown in FIG. 1 of the drawings was prepared (except interlayers **13**, **15** and **18** were omitted) 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-bis-(β-hydroquinoyl-α-methyl) - ethylamino quinizarin dissolved in N-n-butylacetanilide and 4'-methylphenyl hydroquinone, dispersed in gelatin and coated at a coverage of 146 mg. of the cyan dye developer per square foot, 10.5 mg. per square foot of the hydroquinone, and 221 mg. of gelatin 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 bromoiodide (6% iodide) emulsion sensitized to red light was coated at a coverage of 219 mg. of silver per square foot and 86 mg. of gelatin per square foot.

(3) Salt Layer (e.g., Layer No. **14** of FIG. 1).—A coating of sodium alginate coated at a coverage of 27 mg. per square foot. Calcium alginate is formed when layer **4**, containing calcium chloride, is coated over this layer.

(4) Magenta Dye Developer Layer (e.g., Layer No. **16** of FIG. 1).—A coating of the magenta dye developer, 4-isopropoxy-2-[p-(β - hydroquinonylethyl) - phenylazo]-1-naphthol, dissolved in N-n-butylacetanilide, and calcium chloride dispersed in gelatin and coated at a coverage of 44 mg. of the dye developer per square foot, 18 mg. calcium chloride per square foot, and 92.5 mg. of gelatin per square foot. Upon coating, the calcium chloride reacts with the sodium alginate to form calcium alginate.

(5) Green-Sensitive Emulsion Layer (e.g., Layer No. **17** of FIG. 1).—A coating of a developing-out negative gelatino-silver bromoiodide (6% iodide) 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) Yellow Dye Developer Layer (e.g., Layer No. **19** of FIG. 1).—A coating of the yellow dye developer, 1-phenyl-3-hexyl-carboxamide-4 - (p(β'-hydroxyquinolylethyl)phenylazo-5-hydroxy pyrazole, 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.

(7) Blue-Sensitive Emulsion Layer (e.g., Layer No. **20** of FIG. 1).—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 69 mg. of silver per square foot and 49.5 mg. of gelatin per square foot.

(8) 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 10.5 mg. of the auxiliary developer per square foot.

The element prepared is referred to as element A. Element A serves as the control in this example. A second element, element B, was prepared exactly the same as element A except that light fogged silver bromoiodide containing 12 mole percent iodide, in gelatin, was added to the cyan dye developer layer (layer **1**) at the rate of 10 mg. silver per square foot. A third element, element C was prepared exactly the same as element A except

that light fogged silver bromoiodide containing 12 mole percent iodide, in gelatin, was added to the calcium alginate layer, layer 3, at the rate of 10 mg. silver per square foot, together with 2 mg. per square foot of the colorless auxiliary developer, 4'-methylphenylhydroquinone. The resulting photographic elements were each 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 samples of each of the exposed photographic elements were left in contact with the alkaline activator material therebetween for periods of 1, 1¼ and 1½ 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 red D_{max} (i.e., improved cyan dye developer transfer density) and the reduced red emulsion fog that results when fogged silver iodide is present in the emulsion.

TABLE A

Element	Feature	1 Min. Process		Red $D_{max.}$	
		Red $D_{max.}$	Red emul. fog (mg. Ag/ft.²)	1¼ min.	1½ min.
A	Control	1.57	77	1.76	1.93
B	Fogged AgBrI in dye-developing layer.	1.47	37	1.72	1.94
C	Fogged AgBrI in barrier layer.	1.46	27	1.98	2.25

As will be seen in the above table, addition of fogged silver halide in the dye-developer layer reduces fog in the color forming unit below the acid salt layer. A still greater fog reduction occurs when the fogged silver halide is added to the layer containing a polyvalent metal salt of a polymeric carboxylic acid. It was noted that the beneficial effects of the metal salt layer were obtained, i.e., increased magenta D_{max} (in other words improved dye developer image saturation) and reduced magenta "drop-off" (i.e., decreased desaturation of magenta dye developer image resulting from magenta dye developer developing in the red-sensitive emulsion layer). The curves for the red sensitive layers of elements A, B and C, at a processing time of 1¼ minutes, is shown in FIGURE 4. It will be seen that the undesirable unevenness in response in the color-forming unit below the acid salt layer which appears as a "hump" in the curve designated element A, is eliminated by the fogged silver halide in elements B and C. Element C, which contains the fogged silver halide in the metal salt layer, further shows decreased fog and increased D_{max}. In FIG. 4, log E units are given along the abscissa, density units along the ordinate.

EXAMPLE 2

Results similar to those obtained in Example 1 are obtained when layer 3 is replaced with a zirconium-gelatin salt, prepared by overcoating gelatin with a one percent aqueous solution of zirconium sulfate, coated at the rate of 60 mg. zirconium sulfate per square foot.

EXAMPLE 3

When calcium pectinate, plumbous carboxymethyl cellulose, manganous alginate and lead alginate layers are substituted for the calcium alginate interlayer (layer 3) of Example 1, similar results are obtained. These interlayers can be prepared as described in the Becker application referred to above.

Similar results are obtained when, in the above examples, the cyan dye developer used is 5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)ethylamino]-anthraquinone, and the yellow dye developer used is 1-phenyl-3-(N-n-hexylcarboxamido)-4-[p-β'-hydroquinonylethyl)phenylazo]-5-pyrazolone.

The invention has been described in 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 described hereinabove and 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 layer positioned between at least two of said dye image-forming units, said dye image-forming units comprising a light sensitive silver halide emulsion layer and a dye developer contiguous to silver halide of said emulsion, and said salt layer 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 layer 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 layer; and a fogged silver halide salt wherein a substantial amount of said halide is iodide, in at least one layer of said element, other than a light sensitive silver halide emulsion layer thereof, which silver iodide salt develops during development of the element.

2. A photographic element as described in claim 1, having three superposed dye image-forming units capable of recording red, green and blue light respectively and an alkali-permeable, water-insoluble salt layer positioned between at least two of said dye image-forming units, each of said dye image-forming units comprising a light-sensitive 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 layer 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 layer 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 layer.

3. A photographic element as described in claim 2 wherein said water-insoluble salt layer comprises 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; and, said silver halide salt is a silver haloiodide containing at least 5 mole percent iodide.

4. A photographic element as described in claim 2 wherein the polyvalent metal-polycarboxylic acid salt layer is substantially equivalent in permeability to dye developers in aqueous alkaline solution to the calcium alginate formed when a layer consisting essentially of sodium alginate is reacted with calcium chloride coated thereover at a coverage of about 5 to 100 mg. per square foot, and said silver halide is a silver haloiodide containing from about 5 to about 15 mole percent iodide and is coated at a concentration of about 5 to about 20 mg. per square foot.

5. A photographic element as described in claim 2 wherein the water-insoluble salt layer is positioned be-

tween the image-forming units recording red and green light, and the silver halide salt is incorporated in said salt layer.

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

7. A photographic element as described in claim 3 wherein the dye image-forming unit recording blue light is furthest from the support and the dye image-forming unit recording red light is most proximate to the support; said salt layer comprises zirconium gelatinate and is positioned between the said image-forming units recording red and green light; said dye image-forming units comprise a light sensitive 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 continguous silver halide emulsion layer; and, said silver halide salt is incorporated in said salt layer.

8. A photographic element as described in claim 3 wherein the dye image-forming unit recording blue light is furthest from the support and the dye image-forming unit recording red light is most proximate to the support; said salt layer comprises calcium alginate and is positioned between the said image-forming units recording red and green light; said dye image-forming units comprise a light sensitive 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, said silver halide salt is incorporated in said salt layer.

9. A photographic element as described in claim 3 wherein the dye image-forming unit recording blue light is furthest from the support and the dye image-forming unit recording red light is most proximate to the support; said salt layer comprises thorium gelatinate and is positioned between the said image-forming units recording red and green light; said dye image-forming units comprise a light sensitive 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, said silver halide salt is incorporated in said salt layer.

10. A photographic element as described in claim 3 wherein the dye image-forming unit recording blue light is furthest from the support and the dye image-forming unit recording red light is most proximate to the support; said salt layer comprises calcium pectinate and is positioned between the said image-forming units recording red and green light; said dye image-forming units comprise a light sensitive 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, said silver halide salt is incorporated in said salt layer.

11. A photographic element as described in claim 3 wherein the dye image-forming unit recording blue light is furthest from the support and the dye image-forming unit recording red light is most proximate to the support; said salt layer comprises zirconium alginate and is positioned between the said image-forming units recording red and green light; said dye image-forming units comprise 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 continguous silver halide emulsion layer; and, said silver halide salt is incorporated in said salt layer.

12. A photographic element as described in claim 7 wherein the dye developer in the image-forming unit recording red light is 5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone; the dye developer in the image-forming unit recording green light is 4-isopropoxy-2-[p-(β-hydroquinonylethyl)-phenylazo]-1-naphthol; the dye developer in the image-forming unit recording blue light is 1-phenyl-3-(N-n-hexylcarboxamido) - 4 - [p - (β' - hydroquinonylethyl)phenylazo]-5-pyrazolone; and, the silver halide salt is light fogged silver bromoiodide containing from 8 to 15 mole percent iodide and is coated at about 10 mg. per square foot.

13. A photographic element as described in claim 8 wherein the dye developer in the image-forming unit recording red light is 5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone; the dye developer in the image-forming unit recording green light is 4 - isopropoxy - 2 - [p - (β - hydroquinonylethyl) - phenylazo]-1-naphthol; the dye developer in the image-forming unit recording blue light is 1-phenyl-3-(N-n-hexylcarboxamido) - 4 - [p - (β' - hydroquinonylethyl)phenylazo]-5-pyrazolone; and, the silver halide salt is light fogged silver bromoiodide containing from 8 to 15 mole percent iodide and is coated at about 10 mg. per square foot.

14. A photographic element as described in claim 9 wherein the dye developer in the image-forming unit recording red light is 5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone; the dye developer in the image-forming unit recording green light is 4-isopropoxy-2-[p-(β-hydroquinonylethyl)-phenylazo]-1-naphthol; the dye developer in the image-forming unit recording blue light is 1-phenyl-3-(N-n-hexylcarboxamdio) - 4 - [p - (β' - hydroquinonylethyl)phenylazo]-5-pyrazolone; and, the silver halide salt is light fogged silver bromoiodide containing from 8 to 15 mole percent iodide and is coated at about 10 mg. per square foot.

15. A photographic element as described in claim 10 wherein the dye developer in the image-forming unit recording red light is 5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone; the dye developer in the image-forming unit recording green light is 4-isopropoxy-2-[p-(β-hydroquinonylethyl)-phenylazo]-1-naphthol; the dye developer in the image-forming unit recording blue light is 1-phenyl-3-(N-n-hexylcarboxamido) - 4 - [p - (β' - hydroquinonylethyl)phenylazo]-5-pyrazolone; and, the silver halide salt is light fogged silver bromoiodide containing from 8 to 15 mole percent iodide and is coated at about 10 mg. per square foot.

16. A photographic element as described in claim 11 wherein the dye developer in the image-forming unit recording red light is 5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone; the dye developer in the image-forming unit recording green light is 4-isopropoxy-2-[p-(β-hydroquinonylethyl)-phenylazo]-1-naphthol; the dye developer in the image-forming unit recording blue light is 1-phenyl-3-(N-n-hexylcarboxamido) - 4 - [p - (β' - hydroquinonylethyl)phenylazo]-5-pyrazolone; and, the silver halide salt is light fogged silver bromoiodide containing from 8 to 15 mole percent iodide and is coated at about 10 mg. per square foot.

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.

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