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MULTICOLOR DIFFUSION TRANSFER METHOD AND ELEMENT

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This invention relates to photography and, more particularly, to color diffusion-transfer processes employing dye developers.

A principal object of this invention is to provide novel photosensitive elements and composite film units, and color diffusion-transfer processes utilizing said novel composite film units, whereby transfer images having improved photographic characteristics may be obtained.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

This invention is related to color diffusion-transfer processes such as disclosed and claimed in U.S. Patent No. 2,983,606, which issued May 9, 1961, on the copending U.S. application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958, as a continuation-in-part of the earlier U.S. application, Serial No. 415,073, filed March 9, 1954 (now abandoned), and also of the earlier U.S. application, Serial No. 518,979, filed June 29, 1955 (now abandoned), wherein dye developers are utilized to develop an exposed photosensitive emulsion, and a transfer color image is imparted to a superposed image-receiving layer by unreacted dye developer originating from undeveloped areas of the exposed photosensitive emulsion. The dye developers used in such processes are dyes which contain, in the same molecule, a silver halide developing function and the chromophoric system of a dye, i.e., a dye developer is a compound which is both a dye and a silver halide developing agent. A particularly useful class of dye developers are those containing a hydroquinonyl developing radical.

This invention is more particularly related to that embodiment of such color diffusion-transfer processes, also disclosed in said U.S. application, Serial No. 748,421, wherein at least one auxiliary or accelerating silver halide developing agent is used in conjunction with the dye developer. A preferred class of auxiliary silver halide developing agents are those of the benzenoid type, i.e., having an aryl nucleus (benzene or naphthalene) substituted by at least two hydroxyl, amino, and/or alkylamino groups so as to be capable of developing exposed silver halide, such benzenoid developing agents forming quinonoid oxidation products. Other particularly useful auxiliary developing agents are those of the 3-pyrazolidone type, e.g., 1-phenyl-3-pyrazolidone. The use of a benzenoid silver halide developing agent in combination with a 3-pyrazolidone and a dye developer is disclosed and claimed in the copending U.S. application of Howard G. Rogers and Harriet Lutes, Serial No. 654,781, filed April 24, 1957 (now U.S. Patent No. 3,039,869, issued June 19, 1962). Particularly useful multicolor photosensitive elements are those of the multilayer type, as disclosed and claimed in the copending U.S. application of Edwin H.

Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956.

In carrying out the processes mentioned above, a photosensitive element containing a silver halide emulsion is exposed and wetted by an aqueous alkaline processing solution, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred mode of carrying out such processes, the dye developers are disposed in a separate alkali-permeable layer behind the silver halide emulsion layer, and the aqueous alkaline processing solution is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed relationship with an image-receiving element. As the process proceeds, the liquid processing composition permeates the emulsion to initiate development. The dye developer is immobilized or precipitated in developed areas as a function of said development. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by the oxidized developing agent, and/or to a localized reduction in the alkali concentration. In undeveloped and partially developed areas of the emulsion, the dye developer is unreacted and is diffusible. An imagewise distribution of unoxidized dye developer, diffusible in the liquid processing composition, is thus formed under the control of the point-to-point degree of development of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, to provide the desired transfer image.

It has been proposed in the previously mentioned copending U.S. application, Serial No. 748,421, that the auxiliary developer(s) may be disposed in the aqueous alkaline processing solution or in the photosensitive element in either the silver halide emulsion layers or in separate alkali-permeable layers, behind the silver halide emulsions, along with the dye developers which are to be used. It has now been discovered that it is especially advantageous to initially locate an auxiliary developing agent, particularly a benzenoid developing agent, in a layer over the outermost or blue-sensitive silver halide emulsion of a multicolor negative containing the dye developers. In addition, incorporation of the auxiliary developing agent in such an overlayer may permit the use of auxiliary developing agents which tend to be unstable in an alkaline processing solution during storage. Incorporation of some auxiliary developing agents in the silver halide emulsion itself may fog or prematurely develop the silver halide, thus adversely affecting the quality of the transfer image. It has been discovered that incorporation of an auxiliary developing agent in an alkali-permeable layer which is coated over the outermost silver halide emulsion layer gives transfer images of improved color separation and reduced high-light stain. An additional quantity of the same or of another auxiliary developing agent may be incorporated in the processing composition and/or in an interlayer.

The photosensitive elements of this invention are especially useful in those composite film units for use in dye developer processes, wherein all the elements and reagents necessary to produce a colored transfer image are present within the film unit itself. In general, such units comprise a photosensitive element, an image-receiving element and a rupturable container holding an aqueous alkaline processing solution. The rupturable container is as-

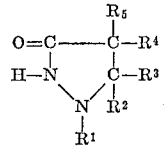
sociated with the photosensitive element and the image-receiving element in such a manner that, upon processing, it may be ruptured and dispense the aqueous alkaline processing solution between the superposed elements. As examples of such rupturable containers, mention may be made of those disclosed in U.S. Patent No. 2,543,181, issued to Edwin H. Land on February 27, 1951, and in U.S. Patent No. 2,634,886, issued to Edwin H. Land on April 14, 1953.

The overlayers, herein disclosed, provide a substantially inert medium into which such developing agents may be disposed until processing is initiated. The auxiliary developing agent may be molecularly dispersed in the overlayer, e.g., in a layer of cellulose acetate hydrogen phthalate, or it may be dissolved in a water-immiscible solvent and the resulting solution dispersed in a suitable carrier, e.g., gelatin. Particularly useful concentrations of the auxiliary developing agent in the overcoat are 5 to 50 mg. per square foot. In general, similar or somewhat lower concentrations of the auxiliary developing agent in the interlayer are useful.

The dye developers, as noted above, are compounds which contain in the same molecule both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide developing function is a hydroquinonyl group. Other suitable developing functions include o-dihydroxyphenyl and o- and p-amino-substituted hydroxyphenyl groups. In general, the developing function includes a benzenoid developing function. Numerous examples of representative dye developers are given in the previously mentioned copending U.S. applications and in other copending U.S. applications referred to therein.

The auxiliary developing agents are substantially colorless, at least in the unoxidized form, and are, of course, soluble and diffusible in the alkaline processing composition. In the preferred embodiment, the auxiliary developing agent is substantially water-insoluble; this group of auxiliary developing agents has been found to give the best results when incorporated in the overcoat.

The auxiliary developing agents accelerate and possibly initiate the action of the dye developer. For this reason they also have been referred to as accelerating developing agents. It is believed that a portion of the dye developer oxidized as a result of the development may be oxidized by an energy transfer from the oxidized accelerating developer. As examples of accelerating developing agents, mention may be made of phenylhydroquinone, metol, amidol, benzylaminophenol and the 3-pyrazolidone developing agents represented by the formula:



in which R^1, R^2, R^3, R^4 and R^5 each represents substituents such as hydrogen, aryl or alkyl groups, including substituted alkyl and aryl groups. The alkyl groups preferably contain from 1 to 4 carbon atoms, inclusive. A large number of developing agents within this class are reported in the literature; see, for example, U.S. Patent No. 2,289,367, issued July 14, 1942, to John David Kendall, and U.S. Patent No. 2,731,300, issued June 19, 1956, to Thomas H. James et al. Particularly useful developing agents of this class are 1-phenyl-3-pyrazolidone and 1-phenyl-4,4-dimethyl-3-pyrazolidone. In general, benzenoid developing agents contain as aryl substituted in the ortho or para positions, with respect to each other, by hydroxyl and/or amino groups, including substituted amino groups, and the nucleus also may have other nuclear substituents, e.g., alkyl, aryl, arylthio, etc.

As examples of auxiliary developing agents which are particularly useful in the processes of this invention, mention may be made of the following:

Phenoxyhydroquinone
Toluhydroquinone
4'-aminophenethylhydroquinone
m-Xylohydroquinone
2-p-toluthiohydroquinone
5,8-dihydro-1,4-naphthohydroquinone
5,6,7,8-tetrahydro-1,4-naphthohydroquinone
Phenylhydroquinone
p-Aminophenylhydroquinone
2,6-dimethylhydroquinone
4'-methylphenylhydroquinone
2-(4'-aminophenethyl)-5-methylhydroquinone
1,4-dihydroxy-naphthalene
2,5-dichlorohydroquinone

The overlayers of this invention may be readily applied to the photosensitive elements by conventional coating and drying techniques, well known to the art. The coating solutions, used, in general, comprise a film-forming material and the desired developing agent or agents. Other reagents, useful in the processes such as antifoggants, etc., may also be incorporated into the coating solution and applied therewith. The film-forming materials which serve as carriers for the developers should be readily permeated by aqueous alkaline solutions. The pH of the carrier material should preferably be neutral or slightly acid in order to provide a substantially inert environment for the developers. When the photosensitive element is to be exposed through the reagent layer, the film-forming material should be substantially transparent to permit the desired exposure. As examples of film-forming materials useful as carriers, mention may be made of sodium carboxymethyl cellulose, polyvinyl alcohol, gelatin, and cellulose acetate hydrogen phthalate.

The use of an overlayer in accordance with this invention is also advantageous in multicolor diffusion-transfer processes employing a photosensitive element comprising at least two selectively sensitized silver halide emulsions, each emulsion being associated with an appropriate dye developer and the emulsions themselves being arranged in the form of a screen on a suitable support, as disclosed in the aforementioned copending U.S. application, Serial No. 748,421, and also in the copending U.S. application of Edwin H. Land, Serial No. 448,441 filed August 9, 1954, now U.S. Patent No. 2,968,554. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of these copending applications, comprises minute red-sensitized emulsion elements, minute green-sensitized emulsion elements, and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern, and each emulsion having in or behind it, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. An overlayer containing an auxiliary developing agent in accordance with the present invention may be coated over such photosensitive screens and the units may be processed as hereinbefore described to produce a multicolor transfer image.

Processes for obtaining multicolor transfer images utilizing dye developers and employing an integral multilayer photosensitive element are disclosed and claimed in the above mentioned copending U.S. application, Serial No. 565,135, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions

having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, e.g., in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from the other sets by suitable spacer strata, for example, by a layer of gelatin or polyvinyl alcohol. They may be further separated by suitable barrier layers, for example, mixtures of cellulose acetate hydrogen phthalate and cellulose acetate. Such layers are used to assist the dye developers to react with the intended silver halide emulsions, and to control permeation rates. In certain instances the interlayers may be left out and useful images obtained.

Other diffusion-transfer processes in which photosensitive elements containing overcoats, in accordance with this invention, are useful are those disclosed and claimed in the copending U.S. application of Howard G. Rogers and Milton Green, Serial No. 50,851, filed August 22, 1960, wherein development with a dye developer is effected in the presence of an onium compound, particularly a quaternary ammonium, a quaternary phosphonium or a teritary sulfonium compound.

The following nonlimiting examples illustrate the use of an overlayer in multicolor diffusion-transfer processes. All percentages are by weight unless otherwise stated.

Example 1

An integral multilayer photosenstive element was prepared by coating a gelatin-coated film support with the following coating solutions, in sequence with intermediate drying of the preceding layer:

(1) Cyan dye developer layer-coating solution comprising 4.5% of 1,4-bis-[β-(2',5'-dihydroxyphenyl)-isopropylamino]-anthraquinone; 0.8% Resoflex R–296 (trade name for an alkyd resinous plasticizer produced by Cambridge Industries Company, Inc., Cambridge, Massachusetts), and 4% cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of acetone and tetrahydrofuran.

(2) Red-sensitized silver halide emulsion coating.

(3) Barrier layer-coating solution comprising 2% of cellulose acetate hydrogen phthalate and 0.75% of cellulose acetate in acetone.

(4) Spacer layer-coating solution comprising 2% polyvinyl alcohol and a small amount of Antarox D–100 (trade name of the Antara Chemical Division of General Dyestuff Corp., New York, N.Y., for a nonionic surface active agent).

(5) Magenta dye developer layer-coating solution comprising 1.75% 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol, 0.4% of Resoflex R–296 and 4% of cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of acetone and tetrahydrofuran.

(6) Green-sensitized silver halide emulsion coating.

(7) Barrier layer-coating solution comprising 2% cellulose acetate hydrogen phthalate and 0.5% cellulose acetate in acetone.

(8) Spacer layer-coating solution comprising 1.5% polyvinyl alcohol and a small amount of Antarox D–100.

(9) Yellow dye developer layer-coating solution comprising 1.5% of 1-phenyl-3-N-n-hexyl-carbamyl-4-[p-(2',5' - dihydroxyphenethyl) - phenylazo]-5-pyrazolone and 4% cellulose acetate hydrogen phthalate in tetrahydrofuran.

(10) Blue-sensitized silver halide emulsion.

(11) Outer layer-coating solution comprising 0.8% of 1-phenyl-3-pyrazolidone, 0.6% of 2,5-dihydroxy-p-benzene diacetic acid and 4% of cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of acetone and tetrahydrofuran.

After a storage period of six weeks, the above photosensitive element was exposed and an aqueous processing solution comprising:

	Percent
Sodium hydroxide	3
Sodium carboxymethyl cellulose	5.0
5-nitrobenzimidazole	0.12

was applied as the exposed photosensitive element was brought into superposed relationship wtih an image-receiving element. The latter element comprised a cellulose acetate-coated baryta which had been coated with a 4% solution of N-methoxymethyl polyhexamethylene adipamide in aqueous isopropanol. After an imbibition period of approximately three minutes, the image-receiving element was separated and contained a multicolored positive image of the photographed subject.

Example 2

A photosensitive element was prepared as in Example 1 except that the coating solution used to prepare the outer reagent layer comprised 0.8% of 1-phenyl-3-pyrazolidone, 0.5% of 2,5-dihydroxy-p-benzene diacetic acid, 0.1% of trimethylhydroquinone and 4.0% of cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of acetone and tetrahydrofuran. After storage for six weeks, the photosensitive element was exposed and processed as in Example 1 to produce a multicolor positive image.

Example 3

A photosensitive element was prepared as in Example 1 except that the coating solution, used to prepare the outer reagent layer, comprised 0.8% of 1-phenyl-3-pyrazolidone, 0.3% of 2,5-dihydroxy-p-benzene diacetic acid, 0.3% of thymolhydroquinone and 4% of cellulose acetate hydrogen phthalate in a 1:1 mixture, by volume, of acetone and tetrahydrofuran. After six weeks' storage, the photosensitive element was exposed and processed as in Example 1 to produce a multicolor positive image.

Example 4

A photosensitive element was prepared as in Example 1 except that the coating solution, used to prepare the outer reagent layer, comprised 0.8% of 1-phenyl-3-pyrazolidone, 0.6% of 2,5-xylohydroquinone and 4% of cellulose acetate hydrogen phthalate in a 1:1 mixture, by vloume, of acetone and tetrahydrofuran. After six weeks' storage, the photosensitive element was exposed and processed as in Example 1 to produce a multicolor positive image.

The multicolor images obtained in Examples 1 through 4 were substantially similar to multicolor images obtained by similar processing of corresponding freshly coated negatives.

Example 5

A multilayer photosensitive element was prepared in accordance with the disclosures of the previously mentioned copending U.S. applications, Serial No. 565,135 and Serial No. 748,421, the same dye developers as in Example 1 being dissolved in a water-immiscible solvent and dispersed in gelatin to provide the dye layers. Thin layers of gelatin were used as spacer layers. This negative was divided in half, one half being overcoated with a thin gelatin layer containing approximately 30 mg. per square foot of 4'-methylphenylhydroquinone dispersed in the gelatin (after being dissolved in a 1:2 mixture, by volume, of methanol and di-n-butyl phthalate), and the second half of the negative being overcoated with a plain gelatin layer as a control. This negative was exposed and developed by application of a layer approximately 0.0040" thick of an aqueous alkaline processing composition while in superposed relationship wtih an image-receiving layer comprising a 1:2 mixture, by weight, of gelatin and polyvinyl alcohol and also containing a small amount of 1-phenyl-5-mercaptotetrazole, as disclosed in

our copending U.S. application, Serial No. 50,849, filed August 22, 1960. The processing composition comprised:

Water	cc.	100
NaOH	g.	5.17
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Delaware, under the trade name Natrosol 250]	g.	4.03
Sodium thiosulfate	g.	1.15
Benzotriazole	g.	2.3
N-benzyl-α-picolinium bromide	g.	2.3

For purposes of comparison, the two negatives were processed with the above composition, and the control negative was also processed with portions of the above processing composition to which had been added, per 100 cc. of the above processing composition, 0.1 g., 0.2 g., and 1.0 g., respectively, of 4'-methylphenyl-hydroquinone. After a 2 minute imbibition period, the image-receiving elements were separated and the degree of color separation in the several images evaluated in terms of magenta "drop-off," i.e., the percentage difference between the magenta density of the area of the transfer image corresponding to no exposure, i.e., the blacks, and the magenta density in the area of the transfer image corresponding to a red and blue exposure:

	Percent drop-off
Control negative	33
Control negative and 0.1 g.	55
Control negative and 0.2 g.	38
Control negative and 1.0 g.	47
Overcoated negative	24

The use of an overcoat containing the 4'-methylphenylhydroquinone gave the least magenta drop-off, thus confirming the improved color separation, and also gave the best maximum density of the several images.

The liquid processing composition herein referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin uniform layer, it may also include a viscosity-increasing compound constituting film-forming material of the type which, when said composition is spread and dried, forms a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble cellulose ether which is inert to an alkaline solution as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents, e.g., polyvinyl alcohol, whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said composition a viscosity in excess of 100 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature. Illustrations of suitable liquid processing compositions may be found in the several United States patents and copending applications herein mentioned and also in examples herein given.

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subtractive color photography, i.e., cyan, magenta and yellow. It should be noted that it is within the scope of this invention to use mixtures of dye developers to obtain a desired color, e.g., black. Thus, it is to be understood that the expression "color" as used herein is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black eye developer.

In all products employed in the practice of this invention, it is preferable to expose from the emulsion side. It is, therefore, desirable to hold the photosensitive element and the image-receiving element together at one end thereof by suitable fastening means in such manner that the photosensitive element and the image-receiving element may be spread apart from their superposed processing position during exposure. A camera apparatus suitable for processing roll film of the type just mentioned is provided by the Polaroid Land Camera, sold by Polaroid Corporation, Cambridge, Massachusetts, or similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof as well as individual processing of an exposed frame by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure rollers which rupture a container associated therewith and effect the spreading of the processing liquid released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

The image-receiving element comprises a sheet of opaque or transparent material which is liquid permeable and dyeable from alkaline solutions. It preferably comprises a support upon which at least one liquid-permeable and dyeable layer is mounted. The support layer may have a water-impermeable subcoat over which the stratum of permeable and dyeable material is applied. In certain instances, the dyeable layer may comprise a layer of the liquid processing composition which is adapted to remain adhered to the support layer upon stripping.

Particularly useful materials for the image-receiving layer are a nylon and preferably a nylon such as N-methoxymethyl polyhexamethylene adipamide, gelatin and polyvinyl alcohol. Suitable mordants, such as poly-4-vinylpyridine may be incorporated in the image-receiving layer, e.g., gelatin or polyvinyl alcohol, as disclosed and claimed in the copending United States application of Howard C. Haas, Serial No. 50,848, filed August 22, 1960, now U.S. Patent No. 3,148,061. Other materials suitable for image-receiving layers comprise a partially hydrolyzed polyvinyl acetate such as that commercially available under the trade name of Vinylite MA–28–18 from Bakelite Division, Carbide and Carbon Chemicals Co.; baryta paper, i.e., a support having a baryta coating thereon; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid, and other materials of a similar nature, as is well known in the art.

While a rupturable container provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition as by coating the composition on said photosensitive element or otherwise wetting said element with the composition following which the permeated, exposed, photosensitive element, still without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

The expression "positive image," as used herein, should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive element. As an example of an alternative meaning for "positive image" assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive element will be a positive and the image produced on the image-carrying layer will be a

negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

This application is in part a continuation of our copending application Serial No. 654,781, filed April 24, 1957, now U.S. Patent No. 3,039,869, issued June 19, 1962.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process of forming multicolor diffusion transfer images comprising the steps of photoexposing a photosensitive element comprising a support bearing, in turn, on one surface thereof

(a) an alkali-permeable layer containing a cyan dye developer,

(b) an alkali-permeable layer containing a red-sensitive silver halide emulsion,

(c) an alkali-permeable layer containing a magenta dye developer,

(d) an alkali-permeable layer containing a green-sensitive silver halide emulsion,

(e) an alkali-permeable layer containing a yellow dye developer,

(f) an alkali-permeable layer containing a blue-sensitive silver halide emulsion, and

(g) an alkali-permeable layer free of dye developer and containing at least one alkali-soluble and alkali-diffusible silver halide developing agent selected from the group consisting of (i) a 3-pyrazolidone silver halide developing agent, and (ii) a benzenoid silver halide developing agent, said benzenoid silver halide developing agent containing an aryl nucleus substituted by at least two substituents selected from the group consisting of hydroxyl and amino groups, one of said substituents being substituted in one of the ortho and para positions with respect to the other of said substituents,

permeating said exposed photosensitive element with an aqueous alkaline processing solution, developing each of said exposed blue-sensitive, green-sensitive and red-sensitive silver halide emulsions, forming in undeveloped areas of said blue-sensitive silver halide emulsion an imagewise distribution of diffusible yellow dye developer, forming in undeveloped areas of said green-sensitive silver halide emulsion an imagewise distribution of diffusible magenta dye developer, forming in undeveloped areas of said red-sensitive silver halide emulsion an imagewise distribution of cyan dye developer, and transferring, by imbibition, at least a portion of each of said imagewise distributions of diffusible dye developers to a superposed image-receiving layer to impart a multicolor diffusion transfer image thereto.

2. A process as defined in claim **1**, wherein said aqueous alkaline processing solution contains, when applied to said photosensitive element, a silver halide developing agent selected from the group consisting of (i) a 3-pyrazolidone silver halide developing agent, and (ii) a benzenoid silver halide developing agent, said benzenoid silver halide developing agent containing an aryl nucleus substituted by at least two substituents selected from the group consisting of hydroxyl and amino groups, one of said substituents being substituted in one of the ortho and para positions with respect to the other of said substituents.

3. A process as defined in claim **1**, wherein said last-mentioned alkali-permeable layer (g) contains a plurality of said silver halide developing agents.

4. A process as defined in claim **1**, wherein said last-mentioned alkali-permeable layer (g) comprises cellulose acetate hydrogen phthalate.

5. A process as defined in claim **1**, wherein said last-mentioned alkali-permeable layer (g) comprises gelatin.

6. A process as defined in claim **1**, wherein said last-mentioned alkali-permeable layer (g) contains 1-phenyl-3-pyrazolidone.

7. A process as defined in claim **1**, wherein said last mentioned alkali-permeable layer (g) contains a hydroquinone silver halide developing agent.

8. A process as defined in claim **7**, wherein said hydroquinone is 4'-methylphenyl hydroquinone.

9. A process as defined in claim **7**, wherein said hydroquinone is trimethyl hydroquinone.

10. A process as defined in claim **7**, wherein said hydroquinone is 2,5-xylo-hydroquinone.

11. A process as defined in claim **1**, including an alkali-permeable spacer layer positioned between said layer (e) of yellow dye developer and said layer (d) of green-sensitive silver halide emulsion, and an alkali-permeable spacer layer positioned between said layer (c) of magenta dye developer and said layer (b) of red-sensitive silver halid emulsion.

12. A process as defined in claim **11**, where each of said alkali-permeable spacer layers comprises gelatin.

13. A process as defined in claim **11**, where each of said alkali-permeable spacer layers comprises polyvinyl alcohol.

14. A process as defined in claim **11**, wherein at least one of said alkali-permeable spacer layers also contains a silver halide developing agent selected from the group consisting of (i) a 3-pyrazolidone silver halide developing agent, and (ii) a benzenoid silver halide developing agent, said benzenoid silver halide developing agent containing an aryl nucleus substituted by at least two substituents selected from the group consisting of hydroxyl and amino groups, one of said substituents being substituted in one of the ortho and para positions with respect to the other of said substituents.

15. A process as defined in claim **1**, wherein said last-mentioned alkali-permeable layer (g) contains from 5 to 50 milligrams per square foot of said silver halide developing agent.

16. A photosensitive element comprising a support bearing, in turn, on one surface thereof

(a) an alkali-permeable layer containing a cyan dye developer,

(b) an alkali-permeable layer containing a red-sensitive silver halide emulsion,

(c) an alkali-permeable layer containing a magenta dye developer,

(d) an alkali-permeable layer containing a green-sensitive silver halide emulsion,

(e) an alkali-permeable layer containing a yellow dye developer,

(f) an alkali-permeable layer containing a blue-sensitive silver halide emulsion, and

(g) an alkali-permeable layer free of dye developer and comprising cellulose acetate hydrogen phthalate and at least one alkali-soluble and alkali-diffusible silver halide developing agent selected from the group consisting of (i) a 3-pyrazolidone silver halide developing agent, and (ii) a benzenoid silver halide developing agent, said benzenoid silver halide developing agent containing an aryl nucleus substituted by at least two substituents selected from the group consisting of hydroxyl and amino groups, one of said substituents being substituted in one of the ortho and para positions with respect to the other of said substituents.

17. A photosensitive element comprising a support bearing, in turn, on one surface thereof

(a) an alkali-permeable layer containing a cyan dye developer,

(b) an alkali-permeable layer containing a red-sensitive silver halide emulsion,

(c) an alkali-permeable layer containing a magenta dye developer,

(d) an alkali-permeable layer containing a green-sensitive silver halide emulsion,

(e) an alkali-permeable layer containing a yellow dye developer,

(f) an alkali-permeable layer containing a blue-sensitive silver halide emulsion, and

(g) an alkali-permeable layer free of dye developer and comprising gelatin and at least one alkali-soluble and alkali-diffusible silver halide developing agent selected from the group consisting of (i) a 3-pyrazolidone silver halide developing agent, and (ii) a benzenoid silver halide developing agent, said benzenoid silver halide developing agent containing an aryl nucleus substituted by at least two substituents selected from the group consisting of hydroxyl and amino groups, one of said substituents being substituted in one of the ortho and para positions with respect to the other of said substituents.

References Cited by the Examiner

UNITED STATES PATENTS

2,543,181	2/51	Land	96—29
2,939,788	6/60	Blout	96—29
2,983,606	5/61	Rogers	96—29
3,019,108	1/62	Dershowitz	96—66
3,039,869	6/62	Rogers et al.	96—3

FOREIGN PATENTS

554,933	8/57	Belgium.
554,935	8/57	Belgium.
221,880	5/59	Australia.
577,021	6/59	Canada.

OTHER REFERENCES

Mees: The Theory of the Photographic Process, Macmillan, N.Y., 1954, pp. 554–563.

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