

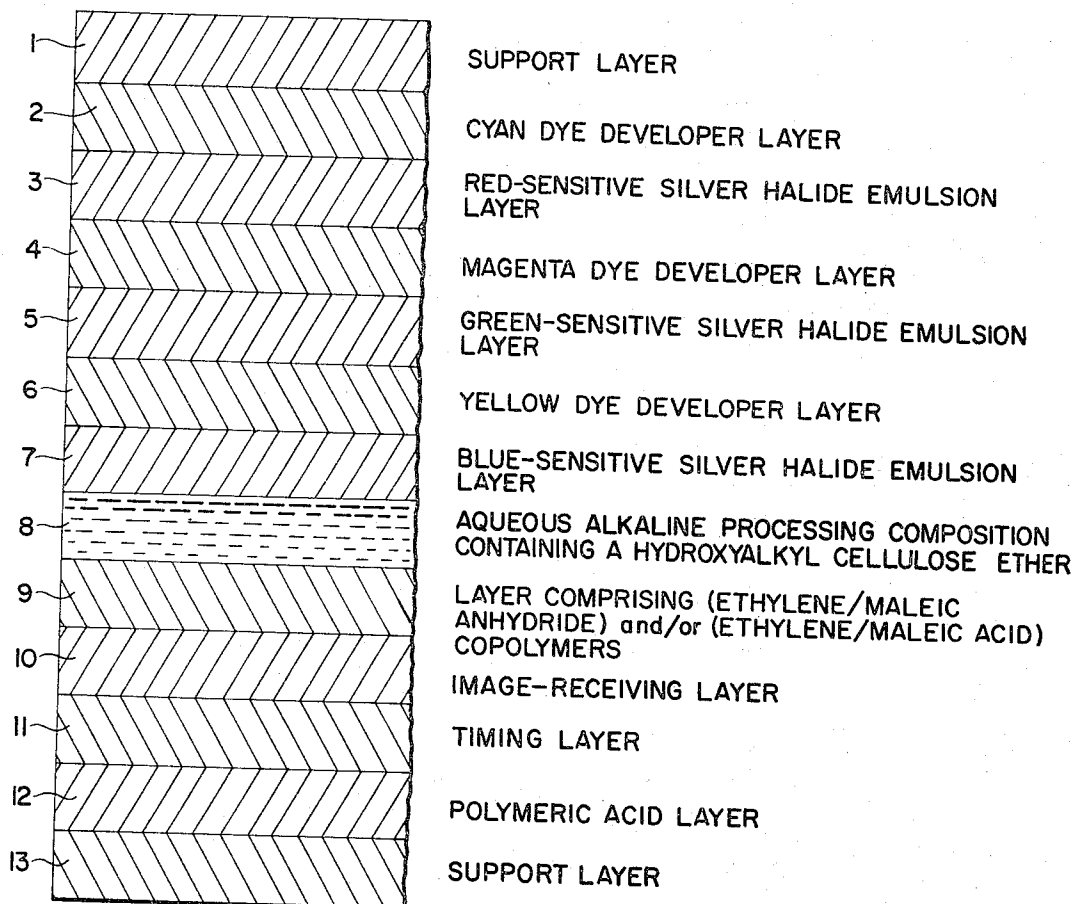
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COLOR DIFFUSION TRANSFER ELEMENTS AND PROCESSES

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COLOR DIFFUSION TRANSFER ELEMENTS
AND PROCESSESLeonard C. Farney, Melrose, Mass., assignor to
Polaroid Corporation, Cambridge, Mass., a cor-
poration of DelawareContinuation-in-part of application Ser. No. 350,704,
Mar. 10, 1964. This application Mar. 25, 1965, Ser.
No. 442,626

5 Claims. (Cl. 96—29)

ABSTRACT OF THE DISCLOSURE

A photographic diffusion transfer image-receiving element comprising, in sequence, a support layer, a polymeric acid layer, a polymeric image-receiving layer and a polymeric layer of 5 to 25 milligrams per square foot of (ethylene/maleic anhydride) or (ethylene/maleic acid) copolymer.

This application is in part a continuation of Ser. No. 350,704, filed Mar. 10, 1964, now abandoned.

The present invention relates to photography and, more particularly, to photographic products particularly adapted for employment in photographic diffusion transfer color processes.

The primary objects of the present invention are to provide photographic products, particularly adapted for employment in diffusion transfer photographic color processes; to provide photographic products which include a photographic diffusion transfer image-receiving element comprising a plurality of essential layers including, in sequence, a support layer, an image-receiving layer and a layer containing (ethylene/maleic anhydride) and/or (ethylene/maleic acid) copolymers; and to provide photographic diffusion transfer color processes employing photo-sensitive film units, including not less than one silver halide emulsion and, as color image-forming components, a dye which is a silver halide developing agent, a transfer image-receptive element of the last-mentioned type and a photographic transfer processing composition which preferably includes a hydroxyalkyl cellulose ether.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components and the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others 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 taken in connection with the accompanying drawing, wherein the figure detailed is a diagrammatic enlarged cross-sectional view illustrating the association of elements during one stage of the performance of a diffusion transfer process, for the production of a multicolor positive transfer print, the thickness of the various materials being exaggerated.

As disclosed in U.S. Patent No. 2,983,606, issued May 9, 1961, a photosensitive element containing a dye developer, that is, a dye which is a silver halide developing agent, and a silver halide emulsion may be exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheet-like support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing

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composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition, positioned intermediate the photosensitive element and the image-receiving layer, permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. 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 oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an image-wise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure 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, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

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 development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

Multicolor images may be obtained using color image-forming components such as, for example, the previously mentioned dye developers, in diffusion transfer processes by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the previously noted U.S. Patent No. 2,983,606. In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of said patent, 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 having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multi-layer photosensitive element, such as is disclosed in the aforementioned U.S. Patent No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawing, 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, for example, 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, for example, 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 other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

Copending U.S. application Ser. No. 234,864, filed Nov. 1, 1962, in the name of Edwin H. Land discloses image-receiving elements, particularly adapted for employment in the preceding diffusion transfer processes, which comprise a support layer possessing on one surface thereof, in sequence, a polymeric acid layer, preferably an inert timing or spacer layer, and an image-receiving layer, adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance.

As set forth in the last-mentioned application, the polymeric acid layer comprises polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium, etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, non-diffusible from the acid polymer layer. In the preferred embodiments disclosed, the acid polymer contains free carboxyl groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives of cellulose modified with sulfo-anhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate;

polyacrylic acid; acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methylvinyl ether/maleic anhydride copolymers; etc.

The acid polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 13 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition. As previously noted, the pH of the processing composition preferably is of the order of at least 13 to 14.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer is kept at a level of pH 12 to 14 until the positive dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about pH 9 to 10, before the positive transfer image is separated and exposed to air. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer. The processing technique thus effectively minimizes changes in color balance as a result of longer imbibition times in multicolor transfer processes using multilayer negatives.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the acid polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the acid polymer layer may be effected by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also disclosed that the layer containing the polymeric acid may contain a water insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats may be employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the aforementioned copending application, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It was stated to

have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylons as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. Preferred materials comprise polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine, as disclosed in the copending U.S. application of Howard C. Haas, Ser. No. 50,848, filed Aug. 22, 1960, now U.S. Patent No. 3,148,061 issued Sept. 8, 1964.

As disclosed in the previously cited patents, the liquid processing composition referred to for effecting monochromatic and multicolor diffusion transfer processes comprises at least an aqueous solution of an alkaline material, for example, diethylamine, sodium hydroxide or sodium carbonate and the like, and preferably possessing a pH in excess of 12. Where this liquid processing composition is to be applied to the photosensitive emulsion stratum by being spread thereon, preferably in a relatively thin and uniform layer intermediate that stratum and a superposed image-receiving layer, it is disclosed to include a viscosity-increasing compound constituting a film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. The preferred film-forming materials disclosed comprise high molecular weight polymers such as polymeric, water-soluble ethers which are inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Additionally, film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time are also disclosed to be capable of utilization. As stated, the film-forming material is preferably contained in the processing composition in such suitable quantities as to impart to the composition a viscosity in excess of 100 cps. at a temperature of approximately 24° C. and preferably in the order of 100,000 cps. to 200,000 cps. at that temperature.

It has now been quite unexpectedly discovered that the aforementioned diffusion transfer color processes may be substantially improved by the employment therein of an image-receiving element which is a laminate comprising a plurality of essential layers including, in sequence, a support layer, an image-receiving layer, and a polymeric layer containing an ethylene/maleic anhydride copolymer and/or an ethylene/maleic acid copolymer.

Specifically, as shown in the drawing in processing relationship, the image-receiving element preferably comprises a plurality of layers including, in sequence, a polymeric support layer 13, a polymeric acid layer 12, an optional polymeric timing layer 11, a polymeric image-receiving layer 10, and a polymeric layer 9 containing an ethylene/maleic anhydride copolymer and/or an ethylene/maleic acid copolymer, and is employed in combination with an aqueous alkaline transfer processing composition 8 preferably containing a hydroxylalkyl cellulose and possessing an initial pH in excess of about 12.

It has now been specifically found that employment of the above-mentioned image-receiving element, in combination with the designated processing composition, facilitates separation of the element from contact with the composition, subsequent to transfer image formation, when processing is effected by distribution of the composition intermediate a photosensitive and an image-receptive element. The aforementioned combination has been found to be uniquely effective in facilitating such separation over an extended range of processing temper-

atures and, especially, for preventing adhesion of the composition to the reception element upon separation at temperatures below 40° F.

For purposes of illustrating the present invention, a series of commercial multicolor diffusion transfer film units of the type available from Polaroid Corporation, Cambridge, Mass. under the trade designation of Type 108, and individually comprising a multicolor, multilayer photosensitive element and an image-receiving element were modified as detailed below. In general, as described in aforementioned U.S. Patent No. 2,983,606 and detailed in the drawing the multicolor, multilayer photosensitive elements comprised a support 1 carrying a red-sensitive silver halide emulsion stratum 3, a green-sensitive silver halide emulsion stratum 5 and a blue-sensitive silver halide emulsion stratum 7. In turn, the emulsions had positioned behind them and contained in layers 2, 4 and 6, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. An interlayer (not shown) was positioned between the yellow dye developer layer and the green-sensitive emulsion stratum, and also between the magenta dye developer layer and the red-sensitive emulsion stratum. The image-receiving elements comprised a support carrying, sequence, a polymeric acid layer, an inert timing or spacer layer and an image-receiving layer, as described in aforementioned U.S. application Ser. No. 234,864.

One group of film units was maintained unmodified for the purposes of control. A second group of film units was modified by coating an acetone solution of (ethylene/maleic anhydride) copolymer (commercially available from Monsanto Chemical Company, St. Louis, Mo., under the trade designation DX-840-11 resin), at a coverage of 8 mgs. per square foot, on the external surface of each film unit's image-receiving layer. A third group of film units was modified by coating, as above, an aqueous solution of (ethylene/maleic acid) copolymer (prepared by aqueous hydrolysis of DX-840-11 resin, supra).

One-half of the film units comprising each group were then each exposed and processed, at 35° F., by spreading an aqueous liquid processing composition comprising:

Water	cc.	100
Potassium hydroxide	grams	11.2
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Company, Wilmington, Del., under the trade name Natrosol 250]	do.	3.8

between each individual image-receiving element and its respective, associated multicolor photosensitive elements as they were brought into superposed relationship. After an imbibition period of about 1 minute, each image-receiving element was separated from the remainder of the film assembly to reveal a transfer image.

The image-receiving elements of the second and third groups of film units exhibited complete separation from the remainder of the film unit, subsequent to processing, in contradistinction to the image-receiving elements of the first group of film units, which exhibited incomplete separation characterized by adhesion of processing composition to the surface of the separated image-receiving elements. In addition, each image-receiving element of the second and third groups of film units exhibited excellent gloss characteristics.

The above-exemplified test procedure was then repeated, processing one-half of the remaining film units at 50° F. and one-half at 72° F., subsequent to effecting accelerated aging of the film units by subjecting them to conditions of 120° F. and 30° relative humidity for a period of 5 days, and provided the results detailed above.

In general, it has been found that the preferred concentration of copolymer forming the stated layer falls within the range of about 5 to 25 mgs. per square foot. Although concentrations in excess of the last-mentioned range may be employed, increasing the concentration be-

yond the designated limits generally provides no additional beneficial results. It will be recognized, however, that in all circumstances, preferred operation of the transfer process requires that the concentration of polymer employed be such as will not interfere with the processing environment by effecting deleterious changes in the pH of same. Conversely, concentrations below the designated range, however, merely decrease the effective ability to separate the image-receiving element from contact with the processing composition, subsequent to transfer processing, at processing temperature extremes.

Substitution of cellulose acetate hydrogen phthalate, polyvinyl alcohol and gelatin, and polyvinyl pyrrolidone and polyvinyl hydrogen phthalate, respectively, for the copolymer detailed above, fails to provide the efficacious separation of the image-receiving element, subsequent to transfer processing, afforded by the instant polymeric composition.

It will be recognized that, where desired, the (ethylene/maleic acid) copolymer may be employed in the form of a salt thereof, for example, an alkali metal, ammonium or amine salt. It will also be recognized that copolymers may be employed which possess varying ratios of maleic anhydride/maleic acid components, for example, copolymers prepared by subjecting of the anhydride to a controlled degree of aqueous hydrolysis to provide the ratio selected, as well as a physical mixture of the anhydride and the free acid copolymers.

The preceding color image-forming components, that is, 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, for example, 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 dye developer.

The dye developers employed may be incorporated in or behind the respective silver halide emulsion. As illustrated, the dye developer may, for example, be in a coating or layer behind the silver halide emulsion and such a layer of dye developer may be applied by the use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer.

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, toluhydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Patent No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethylenimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in the silver halide emulsion strata or the strata containing the dye developers. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the pres-

ence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Ser. No. 50,851, now U.S. Patent 3,173,786, filed Aug. 22, 1960.

In products employed in the diffusion transfer processes 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 film of the type just mentioned is provided by the Polaroid Land Camera, sold by Polaroid Corporation, Cambridge, Mass., or similar camera structure such, for example, as the roll film type camera forming the subject matter of U.S. Patent No. 2,435,717 or the film pack type camera forming the subject matter of U.S. Patent No. 2,991,702. 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 require 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.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, silver halide solvents; etc., other than those specifically mentioned, provided that the pH of the composition is initially in excess of at least 10, for most favorable results, and most preferably in excess of 12. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

The support layers referred to may comprise any of the various types of conventional rigid or flexible supports, for example, glass, paper, metal, and polymeric films of both synthetic types and those derived from naturally occurring products. Suitable materials include paper; aluminums; polymethacrylic acid, methyl and ethyl esters; vinyl chloride polymers; polyvinyl acetal; polyamides such as nylon; polyesters such as polymeric films derived from ethylene glycol terephthalic acid; and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate.

The nature and construction of rupturable containers is well understood in the art; see, for example, U.S. Patent No. 2,543,181, issued Feb. 27, 1951, and U.S. Patent No. 2,634,886, issued Apr. 14, 1953.

It will be apparent that, by appropriate selection of the image-receiving element materials from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency.

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.

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

Throughout the specification and appended claims, the expression "positive image" has been used. This expression 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.

Throughout the specification and claims, the expression "superposing" has been used. This expression is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact or in separated condition and including between them at least one layer or stratum of a material which is a viscous liquid containing a hydroxyalkyl cellulose ether.

In all preferred embodiments of this invention, the polymeric acid layer preferably is thicker than the image-receiving layer and has an appreciably higher mg./ft.² coverage. The image-receiving layer is preferably about 0.25 to 0.4 mil thick, the polymeric acid layer about 0.3 to 1.5 mil thick, and the spacer layer about 0.1 to 0.7 mil thick.

In addition to the described essential layers, it will be recognized that the image-receiving elements may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion.

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 or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process of forming diffusion transfer images in color which comprises, in combination, the steps of exposing a photosensitive element comprising a plurality of layers including a support layer and a silver halide emulsion layer having positioned contiguous thereto a dye which is a silver halide developing agent; developing said element by means of an aqueous alkaline solution containing a hydroxyalkyl cellulose ether and having an initial pH of not less than about 12 positioned intermediate said emulsion layer and the polymeric layer of a superposed image-receiving element which comprises a plurality of essential layers including, in sequence, a support layer, a polymeric acid layer, an image-receiving layer, and a polymeric layer comprising about 5 to 25 milligrams per square foot of a copolymer selected from the group consisting of (ethylene/maleic anhydride) and (ethylene/maleic acid) copolymers; immobilizing said dye in the developed areas of said element, as a result of development, forming thereby an imagewise distribution of

mobile dye, as a function of the point-to-point degree of development of said element; transferring, by imbibition, at least a portion of said imagewise distribution of mobile dye to said superposed image-receiving element, to provide to said element a dye image; and separating said superposed image-receiving element from contact with said processing composition subsequent to transfer image formation.

2. A multicolor diffusion transfer process which comprises, in combination, the steps of exposing a photosensitive element comprising a plurality of layers including blue-sensitive, green-sensitive and red-sensitive silver halide gelatin emulsion layers mounted on a common support, said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers having positioned contiguous thereto, respectively, yellow, magenta and cyan dyes, each of said yellow, magenta and cyan dyes being silver halide developing agents; developing said element by distributing an aqueous alkaline processing composition containing a hydroxyalkyl cellulose ether and having an initial pH of not less than about 12 between said element and superposed image-receiving element comprising a plurality of layers including, in sequence, a support layer, a polymeric acid layer, a polymeric image-receiving layer, and a polymeric layer comprising about 5 to 25 milligrams per square foot of a copolymer selected from the group consisting of (ethylene/maleic anhydride) and (ethylene/maleic acid) copolymers; immobilizing said yellow, magenta and cyan dyes, in exposed areas, as a result of development, thereby forming an imagewise distribution of mobile yellow, magenta and cyan dye, as a function of the point-to-point degree of exposure of said element; transferring by imbibition, at least a portion of each of said imagewise distributions of mobile dye to said superposed image-receiving element, to provide to said polymeric image-receiving layer a multicolor positive transfer dye image; and separating said image-receiving element from contact with said processing composition subsequent to transfer image formation.

3. As a product, an image-receiving element for use in photographic diffusion transfer color processes which comprises a laminate which contains a plurality of essential layers, including, in sequence, a support layer, a polymeric acid layer, a polymeric image-receiving layer, and a polymeric layer comprising about 5 to 25 milligrams per square foot of a copolymer selected from the group consisting of (ethylene/maleic anhydride) and (ethylene/maleic acid) copolymers.

4. As a product, a photographic film unit which comprises, in combination, a photosensitive element containing a plurality of layers including a support layer and a silver halide emulsion layer having positioned contiguous thereto a dye which is a silver halide developing agent; an image-receiving element which comprises a plurality of essential layers including, in sequence, a support layer, a polymeric acid layer, a polymeric image-receiving layer, and a polymeric layer comprising about 5 to 25 milligrams per square foot of a copolymer selected from the group consisting of (ethylene/maleic anhydride) and (ethylene/maleic acid) copolymers; and a frangible container retaining an aqueous alkaline processing composition including a hydroxyalkyl cellulose ether and having a pH of not less than about 12, said frangible container attached to one of said photosensitive elements and an image-receiving element and positioned to distribute its contents, upon application of compressive pressure thereto, intermediate said emulsion layer and the exterior polymeric layer of said image-receiving element.

5. As a product, a photographic film unit which comprises, in combination, a photosensitive element containing a plurality of essential layers including, in sequence, a support layer, a cyan dye containing layer, a red-sensitive silver halide gelatin emulsion layer, a magenta dye containing layer, a green-sensitive silver halide gelatin emulsion layer, a yellow dye containing layer, and a blue-

sensitive silver halide gelatin emulsion layer, each of said cyan, magenta and yellow dyes being silver halide developing agents, and having affixed at one edge thereof an image-receiving element which comprises a plurality of essential layers including in sequence, a support layer, a polymeric acid layer, a polymeric image-receiving layer, and a polymeric layer comprising about 5 to 25 milligrams per square foot of a copolymer selected from the group consisting of (ethylene/maleic anhydride) and (ethylene/maleic acid) copolymers, a frangible container retaining an aqueous alkaline processing composition including hydroxyethyl cellulose and having a pH of not less than about 12, said frangible container attached to

one of said photosensitive element and said image-receiving element and positioned to distribute its contents, upon application of compressive pressure thereto, intermediate said blue-sensitive emulsion layer and the exterior polymeric layer of said image-receiving element.

References Cited

UNITED STATES PATENTS

2,378,629	6/1945	Hanford	-----	260—78.5
2,983,606	5/1961	Rogers	-----	96—3

NORMAN G. TORCHIN, *Primary Examiner.*