

Jan. 18, 1966

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3,230,082

COLOR PROCESSES AND PRODUCTS

Filed May 14, 1962

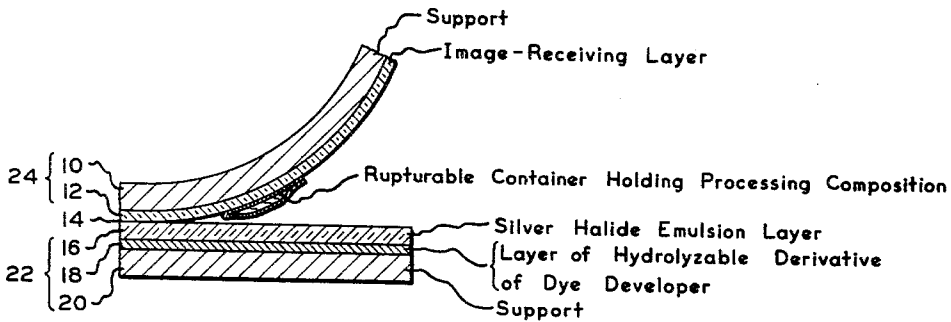


FIG. 1

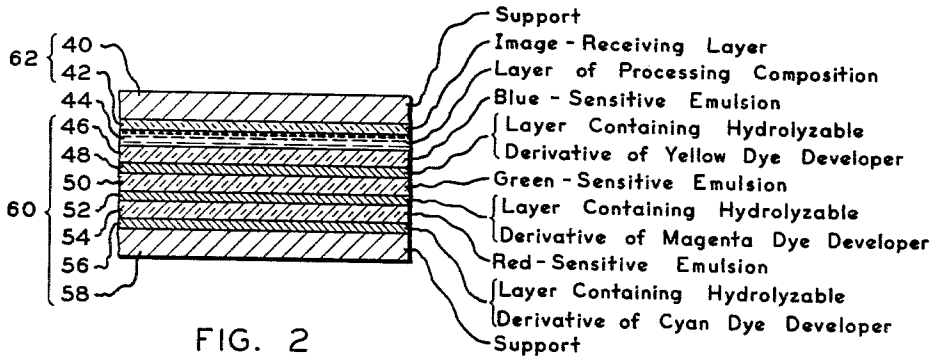


FIG. 2

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3,230,082

COLOR PROCESSES AND PRODUCTS

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 Filed May 14, 1962, Ser. No. 194,359
 18 Claims. (Cl. 96-3)

This application is in part a continuation of our co-pending application, Serial No. 669,542, filed July 2, 1957 (now abandoned) and in part a continuation of our co-pending application Serial No. 565,135, filed February 13, 1956.

This invention relates to photography and, more particularly, to an improvement in photographic diffusion transfer processes for obtaining color images by the utilization of dye developers.

U.S. Patent No. 2,983,606, issued May 9, 1961 to Howard G. Rogers discloses and claims diffusion transfer processes wherein dye developers are utilized in the development of an exposed photosensitive emulsion and a positive color image is imparted to a superposed image-receiving layer by diffusion of unreacted dye developer originating from undeveloped areas of the exposed photosensitive emulsion. The dye developers of this process are dyes which contain, in the same molecule, a silver halide developing function and a chromophoric system of a dye. A particularly useful class of dye developers are those containing a hydroquinonyl developing function.

The processes of the type just mentioned employ dye developers which are initially mobile and diffusible and depend upon the immobilization of the dye developer in exposed areas of the photosensitive emulsion to prevent transfer thereof to the superposed image-receiving layer.

In our copending application Serial No. 565,135, filed February 13, 1956, we have disclosed the use of dye developers to form multicolor transfer images using integral multilayer photosensitive elements and a single image-receiving layer. In multicolor transfer processes of this type, various mechanisms may be used to delay the diffusibility or availability for transfer of nonimmobilized dye developers until after substantial development has occurred. Such delayed or deferred diffusion of unoxidized dye developer greatly increases the control thereof, improving color separation and reducing the possibility of interfering development, i.e., oxidation in an emulsion other than that with which the dye developer is initially associated with. Thus it is desired that the dye developer be retained and reacted in the appropriate emulsion before any large amount of transfer is effected. Such delayed diffusibility insures that the dye developer is reacted to the extent required by the degree of exposure, and that the proper dye developer is reacted as the result of the exposure of silver halide of a given sensitivity.

We have now discovered that delayed diffusibility may be obtained by the utilization of a derivative of a dye developer, which derivative contains a grouping removable during processing by a hydrolysis or displacement reaction, and herein referred to as a "hydrolyzable" derivative, whereby diffusion transfer processes may be substantially improved. Such hydrolyzable derivatives initially are of reduced mobility or substantially immobile, and also may be less reactive until such removal of such grouping is effected.

It is a primary object of this invention to provide novel photographic processes and products whereby improved control of the transfer of unoxidized dye developer to an image-receiving layer may be obtained.

A further object of this invention is to provide novel photographic processes and products for obtaining color images by a diffusion-transfer reversal process wherein the dye developer is initially present in the form of a

hydrolyzable derivative of said dye developer and wherein said hydrolyzable derivative is subjected to hydrolysis conditions during processing.

Another object of this invention is to provide novel photographic processes and products wherein a hydrolyzable derivative of a dye developer is employed and said dye developer is of relatively low mobility until hydrolysis occurs.

A further object of this invention is to provide photographic processes and products wherein hydrolyzable derivatives of dye developers are employed and said dye developers are initially unreactive and are rendered reactive by hydrolysis.

A further object of this invention is to provide photographic processes and products for use in multicolor diffusion transfer processes utilizing dye developers which contain groups removable during processing, whereby improved color separation may be obtained.

A further object of this invention is to provide novel photographic processes and products for obtaining color images by a diffusion transfer process by the utilization of a hydrolyzable ester of a dye developer and, more particularly, a hydrolyzable ester of a polyhydroxy developing function or of an aliphatic hydroxyl group contained in the dye developer molecule.

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 taken in connection with the accompanying drawing wherein:

FIGURE 1 is a diagrammatic cross-sectional view of one embodiment of a photographic product for use in obtaining monochrome images in accordance with this invention and comprising a photosensitive element, an image-receiving element and a rupturable container holding a processing composition; and

FIG. 2 is a diagrammatic cross-sectional view of one embodiment of this invention, for use in obtaining multicolor images, during processing and comprising a multilayer photosensitive element, an image-receiving element and a processing composition.

As stated above, it has been proposed to form color images by a diffusion transfer process utilizing dye developers. In processes of this type, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, 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 embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with an image-receiving element. The liquid processing composition permeates the emulsion to initiate development of the exposed silver halide emulsion. The dye developer is immobilized or precipitated in developed areas as a consequence of the development. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the oxidation product of the dye developer, 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. In undeveloped and partially developed areas of the emulsion, dye developer is unreacted and diffusible, and thus provides an imagewise 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. Under certain conditions, the layer of the liquid processing composition may be utilized as the image-receiving layer. The image-receiving layer receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide a transfer 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 element from the photosensitive element at the end of the suitable imbibition period.

Where such dye developers are initially mobile and free to diffuse to the superposed image-receiving layer in the absence of oxidation or other immobilization reactions, such initial mobility and freedom to diffuse may give rise to premature transfer of dye developer from exposed areas, resulting in highlight stain in the case of monochromes, or in incomplete color isolation in multicolor processes. We have now discovered that dye developers may be rendered initially less mobile or substantially immobile by utilization thereof in the form of a hydrolyzable derivative, i.e., a derivative containing a grouping removable during processing, and particularly in the form of a hydrolyzable ester or salt. In accordance with this invention, the hydrolyzable derivative is substantially immobile or less mobile prior to hydrolysis, and may also be substantially less reactive prior to hydrolysis.

Such hydrolyzable derivatives may be referred to as "hydrolyzable dye developers." In accordance with this invention, a "hydrolyzable dye developer" is a dye developer containing a grouping, removable by hydrolysis, which grouping renders the dye developer substantially less mobile and/or less soluble until such grouping is removed by hydrolysis. It may also be less reactive, as where the developing function is rendered inactive, until hydrolysis occurs. By "hydrolysis," we mean alkaline hydrolysis, i.e., hydrolysis by a solution at least sufficiently alkaline to permit development, including both the splitting of a covalent bond, as in the case of an ester, and displacement, as in the case of the displacement of the anion or cation of a salt. In a preferred embodiment, the desired hydrolysis is initiated without substantial delay after solution in the processing composition, and the hydrolysis of the quantity of dye developer required to provide the desired density should be substantially complete before the completion of the desired imbibition period, which period may be approximately one to ten minutes.

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. Preferred dye systems are azo and anthraquinone dye systems. Examples of representative dye developers are given in the previously mentioned U.S. Patent No. 2,983,606 of How-

ard G. Rogers, and in the copending applications referred to therein.

In one embodiment of this invention, it is contemplated to use the dye developer in the form of a hydrolyzable derivative, which hydrolyzable derivative renders the developing function of said dye developer unreactive until hydrolysis is effected. Thus, a dye developer containing a polyhydroxy developing function, e.g., a hydroquinonyl group, may be employed in the form of a hydrolyzable ester wherein one or more of said hydroxyl groups have been esterified.

Application of the liquid processing composition provides an alkaline solution capable of effecting hydrolysis of such hydrolyzable derivative. The rates of solution and hydrolysis are preferably at least slightly less than the rate of permeation of the emulsion by said processing composition, so that a dye developer is not carried "backwards" into another emulsion by the processing composition. Until hydrolysis occurs, the hydrolyzable dye developer is substantially unreactive and unable to participate in the development of the latent image present in the exposed emulsion, and is also at least substantially less mobile and thus exhibits less tendency of premature transfer. Hydrolyzable dye developers wherein the hydrolyzable grouping is attached to the developing function should exhibit a relatively fast rate of hydrolysis. The unhydrolyzed dye developer is preferably unable to transfer to the image-receiving layer, during the imbibition period, in the absence of such hydrolysis. As hydrolysis occurs and the groups are hydrolyzed off of the developing function, the dye developer is rendered mobile and reactive to participate in the development of the exposed emulsion. It will be noted that such esterified hydroquinonyl dye developers also exhibit reduced initial mobility since the activated hydroquinonyl grouping is unavailable to provide additional solubility or mobility until hydrolysis occurs.

Examples of a suitable hydrolyzable dye developer of this type are ethoxalyl esters of hydroquinonyl-containing dye developers wherein one or both of the hydroxyl groups of the hydroquinonyl portion have been esterified.

The use of a hydrolyzable dye developer wherein the hydrolyzable group or groups are attached to the developing function provides a means of preventing reaction of the dye developer during storage of the photosensitive element. Hydrolyzable dye developers of this type should have faster hydrolysis rates than hydrolyzable dye developers wherein the hydrolyzable grouping is attached to the dye portion.

In another and preferred embodiment of this invention, the hydrolyzable dye developer is initially capable of participating in the development of the latent image and of being oxidized to a less mobile form, but initially contains a grouping removable by hydrolysis, which grouping renders the dye developer initially less mobile or substantially immobile prior to hydrolysis. Thus, one may employ a dye developer containing in the dye portion thereof an aliphatic hydroxyl group which is capable of being esterified to form a hydrolyzable ester, e.g., an oxalyl ester. Such hydrolyzable dye developers have reduced mobility due to the extra bulk provided by the hydrolyzable ester grouping but have the developing function unencumbered and thus remain capable of being oxidized during development of the exposed silver halide emulsion.

Where the hydrolyzable group is attached to the dye portion of the dye developer and thus does not affect the developing function, it is particularly desirable to employ a dye developer which, when hydrolyzed, exhibits an increase in its rate of transfer. Thus, the invention permits the utilization of a dye developer whose rate of diffusion might be too rapid to permit effective control if utilized initially in the free or hydrolyzed form.

The hydrolyzable dye developers of this invention are preferably physically close to the silver halide, e.g., by

being incorporated in the emulsion in the form of particles. They are thus readily available for reaction despite their reduced initial mobility. Where the hydrolyzable grouping is attached to the dye portion, leaving the developing function free to react, such hydrolyzable dye developer may be reacted even before hydrolysis occurs.

Where the developing function is available for reaction, hydrolysis may start immediately but the rate of hydrolysis preferably is initially less than the rate of development but should increase until it approximates the rate of development. Thus, the rate of hydrolysis should exhibit a lag behind the rate of development. In general, if one were to plot the development and hydrolysis rates against time, the development rate curve should have a relatively steep slope, and the hydrolysis rate curve should have a lower slope, or, if it exhibits an induction period, it may have a slope similar to that of the development rate curve. One may increase the rate of hydrolysis by using a hydrolyzable grouping which, when split off by hydrolysis, provides a solvent or cosolvent and thus increases the rates of solution, hydrolysis and transfer. As an example of such process-generated solvents or cosolvents, mention may be made of keto and hydroxy compounds having a solvent effect.

A class of dye developers particularly useful for the preparation of hydrolyzable dye developers are those which contain an aliphatic hydroxyl group capable of reaction, e.g., with an acid chloride, such as an oxalyl chloride, to provide a hydrolyzable ester grouping. Alternatively, the dye developer may contain a suitable aliphatic acid group which may be converted to a hydrolyzable ester.

In a further embodiment of this invention, it is contemplated to employ, as a hydrolyzable dye developer, a dye developer wherein the developing function is attached to the dye function by a hydrolyzable grouping, the rate of hydrolysis being slower than the rate of development. In unexposed areas, hydrolysis will release the dye portion of diffusion to the image-receiving element. In exposed areas, reaction of such hydrolyzable dye developer will so reduce its solubility as to prevent hydrolysis occurring during the imbibition period. Such a hydrolyzable dye developer has advantageous properties for use in multi-color transfer processes, since the diffusible dye portion released by hydrolysis is substantially photographically unreactive and thus would not interfere with development of any other emulsion layer through which it may diffuse. The hydrolyzed grouping containing the developing function preferably is sufficiently immobile as to prevent transfer or reaction in other emulsions.

Another class of hydrolyzable dye developers contemplated in accordance with this invention comprises hydrolyzable salts of dye developers, i.e., dye developers containing displaceable cations or anions. Suitable salts of dye developers include amine salts, e.g., diphenyl guanidine or "rosin amine D" salts of dye developers containing sulfonic acid groups as well as sulfonic acid salts of amine-containing dye developers. ("Rosin amine D" is a product of Hercules Powder Co., Wilmington, Delaware, the main component of which is a $C_{21}H_{30}N$ primary amine.)

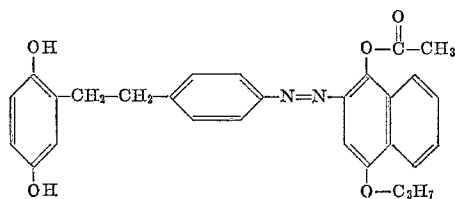
It is also contemplated to employ heavy metal salts of dye developers, e.g., barium salts of carboxy or sulfo-containing dye developers.

Where a hydrolyzable dye developer is too rapidly solubilized by alkali if molecularly dispersed, such hydrolyzable dye developer may be used in the form of particles, thus reducing the rate of solubilization.

In all embodiments of this invention where the developing function is available for reaction prior to hydrolysis, the rate of hydrolysis of the hydrolyzable dye developer associated with exposed areas will be lower due to the exhaustion of alkali due to development and consequent loss of alkali for hydrolysis and for solubiliza-

tion, and also due to the lower solubility of the oxidized form of the hydrolyzable dye developer. In unexposed areas, the rate of hydrolysis will be high as a result of the availability of alkali and the fact that the hydrolyzable dye developer is in the reduced form and thus is substantially more soluble. In addition, as previously mentioned, the hydrolysis rate of such unoxidized, hydrolyzable dye developer may be increased by the generation of a solvent or cosolvent by the hydrolysis of a portion of such developer.

Hydrolyzable dye developers offer a mechanism by which the color of the dye developer may be temporarily shifted toward lower wave lengths whereby their use in a photosensitive element will result in a reduced absorption of light available for exposure of the associated silver halide emulsion or inner silver halide emulsion layers. Hydrolyzable dye developers of this type utilize a hydrolyzable grouping attached to a grouping, e.g., an amino grouping, which is part of the chromophoric system of the dye, and such amino groups may be appropriately acylated, e.g., by a perfluoro acid grouping, to provide a hydrolyzable grouping which serves to shift the absorption properties of the dye to lower wave lengths. The use of hydrolyzable dye developers which exhibit a bathochromic shift in the spectral absorption characteristics is disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 789,080, filed January 26, 1959. An example of a particularly useful hydrolyzable dye developer of this type is:



1-acetoxy-2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-naphthalene

In certain instances, the sensitivity of a silver halide emulsion may be affected by a reaction between the associated dye developer and a sensitizer employed in said silver halide emulsion, or the displacement of sensitizing dye adsorbed on the silver halide, resulting in decreased sensitivity. It has been found that the use of hydrolyzable derivatives of such dye developers offers a means of restricting the mobility of the dye developer and thus avoiding or reducing such desensitization side reactions which occur during storage of the photosensitive product. An example of such a hydrolyzable dye developer is the reaction products of 1,4-bis-[α -methyl- β -(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone and butyl chloroformate.

It will be noted that in the two embodiments of this invention last mentioned above the role of the hydrolyzable dye developer permits the use in such embodiments of a hydrolyzable grouping which has a relatively rapid rate of hydrolysis.

It is also contemplated to employ a hydrolyzable dye developer wherein hydrolyzable groupings are attached to both the developing function and the dye portion of the dye developer. Thus a hydroquinonyl dye developer may have one or both of the hydroxyl groups of the hydroquinonyl portion esterified to form a hydrolyzable ester grouping and may also have an aliphatic hydroxyl group in the dye portion thereof similarly esterified to a hydrolyzable ester grouping. In use, the ester grouping of the hydroquinonyl portion, being aromatic in nature, would have a faster hydrolysis rate than the aliphatic-type ester of the dye portion. Hydrolysis would thus permit reaction of the hydroquinonyl grouping to occur before hydrolysis was completed.

In all embodiments of this invention, the group removable by hydrolysis may provide a means of mordanting the dye developer. It is also within the scope of this invention to have the group which is removable by hydrolysis as a part of the structure of a polymer, e.g., the polymeric carrier material of the emulsion. It will be understood that the grouping removed by hydrolysis should not interfere with processing or be deleterious to the transfer image. Suitable precautions may be taken to avoid transfer of such groupings, e.g., by the use of long chain, relatively nondiffusible groups.

In accordance with this invention, it is contemplated to utilize a hydrolyzable dye developer in both monochromatic and multicolor diffusion-transfer reversal processes. It is contemplated to use at least one of the dye developers employed in multicolor diffusion-transfer reversal processes in the form of a hydrolyzable dye developer. Significant improvements may result from the use of even one hydrolyzable dye developer in multicolor processes. It is also contemplated to employ a plurality of hydrolyzable dye developers containing different types of hydrolyzable groups.

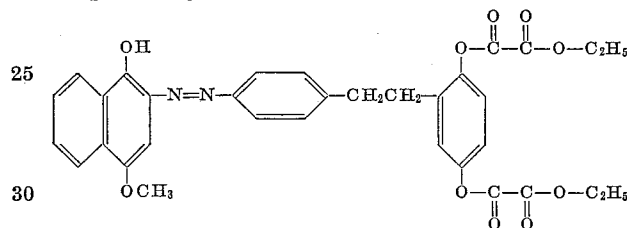
FIGURE 1 of the accompanying drawing illustrates one method of processing a silver halide emulsion to obtain a monochromatic transfer image in accordance with this invention. A photosensitive element 22 comprises a support 20, a layer 18 containing a hydrolyzable derivative of dye developer and a silver halide emulsion layer 16. As shown in the particular embodiment depicted in FIG. 1, the photosensitive element 22 is shown in a spread-apart relationship (as, for example, during exposure) with an image-receiving element 24 having mounted thereon a rupturable container 14 holding a processing composition. The image-receiving element 24 comprises a support 10 and an image-receiving layer 12. After exposure, the image-receiving element 24 is brought into superposed relationship with the photosensitive element 22 and the rupturable container 14 is ruptured by application of suitable pressure, e.g., by advancing between a pair of rollers (not shown), and a layer of the liquid composition is spread between the superposed elements. The processing composition permeates the silver halide emulsion layer 16 and the layer 18 containing the hydrolyzable dye developer. Assuming, for example, that the hydrolyzable dye developer is of the type having the hydrolyzable grouping attached to the dye portion thereof, said hydrolyzable dye developer will exhibit a reduced mobility and/or reduced solubility in the processing composition. The hydrolyzable dye developer, though having a relatively low mobility, is capable of participating in the development reaction since the developing function is free of hydrolyzable groups. In exposed areas, the hydrolyzable dye developer will be reacted, at least to some extent, even before hydrolysis of the hydrolyzable grouping has occurred. Hydrolysis of the hydrolyzable grouping of the dye portion will proceed and as the hydrolyzable dye developer becomes hydrolyzed, its rate of mobility will increase. In unexposed areas, the dye developer will transfer to the superposed image-receiving element 24. Since the hydrolyzable dye developer exhibits "reduced mobility," a portion of the unreacted dye developer which transfers from unexposed areas may transfer in the nonhydrolyzed state. The

image-receiving element 24 is separated from its superposed relationship with the photosensitive element 22 after at least a portion of the unreacted dye developer has been transferred.

The following examples illustrate the use of hydrolyzable dye developers in diffusion transfer processes in accordance with this invention, and are given for purposes of illustration only.

Example 1

A photosensitive element similar to that shown in FIG. 1 is prepared by applying to a support a coating of a hydrolyzable dye developer using a composition comprising 4% of the bis-ethoxalyl ester of 2-[p-(2',5'-dihydroxyphenethyl) - phenylazo] - 4 - methoxy - 1 - naphthol [resulting from the reaction thereof with ethoxalyl chloride, as disclosed and claimed in the copending application of Myron S. Simon et al., Serial No. 813,701, filed May 18, 1959, as a continuation-in-part of, and replacement for, Serial No. 697,808, filed November 21, 1957 (now abandoned)], i.e., the hydrolyzable dye developer having the formula:



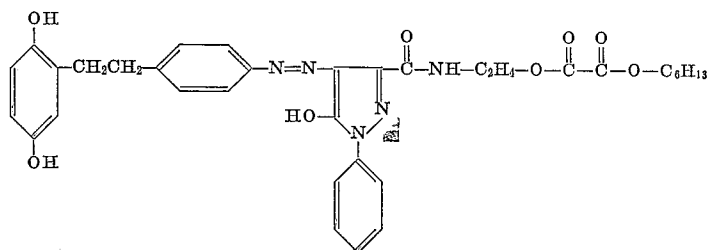
dissolved in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of tetrahydrofuran and acetone. After this coating has dried, a silver iodobromide emulsion is applied. An image-receiving element is prepared by coating a cellulose acetate-coated baryta paper with a solution comprising 4% N-methoxymethylpolyhexamethylene adipamide in ethanol. After exposure, the thus-prepared photosensitive element is brought into superposed relationship with said image-receiving element as an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose (high viscosity) ---	5.0
Potassium bromide -----	0.2
Sodium hydroxide -----	3.0
1-phenyl-3-pyrazolidone -----	0.2

is spread between said elements. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta positive dye image which has a D_{max} of 1.97. The transfer image so obtained is quite similar to that obtained employing the same dye developer initially in the free or non-esterified hydroquinonyl form. The density and contrast obtained clearly demonstrates that the esterified dye developer hydrolyzed during processing.

Example 2

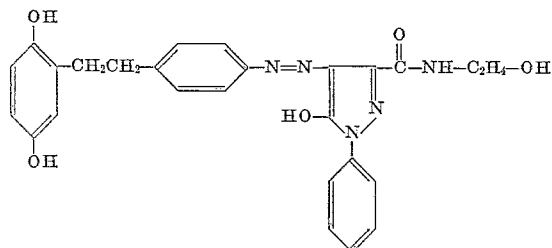
The procedure described in Example 1 is repeated using, as the hydrolyzable dye developer, 5% of a n-hexyloxyalyl ester of a dye developer wherein the ester group is attached to the dye portion, said hydrolyzable dye developer having the formula:



[prepared by reaction of n-hexyloxalyl chloride with the corresponding hydroxyl-containing dye developer, as disclosed and claimed in the copending application of Elkan R. Blout, Saul G. Cohen, Milton Green and Myron S. Simon, Serial No. 813,702, filed May 18, 1959, as a continuation-in-part of, and replacement for, Serial No. 697,809, filed November 21, 1957 (now abandoned)], and an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose (high viscosity) -----	4.5
Potassium bromide -----	0.2
Sodium hydroxide -----	2.5
1-phenyl-3-pyrazolidone -----	0.2

For comparison purposes, a control was run using the corresponding nonesterified dye developer, i.e., the dye developer of the formula:



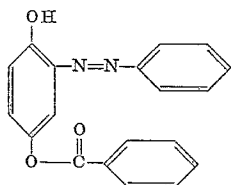
The positive transfer images obtained may be summarized by the following table:

Imbibition Period	D _{max.} -Control	D _{max.} -Esterified Dye Developer
10 seconds.....	0.96	0.70
20 seconds.....	1.51	1.22
1 minute.....	2.0+	2.0+

It will be apparent from the above results that the esterified, hydrolyzable dye developer exhibited initially reduced mobility but that the rate of mobility increased rapidly toward the end of the one minute imbibition period, thus indicating that hydrolysis of the mobility-reducing ester grouping occurred.

Example 3

A photosensitive element similar to that shown in FIG. 1 is prepared by coating baryta paper with a composition comprising 1.0% of phenylazohydroquinone monobenzoate, i.e.



dissolved in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of tetrahydrofuran and acetone. After the layer of hydrolyzable dye developer has dried, a blue-sensitive silver iodobromide emulsion is applied and allowed to dry. The resulting photosensitive element, after exposure, is processed by being brought into superposed relationship with an image-receiving element, as an aqueous liquid processing composition comprising:

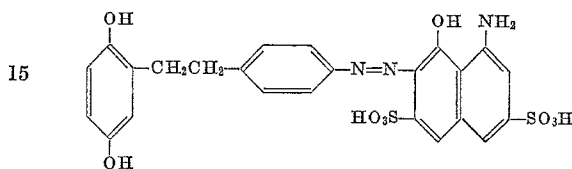
	Percent
Sodium hydroxide -----	10.0
Sodium carboxymethyl cellulose (high viscosity) --	4.0
Potassium bromide -----	0.2
1-phenyl-3-pyrazolidone -----	0.2

is spread between said elements. The image-receiving element is prepared by coating a cellulose-acetate-coated baryta paper with an aqueous 6% polyvinyl alcohol solu-

tion. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a yellow-brown positive dye image.

Example 4

A photosensitive element similar to that shown in FIG. 1 is prepared by coating a support with a composition comprising 7.5% of the diphenylquandine salt of 1-amino-7-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-8-naphthol-3,6-disulfonic acid, i.e., the diphenylquandine salt of:

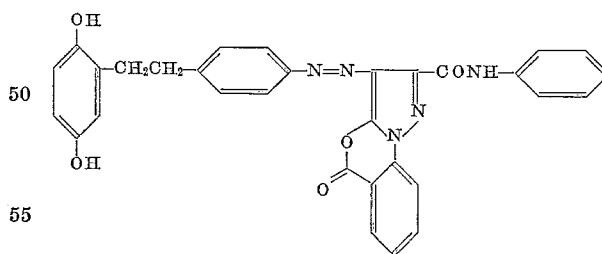


in a 50:50, by volume, acetone-tetrahydrofuran solution containing 2.0% cellulose acetate hydrogen phthalate. After the layer of dye developer has dried, a layer of green-sensitive silver iodobromide emulsion is applied and allowed to dry. The resulting photosensitive element is exposed, and brought into superposed relationship with an image-receiving element as an aqueous liquid composition comprising:

	Percent
Sodium carboxymethyl cellulose (high viscosity) -----	4.0
NaOH -----	1.0
5-nitrobenzimidazole -----	0.1
N-phenethyl- α -picolinium bromide -----	1.0

is spread between said elements. The image-receiving element comprises a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine on a baryta paper support. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magneta positive image.

As an example of yet another type of hydrolyzable dye developer, mention may be made of lactones of 1-o-carboxyphenyl-5-pyrazolone azo dye developers, e.g., 1-(o-carboxyphenyl)-3-carboxanilido-4-[p-(β -hydroxyethyl)-phenylazo]-5-hydroxy pyrazole lactone, having the following structural formula:



the preparation of which are disclosed and claimed in the copending application of Samuel Dershowitz and Robert B. Woodward, Serial No. 101,264, filed April 6, 1961.

It is also contemplated to utilize, particularly in the preparation of monochromatic images, a film structure wherein the silver halide emulsion is coated over the image-receiving layer and the processing composition must permeate through the emulsion before reaching the image-receiving layer. A structure of this type is described, for example, in U.S. Patent No. 2,661,293, issued to Edwin H. Land on December 1, 1953, and particularly with respect to FIG. 7 of said patent.

Multicolor images may be obtained using 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 ar-

ranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the aforementioned U.S. Patent No. 2,983,606 issued to Howard G. Rogers and also in U.S. Patent No. 2,968,554 issued January 17, 1961 to Edwin H. Land. 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 the last-mentioned 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 having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

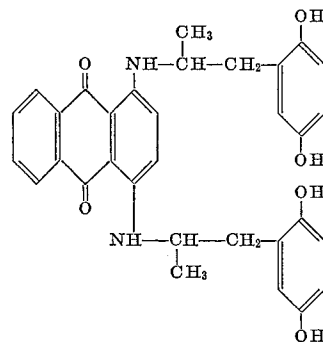
Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element such as disclosed and claimed in our previously mentioned copending application, Serial No. 565,135, wherein at least two selectively sensitized photosensitive strata 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.

A multilayer photosensitive element of the type just described is illustrated in FIG. 2 of the accompanying drawing and is depicted during processing. An exposed photosensitive element 60 comprises: a support 58; a layer 56 containing a cyan hydrolyzable dye developer; a layer 54 of a red-sensitive silver halide emulsion; a layer 52 of a magenta hydrolyzable dye developer; a layer 50 of a green-sensitive silver halide emulsion; a layer 48 containing a yellow hydrolyzable dye developer; and an outermost layer 46 of a blue-sensitive silver halide emulsion. As noted above, each set of silver halide emulsion and associated dye developer strata may be separated from the other sets thereof by suitable spacer strata (not shown), 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 layer and such yellow filter may be incorporated in the spacer layer. Where the yellow hydrolyzable dye developer is of the appropriate color and present in a state capable of functioning as a yellow filter, a separate yellow filter may be omitted.

Referring again to FIG. 2, a multilayer photosensitive element 60 is shown in processing relationship with an image-receiving element 62 and a layer 44 of a processing composition. The image-receiving element 62 comprises a support 40 and an image-receiving layer 42. As noted in connection with FIGURE 1, the liquid processing composition is effective to initiate development of the latent image in the respective exposed silver halide strata and also to effect hydrolysis of the hydrolyzable dye developer. After a suitable imbibition period, during which at least a portion of the dye developer associated with unexposed areas of each of said emulsions is transferred to the superposed image-receiving element 62, the latter element is separated to reveal the positive multicolor image. It will be understood that where the hydrolyzable grouping is attached to the dye portion of the dye developer, the

dye developer transferred from unexposed areas may comprise both hydrolyzed dye developer and non-hydrolyzable dye developer.

It should be noted that it is within the scope of this invention to utilize, in multicolor diffusion transfer processes, one or more of the requisite dye developers in the form of hydrolyzable dye developers. In certain instances, for example, it may be desirable to employ hydrolyzable dye developers in association with the blue-sensitive and green-sensitive silver halide emulsions, together with a non-hydrolyzable dye developer, i.e., a dye developer free of such hydrolyzable groupings. As an example of a suitable cyan dye developer which may be utilized with yellow and/or magenta hydrolyzable dye developers, and which is utilized free of hydrolyzable groupings, mention may be made of 1,4-bis-[α -methyl- β -(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone of the formula:



A further technique for obtaining multicolor images employs a plurality of photosensitive elements associated with appropriate numbers of image-receiving elements and adapted to be treated with one or more liquid processing compositions, the appropriate dye developers being incorporated in the photosensitized elements. Examples of film structures of this type are disclosed in U.S. Patent No. 2,647,049, issued to Edwin H. Land on July 28, 1953.

The dye developers utilized in the processes of this invention may be incorporated in the photosensitive elements, for example, in, on or behind the respective silver halide emulsion. In certain instances, where a plurality of dye developers are employed to obtain a multicolor image and the yellow dye developer is employed in a non-hydrolyzable form, such non-hydrolyzable yellow dye developer may be utilized in the photosensitive element in a manner similar to the other dye developers, or it may be initially contained in the liquid processing composition. The dye developer is preferably 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 dye developer. In a particularly useful embodiment, the dye developer is dissolved in a water-immiscible solvent, the resulting solution is dispersed in gelatin and then coated to provide the dye developer layer.

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 might 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 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 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 1,000 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 patents and copending applications herein mentioned and also in examples herein given. Under certain circumstances, it may be desirable to apply a liquid processing composition to the photosensitive element prior to exposure, in accordance with the technique described in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955 (now U.S. Patent No. 3,078,816, issued April 30, 1963.)

It will be noted that the liquid processing composition may, and in the above examples does, contain an auxiliary or accelerating silver halide developing agent, which is substantially colorless in at least the unoxidized form. Particularly useful accelerating developing agents include 3-pyrazolidone developing agents, and preferably 1-phenyl-3-pyrazolidone which is available under the trade name "Phenidone" from Ilford Limited, 4,4-dimethyl-1-phenyl-3-pyrazolidone, 4'-methylphenylhydroquinone, 2,5-triptycene diol, p-methylaminophenol, benzylaminophenol, phenylhydroquinone. 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 and claimed in the copending application of Howard G. Rogers and Harriet W. Lutes, Serial No. 654,781, filed April 24, 1957, now U.S. Patent No. 3,039,869. 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 or in a stratum over the silver halide emulsion. 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 presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in the copending application of Milton Green and Howard G. Rogers, Serial No. 50,851, filed August 22, 1960 (now U.S. Patent No. 3,173,786, issued March 16, 1965).

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 dye 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 nature and construction of rupturable containers such as that shown in FIGURE 1 is well understood in the art; see, for example, U.S. Patent No. 2,543,181, issued to Edwin H. Land on February 27, 1951, and U.S. Patent No. 2,634,886, issued to Edwin H. Land on April 14, 1953.

The image-receiving element comprises an image-receiving layer of opaque or transparent material which is liquid permeable and dyeable from alkaline solutions and which has been illustrated for purposes of simplicity as comprising a single sheet of permeable material, for example, paper. This element, however, may comprise 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 liquid processing composition which is adapted to remain adhered to the support layer upon stripping.

As examples of useful image-receiving materials, mention may be made of nylon, e.g., N-methoxymethylpolyhexamethylene adipamide, polyvinyl alcohol, and gelatin, particularly polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine. The image-receiving element also may contain a development restrainer, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in the copending application of Howard G. Rogers and Harriet W. Lutes, Serial No. 50,849, filed August 22, 1960. 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.; polyvinyl alcohol with or without plasticizers; 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, such as container 14 in FIGURE 1, 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.

It is also to be understood that the invention may be successfully practiced without the use of a film-forming material in the liquid processing composition. As an il-

illustration, a nonviscous liquid processing composition is particularly applicable with the processing technique last mentioned above and may be applied to the exposed photosensitive element by imbibition or coating practices and may be similarly applied to the image-receiving element before said elements are brought into superposed relation or contact for carrying out the transfer of non-immobilized color-providing substances.

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.

In the use of certain auxiliary developing agents in accordance with this invention, a temporary stain may be observed on the image-receiving layer. This temporary stain disappears within a short time or may be removed immediately by washing or by swabbing with a slightly acidic solution. It has also been found that incorporating these developing agents in the photosensitive element, e.g., in the emulsion or in a layer behind the emulsion, minimizes or eliminates such temporary staining.

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 may be a viscous liquid.

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 transfer images in color comprising the steps of exposing a photosensitive element comprising a silver halide emulsion and a hydrolyzable dye developer, said hydrolyzable dye developer being a compound which is a dye and which compound contains a hydroquinonyl group, at least one of the hydroxyl groups of said hydroquinonyl group being esterified to provide an alkali hydrolyzable ester, applying an aqueous alkaline processing composition to said exposed photosensitive element and thereby hydrolyzing said hydrolyzable ester group to regenerate said hydroxyl groups, developing said exposed emulsion and oxidizing said hydrolyzed dye developer in developed areas as a result of said development, forming an imagewise distribution of diffusible, hydrolyzed, unoxidized dye developer in undeveloped areas as a function of the point-to-point degree of exposure of said emulsion, and transferring, by diffusion, at least a portion of said imagewise distribution of diffusible, hydrolyzed, unoxidized dye developer to a superposed image-receiving layer, to impart thereto a dye image.

2. A process of forming transfer images in color comprising the steps of exposing a photosensitive element comprising a silver halide emulsion and a dye developer, said dye developer being a compound which is both a silver halide developing agent and a dye, said compound also containing an alkali hydrolyzable ester group, permeating said photosensitive element with an aqueous alkali

line processing composition thereby initiating development of the exposed silver halide emulsion and also hydrolyzing at least a portion of said hydrolyzable ester group of said dye developer, oxidizing said dye developer in developed areas as a result of said development and forming, in undeveloped areas, an imagewise distribution of diffusible, unoxidized dye developer as a function of the point-to-point degree of exposure of said emulsion, and transferring, by imbibition, at least a portion of said imagewise distribution of diffusible, unoxidized dye developer to a superposed image-receiving layer to provide a positive dye image, said unoxidized dye developer being substantially nondiffusible to said image-receiving layer until said ester group has been hydrolyzed.

3. A process for forming transfer images in color comprising the steps of exposing a photosensitive element comprising at least two selectively sensitized silver halide emulsions, each of said silver halide emulsions having associated therewith a dye developer of a predetermined color, each said dye developer being a compound which is both a silver halide developing agent and a dye, at least one of said dye developers being present in the form of a hydrolyzable derivative of said dye developer which hydrolyzable derivative contains a grouping removable by alkaline hydrolysis during imbibition, applying an alkaline liquid processing composition to said exposed photosensitive element, developing each of said exposed silver halide emulsions and immobilizing dye developer associated with each emulsion in developed areas thereof as a result of development, hydrolyzing at least a portion of said hydrolyzable derivative, the resulting hydrolyzed dye developer being more diffusible than is said hydrolyzable derivative, forming an imagewise distribution of diffusible, unoxidized dye developer in undeveloped areas of each of said silver halide emulsions as a function of the point-to-point degree of exposure thereof, and transferring, by imbibition, at least a portion of each of said imagewise distributions of diffusible, unoxidized dye developer to a superposed image-receiving layer to form a multicolor, positive dye image, said development, hydrolysis and transfer being effected by the application of a single processing composition.

4. A process of forming transfer images in color as defined in claim 3, wherein said hydrolyzable derivative contains a hydrolyzable ester of an aliphatic hydroxyl group.

5. A process of forming multicolor transfer images comprising the steps of exposing a photosensitive element comprising blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers mounted on a common support, said blue-sensitive, green sensitive and red-sensitive silver halide emulsions having associated therewith, respectively, yellow, magenta and cyan dye developers, each of said yellow, magenta and cyan dye developers being a compound which is both a silver halide developing agent and a yellow, magenta and cyan dye, respectively, each of said dye developers being in a layer behind and contiguous with its respective silver halide emulsion layer, at least one of said dye developers being present in the form of a hydrolyzable derivative thereof, said hydrolyzable derivative containing an ester group removable by alkaline hydrolysis, applying an alkaline processing composition to said exposed photosensitive element and effecting development of said exposed emulsions, immobilizing said yellow, magenta and cyan dye developers, said photosensitive element as a result of the development of their respective silver halide emulsions, hydrolyzing at least a portion of each said hydrolyzable derivative to provide a hydrolyzed dye developer which is more diffusible than said hydrolyzable derivative, forming an imagewise distribution of diffusible, unoxidized, yellow, magenta and cyan dye developers present in undeveloped areas of their respective emulsions as a function of the point-to-point degree of exposure thereof, transferring, by imbibition, at least a portion of each of said imagewise distributions of diffusible dye developer

to a superposed image-receiving layer to form a multi-color, positive dye image, and separating said image-receiving layer from said photosensitive element at some stage of said process after said transfer has been effected.

6. In a process of forming diffusion transfer images in color comprising applying an alkaline processing composition to an exposed photosensitive element including a support carrying a silver halide emulsion and a dye developer, developing said exposed silver halide emulsion, oxidizing said dye developer as a function of said development and thereby forming, in undeveloped areas of said silver halide emulsion, an imagewise distribution of unoxidized dye developer, and transferring said unoxidized dye developer, by diffusion, to a superposed image-receiving layer to provide said transfer color image, said unoxidized, transferred dye developer being a single compound which compound is both a silver halide developing agent and a dye having a predominant spectral absorption within the region of the spectrum to which said silver halide emulsion is sensitive, the improvement wherein said dye developer in said photosensitive element is in a layer positioned between said support and a layer containing said silver halide emulsion, said dye developer initially contains a group removable by alkaline hydrolysis, and including the step of effecting alkaline hydrolysis by means of said alkaline processing composition, after said exposure, of at least a portion of said dye developer containing said hydrolyzable group, said hydrolyzed dye developer being substantially more diffusible than said unhydrolyzed dye developer containing said hydrolyzable group.

7. A process as defined in claim 6, wherein said group removed by hydrolysis provides a solvent for said hydrolyzed dye developer.

8. A process of forming transfer images in color as defined in claim 6, wherein the group removed by said hydrolysis is removed by the breaking of a covalent bond.

9. A process of forming transfer images in color as defined in claim 6, wherein the group removed by said hydrolysis is removed by a displacement reaction.

10. A process of forming transfer images in color as defined in claim 6, wherein said hydrolyzable dye developer is a salt of said dye developer.

11. A process of forming transfer images in color as defined in claim 6, wherein said transfer dye image includes hydrolyzed and unhydrolyzed, hydrolyzable dye developer.

12. A process as defined in claim 6, wherein said development is effected in the presence of a silver halide developing agent which is substantially colorless in at least its unoxidized form.

13. A photosensitive element for use in a diffusion transfer process wherein an exposed photosensitive element is treated with an aqueous alkaline solution to effect devel-

opment and also to effect transfer of diffusible dye developers to a superposed image-receiving layer, said photosensitive element comprising a support carrying at least two unexposed, selectively sensitized silver halide emulsions, each of said silver halide emulsions having associated therewith a dye developer, each of said dye developers being a compound which is both a silver halide developing agent and a dye, each of said dye developers being contained in a layer contiguous its associated silver halide emulsion and positioned between said silver halide emulsion and said support, at least one of said dye developers being present in the form of a hydrolyzable derivative containing a grouping removable by hydrolysis with said alkaline processing composition, the resulting hydrolyzed dye developer being more diffusible in said alkaline solution than is the unhydrolyzed dye developer.

14. A photographic product as defined in claim 13, wherein said hydrolyzable derivative is a salt of said dye developer.

15. A photographic product comprising a photosensitive element as defined in claim 13, a rupturable container holding an alkaline processing composition capable of hydrolyzing said hydrolyzable derivative, and an image-receiving layer comprising a stratum of a dyeable material, said image-receiving layer being adapted to be superposed on said photosensitive element with said rupturable container positioned therebetween, said alkaline processing composition being the only processing composition required to effect development, hydrolysis of said hydrolyzable derivative, and diffusion transfer of said diffusible dye developer.

16. A photographic product as defined in claim 13, wherein said hydrolyzable derivative contains a hydrolyzable ester of an aliphatic hydroxyl group.

17. A photographic product as defined in claim 13, wherein said hydrolyzable derivative contains a hydrolyzable derivative of a hydroquinonyl radical.

18. A process as defined in claim 5, wherein said ester group is an ester of a hydroquinonyl radical.

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