United States Patent

[11] 3,620,731

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[54] **NOVEL PROCESSES FOR FORMING TWO NEGATIVE COLOR TRANSFER IMAGES**
10 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** ..... **96/3, 96/29 D**
[51] **Int. Cl.** **G03c 5/54**
[50] **Field of Search** ..... 96/3, 29 D, 77, 29 R

[56] **References Cited**

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3,196,015	7/1965	Ryan	96/3
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3,443,939	5/1969	Bloom et al.	96/3

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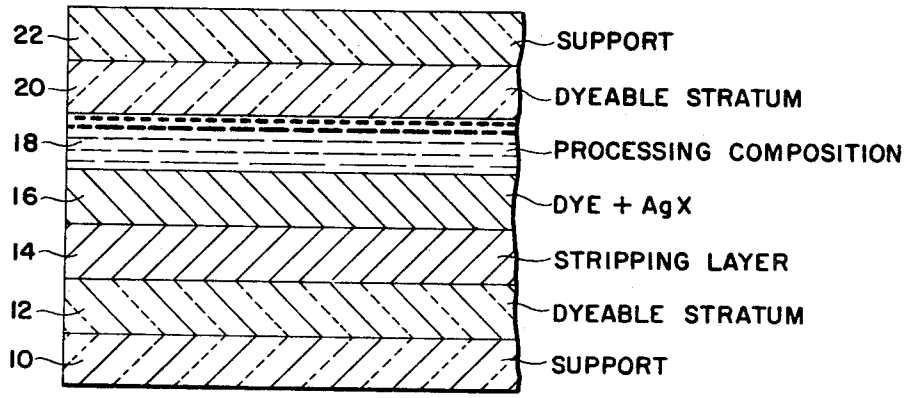
ABSTRACT: Novel systems for preparing a pair of negative images, utilizing film units including a layer of a light-sensitive silver halide, a color-providing material disposed in this layer or in an adjacent layer, which color-providing material is nondiffusible, but, upon oxidation, can release a diffusible color-providing moiety for transfer, said film unit further including a dyeable stratum separable from the aforementioned layer or layers.



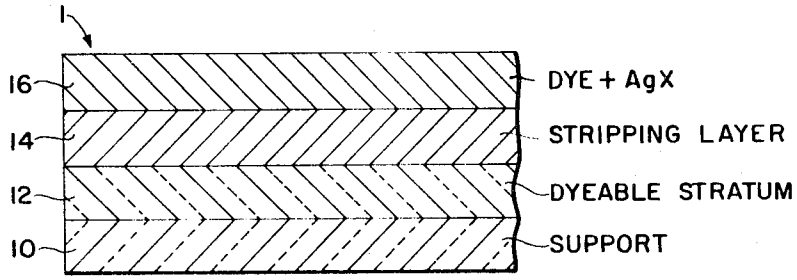


FIG. 1

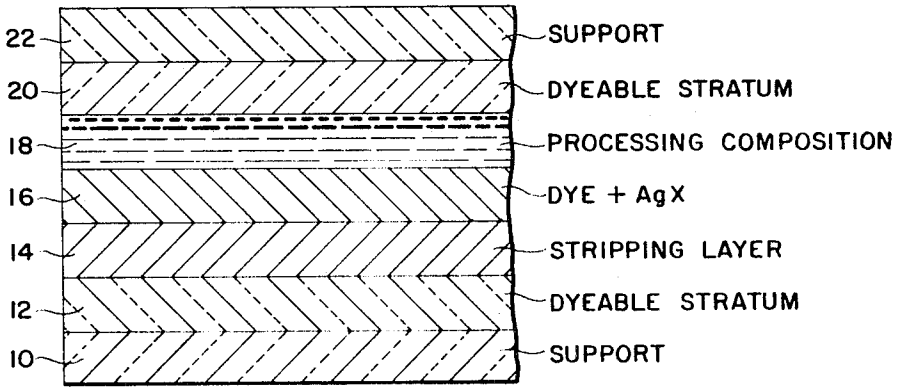


FIG. 2

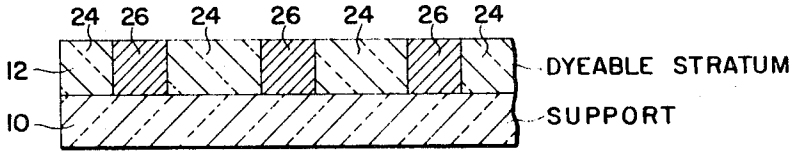


FIG. 3

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NOVEL PROCESSES FOR FORMING TWO NEGATIVE COLOR TRANSFER IMAGES

BACKGROUND OF THE INVENTION

The copending application of Stanley M. Bloom, Ser. No. 655,338 filed July 24, 1967, describes and claims novel compounds containing a color-providing moiety and an "anchoring" or immobilizing moiety. These compounds are immobile and nondiffusible in an aqueous alkaline medium, but are capable of providing, upon oxidation, an oxidation product which may autoreact intramolecularly to form a heterocyclic ring and, as a function of this ring formation, to split off a mobile and diffusible color-providing material. This reaction may also be defined as a ring-closure of the oxidation product resulting in a separation or "freeing" of the mobile color-providing moiety from the "anchoring moiety."

U.S. Pat. No. 3,443,939 issued to Stanley M. Bloom and Robert K. Stephens discloses systems employing the aforementioned nondiffusible compounds to obtain negative color transfer images. According to this copending patent application a photosensitive element containing at least one light-sensitive silver halide emulsion and associated compound of the foregoing description is exposed and then developed with an aqueous alkaline processing composition including a silver halide developing agent which upon development provides an oxidation product capable of being reduced by a redox reaction with the aforementioned compound, the developer further being sufficiently mobile in its oxidized state so as to be capable of migrating to the layer containing the color-providing compound; oxidizing the developing agent as a function of development to provide an imagewise distribution of oxidized developing agent in terms of exposed and developed areas of the emulsion; transferring this imagewise distribution at least in part, to contact the color-providing compound, whereby a redox reaction takes place to reduce the developing agent and to oxidize the color-providing compound to form an oxidation product which then ring-closes to split off the mobile color-providing moiety in turn to form an imagewise distribution of mobile and diffusible color-prodviding compound in terms of exposed areas of the emulsion; and transferring this latter imagewise distribution, at least in part, by imbibition, to a superposed dyeable stratum to impart thereto a negative color transfer image.

The concurrently filed application of Joel M. Peisach, Ser. No. 861,768 relates to the use of a unitary film assembly including a support carrying a light-sensitive silver halide, a color-providing material of the foregoing description in the same or in an adjacent layer, and a dyeable stratum, which film unit may be employed to obtain a negative color transfer image by releasing the diffusible color-providing moiety by the aforementioned redox reaction for transfer to the dyeable stratum.

SUMMARY OF THE INVENTION

The present invention utilizes this unitary film assembly to form a pair of negative color transfer images, the essence of the resent invention over the invention described and claimed in the aforementioned concurrently filed application of Joel M. Peisach, Ser. No. 861,768 being carrying out the development of this exposed film assembly while in superposition with a second dyeable stratum, whereby to form a negative color image on each of these dyeable strata.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the preferred embodiment, at least one of the dyeable strata is contained on a transparent support, whereby to provide a color transparency, and development is effected by spreading an aqueous developing composition in a substantially uniform layer between the exposed film assembly including one of the dyeable strata and a superposed image-receiving element including the other dyeable stratum.

BRIEF DESCRIPTION OF DRAWING

FIG. 1 is a partial schematic, enlarged, fragmentary sectional view illustrating a film assembly for use in this invention;

FIG. 2 is a similar view showing a previously exposed film assembly of FIG. 1 during processing thereof; and

FIG. 3 illustrates the separated negative image obtained from the film assembly after the processing step of FIG. 2.

As was mentioned previously, this invention relates to photography and, more particularly, to novel products and processes for forming color images.

A primary object of this invention, therefore, is to provide novel procedures of the foregoing description.

Another object is to provide novel procedures for forming a pair of negative color images.

A further object is to provide novel procedures utilizing as the color-providing material, a nondiffusible compound containing a diffusible color-providing moiety, e.g., a diffusible dye moiety, which compound is capable of forming by a redox reaction with oxidized silver halide developing agent an oxidization product which can autoreact intramolecularly to effect ring-closure and to eliminate the diffusible color-providing moiety of the compound for transfer.

A still further object is to provide novel procedures whereby a film assembly including a silver halide layer, a color-providing material of the aforementioned description in the same or in an adjacent layer and a dyeable stratum is exposed and then developed to form a negative color transfer image on this dyeable stratum and a second negative color transfer image on a second dyeable stratum contained on a separate element.

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

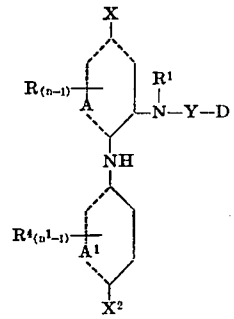
The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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.

As was mentioned previously, the present invention utilizes as the color image-forming component compounds containing a color-providing moiety and an anchoring or immobilizing moiety, which are described and claimed in the aforementioned copending application Ser. No. 655,338. These compounds are immobile and nondiffusible in an aqueous alkaline medium but are capable of providing, upon oxidation, an oxidation product which may autoreact intramolecularly to form a heterocyclic ring and, as a function of this ring formation, to split off a mobile and diffusible color-providing material. This reaction may also be defined as ring closure of the oxidation product resulting in a separation or "freeing" of the mobile color-providing moiety from the "anchoring moiety."

These compounds may be represented by the formula:

(A)

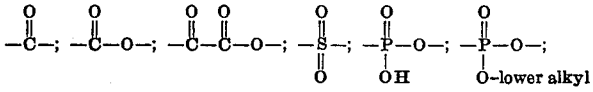


wherein:

A and A^1 each represent the atoms necessary to complete a benzene or naphthalene ring, which ring may be further substituted;

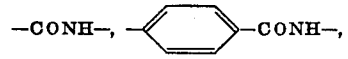
D is a color-provididng moiety, e.g., a complete dye such as a monoazo, disazo or anthraquinone dye which may, if desired, be metallized in known manner;

Y is any substituent which completes or forms an amide with, and reduces the basic character of the amino group in the 3-position, such as the residue of an acid, linking the color-providing moiety D to the 3-nitrogen atom, and which is capable of being eliminated during the ring formation to be described with more particularity hereinafter, e.g.,



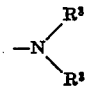
etc.;

R and R^4 each represent an "anchoring" or immobilizing substituent rendering the compound nondiffusible, e.g., higher alkyl such as decyl, dodecyl, stearyl, oleyl, etc. linked directly to the aromatic nucleus or linked indirectly thereto through an appropriate linking group, e.g.,



etc., an aromatic ring, e.g., of the benzene or naphthalene series or a heterocyclic ring, which rings may be either bonded to a single carbon atoms of the aromatic nucleus or fused thereto, i.e., bonded to a pair of adjacent carbon atoms; or R and/or R^4 may be a plurality of short chain radicals which together provide the anchoring moiety, each of said short chain radicals being linked directly or indirectly to a different carbon atoms of the aromatic nucleus formed by the A and/or A^1 moieties;

X is hydrogen, hydroxy, amino, e.g., a primary, secondary or tertiary amino substituent of the formula:



wherein each R^3 may be hydrogen, a hydrocarbon radical, e.g., alkyl, such as methyl, ethyl, butyl, dodecyl, etc., aryl such as phenyl or naphthyl attached through a carbon atom thereof to the nitrogen atom, a cyclic alkyl such as cyclopentyl or cyclohexyl, i.e., where both R^3's are alkylene comprising together with the nitrogen atom a heterocyclic ring, a substituted alkyl, such as hydroxyethyl methoxyethoxyethyl, polyglycoloxyethyl, carboxymethyl, benzyl, phenylethyl,sulfophenylethyl, acetylamino-phenylethyl, succinylamino-phenylethyl, furanemethyl, etc.; or a substituted aryl such as methylphenyl, ethylphenyl, etc., or the anchoring substituent R;

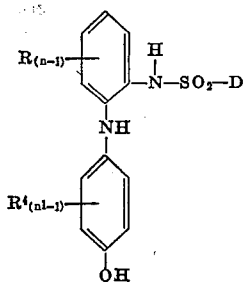
X^2 is hydrogen, hydroxy, an amino group such as may be contained by said X moiety, as previously described, or the anchoring substituent R^4, provided that one of said X and X^2 moieties must be hydroxy or amino;

R^1 is hydrogen, an alkyl such as methyl, ethyl, propyl, butyl, hexyl, octyl, dodecyl, cyclohexyl, etc., or a substituted alkyl such as 2-hydroxyethyl, 3-dihydroxypropyl, carboxymethyl, carboxyethyl, carboxybutyl, carboxydecyl, hydroxyethyl-ether, polyglycoloxyethyl, furanemethyl, benzyl, phenylethyl, carboxyphenylethyl, sulfo-phenylethyl, acylaminophenylethyl, etc., and

n and n^1 each is a positive integer from 1 to 2, provided that when R^1 or R^3 alone or together comprise one of those heretofore named substituents rendering the compound nondiffusible, either or both of *n* and n^1 may be 1 but when R^1 and R^3 alone or together do not provide such an anchoring moiety at least one of *n* and n^1 must be 2.

Preferred are those compounds within the scope of the above formula which are of the following formula:

(B)



wherein the anchoring moiety R or R^4 comprises a long chain amide, e.g., of at least 13 carbon atoms; and nuclear substituted derivatives thereof, e.g., where any of the nuclear carbon atoms not specifically substituted may contain a carboxy, alkyl, alkoxy, amino, chloro, hydroxy or amide substituent.

The present invention utilizes the principles described and claimed in the aforementioned U.S. Pat. No. 3,443,939 in conjunction with the film assemblies described and claimed in the aforementioned copending application Ser. NO. 861,768 to form a pair of negative color images.

The invention will be more readily understood by reference to the accompanying drawing.

As shown in e.g., 1, a film unit 1 for use in this invention contemplates a support 10 carrying, on one side thereof, a dyeable stratum 12, a stripping layer 14, and a layer 16 containing a light-sensitive silver halide and a color-providing material of the foregoing description, e.g. of formulae A or B, which materials are described and claimed in the aforementioned copending application Ser. No. 655,338.

Support 10 may be transparent or opaque, depending upon whether transparencies or reflection prints are contemplated. It may even be translucent so as to provide a support or base sheet for an image viewable either as a reflection print or as a transparency. In any event, it may comprise any of the support materials heretofore employed for such purposes. By way of illustration it may be made of cellulose nitrate, cellulose acetate, polyvinyl acetal, polystyrene, polyethylene terephthalate, polyethylene, polypropylene, polycarbonate, etc., paper, glass or other materials. Translucency may be obtained with any of the foregoing transparent materials by application of a layer of a suitable white pigment, e.g., titanium dioxide.

Dyeable stratum 12 may comprise any of the materials heretofore employed in color transfer processes and may for example comprise a polymeric material such as polyvinyl alcohol or a mixture of polyvinyl alcohol and a polyvinyl pyridine, e.g., a poly-4-vinylpyridine. Such strata are described, for example, in U.S. Pat. No. 3,148,061. The dyeable stratum may also include other reagents performing specific desired functions, e.g., hardeners, cross-linking agents or other reagents to reduce water sensitivity, dye mordants, antifoggants, oxidizing agents, pH adjusters, or the like, all of which additional reagents are known in the art.

Stripping layer 14 is not necessary to the practice of this invention but is preferably employed to facilitate clean separation of the image-containing stratum 12 following processing, as will be described with greater particularity hereinafter. Stripping layers have heretofore been well known in diffusion transfer processes and per se comprise no part of this invention. As an example of such materials, mention may be made of cellulose acetate hydrogen phthalate.

Layer 16 is shown to contain both the silver halide and the color-providing material. The silver halide may be any of the

heretofore employed silver halides, e.g., silver chloride, silver bromide, mixed halides such as silver bromoiodide, silver chlorobromide, or silver chlorobromoiodide. The silver halide is preferably contained in a suitable polymeric matrix, the preferred being gelatino silver halide emulsions such as the known high speed emulsions. The color-providing material may be included in a common matrix with the silver halide or layer **16** may comprise a uniform dispersion of a silver halide emulsion and the color-providing material dissolved or dispersed in a suitable medium. In any event, layer **16** may also include the various other reagents commonly employed in a silver halide layer, e.g., stabilizers, sensitizers and the like and it may also include any of the ingredients needed for development such as the developing agent.

While the color-providing material and silver halide have been shown for purposes of illustration as being in a single layer **16**, they may, if desired, be contained in separate layers.

FIG. **2** illustrates one method of developing a previously exposed element of FIG. **1** to form a pair of negative color images in accordance with this invention. As shown in FIG. **2**, the exposed element is processed by spreading a developing composition **18** in a substantially uniform layer between the exposed element and a superposed dyeable stratum **20** contained on a support **22**. Where a color transparency is desired, it will be appreciated that support **22** should be substantially transparent. In any event, stratum **20** and support **22** may be the same as or different from stratum **12** and support **10** respectively.

Processing composition **18** comprises at least an aqueous medium containing an alkaline material such as sodium or potassium hydroxide, and a silver halide developing agent of the type described in U.S. Pat. No. 3,443,939, which upon development will provide an oxidation product which can undergo a redox reaction with the color-providing material in layer **16**. Such developing agents include dihydroxybenzene developers such as the hydroquinones, aminophenol developers such as metol, and diaminobenzene developers such as 2-amino-5-diethylamino-toluene Any of these ingredients may be present initially in the photographic assembly, e.g., in layer **16**, as noted previously, in which event the developing composition is obtained by applying the aqueous medium to dissolve the component or components so contained. The processing composition may also contain various other reagents performing specific desired functions, e.g., stabilizers, viscous reagents, and the like.

Upon applying the processing composition such as in the manner shown in FIG. **2**, exposed and developable silver halide is developed and as a function of this development an imagewise pattern of oxidized developing agent is formed in terms of developed silver halide. This imagewise pattern of oxidized developing agent then contacts the color-providing material in layer **16**, and this in turn causes turn redox reaction referred to above and in U.S. Pat. No. 3,443,939 to occur, thereby releasing the diffusible color-providing moiety to provide an imagewise distribution of the same, a part of which is then transferred, by diffusion, to stratum **12** to impart thereto a first negative color transfer image, a second part being transferred to stratum **20** to impart thereto a second negative color transfer image. Following development dyeable stratum **12** is separated from the stripping layer to reveal the first image which, as shown in FIG. **3**, comprises layer **12** on support **10**, the image being shown as having dye-containing areas **24** and nonimage or highlight areas **26**; and stratum **20** is separated from layer **16** to reveal the second negative color image which is similar to the first one shown in FIG. **3**.

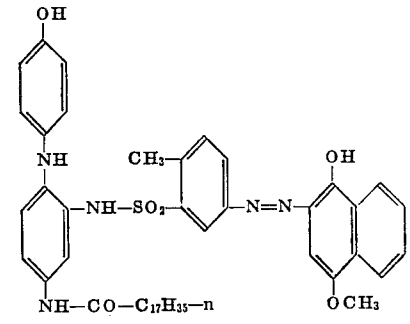
To facilitate separation of this second image, a second stripping layer may be disposed initially on the outer surface of stratum **20**. Alternatively, separation may be effected by washing or equivalent means which will be readily apparent to those skilled in the art.

In the procedures described in he copending application of Joel M. Peisach, Ser. No. 861,768 utilizing a film assembly such as is shown in FIG. **1** to obtain a single negative image, the image so obtained is appreciably denser than either of the images obtainable by the resent invention. When one contemplates that a single imagewise distribution of dye is employed to provide two images rather than one, this fact will be readily understood. However, each of the images obtainable by the present invention is of a usable density and images having densities on the order of about 1.1 have been obtained. While not as satisfactory for some purposes as the image obtained in the aforementioned copending applications, the images obtainable by the present invention are completely satisfactory for other purposes. Accordingly, the present invention affords one an alternative over the invention described in his copending application, namely whether for his individual purposes he desires two images of lesser but usable densities or a single image of greater density. This election may be made after photoexposure namely by selecting an image-receiving element containing a second dyeable stratum, as shown in Fig. **2**, or other processing means, e.g., a spreader sheet, to effect development and single image formation, as described in the copending application.

The following example shows by way of illustration and not by way of limitation the practice of this invention.

EXAMPLE

On a "mylar" (trademark of E. I. duPont de Nemours & Co. for a transparent film of polyethylene terephthalate resin) support sheet was coated a dyeable stratum comprising a mixture of polyvinyl alcohol and poly-4-vinylpyridine at a coverage of about 700 mgm./ft.^{2} of surface area. Over this was applied a stripping layer by coating a solution of cellulose acetate hydrogen phthalate in acetone to provide a layer containing 60 mgm./ft..^{2} of cellulose acetate hydrogen phthalate. 50 cc. of a gelatino high-speed silver iodobromide emulsion containing 5.0 g. of gelatin and 6.0 g. of silver was admixed with 10 cc. of an aqueous dispersion containing 1.1 g. of a dye of the formula:



and "Lomar D"X (trademark of Nopco Chemical Division for a sodium salt of a condensed mononaphthalene sulfonic acid dispersant). The resulting mixture was coated over the stripping layer to provide a layer containing about 300 mgm. of silver and about 70 mgm. of dye per ft.^{2} of surface area. The above element, illustrative of those of the structure shown in FIG. **1**, was exposed to provide a developable image and then processed in the manner shown in FIG. **2** by spreading at a gap of 0.0030 in. between the thus exposed element and a second dyeable stratum (similar to that prepared above) on a "mylar support sheet," a processing composition containing the following proportions of ingredients:

Water	2,000.0 cc.
Hydroxyethyl Cellulose	143.0 g.
Sodium hydroxide	78.0 g.
Metol	32.0 g.
Zinc nitrate	10.0 g.
Sodium bromide	100.0 g.

After an imbibition period of about 90 seconds, the respective dyeable strata were separated to reveal a pair of substantially identical negative color images.

While reference has been made to the formation of monochromatic images for purposes of explaining and illustrating the invention it is contemplated that one may employ two or more silver halide layers with associated color-providing material to obtain multicolor images. Such a film assembly may, for example, include a blue-sensitive silver halide with an associated yellow color-providing material, a green-sensitive silver halide with a magenta color-providing material, and a red-sensitive silver halide with a cyan color-providing material. Such an assembly may, if desired, include one or more spacer layers between the respective silver halide layers.

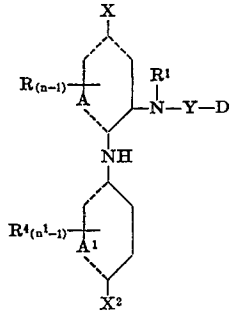
Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for forming two negative color transfer images comprising the steps of exposing to form a developable image on a photographic product comprising a support carrying a dyeable stratum, a light-sensitive silver halide in a layer further from said support than said dyeable stratum and a color-providing material in the same layer as said silver halide or in a contiguous layer, said color-providing material being a nondiffusible material containing a diffusible color-providing moiety, which material is capable of forming by a redox reaction an oxidation product which can autoreact intramolecularly to effect ring-closure and to eliminate the color-providing moiety of said material for transfer; developing said image by applying to the thus exposed product an aqueous alkaline processing composition including a silver halide developing agent which when oxidized is capable of undergoing a redox reaction with said material; as a function of development providing an imagewise distribution of oxidized developing agent in terms of developed areas of said silver halide layer; contacting said nondiffusible material with said imagewise distribution of oxidized developing agent whereby said material is selectively oxidized by a redox reaction with said oxidized silver developing agent to effect said ring-closure and to release said diffusible color-providing moiety in an imagewise pattern corresponding to said imagewise distribution of oxidized developing agent; transferring a part of said released diffusible color-providing moiety imagewise to said stratum to impart thereto a first color transfer image; and transferring a second part of said released diffusible color-providing material imagewise to a second dyeable stratum carried by a second support to impart thereto a second color transfer image.

2. A process as defined in claim 1 wherein said first color image is a negative transparency.

3. A process as defined in claim 1 wherein aid nondiffusible material is a compound of the formula:



wherein:

each of A and A^1 represents the atoms necessary to complete an aromatic ring;

D is a color-providing moiety;

Y is a substituent which completes an amide with and reduces the basic character of the 3-amino-substituent bonded thereto, said Y substituent further being a divalent radical linking said D moiety to said 3-nitrogen atom;

X and X^2 each is hydrogen, hydroxy, amino or the substituent R, provided that at least one of X and X^2 must by hydroxy or amino;

R and R^4 each represents an anchoring moiety rendering said compound nondiffusible;

R^1 is hydrogen, alkyl or substituted alkyl; and

n and n^1 each is 1 or 2, provided that when R^1 is an alkyl radical or X or X^2 is a secondary or tertiary amino comprising an anchoring moiety rendering said compound nondiffusible or when R^1, X and X^2 together contribute an anchoring moiety, n and n^1 may be 1, but when said substituents alone or together do not contribute an anchoring moiety at least one or n and n^1 must be 2.

4. A process as defined in claim 3 wherein said processing composition is applied by spreading between the thus exposed photographic product and a superposed element comprising said second dyeable stratum.

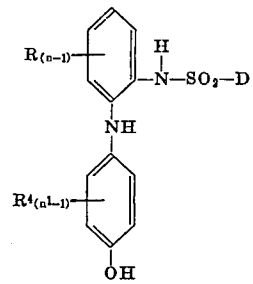
5. A process as defined in claim 4 wherein said element comprises said second dyeable stratum on a substantially transparent support.

6. A process as defined in claim 5 wherein said two color images are substantially identical.

7. A process as defined in claim 5 wherein said photographic product includes a stripping layer disposed over said first-mentioned dyeable stratum.

8. A photographic process comprising the steps of exposing to form a developable image on a photographic product comprising a substantially transparent support containing, in order, a dyeable stratum, a stripping layer, and a layer containing a light-sensitive silver halide emulsion and a nondiffusible material containing a diffusible color-providing moiety, which material is capable of forming by a redox reaction an oxidation product which can autoreact intramolecularly to effect ring-closure and to eliminate the color-providing moiety of said material for transfer; applying between the thus exposed product and a superposed element containing a second dyeable stratum an aqueous alkaline processing composition including a silver halide developing agent which when oxidized is capable of undergoing a redox reaction with said material to form a first negative color transfer image on said first-mentioned dyeable stratum and a second negative color transfer image on said second dyeable stratum.

9. A process as defined in claim 8 wherein said material is a compound of the formula:



wherein:

each of R and R^4 comprises an amide of at least 13 carbon atoms, said amide being bonded directly to a nuclear carbon atom of the shown benzene moiety or linked thereto through a phenylene or alkylene substituent;

each of n and n^1 is 1 or 2, provided that at least one of said n and n^1 is 2; and

D is a monoazo, disazo or anthraquinone dye moiety.

10. In a process for forming color transfer images comprising the steps of providing a photosensitive element comprising at least one light-sensitive silver halide emulsion having associated therewith a layer of nondiffusible material containing a diffusible color-providing moiety, which material is capable of forming by a redox reaction an oxidation product which can autoreact intramolecularly to effect ring-closure and to eliminate the diffusible color-providing moiety of said material for transfer; exposing said photosensitive element to provide a developable image; developing said image and, as a function of said development, selectively oxidizing said material in terms of exposed areas of said photosensitive element by a redox mechanism, thus providing an imagewise distribution of the oxidized material which contains the diffusible color-providing moiety, said oxidized material thereby autoreacting intramolecularly to effect ring-closure and to eliminate said diffusible color-providing moiety in imagewise distribution; and transferring this imagewise distribution of eliminated diffusible color-providing moiety, at least in part, by imbibition to a superposed stratum to impart thereto a negative color transfer image; the improvement which comprises the step of substantially simultaneously forming a second negative color transfer image on a second dyeable stratum carried by a second support.

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