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PHOTOGRAPHIC COLOR REPRODUCTION PROCESS

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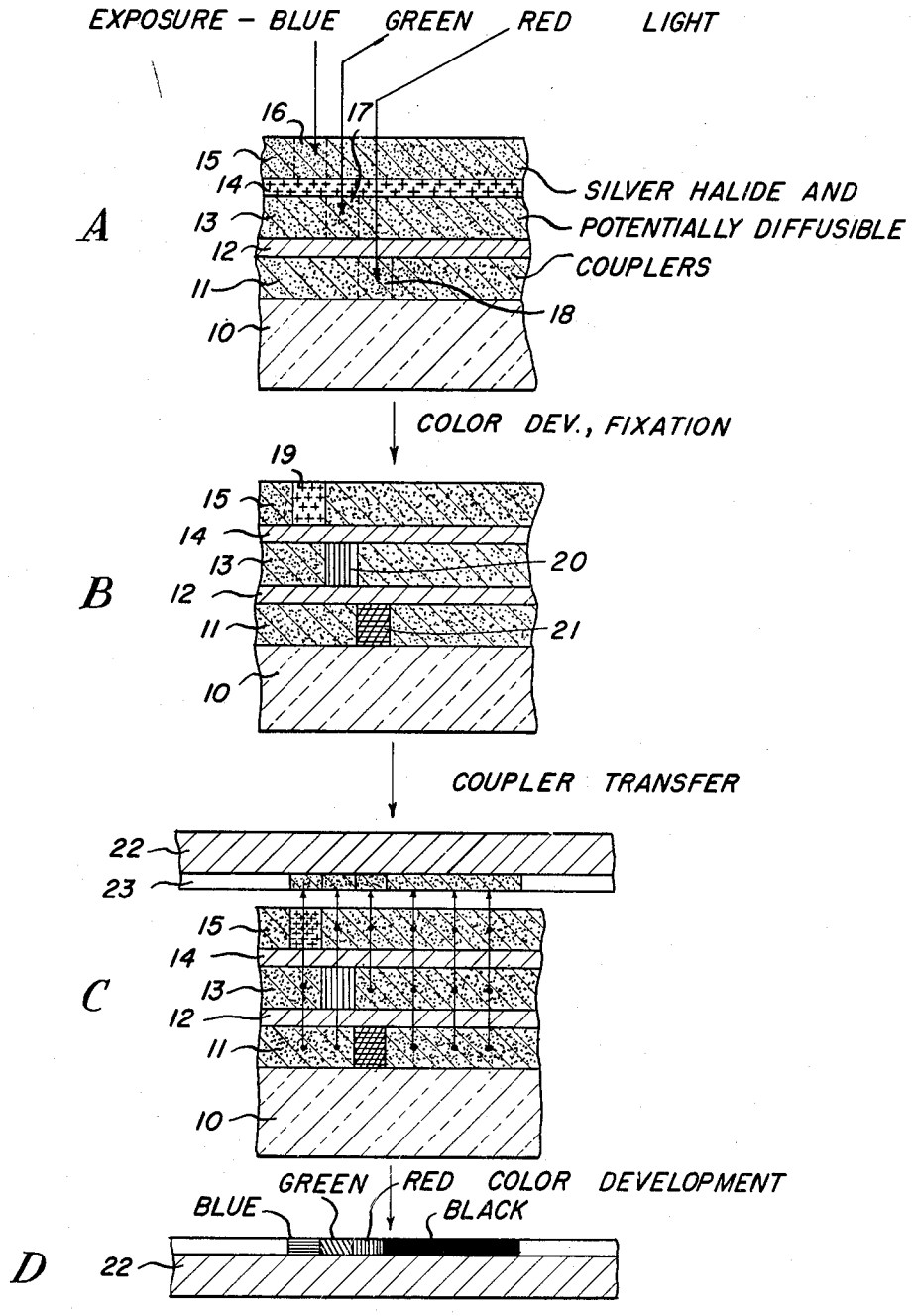


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# PHOTOGRAPHIC COLOR REPRODUCTION PROCESS

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This invention relates to a process in color photography wherein colored reproductions are made by image-wise imbibition transfer of coloring materials from multilayer photographic elements.

Processes for preparing a positive photographic reproduction of an original have been known for a long time, according to which a silver halide emulsion layer is exposed to the original subject, developed to a negative, and a positive image transferred to a receiving sheet by placing the receiving layer in close contact with the emulsion layer under suitable conditions. Several of these procedures depend upon development of a negative image in the silver halide emulsion layer, using up silver halide or developing agents in the areas of the negative image, transferring to the receiving sheet the residual silver halide or developing agent as a positive image, the silver halide being reduced or the developing agent being used to form a visible density by reducing silver halide, heavy metal salts, or by forming a dye. A recent process of that type produces a colored positive image by transferring unused color developer and color coupler from the sensitive layer to the receiving sheet where they are later caused to form a dye by treatment with an oxidizing agent. For obtaining multicolor positive images in that process, a plurality of receiving sheets, each containing a color separation dye image, are superimposed or successive registered transfers are made to a receiving sheet from several negative elements. So far as I am aware, none of these processes can be manipulated so as to yield a multicolor image by transfer of color-yielding substances from a single photographic element.

One object of my invention, therefore, is to provide a process which utilizes a single light-sensitive photographic element for recording several negative color-separation aspects of a colored subject and directly utilizing certain color-yielding materials in all regions of the element not occupied by the negative records of the subject, for producing a positive multicolor reproduction of the subject. Another object is to provide a means by which a plurality of color reproductions can be made from the coloring materials in a single light-sensitive photographic element. Other objects of my invention will become apparent by consideration of the following description of my invention.

In the broadest aspects of my invention, the objects are accomplished by exposing to a colored subject a photographic element containing at least two silver halide emulsions sensitized to different regions of the visible spectrum and each emulsion having intimately associated with it a potentially diffusible coloring material which is non-wandering during coating and development, developing the exposed photographic element with a solution of a silver halide developing agent which renders said coloring material non-diffusible only in the regions of exposure and development of the emulsions, rendering the coloring material only in the unexposed regions of the emulsions diffusible and placing the emulsions in intimate contact with an absorbent surface to simultaneously cause the diffusible coloring material in the emulsions to diffuse imagewise into the absorbent surface.



For a proper understanding of my process, it is necessary to consider that in color processes in general, to maintain color separation it is necessary to set up some mechanism according to which the appropriate dye or color former is associated image-wise with the photosensitive emulsion of complementary sensitization. In a three-layer silver halide material for subtractive color photography the blue-, green- and red-sensitive layers normally contain, respectively, yellow, magenta and cyan dyes or color formers. These dyes or color formers must be such as to be non-wandering during the coating operations and usually during at least the early stages of negative development. This is conventionally accomplished by any of several means, namely, using very large molecules, molecules containing groups which are substantive to gelatin or the vehicle, molecules containing groups which can be mordanted by conventional cation or anion mordants, etc. In my invention, dyes or color formers are selected such that they will not diffuse from layer to layer during coating or negative development, with the additional characteristic that by an appropriate step in the processing they can be made to diffuse easily so that after a negative development the release mechanism can be called into operation so that unaltered dye or color former can thereupon diffuse readily to a receiving sheet which has been placed in contact with the emulsion layers. It is also necessary that the dyes or color formers be rendered non-diffusible or non-wandering as a function of the negative development, as by coupling according to one mechanism or another, to form a larger molecule. It is equally useful if the dyes are rendered colorless or the coupler formers rendered incapable of forming a dye as a function of the formation of negative silver images in the emulsion layers. It will be noted that it is important that the particular dye or color former be so associated with the appropriately sensitized silver halide system that the dye or color former can be made insoluble or non-diffusing at the site of negative development of the silver halide, being released to wander by the secondary mechanism only after it has been immobilized at the negative silver image. If dyes or couplers are used which diffuse at too early a stage, i. e., during coating or development, then the association between the appropriate dye and silver halide is lost and color separation will not be obtained. The dyes or color formers may be rendered non-wandering during coating by many techniques which would include mordanting, precipitation with metallic ions, and the like. Similarly, dyes or color formers can be used in chemical combinations, such as esters which are hydrolyzed at an appropriate step in the processing to release the dye or color former as a smaller molecule to wander. The mechanism of immobilization of the dye or color former at the site of the negative image can be accomplished by reaction with the oxidized form of the developing agent, as in the typical color development with p-phenylenediamine developers using couplers with active methylene groups. It should be remembered, however, that any oxidized developer capable of combining with the dye or color former may be used regardless of the color of the reaction product in the negative image, since the color to be formed in the transferred image by diffusion of the dye or color former can be obtained by other means. Therefore, the choice of developing agent will depend upon other factors not necessarily important in choosing developing agents for conventional color processes and restrictions imposed in the conventional systems on the choice of developer molecule, which have to do with color and stability of the final dye, are not necessarily applicable. Thus, the developing agents can be not only p-phenylenediamine

or its derivatives but any other developing agent having oxidation products reactive with the dye or color former in question. For instance, conventional tanning developers such as derivatives of hydroquinone, catechol or pyrogallol may react with dye or coupler formers containing amino groups to cause image differentiation as a result of the coupling action.

If colorless coupler-type color formers are used in the respective layers, then they should be of such type that they are non-diffusing during coating and development but released by a definite mechanism to allow transfer later to a receiving sheet where they could be coupled with an oxidized p-phenylenediamine or possibly with a diazonium salt to give an appropriately colored image. Thus the receiving sheet in this case should contain, possibly a mordant, but also either an oxidizing agent to provide the oxidized form of the p-phenylenediamine developer if that is used during negative development, or at least a suitable agent for converting the color former after diffusion to a suitable dye image.

Examples of suitable coupler systems which can be employed in the sensitive elements employed in my invention are to be found in the Peterson U. S. Patents 2,353,754, July 18, 1944, and 2,296,306, September 22, 1942, and particularly in the Weissberger et al. U. S. Patent 2,412,700, December 17, 1946. These couplers are capable of forming a dye with the oxidation products of a primary aromatic amino silver halide developing agent. The couplers of the two former patents have attached to their molecules a heavy metal salt, for example, a silver salt, of a heterocyclic compound having an imino or mercapto group. Examples of these couplers are:

6-benzoylacetamino indazole
6-(o-hydroxybenzoylamino) indazole
5 - (4' - benzoylacetaminobenzenesulfonamido) - 2 - mercaptobenzimidazole

Couplers of the latter patent have attached to their reactive coupler molecules, heavy metal-containing thioglycolyl groups such as the couplers of the following examples and

1-phenyl-3-(thioglycolylamino)-5-pyrazolone
ω-benzoylacetamino-p-thioglycolic anilide
2-hydroxy-4-methyl-5-chlorothioglycolic anilide
5-(thioacetylamino)-1-naphthol

Accordingly, the above potentially diffusible couplers have attached to their molecules the heavy metal-substituted mercapto or imino groups. These couplers form conventional negative color images in the original photosensitive layer, can be released to wander by treatment with hypo, iodide or other agents of this type, and converted to dyes after diffusion to the receiving layer, by treatment with oxidized p-phenylenediamine developing agents.

In my invention a developing agent may be incorporated into one or more layers of the sensitive negative element containing such coupler compounds. Thus, after exposure development can be initiated by use of stable solutions particularly alkaline solutions free of coupler or developing compounds. Accordingly, the emulsion layers of the multilayer sensitive elements can contain different developing agents which allow for greater latitude in choice of dyes and color formers in the respective layers.

As will be apparent, my invention can be carried out with sensitive elements containing superposed emulsions containing potentially diffusible coloring materials or by means of one or more sensitive layers of the mixed grain or mixed packet type such as disclosed in the Godowsky U. S. patent application Serial No. 156,066, filed April 15, 1950, now U. S. Patent 2,698,794, granted January 4, 1955, or in Godowsky U. S. Patent 2,548,526, granted April 10, 1951. In this case, the sensitive elements have the potentially diffusible coloring materials in intimate association with the silver halide particles and after exposure and development to insolubilize the coloring materials, the coloring materials remaining in the unexposed regions are liberated and transferred simultaneously image-wise to a receiving sheet. In all of the processes of my invention, since a single transfer of the coloring materials to a receiving sheet does not deplete the negative element, further transfers to separate receiving sheets can be made in the same manner.

The following examples illustrate in more detail the operation of my invention and from which my invention can readily be understood, particularly when consideration is given to the accompanying drawings. In the drawings is shown in greatly enlarged cross-sectional view the appearance of typical photographic elements used in my process at various stages in the reproduction of a colored subject.

## EXAMPLE 1

This example illustrates the use of the mentioned coupler compounds containing metallic salts of heterocyclic compounds having mercapto groups, in a 3-layer photographic element sensitized in the natural order.

*Red-sensitive emulsion*

A fine-grain silver chloride dispersion was prepared by adding simultaneously and at a moderate rate a mixed solution of 70.0 cc. of a 1 N KCl solution and 25.0 cc. of a .2 N KBr solution diluted to a total volume of 125 cc. and 80 cc. of a 1 N $AgNO_3$, also diluted to a total volume of 125 cc. to a well agitated solution of 250.0 g. of a 10% de-ashed gelatin solution and 500 cc. of water. The total weight of the silver chloride dispersion was 1000 g.

A mixture of 5.35 g. of 5-chloro-2-hydroxy-4-methylthioglycolic anilide, 40.0 cc. of ethyl alcohol and 4.4 cc. of a 20% aqueous NaOH solution was heated to 110–120° F. for 5–8 minutes. To the clear solution was then added 35.0 cc. of water and the whole added slowly with very good stirring to 400.0 g. of AgCl dispersion described above. Total weight 480.0 g. A dispersion of the silver salt of the cyan coupler is thus obtained.

A fast bromo-iodide gelatin emulsion sensitized to red light with 5-[(ethyl-2(3)-α-naphthoxazolylidene)-ethylidene]-3-n-heptyl-1-phenyl-2-thiohydantoin is then provided and 112 grams of it combined with 194 grams of the coupler dispersion prepared as above, together with suitable quantities of mucochloric acid hardening agent, antifoggant and saponin spreading agent. The coupler-containing emulsion is then coated on a film support at a rate of 11.3 cc. per square foot. This red-sensitive emulsion layer is then coated with 10 cc. per square foot of the following gelatin solution:

| | | |
|---|---|---|
| Gelatin | grams | 113 |
| Water | cc. | 290 |
| Saponin solution (7%) | cc. | 15 |
| Mucochloric acid | grams | .064 |

*Green-sensitive emulsion*

A mixture of 5.5 g. of p-acetylthioglycolylamino-ω-cyanoacetophenone, 40.0 cc. of ethyl alcohol, and 8.0 cc. of a 20% aqueous NaOH solution was heated to 130–140° F. and maintained at that temperature for 10 minutes. The solution was intermittently hand-stirred during this period. To the clear solution was added 35.0 cc. of water and the whole then added slowly with very good stirring to 400.0 g. of AgCl dispersion described above. Total weight 480.0 g.

75 grams of the silver salt of the magenta coupler dispersion thus obtained is then mixed with 56 grams of fast bromoiodide gelatin emulsion sensitized to green with 5 - [4 - (3 - ethyl - 2(3) - benzothiazolylidene) - 2 butanylidene] - 3 - n - heptyl - 1 - phenyl - 2 - thiohydantoin

together with suitable quantities of mucochloric acid gelatin hardening agent, antifoggant and saponin spreading agent. This couplier-containing emulsion is then coated over the gelatin layer on the red-sensitive emulsion layer of the above element at the rate of 10 cc. per square foot. Following this, the green-sensitive emulsion layer is coated with a filter layer containing a dispersion of yellow colloidal silver such as Carey-Lea silver in gelatin.

*Blue-sensitive emulsion*

A mixture of 2.2 g. of ω-benzoyl-4-(p-acetylmercaptoethanesulfonamido)acetanilide, 16.0 cc. of ethyl alcohol, and 1.54 cc. of a 20% aqueous sodium hydroxide solution was heated with intermittent hand stirring to 125–130° F and maintained at that temperature for 10 minutes. After the addition of 5.0 cc. of distilled water, the clear solution was poured slowly into 100.0 g. of a well-stirred silver chloride dispersion prepared in the manner described above. The total weight of the dispersion was 140.0 g.

140 grams of the silver salt of the yellow coupler thus obtained are combined with 91 grams of a blue-sensitive silver halide emulsion together with suitable quantities of antifoggant, saponin spreading agent and mucochloric acid hardening agent. The resulting emulsion is then coated over the yellow filter layer of the above film to provide the element shown in Fig. 1 of the accompanying drawings. In the figure the support **10** is shown as carrying the red, green and blue-sensitive emulsion layers **11**, **13** and **15**, separated by the gelatin layer **12** and the yellow filter layer **14**, the emulsions containing the potentially diffusible couplers for forming substractively colored dye images of color complementary to the sensitivity of the respective emulsion layers containing the couplers. In addition, stage A shows the blue, green and red-sensitive emulsion layers being exposed in regions **16**, **17** and **18** respectively by light of those colors reflected from or transmitted by a colored subject.

In the manner of my invention, the exposed photographic element of this example and shown in stage A can be processed as follows to yield a positive color reproduction:

The film is developed for 5 minutes in the following color developer composition:

| | | |
|---|---|---|
| Benzyl alcohol | cc. | 15 |
| Trisodium phosphate | grams | 100 |
| Potassium bromide | do | 2.5 |
| Sodium sulfite | do | 1.5 |
| d-iso-Ascorbic acid | do | 0.25 |
| N - ethyl - β - methanesulfonamidoethyl - 4 - amino aniline | grams | 4.0 |

Water to 1000 grams.

The developed film is then fixed for a short time in a non-hardening acid fixing bath containing a silver solvent such as acid hypo, for example, for 1 minute in the following bath:

| | Grams |
|---|---|
| Sodium thiosulfate | 240 |
| Sodium sulfite | 10 |
| Sodium bisulfite | 25 |

Water to 1000 cc.

The result of fixation, in addition to removing unused silver halide from the film, is to remove silver from the unused couplers in the unexposed regions of the film and to render them diffusible in the presence of alkali. The film may then be washed for about 1 minute and appears substantially as shown in stage B of the drawings wherein areas **19**, **20** and **21** contain the non-diffusible yellow, magenta and cyan dye images obtained by color development of the exposed regions of the film and in the remaining areas of the layers **11**, **13** and **15** are present the water-insoluble couplers which are diffusible in the presence of alkali.

The washed film, while still moist, is then placed with its emulsion surface in intimate contact with an absorbent surface, for example, an alkaline receiving sheet **22** having an absorbent surface or layer **23**, such as a baryta-coated paper which has been soaked in a 10 percent solution of trisodium phosphate. As shown in stage C of the drawings, the result is that the cyan, magenta and yellow couplers which are present in the undeveloped areas of the emulsion layers, in the presence of alkali, diffuse simultaneously image-wise to the surface of the alkaline receiving sheet **22** along substantially rectilinear courses as illustrated. The receiving sheet **22** is then treated with a solution of a primary aromatic amino silver halide developing agent, such as the formula above, for 1 minute, and then with a solution of an oxidizing agent for the color developing agent. For this purpose, a 2 percent solution of potassium ferricyanide is satisfactory. The oxidation products of the color developing agent then couple immediately with the couplers which have transferred to sheet **22** to form dye images substantially as shown in stage D. At this point it is preferable to treat the receiving sheet containing the dye images with a silver bleaching solution followed by hypo solution and washing to remove any silver and silver salts which are present in element **22**.

Inasmuch as the colored reproduction obtained as above has not depleted the diffusible couplers, one or more other reproductions can be made from the element of stage C by repeating the transfer step using a fresh receiving sheet followed by treatment of the transferred coupler images as described.

In a variation of the process of this example which is in certain instances preferred to the end of obtaining improved definition in a final colored image, after initial color development of the light-sensitive element of stage A, it is squeegeed down on to a receiving sheet such as a baryta-coated sheet **22** which has been soaked in an alkaline solution of a silver solvent such as alkali metal or ammonium thiosulfate solution with the result that silver is removed from the potentially diffusible coupler molecules and in the presence of alkali the diffusible couplers obtained transfer at once image-wise to the receiving sheet. Treatment of the transferred coupler images with the color developing agent and oxidizing bath yield the desired dye images. As above, silver bleaching and fixing solutions may then be employed to remove metal salts from the color reproduction.

In the above processes, as mentioned, the initial development of the exposed element of stage A is not especially critical in the respect that either color developing agents or well-known colloid tanning silver halide developing agents can be used to immobilize the coupler compounds in the exposed regions. Also, the light-sensitive emulsions prepared as above can contain other metal salt couplers as disclosed in the Peterson and Weissberger et al. inventions. Naturally, if the process outlined above employs a film containing only one or two superposed emulsion layers, the final reproduction is in either a single color or essentially 2-color. Other well-known color developing agents such as disclosed in the above Weissberger U. S. Patent 2,193,015 and others well known in the art are suitable for use in the initial development step or for use in the treatment of the transferred coupler images on the receiving sheet.

When my invention is applied to mixed grain or mixed packet systems, for example, of the Godowsky inventions above, I merely incorporate dispersions of the metal salts of the potentially diffusible couplers such as of the Peterson U. S. Patents 2,296,306 and 2,353,754 and the Weissberger et al. U. S. Patent 2,412,700 into suitable emulsions before mixing them as specifically described in the Godowsky U. S. Patent 2,548,526. The resulting photographic element thus contains at least two silver halide emulsions each having a coupler intimately associated with its silver halide grains.

*Example 2*

This example illustrates the use of water-insoluble salts of acid dyes as the potentially diffusible coloring materials for the light-sensitive element.

A solution of 2 grams of Erio Fast Cyanine dye (4,8-diamino - 1,5 - dihydroxy anthraquinone - 2,6 - disulfonic acid) is prepared in 495 cc. of water and the pH adjusted to 5.6 by addition of pyridine. 112 cc. of this solution are then added to 78 grams of a red-sensitive bromo-iodide gelatin emulsion, then with stirring, is added 4 cc. of a 10 percent barium chloride solution, 8 cc. of saponin solution and .0425 gram of mucochloric acid. The emulsion is then coated on a film base at a rate of 12.2 cc. per square foot. A thin gelatin layer is then coated over the emulsion layer from a solution such as given above.

A green-sensitive gelatino silver halide emulsion is then prepared in a similar manner using the barium salt of the magneta dye 6-amino-1-hydroxy-2-p-sulfophenyl-azonaphthalene-3-sulfonic acid. This emulsion is then coated over the gelatin layer of the element immediately above. If desired to produce a 3-color system, a yellow gelatin filter layer such as that above and a blue-sensitive emulsion layer containnig a potentially diffusible metal salt of a suitable yellow dye can be coated over the green-sensitive emulsion layer. After exposure to the colored subject, development is carried out for 3 minutes in a gelatin-tanning silver halide developing solution of the composition:

*Solution A*

| | Grams |
|---|---|
| Pyrogallol | 6 |
| Elon | 6 |
| Ascorbic acid | 2 |
| Methyl benzotriazole | 0.1 |
| Potassium bromide | 2 |
| Water to make 1000 cc. | |

*Solution B*

| | Grams |
|---|---|
| Sodium carbonate monohydrate | 216 |
| Quadrafos | 10 |
| Water to make 1000 cc. | |

Mix 1 part A with 2 parts B just before use. After a 1-minute wash, 2 minutes in dilute acetic acid solution and washing 1 minute, the element is soaked for 1 minute in a working solution of 3 parts water and 1 part of the following conditioning solution:

| | Cc. |
|---|---|
| Glycerin | 100 |
| Acetic acid (glacial) | 4 |
| Ammonium hydroxide (conc.) | 13 |
| Formaldehyde (40%) | 20 |
| Water | 800 |

A baryta-coated receiving sheet is provided containing an acid dye mordant such as a polymerized quaternized vinyl-substituted azine dye-mordant, for example, quaternized polyvinyl pyridine as described in Sprague et al. U. S. Patent 2,484,430. The receiving sheet which has previously been soaked for at least 30 minutes in the above acidic working solution is then squeegeed against the moist emulsion layers with the result that the solubilized dyes in the emulsion layers transfer image-wise to the receiving sheet and are mordanted therein.

If desired, in the above process the green-sensitive emulsion layer may contain phenosafranine as the potentially diffusible magneta coloring material. Development of the exposed emulsion layers with the above developer is believed to yield in this layer a product which facilitates insolubilization of the dye in the exposed region. When this dye is used, an efficacious additional mordant for the receiving sheet is silver halide.

In this example, while a tanning developer composition is employed, the image-wise tanning of the gelatin appears to be an incidental feature of the developer. A more important feature appears to reside in the reaction of the oxidized developing agent with free amino groups of the dyes to form non-diffusible compounds. Accordingly, the effective potentially diffusible dyes contain free amino groups, dyes free of amino groups or containing only alkylamino groups are not useful in the process. Thus representative dyes useful in the process, as exemplified above, are anthraquinone, azo and safranine dyes containing primary amino groups.



As will be apparent, the process of this example can be used for making monochrome or 2-color transfers by utilizing any one or two of the above emulsion layers for the negative element, insolubilizing the dye salt locally and transferring the residual dye as described.

What I claim is:

1. A photographic color reproduction process which comprises exposing to a colored subject a photographic element having at least two superposed silver halide emulsion layers sensitized to different regions of the visible spectrum and each containing a coupler compound capable of forming a dye with the development products of a primary aromatic amino silver halide developing agent and having attached to the coupler molecule a group of the class consisting of heavy metal-substituted imino and mercapto groups, developing the exposed emulsion layers with a solution of said developing agent to form non-diffusible dye images only in the exposed regions of the emulsion layers, transforming the coupler compounds in the unexposed regions of the emulsion layers to diffusible couplers, placing the emulsion layers in intimate contact with an absorbent surface to simultaneously cause the diffusible coupler compounds in the emulsion layers to diffuse image-wise into the absorbent surface, and reacting the diffused couplers in the absorbent surface with the oxidation products of a primary aromatic amino silver halide developing agent to form dye images.

2. The process of claim 1 wherein the photographic element has three superposed emulsion layers each sensitized to one of the primary regions of the visible spectrum and each contains the designated coupler compound for forming subtractively colored dye images.

3. A photographic color reproduction process which comprises exposing to a colored subject a photographic element having at least two superposed silver halide emulsion layers sensitized to different regions of the visible spectrum and each containing a coupler compound capable of forming a dye with the development products of a primary aromatic amino silver halide developing agent and having attached to the coupler molecule a group of the class consisting of silver-substituted imino and mercapto groups, developing the exposed emulsion layers with a solution of said developing agent to form non-diffusible dye images only in the exposed regions of the emulsion layers, treating the developed emulsion layers with an acid fixing solution to form diffusible coupler compounds in the unexposed regions of the emulsion layers, placing the emulsion layers in intimate contact with an alkaline absorbent surface to simultaneously cause the diffusible coupler compounds in the emulsion layers to diffuse image-wise into the alkaline absorbent surface, and reacting the diffused couplers in the alkaline absorbent surface with the oxidation products of a primary aromatic amino silver halide developing agent to form dye images.

4. A photographic color reproduction process which comprises exposing to a colored subject a photographic element having at least two superposed silver halide emulsion layers sensitized to different regions of the visible spectrum and each containing a coupler compound capable of forming a dye with the development products of a primary aromatic amino silver halide developing agent and having attached to the coupler molecule a group of the class consisting of heavy metal-substituted imino and mercapto groups, developing the exposed emulsion layers

with a solution of said developing agent to form non-diffusible dye images only in the exposed regions of the emulsion layers, placing the emulsion layers in intimate contact with an absorbent surface containing an alkaline fixing solution to render the coupler compounds diffusible in the unexposed regions of the emulsion layers and to cause them to diffuse image-wise into the absorbent surface, and reacting the diffused couplers in the absorbent surface with the oxidation products of a primary aromatic amino silver halide developing agent to form dye images.

5. The process of claim 1 wherein the potentially diffusible coupler compounds contain a silver-substituted thioglycolyl group.



6. The process of claim 1 wherein the developing agent is contained in the emulsion layers and following exposure, development is initiated with an alkaline solution.

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