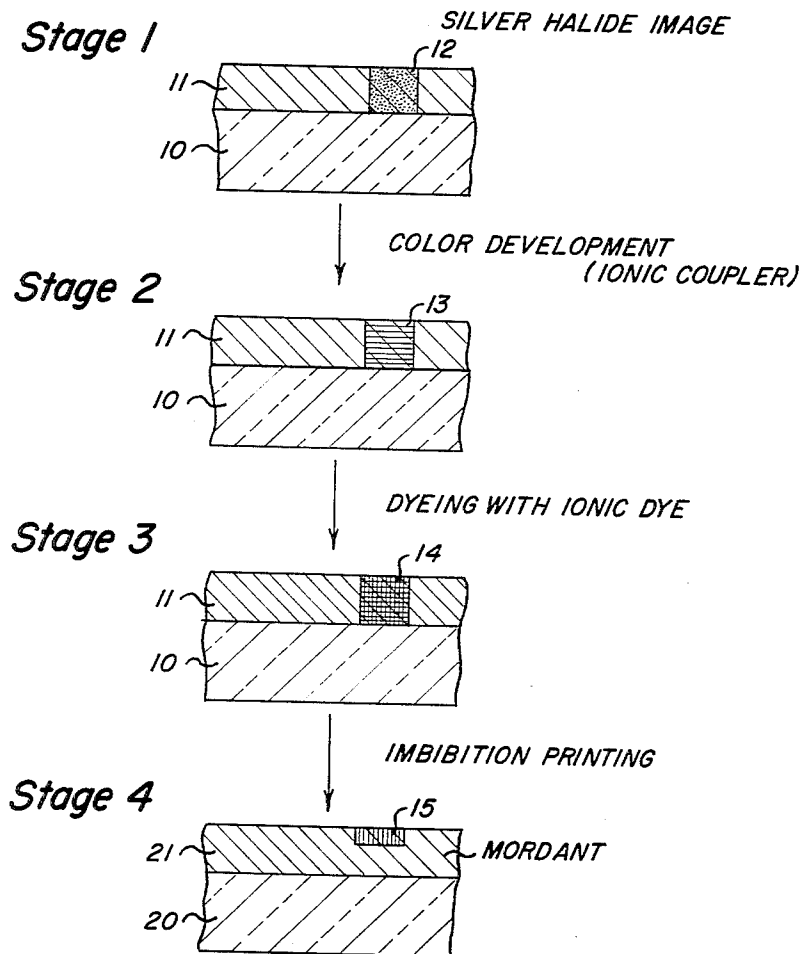


June 14, 1960

K. E. WHITMORE ET AL
PLANOGRAPHIC DYE TRANSFER PROCESS

2,940,849

Filed July 10, 1957



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PLANOGRAPHIC DYE TRANSFER PROCESS

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Filed July 10, 1957, Ser. No. 670,896

18 Claims. (Cl. 96—3)

This invention relates to a photographic process for reproducing subjects which involves the preparation of ionic dye images in photographic emulsion layers, the dyeing of the images with ionic dyes and printing from the dyed images by imbibition dye-printing methods.

The imbibition dye-printing process of color photography is well known. In a common form of the process, colloid matrices such as gelatin relief images are prepared from color-separation images and after dyeing the matrices with dyes of appropriate colors, the dyes are transferred imagewise by imbibition from the matrices to a mordanted receiving surface in register. Dye transfer processes of this type depend on the formation of a relief image in gelatin by a variety of means which have one point in common, the exposure of an emulsion containing such a high concentration of dye or pigment that the exposure varies rapidly with the distance to which light has penetrated the emulsion. By means such as a tanning developer, a tanning bleach bath, or an etch bath regulated by concentration of silver, the gelatin of the emulsion at points containing a critical concentration of silver is either tanned or made soluble, so that on development with hot water a relief image is formed in varying thicknesses of gelatin. This is used to absorb dye which is transferred to a receiving sheet. These relief processes have been and are used on a large scale commercially, but they have several difficulties. In the first place, the high light-absorption of the emulsion greatly decreases its sensitivity, and, combined with the hot water development, gives a very unfavorable relation of speed to definition. The images are physically soft, and all types of these processes are difficult to control, especially with the precision necessary for three-color photography. When used for cine film or other small images, the relief image may give difficulty of contact with the blank.

We have discovered a process of transferring dye images by imbibition from planar colloid surfaces as opposed to the colloid relief image surfaces. The process employs ordinary silver halide emulsion which need not contain a dye or pigment to lessen speed. Other disadvantages mentioned above associated with the exposure, tanning development and bleaching operations of the colloid matrix processes are avoided in the process of the invention.

According to our invention an imagewise distribution of developable silver halide is prepared in an organic colloid layer, for example, by means of light exposure of an ordinary silver halide emulsion layer. The silver halide image is then developed with a color developing solution containing a primary aromatic amino silver halide developing agent, in the presence of an ionic coupler compound such as a sulfonated pyrazolone coupler below, reactive with the oxidation product of the developing agent to form an ionic dye image in the layer which is substan-

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tially non-diffusing or has a low rate of diffusion in the colloid layer particularly with regard to the dye subsequently used in the process. The ionic character may be imparted to the dye either by use of an ionic coupler or ionic developing agent, or by both. The color of the ionic dye image is not important. Thereafter, the ionic dye image is dyed up with a diffusible ionic dye of charge opposite to that of the dye image, for example, a basic dye if the image is anionic thereby forming a salt of the ionic dye and the dye of opposite charge. Thereafter the colloid layer containing the dye image is placed in contact with a receiving element containing a mordant for the ionic dye and a transfer of the ionic dye is made to the receiving element by imbibition methods. Repeated transfers can be made similarly by merely recharging the ionic dye image with the ionic dye. Accordingly, the process employs an ionic dye image in place of the usual colloid matrix for obtaining an imagewise distribution of transferable dye.

The invention is illustrated in the accompanying drawings wherein in Stage 1 is shown in greatly enlarged cross-sectional view the appearance of a typical photographic element comprising a support 10 such as a cellulose acetate film support, carrying the hydrophilic organic colloid layer containing a developable silver halide image 12 such as contained in an exposed silver halide emulsion layer. The silver halide image is developed with a color-forming developer composition in the presence of the ionic coupler compound (anionic or cationic) to obtain the element shown in Stage 2 containing the dye image 13 in layer 11. Thereafter the element of Stage 2 is treated with a solution of an ionic dye of charge opposite to that of the dye image 13 producing the composite dye image 14 as shown in Stage 3. Subsequently, layer 11 of the dyed element while moist is placed into contact with the imbibition blank shown in Stage 4 having a support 20 and organic colloid layer 21 containing a mordant for the ionic dye, with the result that the imbibition dye image 15 is obtained in the imbibition blank.

In the process of the invention, various photographic elements containing the imagewise distribution of developable silver halide may be used. The element may take the form of a sensitive film which has been exposed and a silver image developed therein leaving the usual undeveloped silver halide image in the emulsion for use in the process. This procedure is particularly useful to replace the well-known imbibition dye-printing process employed for the production of colored motion-picture films. In that process, gelatin relief matrices corresponding to primary color-separation images are prepared for example from color-separation negatives. The matrices are then dyed with subtractively colored dyes and the respective dye images printed successively by imbibition in register on an imbibition blank. According to the present invention, in a similar process the gelatin matrices may be replaced by an equal number of silver halide emulsions in which have been recorded the color-separation images followed by color development of ionic dye images in each, dyeing each of the resulting ionic dye images subtractively with an ionic dye of charge opposite to that of the dye images and then printing each dye image onto a mordanted imbibition blank in register. This color reproduction process may be carried out by making original color-separation negatives directly from a scene being photographed and printing positive films therefrom which are separately color-developed to produce the ionic dye images for use as described; otherwise the color-separation

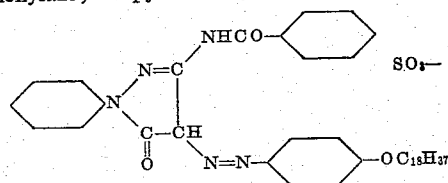
images to be color-developed to ionic dye images may be derived by the filtered exposure of sensitive films to color transparencies such as the "Eastman Color Negative" described by Hanson and Kisner, J.S.M.P.T.E. 61, 667-701 (1953). Color negatives of that type contain color-separation images recorded in a multilayer color film in the form of subtractively colored negative dye images. Such color negatives can therefore be used to print color-separation positive images into separate sensitive films which, according to the present invention, are then color-developed to produce the ionic dye images in each which are then dyed with subtractively colored dyes of opposite charge and thereafter each dye image is printed by imbibition methods onto a mordanted imbibition blank in register to obtain a positive subtractively colored image in natural color. This procedure is described in more detail in Example 1 hereinafter.

Similarly, the reproduction may be made from a positive image by using reversal methods or by the use of direct positive emulsions. Thus a positive image may be used to expose an emulsion which is then developed with a black-and-white developer followed by reversal exposure and color development to produce the ionic dye image which is utilized to make a dye transfer print as described. When the positive consists of a positive color transparency such as is produced by well-known methods in multilayer subtractive color films; and a subtractively colored print is desired, the same may be obtained by the process of the invention by recording color-separation negative images in separate films by filtered exposure of the transparency, developing each film to silver images, reversal exposing, color developing the same or a different ionic dye image in each of the films using a suitable ionic coupler, followed by dyeing the ionic dye images subtractively and transferring the dyes to an imbibition blank in register.

The process may be carried out similarly by starting from any silver image such as a silver color-separation image and merely bleaching the silver image by well-known methods to produce an imagewise distribution of developable silver halide in the film which is then color-developed to produce the ionic dye image which is then used as a planographic element for printing a dye image on an imbibition blank as described. Thus, well-known motion-picture color-separation colloid relief matrices containing silver images, formerly used for the printing of subtractively colored dye images by the inhibition dye-printing process, may be bleached to produce silver halide images distributed in the films in proportion to the silver and colloid relief images therein and the silver halide images developed to ionic dye images which are then dyed subtractively with ionic dyes and printed by imbibition. This process is therefore not dependent upon the absorption of the image dye by the colloid relief image and the transfer of the dye therefrom is not dependent upon the relief image itself. Rather, the image dye may be controlled by the ionic dye image alone independent of the colloid relief image; although unusual effects are obtainable by use of a mixture of dyes for coloring the relief images containing the ionic dye image such as one dye which is controlled by the ionic dye image itself and another dye controlled by the colloid relief image. Accordingly, a much wider choice of dyes can be employed and the undesirable effects upon definition of imbibition prints associated with dye transfer from relief images are obviated by the present planographic dye transfer process.

The process of the invention can be carried out in a somewhat different manner by employing as the sensitive element in which the imagewise distribution of developable silver halide is formed, an emulsion containing a substantially non-diffusing anionic coupler compound having an acid group in a non-coupling position and which coupler is reactive with a color-forming developing agent present in the developer solution to produce a dye image readily soluble in the alkaline processing solutions. Such a cou-

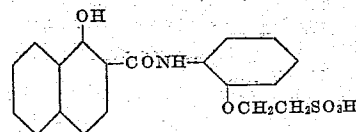
pler is 1-phenyl-3-(3-sulfobenzamido)-4-(4-octadecyloxyphenylazo)-5-pyrazolone, having the formula:



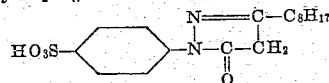
The result is that during color development of the emulsion containing the coupler and subsequent processing steps; the dye image obtained in the developed area washes out of the emulsion leaving an imagewise distribution of the original anionic coupler in the emulsion which may be dyed with a basic dye for transfer by imbibition to a mordanted receiving sheet as shown in Example 6 hereafter.

Similarly, the anionic coupler may contain the acid group in a coupling position as present in the compound 1-hydroxy-4-sulfo-2-naphthoylethylamide with the result that when the coupler is present in the emulsion, color development splits off the sulfonic acid group in the developed area of the emulsion leaving the original anionic coupler image in the remaining area to be dyed up and used in imbibition printing as described.

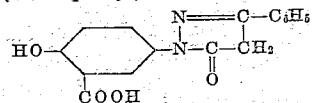
Representative anionic coupler compounds useful in a preferred embodiment of the invention to form the anionic dye images are as follows:



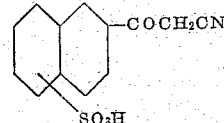
1-hydroxy-N-[2-(β-sulfoethoxy)phenyl]-2-naphthamide



1-(4-sulfophenyl)-3-octyl-5-pyrazolone



1-(3-carboxy-4-hydroxyphenyl)-3-phenyl-5-pyrazolone



2-cyanoacetyl-x-sulfonaphthalene

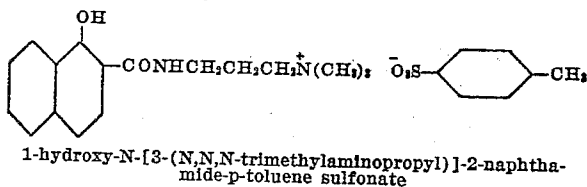
Other useful anionic couplers are as follows:

- 1-phenyl-[3-(3-sulfobenzamido)-1]-5-pyrazolone
- 2-(3,5-disulfobenzamido)-5-methylphenol
- 1-hydroxy-N-[β-(3-sulfobenzamido)ethyl]-2-naphthamide
- 1-hydroxy-N-(β-sulfoethyl)-2-naphthamide
- 1-hydroxy-N-(4-hydroxy-3-carboxyphenyl)-2-naphthamide
- 1-(3-phosphonophenyl)-3-undecyl-5-pyrazolone
- 1-hydroxy-N-(2,3-dicarboxyphenyl)-2-naphthamide
- 1-hydroxy-N-[4-(β-sulfoethoxy)phenyl]-2-naphthamide
- 1-hydroxy-2-naphthoic acid
- 5-methoxy-2-(3-sulfobenzamido)phenol
- 1-hydroxy-N-(m-hydroxyphosphonophenyl)-2-naphthamide
- 1-hydroxy-N-{o-[β-(β-sulfoethoxy)ethoxy]phenyl}-2-naphthamide
- 1-hydroxy-3'-(β-sulfoethyl)sulfamylphenyl-2-naphthamide
- 1-hydroxy-N-[β-(3,5-disulfobenzamido)ethyl]-2-naphthamide
- 1-(m-sulfomethylphenyl)-3-undecyl-5-pyrazolone

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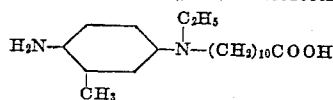
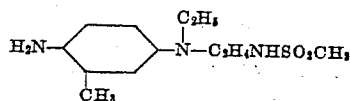
2 - [3-(3,5-disulphobenzamido)benzamido]-5-methylphenol
2-octanamido-5-(3,5-disulphobenzamido)phenol

Typical cationic coupler compounds useful in the invention with acid dyes are



Accordingly, it will be understood that the ionic couplers, in addition to possessing ability to couple with color developing agents, contain in the case of the anionic couplers, a negative charge for example due to the presence in the molecule of an acid group such as SO_3H , $\text{P}(\text{OH})_3$, $\text{As}(\text{OH})_3$, COOH etc., attached either directly to the nucleus or to a side chain in a non-coupling position, or in the case of the cationic couplers possessing a positive charge due to the presence of the coupler molecule of a basic group such as an ammonium group in a non-coupling position of the molecule.

The well-known primary aromatic amino silver halide developing agents of the para-phenylenediamine type are useful in developing the ionic dye images with the ionic coupler compounds, for example, 2-amino-5-diethylamino toluene as well as



Other very useful developing agents are as follows:

4-amino-N-(10-carboxydecyl) aniline

4-amino-N-(5-carboxyamyl)-N-ethyl-3-methyl aniline

4-amino-N,N-diethyl-3-(β -propylsulfonamido) ethyl aniline

4-amino-N,N-diethyl-3-[β -(p-tolylsulfonamido) ethyl aniline

4-amino-N-(10-carboxydecyl)-N-ethyl aniline

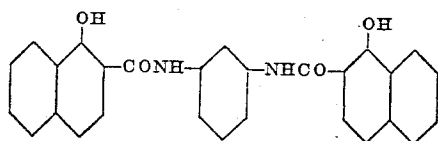
4-amino-N-(10-carboxydecyl)-N-ethyl-3-methoxy aniline

4-amino-N-ethyl-3-methoxy-N-(β -sulfoethyl) aniline

6-amino-1-(β -sulfoethyl)-1,2,3,4-tetrahydroquinoline

4-amino-N-ethyl-3-methyl-N-(β -sulfoethyl) aniline

In case the coupler compound used is non-ionic or not strongly anionic such as



the color developing agent should be an ionic one such as 4-amino-N-(10-carboxydecyl)-N-ethyl-3-methyl aniline above as shown in Example 2 below.

Representative basic dyes suitable for dyeing up the anionic dye images include the following

Acridine Yellow (Color Index 785)

Auramine G (Color Index 656)

Auramine O (Color Index 655)

Capriblau GON (Color Index 876)

Chrysoidine Y (Color Index 20)

Methylene Blue GX (Color Index 922)

New Fast Green 2B (Color Index 659)

Rhoduline. Blue. 6GA (Color Index 658)

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Thioflavine T (Color Index 815)

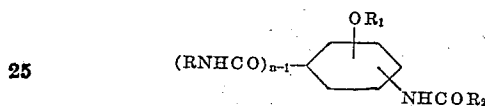
Malachite Green (Color Index 657)

Acriflavine (Color Index 790)

Astraphloxine FF (Schultz-Lehmann 930)

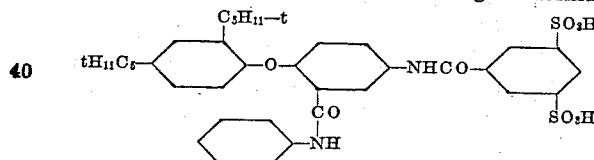
Brilliant Alizarine Light Red 4B, is a typical magenta acid dye useful for dyeing up the cationic dye images produced in the process of the invention imbibition transfer as described. Other acid dyes are readily selected to provide subtractively colored cyan and yellow acid dye images.

The mordants useful in the imbibition blanks to which the basic dye images are transferred include those known in the art for example silicotungstic acid, phosphomolybdic acid, phosphotungstic acid, a styrene-maleic anhydride copolymer (1 to 1), polyvinyl phthalate, sulfonated polystyrene, or other high molecular weight anionic material which combines with the cation of the basic dye. Particularly effective mordants may be selected from the sulfonated and carboxylated compounds disclosed in the Saunders et al. U.S. Patent 2,756,149 having the general formula

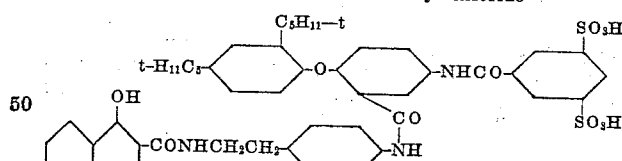


wherein n is a positive integer of from 1 to 2, R and R_1 each represent monocyclic aryl groups of the benzene series, one or both of which contain one or more alkyl groups of at least four carbon atoms such as n -butyl, n -amyl, t -amyl, n -hexyl, lauryl and cetyl. R_2 represents either a monocyclic sulfoaryl or carboxyaryl group of the benzene series, such as mono or disodium sulfophenyl or mono or disodium carboxyphenyl groups.

Representative compounds of this class of mordants are compounds I and III of that patent having the formulas

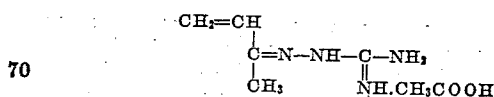


5-[4-(2,4-di-tert-amylphenoxy)-3-(phenylcarbonyl) phenyl-carbonyl]-1,3-benzenedisulfonyl chloride



1-hydroxy-4-chloro-N-[4-[2-(2,4-di-tert. amylphenoxy)-5-(3,5-disodium sulfobenzamido) - benzamido] - phenethyl]-2-naphthamide

In the variation of the process of the invention using a cationic coupler to form cationic dye images which are dyed with acid dyes for transfer to the imbibition blank, a basic mordant should be used in the imbibition blank such as polymers of amino guanidine derivatives of vinyl methyl ketone such as described in the Minsk U.S. Patent application Serial No. 544,111 filed December 19, 1955, now 2,882,156, having the structure



Other mordants include the 2-vinyl pyridine polymer metho-p-toluene sulfonate and similar compounds described in Sprague et al. U.S. Patent 2,484,430, granted October 11, 1949.

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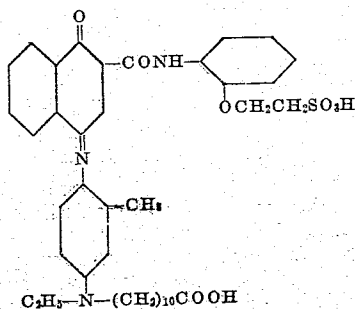
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Specific examples illustrating the invention are provided as follows:

Example 1

A fine-grain positive film was exposed to a negative such as a red-light color-separation image from a multi-layer color negative, followed by development at 80° F. for 10 minutes in a conventional alkaline carbonate developing solution containing 3.4 grams per liter of the developing agent 4-amino-N-(10-carboxydecyl)-N-ethyl-3-methyl aniline and 2.75 grams per liter of the anionic coupler 1-hydroxy-N-[2-(β-sulfoethoxy)phenyl]-2-naphthamide to form the anionic dye image in the exposed area, followed by rinsing the film for 30 seconds, fixing it for 3 minutes in conventional hypo solution, washing for 3 minutes, bleaching for 1 minute in a ferricyanide-bromide bleach solution of composition given in Example 6 rinsing for 30 seconds, and refixing the strip for 1 minute before the final wash.

The resulting dye matrix, containing the anionic dye image



was bathed 2 minutes in a solution of Methylene Blue dye, removed from the dye bath, rinsed for 90 seconds and placed in contact with a receiving film which had been preconditioned with acetic acid solution before use and having a gelatin coating containing an acid mordant, e.g., 1-hydroxy-4-chloro-N-{4-[2(2,4-di-tert-amylphenoxy)-5-(3,5-disodium-sulfobenzamido)-benzamidol]-phenethyl}-2-naphthamide (Sanders et al. U.S. Patent 2,756,149). The dye transferred from the anionic dye image to the receiving surface with good definition. Additional prints were obtained by repeating the dye bathing, rinsing and transferring steps to obtain a series of cyan colored prints of nearly identical density and contrast.

In a similar manner, green and blue light color-separation images of the same subject were used for the preparation of anionic dye images in separate sensitive films and dyed respectively with magenta and yellow basic dyes such as Sevron Brilliant Red 4-G, Genacryl Yellow 3G or Sevron Yellow R. The magenta and yellow dyes were then transferred to the mordanted receiving film in register with the cyan image from the red color-separation to obtain a full-color reproduction of the subject.

As mentioned in these examples, a variety of means may be used for supplying the silver halide image which is developed to the ionic dye image. Color-separation negatives or positives and filtered negative or positive color transparencies may be used for exposure of the sensitive elements in which the ionic dye images are formed. When desired, reversal processing may be employed, for example, when preparing the ionic dye images by printing directly from positive originals.

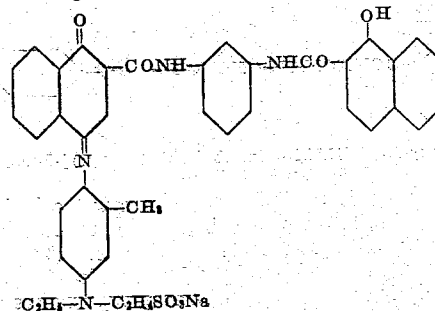
Example 2

A fine-grain positive film was exposed to a negative such as a red-light color-separation image, developed 5 minutes at 90° F. in a conventional alkaline carbonate developer solution containing 3.0 grams per liter of 4-amino-N-β-sulfoethyl-N-ethyl-3-methyl aniline and 3 grams per liter of 1,3-di(1-hydroxy-2-naphthamido)-benzene, fixing in a conventional hypo bath, washing 3 minutes, bleaching in an ordinary ferricyanide-bromide

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bleaching solution as given below, rinsing for 30 seconds and refixing for 1 minute before finally washing.

The resulting dye matrix, containing an anionic dye image of the probable structure



was bathed in a solution of Methylene Blue dye, removed from the dye bath, rinsed and placed in contact with a receiving film (preconditioned to acetic acid) having a gelatin coating containing an acid mordant, e.g., phosphotungstic acid. The dye bathing, rinsing, and transferring operation was repeated several times yielding a series of monochrome cyan prints of very nearly identical density and contrast.

In a similar manner, green and blue-light color-separation images of the same subject were used for preparation of anionic dye images in separate sensitive films and dyed with magenta and yellow dyes of Example 1 and transferred in register to the imbibition blank containing the cyan image to obtain a full-color reproduction of the subject.

Example 3

The process of Example 1 was carried out except using positive images for exposure of the films, developing the films in a conventional black-and-white developing solution for 10 minutes at 68° F., washing 5 minutes, reversal exposing each film followed by the same color developing, fixing, bleaching, washing, drying and transfer steps of Example 1 to obtain registered subtractively colored images corresponding to the original positive images.

Example 4

This example illustrates a typical procedure employing a cationic dye image and acid dyes.

A fine-grain positive film was exposed to a negative such as a red-light color-separation image, developing for 10 minutes at 68° F. in an alkaline carbonate developer containing 3.4 grams per liter of 4-amino-N-(10-carboxydecyl)-N-ethyl-3-methylaniline and 3.0 grams per liter of 1-hydroxy-N-[3-N,N,N-trimethylaminopropyl]-2-naphthamide iodide, rinsing the strip for 30 seconds, fixing it for 3 minutes in hypo, washing for 3 minutes, bleaching for 30 seconds in the ferricyanide-bromide bleach, and refixing the strip for 1 minute before the final wash.

The resulting dye matrix containing a cationic dye image was then bathed in a solution of Brilliant Alizarin Light Red 4B magenta dye, removed from the dye bath, rinsed and placed in contact with a receiving film having a gelatin coating containing a polyvinylaminoguanidine mordant mentioned above. The dye bathing, rinsing, and transferring operation was repeated several times yielding a series of monochrome magenta prints of very nearly identical density and contrast.

In a similar manner green and blue-light color-separation images of the same subject may be utilized to obtain cationic dye images for dyeing with magenta and yellow acid dyes for transfer in register to the cyan image on the receiving film.

Example 5

The procedure of Example 4 was carried out except using the cationic coupler 1-hydroxy-N-(2-pyridyl)-2-

naphthamide methyl p-toluene sulfonate in the color developing solution for each film in place of the quaternary ammonium coupler and replacing the color developing agent with a like amount of 2-amino-5-diethylaminotoluene.

The procedures of Examples 4 and 5 can be carried out similarly employing positive originals and using the reversal process, by interposing black-and-white development and reversal exposure steps before color development.

Example 6

The mentioned variation of the invention wherein the emulsion contains an anionic coupler containing an acid group in a non-coupling position of the molecule is illustrated in this example.

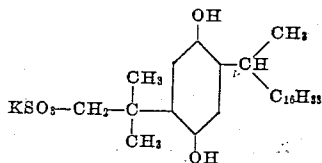
400 milligrams of the coupler 1-phenyl-3-(3-sulfo-benzamido)-4-(4-octadecyloxyphenylazo)-5-pyrazolone was moistened with ethyl acetate and ethyl alcohol with the addition of concentrated ammonia to effect solution. This solution was added to 20 cc. of 10 percent aqueous gelatin solution and to this was added a small amount of a spreading agent. The pH of the solution was then adjusted to 6.5 and 30 cc. of a silver bromide emulsion added followed by stirring for 10 seconds, holding for 15 minutes at 40° C. and coating on a cellulose acetate film base.

Samples of the resultant film were then exposed with white light to color-separation positive images which had been made from a multilayer positive color transparency. Each sample was then treated in the following process at 70° F. (unless otherwise indicated):

Develop	10 min.
Rinse	1 min.
Fix	1 min.
Wash	3 min.
Bleach	1 min.
Wash	10 min.
Harden	4 min.
Dry.	
Wash	10 min.
Bleach (15% HCl)	5-10 sec. at 40° F.
Wash.	
Dry.	

The film now containing anionic positive dye images composed of the residual color coupler (the dye formed in color development having washed out of the emulsion) was then dyed for 5 minutes in 0.25 percent aqueous solutions of dyes complementary in color to each color separation, that is, Methylene Blue, Safranine O and Acraflavine dyes, followed by rinsing 3-20 seconds in 0.5 percent acetic acid solution. Thereafter, in order to obtain a multicolor reproduction in full color the yellow, magenta and cyan dye images were transferred from the films for 5 minutes each in register on a mordanted imbibition blank prepared as follows:

300 milligrams of the mordant



2-(2-octadecyl)-5-sulfo-tert-butyl hydroquinone (potassium salt)

were dissolved in 30 cc. of 5 percent gelatin solution, a spreading agent was added and the composition coated onto an opaque white cellulose acetate film support and the coating after drying hardened with the formaldehyde hardener solution given below. Just before transferring the dye images, the imbibition blank was conditioned with a solution of a mixture of one part of 28 percent acetic acid, one part of 1 percent aqueous sodium carboxymethyl cellulose solution and two parts of water.

The processing solutions used in the above process had the following compositions:

Developer:		G.
5	Calgon	1.0
	Sodium sulfite	4.0
	2-methyl-4 N,N-diethylamino-aniline hydrochloride	3.0
	Sodium carbonate (mono.)	20.0
10	Potassium bromide	2.0
	Sodium thiocyanate	2.0
	Water to 1.0 liter.	

Formalin hardener:		G.
15	Calgon	0.6
	Sodium bisulfite	5.0
	Sodium carbonate	5.0
	Potassium bromide	1.0
	40% formaldehyde	20.0
	Water to 1.0 liter.	

Bleaching solution:		G.
20	Potassium ferricyanide	30
	Sodium bromide	13
	Borax	7.3
25	Boric acid	15
	Sodium nitrate	30
	Water 1 liter.	

Fixing solution:		G.
30	Sodium thiosulfate (hypo)	240
	Sodium sulfite (des.)	10
	Sodium bisulfite	25
	Water 1 liter.	

In the above processes the "bleach (15 percent HCl)" is used to remove any residual color-developed dye which may not have washed out of the film previously.

It will be apparent that if the coupler-containing films are to be exposed to color-separation negatives for the production of multicolor prints, the black-and-white development and reversal exposure steps of the reversal technique can be employed in the process of this example prior to the color-development step.

The ionic dye images prepared as described above are useful in a similar color process. That is, in multilayer color films in which the blue-sensitive emulsion layer for the production of the yellow image is outermost, the emulsion causes scattering of light which exposes an underlying emulsion layer thereby causing a loss in definition. To remedy this effect, the silver halide content of the blue-sensitive emulsion layer may be reduced appreciably to reduce the light scattering and a yellow ionic dye image of low density developed in the layer using an ionic yellow-forming coupler such as α -benzoyl-4-(3-chlorosulfonylbenzamido) acetanilide and developing with, for example, 2-amino-5-diethylaminotoluene monohydrochloride. The resulting yellow ionic dye image may then be dyed to the required density and contrast using a solution of a yellow dye of opposite charge such as those above mentioned.

What we claim is:

1. A photographic reproduction process which comprises developing a gelatino layer containing an image-wise distribution of developable silver halide, with a silver halide developing solution containing a primary aromatic amino silver halide developing agent in the presence of a coupler compound reactive with the oxidation product of said developing agent to form an image-wise distribution of a substantially non-diffusing dye of the class consisting of acid and basic dyes in the layer, bleaching the resultant silver image and fixing, dyeing the dye image thus formed with a diffusible dye which forms a salt with said dye image, placing the colloid layer while moist into contact with a receiving layer containing a mordant for said last-mentioned dye and transferring the dye image-wise by imbibition to the receiving layer.
2. A photographic reproduction process which com-

prises developing an exposed gelatino silver halide emulsion layer with a silver halide developing solution containing a primary aromatic amino silver halide developing agent and a coupler compound reactive with the oxidation product of said developing agent to form an image-wise distribution of a substantially non-diffusing dye of the class consisting of acid and basic dyes in the layer, bleaching the resultant silver image and fixing, dyeing the dye image thus formed with a diffusible dye which forms a salt with said dye image, placing the emulsion layer while moist into contact with a receiving layer containing a mordant for said last-mentioned dye and transferring the dye imagewise by imbibition to the receiving layer.

3. A photographic reproduction process which comprises exposing a gelatino silver halide emulsion layer to a color separation image of a colored subject, developing the exposed emulsion layer with a silver halide developing solution containing a primary aromatic amino silver halide developing agent and a coupler compound reactive with the oxidation product of said developing agent to form an image-wise distribution of a substantially non-diffusing dye of the class consisting of acid and basic dyes in the layer, bleaching the resultant silver image and fixing, dyeing the dye image thus formed with a diffusible dye which forms a salt with said dye image, placing the emulsion layer while moist into contact with a receiving layer containing a mordant for said last-mentioned dye and transferring the dye image-wise by imbibition to the receiving layer.

4. A photographic reproduction process which comprises exposing a plurality of gelatino silver halide emulsion layers on separate supports each to different primary color separation images of a colored subject, developing each of the exposed emulsion layers with a silver halide developing solution containing a primary aromatic amino silver halide developing agent and a coupler compound reactive with the oxidation product of said developing agent to form a dye image of a substantially non-diffusing dye of the class consisting of acid and basic dyes in each emulsion layer, bleaching the resultant silver image and fixing, dyeing each of the resulting dye images with a diffusible dye which forms a salt with said dye image and which has a color complementary to the color of light used in forming each color separation image, and transferring the last-mentioned dyes from each layer by diffusion to an imbibition blank in register, said imbibition blank containing mordants for said last-mentioned dyes.

5. The process of claim 4 wherein the colored subject is a photographic color transparency.

6. The process of claim 4 wherein the colored subject is a negative color transparency.

7. The process of claim 2 wherein the coupler compound is strongly acidic and reacts with the developing agent to form a strongly acidic dye image which is dyed with a basic dye.

8. The process of claim 2 wherein the coupler compound is basic and reacts with the developing agent to form a basic dye image which is dyed with an acid dye.

9. The process of claim 1 wherein the gelatin layer containing an imagewise distribution of developable silver halide is a silver halide emulsion layer which has been exposed, developed, and the residual silver halide reversal exposed.

10. The process of claim 1 wherein the gelatin layer containing an imagewise distribution of developable silver halide is a silver halide emulsion layer which has been exposed to a color separation image of a positive color transparency, developed, and the residual silver halide reversal exposed.

11. The process of claim 2 wherein the coupler compound is 1,3-di(1'-hydroxy-2'-naphthamido)benzene and the developing agent is 4-amino-N-ethyl-3-methyl-N-(β -sulfoethyl)aniline.

12. The process of claim 2 wherein the coupler compound is 1-hydroxy-N-[2-(β -sulfoethoxy)phenyl]-2-naphthamide and the developing agent is 4-amino-N-(10-carboxydecyl)-N-ethyl-3-methylaniline.

13. The process of claim 2 wherein the developing agent is strongly acidic and reacts with the coupler compound to form a strongly acidic dye image which is dyed with a basic dye.

14. The process of claim 2 wherein the coupler compound is one containing a phenolic hydroxy group.

15. The process of claim 2 wherein the coupler compound is a 5-pyrazolone.

16. The process of claim 2 wherein the coupler compound is one containing an open-chain reactive methylene group.

17. A photographic reproduction process which comprises exposing a gelatino silver halide emulsion layer containing a strongly acidic coupler compound reactive with the oxidation product of a primary aromatic amino silver halide developing agent to form an alkali-soluble dye image, developing the exposed emulsion layer with a silver halide developing solution containing said developing agent and washing the resulting alkali-soluble dye image out of the emulsion layer, bleaching the resultant silver image and fixing, dyeing the residual coupler compound with a basic dye, placing the emulsion layer in contact with a receiving layer containing a mordant for said basic dye and transferring the basic dye imagewise by imbibition to the receiving layer.

18. A photographic reproduction process which comprises exposing a gelatino silver halide emulsion layer containing a strongly acidic coupler compound reactive with the oxidation product of a primary aromatic amino silver halide developing agent to form a dye, said coupler having an acid group in the coupling position of its molecule, which group is split off during development of the emulsion layer with said developing agent, developing the emulsion layer with a silver halide developing solution containing said developing agent to split off said group from the coupler compound, to form said dye image and coupler image in the layer, bleaching the resultant silver image and fixing, dyeing said coupler image with a basic dye, placing the emulsion layer in contact with a layer containing a mordant for said basic dye and transferring the basic dye imagewise by imbibition to the receiving layer.

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