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PHOTOGRAPHIC DYE TRANSFER PROCESS

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This invention relates to a photographic dye transfer process of particular use in color photography.

A number of methods for monochrome and color photography by transfer of dye images have been devised. Most of these 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.

Another type of transfer process, represented by bromoil transfer of Pinatype, depends on differential attraction of wet tanned and untanned gelatin for greasy inks, or for certain types of dyes. These processes are notoriously difficult to control; the Pinatype process is no longer in use, and bromoil transfer is used only in a very limited way for artistic effects.

We have discovered a process of transferring dye images by imbibition from planar surfaces, which employs a silver image formed in an ordinary silver halide emulsion layer which need not contain a dye or pigment to lessen emulsion speed. The process includes bleaching a developed silver image in a fixed-out emulsion layer to silver halide in a well known manner, then treating the silver halide image thus obtained with a basic dye in the presence of a water soluble halide salt such as an alkali metal chloride, bromide or iodide. As a result, the dye becomes adsorbed on the negatively charged silver halide image. The dyed silver halide image can then be used for making a multiplicity of imbibition dye prints by merely pressing the image into contact with a mordanted receiving sheet in the presence of a soluble silver salt. The function of the silver salt is to reverse the charge on the silver halide and allow diffusion of the dye to the receiving sheet.

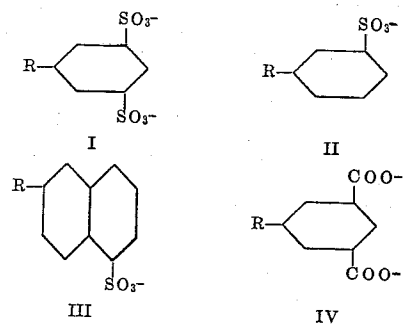
According to the process, a normal silver image is formed in an emulsion by exposure and development in a standard developer such as a Metol-hydroquinone developer followed by fixing and washing. The resulting element appears substantially as shown in greatly enlarged cross-sectional view in Stage 1 of the drawings

wherein layer **10** is the emulsion support such as paper, cellulose ester or synthetic resin carrying a fixed-out hydrophilic organic colloid-silver halide emulsion layer **11** containing the silver image **12**. The silver image is then oxidized to silver halide such as silver bromide or silver iodide and the element appears substantially as shown in Stage 2 of the drawings, emulsion layer **11** now containing the silver halide image **13**. The silver halide image is then dyed with a basic dye such as the following representative dyes:

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)
Thioflavine T (Color Index 815)
Malachite Green (Color Index 657)
Acriflavine (Color Index 790)
Astraphloxine FF (Schultz-Lehmann 930)

The dyeing of the silver image with the basic dye is carried out in the presence of a salt containing an anion which is absorbed by the silver halide, e. g., soluble iodide salt such as an alkali-metal idoide. It appears essential that the anion of the salt such as iodide can be present when dyeing the silver halide image in order to maintain satisfactory absorption of the basic dye on the silver halide. The dyed element is shown in Stage 3 of the drawings as containing the image **14** of silver halide on which the dye has been absorbed.

A receiving sheet is prepared, for example, by coating on a paper or film support a gelatin layer containing a mordant for the basic dye to be transferred. Suitable mordants for the basic dyes are, 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. Further examples of suitable mordants for the basic dyes include alkali metal or amine salts of compounds having the general formulas:



wherein R is a radical having a molecular weight of the order of 350 or larger, e. g.

5-[2-(2,4-di-tert - amylphenoxy)phenylcarbamyl]-1,3-benzene sodium disulfonate

3-[4-(2,4-di-tert-amylphenoxy)-3-(3-sodiumsulfophenylcarbamyl)phenylcarbamyl]-benzene sodium sulfonate

5-[4-(2,4 - di-tert-amylphenoxy)-3-(phenylcarbamyl)-phenylcarbamyl]-1,3-benzene sodium disulfonate

5-[4-(2,4 - di-tert-amylphenoxy)-3-(2-hydroxy-3,5-dichloro - 4 - methylphenylcarbamyl)phenylcarbamylmethyleneoxy]-1,3-benzene sodium dicarboxylate

5-[4-(2,4-di-tert-amylphenoxy) - 3 - (4-{1-hydroxy-4-chloro - 2-naphthyl}carbamylethyl)phenylcarbamyl]-1,3-benzene soduim disulfonate

3-[4-(2,4-di-tert-amylphenoxy) - 3 - (2-hydroxy-3,5-dichloro - 4 - methylphenylcarbamyl)phenylcarbamyl]-benzene sodium sulfonate.

The alkali metal or amine salts of sulfonated naphthalene-formaldehyde condensates such as sold under the trade name Tamol P by the Rohm and Haas Company and under the trade name Daxad 11 by the Dewey and Almy Chemical Co., and also useful as mordants in our process.

Stage 4 simulates the appearance of the receiving sheet after transfer thereto of the dye image from the element of Stage 3, according to which layer **15** is the support, such as paper, carrying a thin hydrophilic organic colloid coating **16**, such as gelatin, containing the mordant and soluble silver salt and to which the dye image **17** has transferred by imbibition.

Repeated transfers can be made from the same element containing the silver halide image by merely washing the element with dilute acid to remove the soluble silver salt and again treating with the basic dye solution in the presence of soluble iodide salt followed by transferring the dye to a mordanted receiving sheet in the presence of soluble silver salt.

The amount of dye adsorbed by the silver halide image is so high that the amount of dye needed for maximum density in a final image can be transferred from a silver halide image which had an optical density of about 1.0 as a silver image.

While the process can be used for making monochrome reproductions as indicated above, the process is particularly adapted to the preparation of subtractively colored dye images from silver color separation negatives. To this end, color separation records are prepared in the usual manner on fine-grained panchromatic emulsions, for example, by exposing under a color transparency to the red, green and blue primary regions of the spectrum and developing the records to low contrast. Good definition in the process is maintained by utilizing thin, well hardened colloid layers both for the silver halide color separation films and the receiving sheet.

Example I

Color-separation images are prepared on a suitable emulsion (for example, a fine-grained sound recording or duplicating negative film), and developing to a gamma of about 0.5. After normal fixing and washing, these images are converted to silver iodide by bathing for two minutes at 70° F. in a solution of 20 g. $K_3Fe(CN)_6$ and 20 g. KI in 1.0 liter of water. The film is then washed in running water for five minutes. The red separation image is dyed for 1½ minutes in a bath of 10 cc. glacial acetic acid, 0.30 g. KI and 5.0 g. Malachite Green or Rhoduline Blue 6GA in 1.0 liter of water. It is then washed in at least two changes of a solution of 10 g. acetic acid per liter of water, to remove dye and iodide from the gelatin. A typical receiving sheet may contain 20 g. of the sodium salt of phosphotungstic acid per 100 g. of deashed gelatin, coated at 0.42 g. gelatin per square foot. This sheet is soaked for three minutes in a solution of 10 g. acetic acid and 17 g. silver nitrate per liter of water and the excess removed. The cyan dyed image is rolled into contact with the receiving sheet; transfer is complete in three minutes or less. The red separation image is then removed and washed in three changes of acetic acid 10 g. per liter, to remove silver nitrate, before dyeing again. The receiving sheet is reconditioned by soaking again in the acid solution of silver nitrate.

The green separation negative is dyed and transferred like the red, except that Astraphloxine FF is used instead of Malachite Green. The receiving sheet and separation image are washed and reconditioned as before. The blue separation image is transferred in the same way except Acriflavine is used as the dye. Finally, the receiving sheet with the complete image is washed thoroughly in dilute acid to remove excess silver salt, and dried. The transfer should be carried out under light from which ultraviolet and violet have been removed although white light can be used momentarily to judge color balance.

An alternative method for removing soluble silver salts from the separation images after transfer is to bathe in one or more changes of a solution of 20 g. sodium sulfite in 1.0 liter of water, followed by washing in water. The image can then be dyed as described above.

Example II

A receiving sheet is prepared as follows:

13.0 g. 5-[4-(2,4-di-tert-amylphenoxy)-3-(2-hydroxy-3,5-dichloro-4-methylphenylcarbamyl)phenylcarbamyl]-1,3-benzene disulfonyl chloride was hydrolyzed by boiling 5 minutes in a solution of 15 cc. of 20% sodium hydroxide and 50 cc. of ethyl alcohol.

The solution for coating was prepared by adding the above to a solution of 40 g. gelatin, 0.6 g. saponin (spreading agent), 0.3 g. mucochloric acid (hardening agent), and 690 g. water.

The final solution was coated on a film base of cellulose acetate at 1 lb. dry gelatin per 600 sq. ft.

A silver image in gelatin on film base was bleached 2 minutes in 1% potassium iodide—1% potassium ferricyanide solution in water to produce a silver iodide image. After washing in running water 2 minutes, the sample was bathed 2 minutes in a water solution containing 0.25% Malachite Green, 1% acetic acid, 12% ethanol, and 0.05% potassium iodide. A 3-minute wash in running water followed, leaving an image consisting of dye adsorbed to silver iodide.

The receiving sheet (mordanted blank prepared above) was conditioned by treating first 2 minutes in a hardening bath consisting of 0.5 g. sodium hexametaphosphate, 5.0 g. sodium bisulfite, 5.0 g. sodium carbonate monohydrate, 1.0 g. potassium bromide, 150 g. sodium sulfate and 20 cc. formalin (40%) made up to one liter with water. This was followed by a 1-minute water wash and a 3-minute bath in 0.1 N silver nitrate in 1% acetic acid.

The wet image sample was rolled into contact with the wet, treated receiving sheet and after 2 minutes removed. The receiving sheet, containing the transferred image was washed in running water 1 minute and dried.

It was observed that all the dye had transferred and that the final image had appreciably better definition than images obtained similarly using other classes of non-diffusing acid mordants in the receiving sheet.

What we claim is:

1. A photographic reproduction process which comprises oxidizing a silver image contained in a developed and fixed silver halide emulsion layer, to a silver halide image, dyeing the silver halid image with a basic dye in the presence of a water-soluble halide salt, washing excess dye and halide salt from the emulsion layer, pressing the emulsion layer while moist into contact with a moist mordanted receiving sheet in the presence of a water-soluble silver salt to transfer the dye image-wise from the silver halide image to the receiving sheet by imbibition.

2. A photographic reproduction process which comprises oxidizing a silver image contained in a developed and fixed silver halide emulsion layer, to a silver iodide image, dyeing the silver iodide image with a basic dye in the presence of an alkali metal iodide, washing excess dye and alkali metal iodide from the emulsion layer, pressing the emulsion layer while moist into contact with a moist mordanted receiving sheet in the presence of silver nitrate to transfer the dye image-wise from the silver iodide image to the receiving sheet by imbibition.

3. A photographic reproduction process which comprises preparing a set of silver color-separation records in fixed-out silver halide emulsion layers on separate

supports, oxidizing each silver color-separation record to silver halide, dyeing the silver halide records thus formed respectively with subtractively colored basic dyes in the presence of an alkali metal iodide, washing excess dye and alkali metal iodide from each dyed silver halide record, pressing the moist dyed and washed records successively into contact with a moist mordanted receiving sheet in the presence of a soluble silver salt to form a subtractively colored picture on the receiving sheet.

4. The process of claim 3 wherein red, green and blue color separation records of silver, after oxidizing each to silver halide, are dyed with Rhoduline Blue 6GA, Astraphloxine FF, and Acriflavine dyes respectively.

5. The process of claim 1 wherein the water-soluble halide salt is an alkali metal chloride.

6. The process of claim 1 wherein the water-soluble halide salt is an alkali metal bromide.

7. The process of claim 1 wherein the water-soluble halide salt is an alkali metal iodide.

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