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# DYE IMBIBITION TRANSFER BLANK

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## ABSTRACT OF THE DISCLOSURE

A photographic transfer blank, a composition for preparing the same, and a photographic dye transfer process utilizing the same wherein said transfer blank comprises a support base with a transfer layer thereon, such transfer layer including a colloidal carrier homogeneously intermixed with a stabilizing material consisting essentially of sodium acetate, sodium citrate and citric acid.

This invention relates to a photographic process, transfer blank and coating composition therefor, and product thereof, and relates more particularly to a photographic dye transfer process utilizing a transfer blank having a novel transfer layer thereon which results in a brilliant, sharply detailed, colored print.

In a conventional dye transfer or imbibition process, one or more dye matrices is pressed into contact with a transfer blank having a colloidal carrier frequently including various materials which increase the definition or sharpness of the dye transferred onto the blank to form a print. Such materials are known as stabilizing materials. In the well-known three-color photograph system, the transfer layer receives blue, yellow and red records printed or otherwise produced in yellow, magenta and cyan coloring matters, normally dyes. The matrices carry images in colloidal relief, dyed with a coloring material which, in part, is transferred on contact with the transfer layer of the blank for the production of a color print.

Various prior art patents to Ives and others provide the basic background teachings for the conventional imbibition procedure. Such processes have suffered from numerous disadvantages. For example, the resultant product has not been clearly defined, the dye materials having a tendency to go out of registration during transferring to provide images incapable of consistent reproduction. The definition of the product as well as the contrast and transparency of the same have been poor, and prior art techniques have frequently results in strained or foggy prints. Further, such products have been particularly difficult to bleach and reprint or retouch in general, or specifically for taking out or putting in images of various subjects as is necessary, for example, in many commercial art procedures. Moreover, the processes themselves have been relatively time consuming requiring air brushing with pigments thereby rendering the same commercially prohibitive.

The primary object of this invention is the provision of, materials used in a process, which are free from the foregoing and other disadvantages.

A further object of this invention is the provision of a transfer blank and a coating composition therefor which procesess of the type described and which prowhich is particularly adapted for use in a dye transfer process of the type described and which provides an extremely desirable final product.

Yet another object of this invention is the provision of a transfer blank and composition therefor having therein a stabilizing material uniquely compatible with various dye solutions in a dye transfer process requiring less



printing time and resulting in better film products than heretofore obtainable.

Other and further objects reside in the combination of materials and quantitative amounts of the same in the coating composition and in the transfer blank:

Still other objects will, in part, be obvious, and, in part, be pointed out, as the description of the invention proceeds.

It is to be understood that the instant inventive concept is equally applicable to all types of photographic procedures from the production of 35 millimeter transparencies to 8 x 10 inch and larger reflected prints or to motion picture production, which, in effect, is merely the production of a plurality of individual film plates. Moreover, although the specification is particularly described in terms of a conventional three dye system, it will be seen that the materials herein can be utilized to produce a single color product, or one having any number of superimposed transferred images of different colors.

Referring first to the transfer blank of the instant invention, it is comprised basically of a support base having thereon a transfer layer including a colloidal carrier homogeneously intermixed with a stabilizing material adapted to provide better and clearer transfer of dye substances as will be explained in more detail hereinafter.

While the support base may take any form, such as even paper or the like, it is preferably formed of a dimensionally stable film of a polyester such as polyethylene terephthalate of any desired thickness. Various commercially available products such as Cronar, Dacron and Mylar, produced by Du Pont, Terylene produced by I.C.I. or the French Tergal are all useful although Cronar has been found particularly advantageous. Since this material has no plasticizer, it is substantially dimensionally stable having high tensile strength and high abrasion resistance. Moreover, it is not readily hydrolyzed nor is it deleteriously affected by most acids and organic solvents or conventional oxidation and reduction agents.

In order to provide for best saturation of the color dyes and for the reflection of a bright image, the support base is preferably first coated with a background layer which may consist essentially of a colloidal carrier such as an aqueous dispersion of gelatin or a gelatin substitute which has been homogeneously intermixed with a white pigment such as barium sulphate, titanium dioxide or zinc oxide.

Superimposed over this background layer is the transfer layer which is formed from the photographic transfer blank coating composition of the instant invention. This composition is comprised of an aqueous dispersion of a colloidal carrier, such as gelatin or a gelatin substitute, homogeneously intermixed with the stabilizing material of this invention. While gelatin itself, preferably of a fairly high grade, has been found to be most acceptable for use in the instant inventive concept, various of the conventional gelatin substitutes such as other water permeable colloids including albumin, casein, polyvinyl alcohol or the like may be utilized. For each kilogram of coating composition, the optimum quantitative ratio of ingredients has been found to be approximately 80 grams of gelatin, approximately 4 grams of formaldehyde, approximately 2.4 grams of sodium acetate, approximately 3.6 grams of sodium citrate and approximately 4.3 grams of citric acid, the remainder being water and various wetting agents. While the above ratios are optimum and produce the best product, they may be somewhat varied slightly while still producing an acceptable color print. However, if the materials are present in a substantial excess, the transparency of the final product may be relatively poor, while if they are present in insufficient quan-

tity, the image itself may be very difficult to define. The following ranges of ingredients must be maintained to insure a commercially acceptable product; for each kilogram of coating composition, from approximately 72 to approximately 88 grams of gelatin, from approximately 3.2 to approximately 4.8 grams of formaldehyde, from approximately 1.9 to approximately 2.9 grams of sodium acetate, from approximately 2.9 to 4.3 grams of sodium citrate, and from approximately 3.4 to approximately 5.2 grams of citric acid. The quantitative ratio between these ingredients should be carefully adjusted to produce a composition having a pH of from 3.0 to 6.5, the optimum value being 5.2.

The coating material is prepared by intermixing the wetting agents, of which saponin and Tergitol, a Union Carbide Corporation surface active agent, have been found most useful, with 37 percent formaldehyde or formalin in an aqueous solution. The gelatin is dispersed in water and heated under stirring to boiling. The solution of stabilizing material is prepared by dissolving the sodium acetate, sodium citrate, and citric acid in water and this solution is then substantially homogeneously intermixed under heat and stirring with the aqueous dispersion of gelatin and with the solution of formaldehyde and wetting agents. The composition is then filtered in preparation for use.

Various procedures may be utilized for coating the support base with the transfer layer. For example, the base may be passed beneath ebonite rollers which dip into a trough of the coating composition removing and transferring a desired quantity. Alternately, an auxiliary roller may be provided which dips into a reservoir of the coating composititon and deposits the same on a main roller which rotates in juxtaposition to the support base without actually contacting the same, a triangular space being defined between the support base and the main roller which is maintained filled with coating composition to produce a desired thickness of transfer layer. The composition may merely be sprayed upon the support base or it may be transferred by a roller which is doctored by an actual knife or by a "blade" of compressed air. An air knife is preferably used such as in the conventional Brookfield coating devices.

The transfer blank thus formed is utilized in the photographic dye process of this invention by contacting the same with at least one matrix having an image impregnated with a dye solution compatible with the stabilizing material in the transfer layer. While other compatible dyes have been found useful, optimum results have been attained by dying three-color separation matrices respectively with cyan, magenta, and yellow dye materials compatible with the stabilizing material, homogeneously intermixed with an aqueous solution of sodium citrate, formaldehyde and citric acid in a quantitative ratio to give proper dye contrast, each liter of the dye solution consisting essentially of approximately 10 grams of sodium citrate and from approximately 25 to 50 milliliters of a preservative solution formed by intermixing approximately 20 percent formalin and approximately 80 percent of an approximately 10 percent citric acid solution. The cyan dye solution, for each liter, includes approximately 2.9 grams of Anthraquinone Blue 3G, approximately 0.05 gram of Pontacyl Green-Blue, both Du Pont dye materials. Each liter of the magenta dye solution includes approximately 0.08 gram of Pontacyl Rubine R, and a approximately 0.02 gram of Pontacyl Carmine 2B, also Du Pont products. The yellow dye solution, for each liter, includes approximately 3.0 of tartrazine, which is a phenyl hydrazine.

The transfer blank, immediately before use, is immersed in plain water for a short time and squeezed lightly. Each of the matrices are immersed in a weak acetic acid solution until ready to print. The cyan, magenta, and yellow matrices are successively pressed into contact with the transfer blank with the images in registry for a time sufficient to transfer the respective dyes to the transfer layer.



A color print made from the transfer blank of the instant invention, even if it is retouched to any extent, can be used to directly make high fidelity contact separations or contact plates by masking in a conventional manner. This is true both of a transparency and even of a reflected copy. This process comprises passing light through selective color filters and the image on the transparency or the reflected copy diretly onto a positive. The positive image produced by this technique is of much higher fidelity and quality than is available through any known prior art methods.

The following representative examples are set forth to facilitate understanding of this invention, although it is to be understood that the examples are only presented to illustrate the various concepts disclosed herein rather than to limit them.

## EXAMPLE I

A coating composition is prepared utilizing the following ingredients:

Coating composition

Water—10,700 milliliters
Gelatin (Knox, Gel B10)—1,428 grams
Mordant solution—5,360 milliliters
Saponin—117 milliliters
Tergitol—540 milliliters
Formalin—72 milliliters

Stabilizing solution

Water—125 milliliters
Sodium acetate—1.0 grams
Sodium citrate—1.5 grams
Citric acid—1.8 grams

The saponin and Tergitol wetting agents are mixed with the formalin in water and the gelatin is dispersed in water, heated and stirred at approximately 225° F. The stabilizing solution is then added to the entire mixture, heated and stirred briskly, followed by filtering. The pH is checked and adjusted to from 3.0 to 6.5, if necessary, with citric acid or sodium hydroxide.

A film of Cronar is first coated with a gelatin carrier homogeneously intermixed with titanium white to provide a background layer by the conventional Brookfield coating machine.

After drying of the background layer, it is then superimposed with the transfer layer at approximately 100° F. and 1.5 atmospheres pressure. The coating operation proceeds at approximately 72 feet per minute providing a viscosity rating of 13.5 on the Brookfield scale. Approximately 25 kilograms of the coating composition is utilized to provide a transfer layer on a 44 foot wide, 1000 foot long, roll of Cronar thereby resulting in a uniform layer of from 0.5 to 0.6 gram of coating composition for each square foot of support base.

Three separate matrices are formed by immersing properly prepared gelatin reliefs in dye baths of the following composition:

Cyan

| | Grams |
|---|---|
| Anthraquinone Blue 3G | 2.9 |
| Pontacyl Green-Blue | 0.05 |

Magenta

| | |
|---|---|
| Pontacyl Rubine R | 0.08 |
| Pontacyl Carmine 2B | 0.02 |

Yellow

| | |
|---|---|
| Tartrazine | 3.0 |

With each of the above dye materials, a liquid buffer solution as follows is added:

Sodium citrate—10.0 grams
Distilled water to make—1.0 liter
Preservative solution—50 milliliters

Preservative solution

Formaldehyde (37%)—300 milliliters
Citric acid (10%)—1200 milliliters.

The imbibition or dye transfer printing operation is performed by dipping a sheet of the transfer blank in plain water for 15 seconds and squeezing the same. The dye matrices are each immersed in approximately ¼ to ½ percent acetic acid solution and are then successively rolled into contact with the transfer blank in registry to apply pressure for a time sufficient to transfer the dye to the blank.

The resultant product is found to have extremely good definition and brilliant colors with no staining, fogging, or spreading of the dyes. The product may be utilized either as a transparency or as a reflected print.

When the product is bleached by an overall bleach which reduces the three colors simultaneously, the artist or retoucher can control the bleaching process by varying the strength of the bleach with water. The use of a full strength bleach will entirely remove the image and the transfer blank may be reutilized for subsequent printing.

Alternately, individual red, yellow and blue bleaches are used to reduce or remove specific colors. For example, Kodak's Photoflow may be utilized to bleach the red dye, ammonia or Clorox for the yellow dye and potassium permanganate for the blue dye.

The product is found to be capable of bleaching and retouching or reprinting invisibly. Any corrections such as photocomposing, taking out or putting in of images, or other artwork may be readily accomplished by simple use of bleaches and dyes without the necessity of various etching techniques or the like.

By passing light through selective color filters and the image on the above product, both before and after retouching, masked in a conventional manner, direct contact separations and contact plates of extremely high fidelity are produced.

## EXAMPLE II

Example I is reproduced replacing the Cronar with various other support bases. While the use of other polyester materials is substantially comparable with Cronar, the use of absorbent bases such as paper or the like is found to result in a product which is not as clearly defined since there is a tendency for bleeding or spreading of the dyes into the base.

## EXAMPLE III

Example I is substantially repeated modifying the concentration of the citric acid in the preservative solution by increasing the same or neutralizing a portion of the same with small amounts of a 5–7 percent sodium hydroxide solution. Increased citric acid concentration is found to increase the dye contrast in the final product while decreased citric acid concentration decreases the dye contrast.

## EXAMPLE IV

The process of Example I is repeated varying the chemical ingredients in the transfer layer by as much as plus or minus 20 percent. As the upper limit of the ranges is approached, the transparency of the final product is substantially diminished. On the other hand, as the lower limit of the ranges is reached, the image is so vague and poorly defined as to be incapable of commercial use.

The quantitative ratios set forth in Example I are found to be optimum in all respects.

It will now be seen that there is herein provided an improved photographic dye transfer process utilizing a novel transfer blank having a unique transfer layer applied thereto, and resulting in a substantially more desirable film product than has been possible with prior art techniques. The inventive concepts disclosed herein, therefore, satisfy all of the objectives of this invention, including many advantages of great practical utility and commercial importance.

While the transfer blank has been particularly described as useful in a dye transfer printing process to produce a high fidelity product, the blank can also be utilized in the well-known silk screen and photo-gelatin processes for display and light box advertising purposes.

What is claimed is:

**1.** A photographic transfer blank comprising a support base, a transfer layer carried thereby, and a white background layer interposed between said support base and said transfer layer, said transfer layer including a colloidal carrier homogeneously intermixed with a stabilizing material consisting essentially of sodium acetate, sodium citrate and citric acid.

**2.** The blank of claim **1** wherein said support base is a substantially dimensionally stable film of polyethylene terephthalate.

**3.** The blank of claim **1** wherein said carrier is selected from the group consisting of gelatin and other water-permeable colloids.

**4.** The blank of claim **3** wherein said carrier is gelatin.

**5.** The blank of claim **1** wherein said background layer consists essentially of a colloidal carrier homogeneously intermixed with a white pigment.

**6.** The blank of claim **5** wherein said white pigment is selected from the group consisting of barium sulfate, titanium dioxide and zinc oxide.

**7.** The blank of claim **1** wherein said transfer layer consists essentially of a homogeneous intermixture of a water permeable colloidal carrier selected from the group consisting of gelatin and other water-permeable colloids formaldehyde, and a stabilizer material consisting essentially of sodium acetate, sodium citrate and citric acid.

**8.** A photographic transfer blank comprising a substantially dimensionally stable support base, a background layer carried by said support base and consisting essentially of a colloidal carrier homogeneously intermixed with a white pigment, and a transfer layer superimposed on said background layer, each kilogram of which upon application consists essentially of an aqueous dispersion of from approximately 72 to approximately 88 grams of a colloidal carrier selected from the group consisting of gelatin and other water-permeable colloids, from approximately 3.2 to approximately 4.8 grams of formaldehyde, and an aqueous stabilizer solution consisting essentially of from approximately 1.9 to approximately 2.9 grams of sodium acetate, from approximately 2.9 to approximately 4.3 grams of sodium citrate, from approximately 3.4 to approximately 5.2 grams of critric acid, the remainder being water and wetting agents, said transfer layer having a pH of from approximately 3.0 to approximately 6.5.

**9.** The blank of claim **8** wherein said transfer layer is of a substantially uniform thickness, each square foot of support base carrying approximately 0.5–0.6 gram of transfer layer.

**10.** A photographic transfer blank comprising a support base, a transfer layer carried thereby, and a white background layer interposed between said support base and said transfer layer, said transfer layer including a colloidal carrier comprising gelatin homogeneously mixed with the stabilizing material consisting essentially of sodium acetate, sodium citrate, and citric acid, wherein a kilogram of said transfer layer upon application consists essentially of approximately 80 grams of gelatin, approximately 4 grams of formaldehyde, approximately 2.4 grams of sodium acetate, approximately 3.6 grams of sodium

citrate, and approximately 4.3 grams of citric acid, the remainder being water and wetting agents.

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