This invention relates to the formation of photographic images by diffusion transfer processes, and particularly to processes wherein the surface of a diffusion transfer image is after treated with a liquid coating composition.

The formation of transfer images by diffusion transfer processes is now well known. The formation of silver halide transfer images, wherein an exposed silver halide emulsion is developed and a soluble complex of unexposed silver halide is transferred to a superposed image-receiving layer to provide a silver transfer image is described in a number of patents; see, for example, U.S. Patent No. 2,543,181, issued to Edwin H. Land, February 27, 1951; U.S. Patents Nos. 2,698,237, 2,698,238 and 2,698,245, all issued December 28, 1954, to Edwin H. Land; U.S. Patent No. 2,774,667, issued December 18, 1956, to Edwin H. Land and Meroe M. Morse; U.S. Patent No. 2,923,122, issued February 11, 1958, to Edwin H. Land; etc. Color images also may be formed by diffusion transfer processes; see, for example, the aforesaid U.S. Patent No. 2,543,181; U.S. Patent No. 2,559,643, issued to Edwin H. Land on July 10, 1951; U.S. Patent No. 2,661,295, issued to Edwin H. Land on December 1, 1953; U.S. Patent No. 2,774,668, issued on December 18, 1956, to Howard G. Rogers; U.S. Patent No. 2,968,554, issued January 17, 1961 to Edwin H. Land; the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 365,135, filed February 13, 1956; and the copending U.S. application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958 (now U.S. Patent No. 2,983,606 issued May 9, 1961).

It is frequently desirable to apply a liquid coating composition to a diffusion transfer print to improve its stability. It is particularly important to protect the print from the hazards encountered in handling and storage, such as dirt or dust, fingerprints, scratches, and the like. Such a photographic transfer image ordinarily retains at least traces of photographic reagents with which it has been processed, the continued presence of which may adversely affect the quality and stability of the image. For example, the oxidation products of some silver halide developing agents tend to oxidize silver and thus may cause a loss of density in a silver transfer image. Reaction products from residual sodium thiosulfate also may act adversely by oxidizing silver. In addition, oxidation by atmospheric oxygen of unreacted developing agent or other components of the processing composition may impart a stain or otherwise discolor a transfer image, particularly the highlights thereof, whether the image is composed of silver or dye. Application of the liquid coating composition is effective to render such residual processing reagents relatively innocuous, and also may physically remove such residual reagents by a washing action, particularly water-soluble residual processing reagents. If padding a physical protective layer to the surface of the image, may also increase the glossy appearance of the print. It has been found convenient and more efficient when applying such a liquid coating composition, and particularly one which includes a polymeric material, to employ an applicator such as that disclosed in U.S. Patent No. 2,788,408, issued to Charles A. Goyatos on October 30, 1957. The applicator comprises a rigid holder and an absorbent element retained within the holder. The absorbent element may be of any appropriate absorbent material which will serve to retain a quantity of the liquid coating composition, and may be of cotton or wool in any form, such as woven or nonwoven fabric or felt or a batt of such material. The mass of the absorbent element is preferably proportioned so that it can contain a volume of liquid composition sufficient to coat a plurality of photographic prints, or, for example, the number of prints obtained from one roll of film. In use, a quantity of the liquid composition is applied to the photographic print by squeezing or applying to the holder portion of the applicator, and the liquid composition is spread over the surface of the photographic print by passing the absorbent element portion of the applicator over the surface of the print while in frictional pressure contact therewith. A number of such coating compositions particularly suitable for use with silver transfer prints have been disclosed; see, for example, U.S. Patent No. 2,719,791, issued October 4, 1955, to Edwin H. Land; U.S. Patent No. 2,794,740, issued June 4, 1957, to Edwin H. Land and Milton Green; U.S. Patent No. 2,830,900 issued April 15, 1958, to Edwin H. Land, Elkan R. Blout and Howard C. Haas; U.S. Patent No. 2,855,298, issued October 7, 1958, to Edwin H. Land; U.S. Patent No. 2,866,705, issued December 30, 1958, to Edwin H. Land and Meroe M. Morse; and U.S. Patent No. 2,874,045 issued February 17, 1959, to Edwin H. Land. Examples of coating compositions useful in imparting a protective action to color transfer images are disclosed in the copending U.S. application of Howard G. Rogers, Serial No. 93,309 filed March 6, 1961.

It has been found that while these coating compositions do provide a desirable protective action, the benefits of applying the coating composition are dependent to a substantial degree upon the efficiency with which the user applies the liquid coating composition to the transfer image. While the user may believe that he has in fact uniformly applied the composition over the entire surface, it may happen that the amount of the liquid coating composition applied was insufficient, or that the quantity applied was not so distributed as to properly coat the transfer print despite what visually may appear to have been a uniform application. In addition, it is desirable that the border areas also be coated with the liquid coating composition to insure that the corner areas of the image area have been coated, and also to avoid any possibility of introduction of contaminants into the border areas from which they might diffuse laterally into the picture area to adversely affect its quality or stability. In addition, the user may simply forget to apply the print coating composition.

It has now been found that the efficiency of the print coating operation may be substantially increased by incorporating a visual indicator, removable by the liquid coating composition, in or on the surface of the image-receiving layer. Accordingly, primary objects of this invention are to provide an improved process for applying a liquid coating composition to a diffusion transfer image and to provide an image-receiving element particularly useful in such after coating processes.

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

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

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

In accordance with this invention, a colored reagent
serving as a visual indicator or guide to the efficacy with which the liquid coating composition has been incorporated in or on the image-receiving layer of the image-receiving element. The presence of this colored reagent serves as a visual reminder to the user to apply the liquid coating composition and also serves to indicate the uniformity and thoroughness with which the liquid coating composition has been applied. This colored reagent is present in a substantially uniform concentration to give an overall coloration, and preferably is a dye which is photographically inert in the particular transfer process. While this dye may be included in the image-receiving layer, in a preferred embodiment the dye is included in a striping layer coated over the image-receiving layer. The use of such striping layers to facilitate separation of the image-receiving layer from the photosensitive layer and the layer of processing composition is well known in the diffusion transfer art; note, for example, U.S. Patent No. 2,759,825 issued to Edwin H. Land on August 21, 1956, as well as each of stripping layer 15a in FIGURE 1 of the previously mentioned U.S. Patent No. 2,719,791, FIGURES 2 and 3 of the previously mentioned U.S. Patent No. 2,774,667, and FIGURES 3 and 4 of the previously mentioned U.S. Patent No. 2,823,122.

The visual indicator, or coating guide, may be a dye or other colored substance.

While the dye may be of any desired color, it preferably is of a color esthetically acceptable as a "tint" in the normally white border areas of the transfer image. It is a feature of this invention that the coating guide dye is removed from the image areas of the image-receiving layer during formation and formation of the transfer image. As a result, the separated transfer print has a normal appearance except for the colored border areas. The dye preferably is removed from the image areas by virtue of its solubility in the alkaline processing composition. In the preferred embodiment the dye does not undergo a color change or decomposition during formation but is merely dissolved out of the image-receiving element into the processing composition. It will be understood, however, that, where desired, one may use dyes which undergo a color change in alkaline environment, or which are bleached or otherwise chemically reacted to yield fragments which are colorless and/or insoluble in the transfer processing composition. It will be apparent that if the dye used as the coating indicator is one which undergoes a chemical reaction in the presence of the alkaline processing composition, the resulting process reagent should have no adverse effect upon either the formation of the transfer image, or upon its stability should they remain in the transfer print. Since the alkaline processing composition does not come into contact with the border areas of the print (by virtue of a "mask" as is well known in the art), the dye in the border areas is unaffected and remains to act as a visual indicator and reminder that the protective liquid coating composition has not been applied.

It is frequently desirable, particularly where the aftertreatment of the transfer image with a liquid coating composition serves at least in part to wash out residual photographic reagents, to pass the applicator over the surface of the transfer image several times, e.g., 4 or 6, and, more preferably 6 to 8 times, to insure that an adequate treatment has been accomplished. A plurality of passes of the applicator also serves to minimize the possibility that areas of the transfer print will not be coated in any individual pass. It is therefore a further feature of this invention that the amount of dye used and/or the solubility of said dye in the coating composition are so adjusted or selected that the desired minimum number of passes of the print coat must be made in order to remove the dye from the border areas of the transfer print. It will be apparent that the quantity of dye may be readily varied, and that the amount of any given dye necessary to provide the desired color level will vary with the spectral efficiency (e) of the respective dye. The amount of dye used is preferably just sufficient to impart a clearly visible but relatively light tint, so that it will be esthetically acceptable.

As an example of an embodiment of this invention, 23 g. of a dye sold by General Aniline & Film Co., Binghamton, N.Y., under the trade name "Wool Green BSNA" (Extra Concentrated) were added to 5 gallons of a gum arabic striping layer coating composition. The resulting image-receiving element had a light blue tint. When processed in a silver transfer process in accordance with the previously noted patents, the image area of the separated transfer print was substantially completely free of any coloration from the "Wool Green BSNA" dye, while the border areas of the print retained the same blue tint as before processing. Several passes of a liquid coating composition, such as one of those disclosed in the aforementioned patents for aftertreatment of a silver transfer image, removed the dye from the border areas of the print also. Examination of the print coat showed a blue coloration of the absorbent cotton batting, indicating that the dye was not destroyed or otherwise reacted during the print coat treatment. "Wool Green BSNA" is the trade name of General Aniline & Film Co., Binghamton, N.Y., for a dye having the structure:

This dye is listed in the Colour Index, 2nd edition, 1956, as C.I. Acid Green 50 and as C.I. 44000. Transfer prints made using image-receiving elements containing this dye in the strip coat and aftercoated in the usual manner showed no difference in image stability in accelerated aging tests as compared with similar prints made without the blue dye in the strip coat.

Image-receiving elements containing useful concentrations of the "Wool Green BSNA" were found to exhibit a reflectance density at 650 mμ (measured above a magnesium carbonate standard) of from 0.10 to about 0.45. The preferred reflectance density was about 0.25.

As an example of another dye which has been found useful in this invention, mention may be made of Pontacryl Green SN-Extra, C.I. No. 737 (Colour Index, 1st edition). Other dyes useful in this invention will be apparent or may be readily determined by simple experiments.

The advantages of the incorporation of a print coating guide dye were demonstrated in two experiments. In the first of these experiments, two sets of 896 silver transfer images were printed coated. One set was made using an image-receiving element which contained no dye or other visual coating guide, and 230 of these prints were found to have been inadequately coated. By comparison, only 43 of the 896 transfer images made on an image-receiving element containing the "Wool Green BSNA" dye were found to have been inadequately coated.

In the second experiment, 480 silver transfer images were made on each of the aforementioned types of image-receiving elements. 83 of the transfer prints made on the normal image-receiving sheet were found to have been inadequately coated, but only 8 of the pictures made on the "Wool Green BSNA" colored receiving sheet had any print defects.

The efficiency with which the dye is removed from the image-receiving sheet will be enhanced if the dye exhibits...
a preferential affinity for the absorbent material of the print coater, for the film-forming material, e.g., carboxymethyl cellulose or hydroxyethyl cellulose, employed in the transfer processing composition, and/or for the gelatin or other polymeric materials of the photosensitive element.

It will be noted that the dye incorporated in the image-receiving sheet as the print coating guide is substantially completely removed from the image area during formation of the transfer image, and from the border area by the aftertreatment with the liquid coating composition. If any of the dye remains in the image area or in the border areas after the transfer image has been properly print coated, the amount of the residual dye is insufficient to give any appreciable visual coloration, so that for practical purposes, the whites are uncolored.

While the invention has been illustrated with respect to a silver transfer image which is subjected to an aftertreatment with a liquid coating composition contained in an applicator or print coater, it will be understood that the invention is also applicable where the aftertreatment constitutes immersing the separated image-receiving element in a suitable liquid, for example, as described in the U.S. Patent No. 2,662,822, issued December 15, 1953, to Edwin H. Land. A device suitable for effecting such an immersion is disclosed in U.S. Patent No. 2,873,666, issued to Edwin H. Land and Vaito K. Eloranta on February 17, 1959.

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

What is claimed is:

1. In a process of forming a photographic image by diffusion transfer, wherein an exposed photosensitive emulsion is developed with an alkaline processing composition, an imagewise distribution of a diffusable image-forming component is transferred by diffusion to an image-receiving element carrying an image-receiving layer in superposed relationship with said photosensitive emulsion to provide a visible transfer image, and said transfer image is subjected to an aftertreatment with a liquid composition to remove or render innocuous residual processing reagents, the improvement wherein the image-receiving element containing said image-receiving layer also initially includes a substantially uniformly distributed colored substance, said colored substance is substantially completely removed from the image areas of said image-receiving element during said development and transfer, said colored substance is retained in the nonimage, border areas of said image-receiving element, and said after-treatment substantially completely removes said colored substance from said border areas.

2. A process as defined in claim 1, wherein said diffusable image-forming component is a water-soluble complex of silver halide, and said transfer image is a silver image.

3. A process as defined in claim 1, wherein said liquid coating composition is applied to said image-receiving element by means of a print coater including an absorbent material releasably containing said liquid composition, said colored substance having an affinity for said absorbent material.

4. A process as defined in claim 1, wherein said colored substance is contained in a layer over said image-receiving layer.

5. A process as defined in claim 1, wherein said colored substance is removed from said image area by being dissolved in said alkaline processing composition.

6. A process as defined in claim 1, wherein said colored substance is a dye having the structure:

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,114,636

December 17, 1963

Edwin H. Land

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 62, after "If" insert -- the liquid coating composition also includes a water-insoluble organic polymer, a protective coating of this polymer will also be applied, which, in addition to im-- --; column 6, line 4, for "substantilly" read -- substantially --; line 11, for "image receiving" read -- image-receiving --; line 44, for "Govatsos" read -- Govatsos --.

Signed and sealed this 23rd day of June 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents