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DIFFUSION TRANSFER WITH 4-METHYLPHENYL-HYDROQUINONE IN THE EMULSION AND N,N-DIETHYLHYDROXYLAMINE IN THE PROCESSING FLUID

Edwin H. Land, Cambridge, Mass., assignor to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Diffusion transfer processes for forming silver transfer images are disclosed wherein the photosensitive element includes a first silver halide developing agent (e.g., 4'-methylphenyl hydroquinone) which is a strong silver halide developing agent and is substantially nondiffusible from the photosensitive element to the silver-receptive stratum during processing, and the processing composition includes a second silver halide developing agent (e.g., N,N-diethylhydroxylamine) which is volatilizable at room temperature and is effective to reduce the transferred silver complex. The second developing agent is volatilized from the silver receptive stratum after the transfer image is formed and said stratum is separated from the developed photosensitive element.

This invention relates to photography and more particularly to the formation of silver images by diffusion transfer processes.

This application is a continuation-in-part of my copending application, Ser. No. 854,551, filed Nov. 23, 1959.

Processes for forming transfer images by the formation of a diffusible complex of unexposed silver halide and transferring said silver complex to a stratum where the silver of said complex is precipitated to form a visible image are now well known. It is a principal object of this invention to provide improvements in said transfer processes, whereby the exposed photosensitive silver halide emulsion is developed by a substantially nondiffusible silver halide developing agent, and the transferred silver complex is developed by a substantially volatile silver halide developing agent. A further object of the invention is to provide silver transfer images of substantially improved stability, as well as substantially reduced stain in the transfer image. A further object of this invention is to provide photographic processes and products utilizing a novel combination of silver halide developing agents to form transfer images in silver.

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

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 disclosure, and the scope of the application of which will be indicated in the claims.

As noted above, the formation of transfer images in silver is now well known. In accordance with said processes, an exposed silver halide emulsion is developed and a diffusible water-soluble complex is formed with unexposed silver halide. This water-soluble silver complex is transferred by diffusion to a stratum in superposed relationship with said exposed silver halide emulsion. The transferred silver complex is precipitated or reduced to provide a visible image. The superposed stratum to which the soluble silver complex is transferred is frequency referred to as a silver-receptive layer and preferably includes reagents

which act to increase the precipitation of the silver of said silver complex. In a typical embodiment of this silver transfer process, a processing fluid is spread in a uniformly thin layer between the exposed silver halide emulsion and another sheet-like element which may include the silver-receptive layer, for example, by advancing the elements between a pair of pressure-applying rollers. The elements are maintained in superposed relation for a predetermined period, preferably of the order of 10 to 120 seconds in duration during which exposed silver halide is developed, and undeveloped silver halide forms a water-soluble complex silver salt which is transferred through the layer of processing fluid to the silver-receptive layer where it is reacted to form a visible print. At the end of this imbibition period, the silver halide emulsion is stripped from the silver-receptive layer. Materials useful in one such transfer process and described in my U.S. Patent No. 2,543,181, issued Feb. 27, 1951.

A wide variety of silver halide developing agents have been disclosed as useful in such diffusion transfer processes. It has been customary to incorporate the silver halide developing agent or agents in the processing fluid, and said silver halide developing agents have been effective in reducing the transferred soluble silver complex to silver in addition to reducing the exposed silver halide of the negative to silver. In has been recognized that one source of potential staining and/or instability of the resulting silver transfer image has been residual silver halide developing agent present in or on the stripped silver-receptive layer. A number of proposals have been made for preventing or minimizing said staining and instability. Thus, it has been found that the stability and stain resistance of the silver transfer image may be substantially improved by swabbing the stripped silver-receptive layer with an aqueous solution of a polymeric material which upon drying provides a protective plastic layer. The swabbing of the stripped silver-receptive layer with such a composition is also effective to remove at least part of any silver halide developing agent or other components of the processing fluid which may adhere to the stripped silver-receptive layer. Examples of such processes are disclosed in U.S. Patents Nos. 2,719,791, 2,794,740, 2,852,372, 2,855,298, 2,866,705 and 2,874,045.

It has also been proposed in U.S. Patent No. 2,740,717, issued to H. C. Yutzy et al. on Apr. 3, 1956, to reduce staining of the silver transfer image by effecting development with a substantially nondiffusing development agent contained in the silver halide emulsion. While such a procedure may minimize the amount of silver halide developing agent which may be present in the stripped element containing the silver transfer image, it must depend upon the action of the silver precipitating agent present in the silver-receptive layer to convert the transferred silver complex to a visible image. The resulting absence from the silver-receptive stratum of a silver halide developing agent substantially decreases the overall effectiveness of the process.

A further method of preventing staining of the silver transfer image by the silver halide developing agent has been to employ a volatile silver halide developing agent, particularly in combination with a volatile nitrogenous base. Examples of such volatile silver halide developing agents and volatile nitrogenous bases may be found in U.S. Patent No. 2,857,276, issued to Edwin H. Land et al. on Oct. 21, 1958. These volatile silver halide developing agents are very effective in reducing the transferred silver complex, but they are not as effective in developing the exposed silver halide, and the resulting silver transfer images are formed at relatively low film speeds or exposure indices.

I have now unexpectedly found that the use of a sub-

stantially nondiffusing silver halide developing agent to develop the exposed silver halide emulsion in combination with a volatile silver halide developing agent to develop the transferred silver complex is effective to provide good quality silver transfer images having substantially improved stability and minimal stain. In addition, the use of such a combination of silver halide developing agents is effective to give good quality transfer images at substantially lower illumination levels than are obtained using the volatile silver halide developing agent alone. This combination of silver halide developing agents is effective to provide silver transfer images of immensely greater density and contrast than the trace images which can be obtained using the same nondiffusing silver halide developing agent alone.

As used herein, the expression "nondiffusing silver halide developing agent" is intended to include silver halide developing agents which, when incorporated in the photosensitive element containing the silver halide emulsion, are substantially nondiffusible from the photosensitive element to the silver-receptive layer during processing, so that the silver-receptive layer is substantially free of this developing agent. It will be understood that this "nondiffusibility" is a relative term, as this developing agent must have sufficient solubility to reach the exposed silver halide and rapidly reduce it, without transferring to the silver-receptive stratum to any appreciable extent within the imbibition period. The nondiffusing silver halide developing agent may be initially located in the silver halide emulsion stratum or in a stratum coated over or behind the silver halide emulsion. The nondiffusing developing agent should be one which rapidly develops the exposed silver halide, and may be a hydroquinone or aminophenol. 4' - methylphenyl - hydroquinone has been found to be particularly useful as such a negative developing agent. Other nondiffusing silver halide developing agents are well known in the art and may be selected to meet the requirements of any particular silver halide emulsion, emulsion thickness, alkali concentration of the processing composition, etc.

Examples of volatile silver halide developing agents are also well known and may be selected to meet the requirements of the particular embodiment by which this invention is practiced. In particular, mention may be made of the volatile silver halide developing agents disclosed in U.S. Patent No. 2,857,276, issued to Edwin H. Land et al. on Oct. 21, 1958, and, in particular, the volatile hydroxylamines. As an example of particularly useful volatile silver halide developing agents, mention may be made of the N- lower alkyl hydroxylamines, and particularly of N,N-diethylhydroxylamine. As used herein, the expression "volatile silver halide developing agent" is intended to include silver halide developing agents which are effective to reduce the soluble silver complex which is transferred to the silver-receptive layer, and which will be volatilized from the stripped silver-receptive layer within a short time at room temperature. Such volatile silver halide developing agents are soluble in the processing fluid and readily volatilize from the separated silver-receptive layer at room temperature.

In a particularly useful embodiment of this invention, the processing fluid is caused to adhere to the silver-receptive layer when said silver-receptive layer is separated from the developed silver halide emulsion. Techniques for causing the preferential adhesion of the solidified layer of processing fluid to the silver-receptive layer upon stripping are known to the art. The solidified layer of processing fluid is effective to provide a protective coating to the silver transfer image. In this embodiment, the nondiffusing silver halide development agent also should not diffuse into the processing fluid to any appreciable extent. Since the silver halide developing agents are either nondiffusible from the photosensitive element into the silver-receptive layer or are volatilized from it subsequent to image formation, any tendency of residual components of the processing fluid to stain or attack the silver image is minimized.

The following examples are illustrative of this invention.

Example 1

An exposed silver halide emulsion is developed in a solution of Kodak DK–50 developer [1] for 3 minutes and rinsed. The thus-developed negative, in the dark and without being fixed, is then processed with a solution comprising:

Sodium hydroxide	g	11.25
Sodium thiosulfate	g	11.97
Sodium carboxymethyl cellulose (medium viscosity)	g	20
Sodium carboxymethyl cellulose (high viscosity)	g	2
N,N-diethylhydroxylamine	cc	15

Water to make 300 cc.

while superposed on an image-receiving element, the silver-receptive layer of which contained silver precipitating agents. After an imbibition period of approximately 1 minute, the image-receiving element, with the solidified layer of processing composition adhered to the silver-receptive layer, was stripped from the photosensitive element.

Example 2

A photosensitive silver emulsion, approximately seven feet in length and three and fifteen-sixteenths inches in width, was coated with approximately 8 cc. of a gelatin solution having 4'-methylphenyl-hydroquinone dispersed therein at a concentration of approximately 0.0395 g. per cc. of gelatin solution and allowed to dry. After exposure, the negative and an image-receiving element containing silver precipitants were subjected to the viscous processing fluid set forth in Example 1 applied in a layer approximately 0.0022 inch thick as the exposed negative and the image-receiving layer were advanced between a pair of pressure-applying rollers. After an imbibition period of approximately 1 minute, the image-receiving layer, with the solidified layer of processing fluid adhered to its surface, was stripped from the developed negative. The resulting positive image had a $D_{max.}$ of 1.17, a $D_{min.}$ of 0.03, and a slope of 0.84.

Example 3

When the procedure described in Example 2 was repeated without the N,N-diethylhydroxylamine, a pale positive image was obtained, indicating that only a very small amount of the 4'-methylphenylhydroquinone had diffused to the silver-receptive layer.

Silver transfer images obtained in accordance with the procedure described in Example 2, and which were not given any additional treatment after stripping, have been found to be more stable than similar images made following the conventional practice of including hydroquinone-type silver halide developing agents in the processing fluid and wherein the resulting silver image was not subjected to an aftertreatment such as previously described. The silver images obtained by this invention were particularly resistant to fading, and showed marked stain reduction.

Photosensitive emulsions are customarily assigned an A.S.A. Exposure Index according to an established standard procedure. This A.S.A. Exposure Index is an indication of the relative sensitivity, and when employed in combination with an appropriately calibrated exposure meter permits the user to determine the proper exposure. The term "Diffusion Transfer Process Exposure Index"

[1] Kodak DK–50 developer has the following composition: to 500 cc. of water are added 2.5 g. of Elon (N-methyl-p-aminophenol sulfate); sodium sulfite (desiccated) 30.0 g.; hydroquinone 2.5 g.; Kodalk 10.0 g.; potassium bromide 0.5 g. The resulting solution is diluted with water to make 1000 cc., and is used without further dilution.

is to be distinguished from the A.S.A. Exposure Index, and is the exposure index to which an exposure meter, calibrated to the A.S.A. Exposure Index, must be set in order that it give the correct exposure data for producing transfer prints of satisfactory high quality; this exposure index is sometimes referred to as the "equivalent A.S.A. Exposure Index." A description of the methods of determining these exposure indices may be found in the copending application of Milton Green, Ser. No. 834,262, filed Aug. 17, 1959 now Patent 3,108,001.

It has been found that this invention provides unexpectedly high exposure indices. Thus, the following Diffusion Transfer Process Exposure Indices were obtained for the procedures of Examples 1 and 2, and for a control which duplicated Example 2 omitting the overcoat of 4'-methylphenyl-hydroquinone, i.e., the sole developing agent present in the control was N,N-diethyl hydroxylamine:

Control	3.3
Example 1	3500
Example 2	1960

The "shoulder speed" of the silver transfer image obtained in Example 2 was 0.00029 meter-candle-seconds. "Shoulder speed" is the minimum amount of exposure in meter-candle-seconds which can be used to expose the negative emulsion and give a transfer image in which there is the minimum contrast which the eye can distinguish, i.e., there is visible detail in the shadow regions of the transfer image.

It will thus be noted that the use of a strong negative developing agent which is not diffused out of the negative in combination with a volatile developing agent to develop the transferred silver halide complex has resulted in superior transfer images without the disadvantages normally expected of the developing agents employed.

It should be noted that no antifoggant was present in the processing set forth in Example 2 or in the "volatile developer" composition set forth in Example 1.

While, in the preferred embodiment of this invention, the solidified layer of processing fluid is caused to preferentially adhere to the surface of the silver-receptive layer, it is also contemplated to so perform the process as to cause said solidified layer or processing fluid to preferentially adhere to the developed negative. In this last-mentioned embodiment, the stripped silver transfer image then may be given a protective plastic layer, in accordance with the previously mentioned patents.

The processing fluid is preferably contained in a frangible or rupturable container which may be constructed in accordance with the disclosures set forth in U.S. Patent No. 2,634,886. The silver halide emulsion and/or the silver-receptive layer may be mounted on opaque or transparent supports, thus permitting exposure from either side as desired, and permitting the formation of reflection prints or transparencies.

As previously noted, the print-receiving stratum preferably contains silver precipitating agents or nuclei, whose presence during the transfer process has a desirable effect on the amount and character of the silver precipitated during positive print formation. Examples of such silver precipitating agents are the metallic sulfides and selenides, thiooxalates, and thioacetamides, and colloidal metals disclosed in U.S. Patents Nos. 2,698,237 and 2,774,667. It is also desirable, as disclosed in said patents, to provide, as the vehicle for the silver precipitating agents, a macroscopically continuous film that consists of submacospic agglomerates of minute particles of a suitable water-insoluble, inorganic, preferably siliceous, material such as silica aerogel. The use of such a vehicle for the precipitating agents tends to aggregate the silver that is precipitated into its most effective condition for print formation.

Suitable silver halide solvents, which may be incorporated in the processing composition or in one of the photosensitive and receiving elements, include conventional fixing agents such as sodium thiosulfate, sodium thiocyanate, ammonium thiosulfate, or associations of cyclic imides and nitrogenous bases such as associations of barbiturates or uracils and ammonia or amines. Of these, the conventional fixing agents specified are preferred. Preferably, the solution also contains a film-forming material such as water-soluble plastic, such as sodium carboxymethyl cellulose or hydroxyethyl cellulose, starch or gum imparting a viscosity of from 1000 to 200,000 centipoises at a temperature of 20° C. in order to permit the solution to be readily controlled during and after spreading.

It will be apparent that the relative proportions of the agents of the developer composition set forth herein may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, silver halide solvents, etc., other than those specifically mentioned. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of developing agent may be varied over a wide range.

Since certain changes may be made in the above products and processes 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. A process of forming silver transfer images comprising exposing a photosensitive element containing a silver halide emulsion and 4'-methylphenyl-hydroquinone, developing said exposed emulsion with said 4'-methylphenyl-hydroquinone, forming a soluble silver complex by reaction of unexposed silver halide with a silver halide solvent, transferring said soluble silver complex to a silver-receptive stratum in superposed relationship with said silver halide emulsion, reducing said soluble silver salt with N,N-diethylhydroxylamine to form a silver-containing positive image and separating said silver-receptive stratum from said silver halide emulsion after said positive image has been formed, said process including the step of volatilizing said N,N-diethylhydroxylamine from said silver-receptive stratum.

2. A photographic process of forming positive silver transfer images comprising the steps of exposing a photosensitive element containing a silver halide emulsion and 4'-methylphenylhydroquinone, applying to said exposed photosensitive silver halide emulsion a processing composition including sodium thiosulfate, a film-forming polymeric material and N,N-diethylhydroxylamine, developing the exposed silver halide and forming a soluble silver complex of unexposed silver halide with said sodium thiosulfate, transferring said soluble silver complex to a silver-receptive stratum in superposed relationship with said silver halide emulsion, reducing said soluble silver complex to form a visible silver-containing positive image and separating said silver-receptive stratum from said silver halide emulsion, said process including the step of volatilizing said N,N-diethylhydroxylamine from said silver-receptive stratum.

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NORMAN G. TORCHIN, *Primary Examiner.*

D. LEVY, *Assistant Examiner.*