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E. H. LAND ETAL
DIFFUSION-TRANSFER REVERSAL PROCESSES AND
ELEMENTS USEFUL IN SUCH PROCESSES
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3,234,022

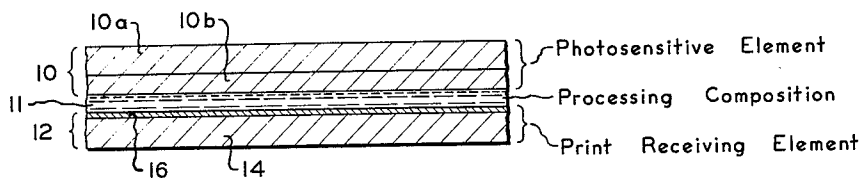


FIG. 1

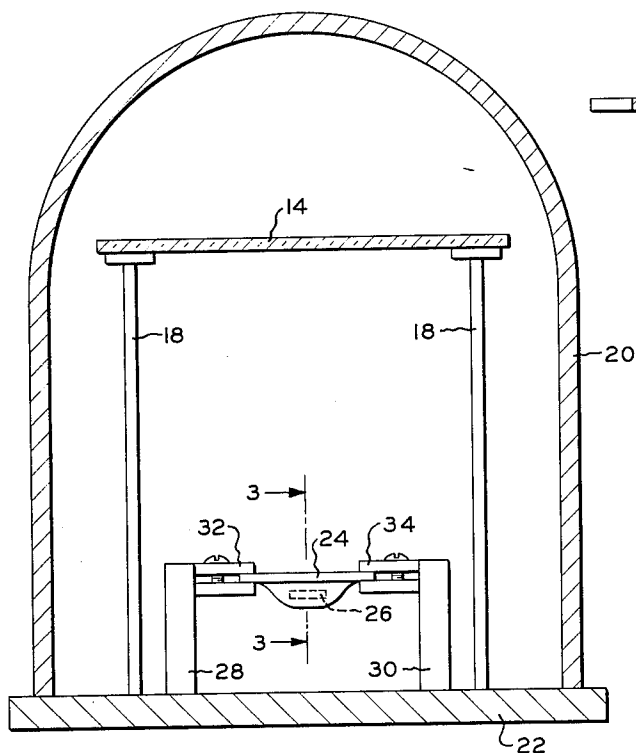


FIG. 2

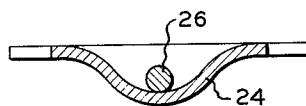


FIG. 3

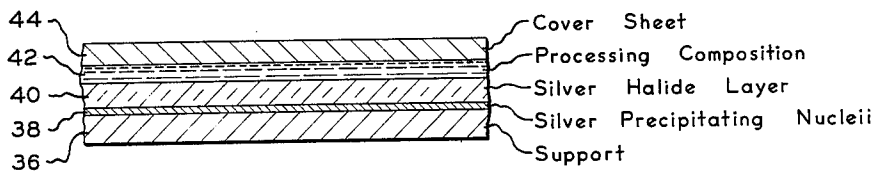


FIG. 4

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DIFFUSION-TRANSFER REVERSAL PROCESSES AND ELEMENTS USEFUL IN SUCH PROCESSES

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Continuation of abandoned application Ser. No. 625,981, Dec. 3, 1956. This application Aug. 8, 1960, Ser. No. 48,327

16 Claims. (Cl. 96—29)

This application is a continuation of application Serial No. 625,981 filed December 3, 1956, now abandoned.

This invention relates to photographic processes and products and more particularly to diffusion-transfer reversal processes and to print-receiving elements useful in such processes.

Photographic processes for giving positive images directly and involving the development of a latent image in a silver halide emulsion and the transfer by diffusion of components from said emulsion to another layer to effect the formation of the positive print are now well known. One species of this type of processing involves the transfer of silver from the silver halide emulsion in the form of a soluble silver complex and the formation of a print by means of the silver of said complex in or on a suitable print-receiving element. In a preferred form of this type of process, the silver of the complex is precipitated as metallic silver and the pictorial quality of the print obtained in this way is, in a large measure, dependent on the nature of the silver precipitating environment provided by the print-receiving element.

It is one object of the present invention to provide a novel silver precipitating mechanism useful in silver diffusion-transfer reversal processes. More specifically, it is an object of the present invention to provide a novel process wherein silver is transferred to and precipitated on silver precipitating nuclei created by the evaporation upon a support of silver precipitating agents, the evaporation providing simply and economically an advantageous distribution of the silver precipitating nuclei.

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.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

FIGURE 1 is a diagrammatic, enlarged, sectional view illustrating the association of elements during one stage of the performance of a transfer process according to the present invention and showing as one of the elements an embodiment of the novel silver precipitating element of the invention, the relative thickness of the various layers of said element being, in some cases, exaggerated;

FIG. 2 is a sectional view illustrating diagrammatically apparatus suitable for producing the print-receiving element shown in FIG. 1;

FIG. 3 is a sectional view taken substantially along line 3—3 of FIG. 2 and showing a detail of the filament of such apparatus; and

FIG. 4 is a diagrammatic, enlarged, sectional view illustrating the association of elements during one stage of the performance of another embodiment of a transfer process using the novel silver precipitating element of the invention.

The improvements comprehended by the present invention are particularly useful in processes wherein a positive print is obtained in a single step by suitable treating the silver halide emulsion with a uniformly applied layer of processing liquid, said liquid being preferably viscous and being spread in a layer over the surface of the photosensitive element. The liquid in its viscous condition may be distributed between the print-receiving element and the photosensitive element from a container located between said elements, the process in this form being particularly suited for performance directly in a camera. However, it is to be expressly understood that the present invention is not limited to use in this type of transfer process but finds general utility in any process in which a soluble silver complex is to be reduced at a predetermined site to silver to provide a record image.

According to the present invention, a silver precipitating agent is deposited by evaporation upon a suitable support, thereby providing said support with silver precipitating nuclei in a highly dispersed state and essentially free of protective colloid and forming a silver precipitating element especially adapted for use in a silver diffusion-transfer reversal process. The silver precipitating agent may be one of the compounds and elements which have previously been described as useful for improving the amount and kind of silver precipitate obtained in a process of this type. However, the present invention is especially adapted to provide a mechanism for simply and directly making use of silver precipitating agents which are relatively water-insoluble and refractory in character, such, for example, as the metals and the sulfides and selenides of heavy metals. Among these may be mentioned metallic silver, gold, platinum, palladium, mercury, copper, aluminum, zinc, lead and iron; the sulfides of zinc, chromium, gallium, iron, cadmium, cobalt, nickel, lead, antimony, bismuth, silver, cerium; and the selenides of lead, zinc, antimony and nickel. Among the metals, best results are obtained from the more noble metals and especially by the evaporation of one or more of gold, platinum, silver, palladium, mercury and copper.

Some of the aforesaid metals, e.g., aluminum and zinc, are oxidizable in ordinary atmospheres, and with respect to such materials it is desirable that the print-receiving element be used soon enough after the deposition of the materials thereon to be free of any substantial amount of the oxidized metal. The deposit of metal or other silver precipitating agent is preferably kept very thin so that even when depositing materials of relatively high optical density, the deposit does not appreciably affect the visual transparency of a transparent support when the deposit is made on such a support or the visual lightness of an opaque support for a reflection print when the deposit is made on such a support. It is desirable, too, that the support upon which the deposit is made have a surface which is relatively smooth. The support may be any solid material which is otherwise appropriate as a support for a photographic print. Glass and smooth-surfaced organic plastics are very satisfactory in this regard, as are papers whose surfaces are suitably treated to make them smooth.

Some of the above-mentioned silver precipitating agents, when deposited in accordance with the present invention and used in diffusion-transfer reversal processes, tend to give silver images which are non-homogeneous in hue and, to correct for this tendency, there may be incorporated in or on the print-receiving element or in or on the photosensitive element or in the processing composition a suitable blue-black toning agent. Especially effective for this purpose are: cysteine, mercaptobenzthiazol and thiobarbituric acid.

Referring now to the drawing, FIG. 1 illustrates diagrammatically an assembly of elements, including the

novel print-receiving element of the present invention, as they might be used in one form of silver diffusion-transfer reversal. In this embodiment, 10 represents a photosensitive element comprising a support 10a and a photosensitive emulsion layer 10b, 11 represents a layer of relatively viscous processing composition, and 12 is one embodiment of the novel print-receiving element of the invention. As shown, print-receiving element 12 comprises a suitable support 14 and a silver precipitating layer 16 comprising the thin, highly dispersed film of evaporated silver precipitating nuclei.

Liquid layer 11 may be obtained by spreading the processing composition, for example, in the manner disclosed in U.S. Patent No. 2,647,056, issued July 28, 1953, to Edwin H. Land, and the processing composition may be one of the film-forming compositions disclosed in said patent. It may comprise, for example, a developing agent such as hydroquinone, an alkali such as sodium hydroxide, a substance, such as sodium thiosulfate, for forming a soluble silver complex with unexposed silver halide, and a thickening agent, such as the high molecular weight film former, sodium carboxymethyl cellulose. All of these materials are preferably in aqueous solution. It is, of course, to be understood that, instead of being contained in the processing liquid as it is applied to the photosensitive element, these various photographic reagents may be in part or wholly added to the processing liquid after it is applied by being dispersed in or on one or both of elements 10 and 12. The liquid processing agent may be spread as layer 11 from an elongated container of the type and in the manner described in U.S. Patent No. 2,543,181, issued February 27, 1951, to Edwin H. Land.

In the type of process performed as illustrated in FIG. 1, the developing agent rendered active by the spreading of layer 11 develops the latent image record in emulsion 10b and causes soluble silver complexes to form with the undeveloped grains of the emulsion. The silver complexes dissolve in the liquid of layer 11 and diffuse to silver precipitating layer 16, the silver thereof being there precipitated, preferably as metallic silver or less preferably as a silver salt, to form the positive print. Under ordinary circumstances and for normal processing, the formation of the positive print takes approximately a minute and, upon completion thereof, print-receiving element 12 is stripped from photosensitive element 10. Depending upon the specific process involved, the residual film created by the spreading of layer 11 is peeled either with element 10 or with element 12.

FIG. 2 illustrates diagrammatically an apparatus suitable for use in the preparation of print-receiving element 12 according to the invention. Support 14, which as noted above may be glass, an organic plastic or a suitably surfaced paper, is shown as mounted on suitable supports 18 within a bell jar 20, which is supported, for example, on a base plate 22. Bell jar 20 is evacuated by suitable means, not shown, and maintained thereby at the desired high vacuum during the evaporation process. A filament 24, for example of tantalum, shaped into the form of a vessel (FIG. 3) and containing the charge of material 26 to be evaporated, is supported within the said bell jar between two electrodes 28 and 30. As shown, said filament is secured at each end to the said electrodes by suitable holding means, as for example a pair of jaws 32 and 34, affixed respectively to electrodes 28 and 30. An electric potential applied across said electrodes heats filament 24 and the charge 26, e.g., gold, contained therein. Lead wires, not shown, connect the two electrodes 28 and 30 in a conventional manner and connect said electrodes, in turn, to a source of electric potential, preferably through a suitable rheostat control. Another arrangement suitable for holding and heating the charge of material to be evaporated and especially for evaporating certain of the salts which can be usefully employed in the process involves a crucible for containing the charge and separate heating filaments associated with said

crucible for volatilizing the charge. This type of arrangement is shown diagrammatically in U.S. Patent No. 2,447,831.

In general, when depositing metals, e.g., gold, on a support, especially a transparent support, it is preferable to include within the evaporation mechanism a test strip of white, opaque paper, a portion of which is shielded by a suitable obstacle from the evaporating charge. When a detectable difference in density begins to exist between the protected and unprotected areas of this test strip, evaporation is sufficient. Although a density difference can be detected between the coated and the uncoated surfaces, this difference is actually so slight as not to have any adverse effect on the highlight regions of a support which is uniformly coated with a deposit of the optical density under consideration. While the method of deposition is here described in connection with laboratory apparatus and laboratory controls, it can obviously be performed by production equipment, for example continuously on supports of paper or plastic.

It is to be understood that the print-receiving element of the present invention may be used in conjunction with a photosensitive element to produce prints by diffusion-transfer in any of the variety of physical arrangements that have heretofore been proposed for this purpose and is not restricted to the type of process illustrated in FIG. 1. For example, an especially useful arrangement employing the novel silver precipitating environment of the present invention is the one illustrated in FIG. 4, which comprises a suitable support 36 upon which a layer 38 of highly dispersed silver precipitating nuclei has been deposited by evaporation. Upon this layer, a silver halide emulsion 40 is cast or otherwise directly applied. If desired, there may be interposed between layer 40 and layer 38 a stripping layer which will facilitate the separation of layers 40 and 38 upon the completion of the formation of the positive image. Suitable stripping layers for this purpose are disclosed in U.S. Patent No. 2,759,825, issued August 21, 1956, to Edwin H. Land.

To process this element, a layer 42 of processing composition, preferably the viscous processing composition hereinabove referred to, is spread between the said element and a cover sheet 44, the latter serving to facilitate spreading and to separate the undesired strata from the print-receiving element upon the completion of the transfer. The liquid content of layer 42 permeates through photosensitive silver halide emulsion 40, developing the latter and providing the soluble silver complexes which transfer to print-receiving layer 38 to be there precipitated as silver. On the formation of the silver print in layer 38, the print-receiving element comprising support 36 and layer 38 is stripped from the remainder of the lamination, the photosensitive element adhering preferentially to layer 42. It is also possible to obtain a useful positive print without separating layers 38 and 40 by taking advantage of the more dense deposits of silver which are obtained when the silver is transferred and reprecipitated on a vigorous silver precipitating environment of the type created by the deposition techniques of the present invention. Processes of this type are disclosed in the copending application of Edwin H. Land, Serial No. 466,889, filed November 4, 1954, now U.S. Patent No. 2,861,885, issued November 25, 1958.

A useful application of this last-mentioned species of the transfer process is described in Patent No. 2,726,154, issued December 6, 1955 to Edwin H. Land. The process is, however, generally useful wherever high resolving power and freedom from grain are desired. It is preferable for optimum results to have layers 36 and 38 transparent so that the surface of photosensitive emulsion 40 adjacent layer 36 can be exposed through said layer. This type of exposure, as opposed to exposure of layer 40 through the other side thereof, gives higher resolution.

The print-receiving elements formed by evaporation may be used in a diffusion-transfer process, for example,

of the type illustrated in FIG. 1. A print-receiving element so formed may serve as the element 12, and the processing composition of layer 11 may comprise:

	Grams
Water	1860
Sodium carboxymethyl cellulose	117
Sodium sulfite	78
Sodium hydroxide	74.6
Sodium thiosulfate	14.5
Citric acid	38.5
Hydroquinone	52

It is prepared by dissolving the sodium carboxymethyl cellulose, for example the commercially available Hercules 1362 medium viscosity type, in the water in a mixer at room temperature, and the solution is mixed therein for approximately one hour. Thereafter, the sodium sulfite, sodium hydroxide, sodium thiosulfate and citric acid are added to the solution, the addition being effected in an inert atmosphere, for example of nitrogen. Upon dissolution of these materials, the hydroquinone is added and the solution is further mixed for an hour at approximately room temperature in a nonoxidizing atmosphere of nitrogen.

Layer 11, upon spreading, is approximately .002-.003" in thickness. Emulsion 10b is a relatively high-speed orthochromatic emulsion, like the emulsion of Eastman Kodak Verichrome film, and has been exposed to predetermined subject matter to form therein a latent image of said subject matter, support 10a for said emulsion being a white paper. The laminations formed by the spreading of the processing agent in a layer 11 between elements 10 and 12 is kept intact for approximately one-half to one and one-half minutes, preferably one minute, and at the end of this time element 12 is stripped from element 10. Element 12, when so stripped, carries a positive print in silver of the subject matter of the latent image in emulsion 10b. The sodium carboxymethyl cellulose of layer 11 and adheres to coating 16 of element 12 and solidifies to form a film thereon.

In still another embodiment of the invention, the silver precipitating agents herein described may be evaporated directly on the emulsion surface of the photosensitive element. This provides a silver precipitating stratum directly on the emulsion, and a composite structure so constituted may be used in a diffusion-transfer reversal process to form a positive image in said stratum which is thereafter peeled from the emulsion. Preferably, however, this composite structure is used to produce a print which requires no separation of the print-receiving stratum from the photosensitive emulsion in accordance with the processes disclosed in the aforementioned copending application of Edwin H. Land, Serial No. 466,889.

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 or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of forming images by diffusion-transfer which comprises condensing silver precipitating nuclei from the vapor phase on a support in a highly dispersed state and essentially free of protective colloid to form a print-receiving element, developing a latent image in an exposed silver halide layer, forming a transferable silver complex with part at least of the undeveloped silver halide of said layer, transferring at least part of said complex to said print-receiving element, and forming

on said support by means of the silver transferred to said nuclei an image comprising silver.

2. The process of claim 1 wherein said silver precipitating nuclei are formed of a relatively water-insoluble and refractory substance.

3. The process of claim 1 wherein the silver precipitating nuclei are at least one substance from the class consisting of metallic sulfides and selenides and metals.

4. The process of claim 1 wherein the silver precipitating nuclei are a noble metal.

5. The process of claim 1 wherein the silver precipitating nuclei are gold.

6. The process of claim 1 wherein the silver precipitating nuclei are silver.

7. The process of claim 1 wherein the silver precipitating nuclei are mercury.

8. The process of claim 1 wherein the silver precipitating nuclei are copper.

9. The process of claim 1 wherein the silver precipitating nuclei are aluminum.

10. A photosensitive element comprising a support carrying, in sequence, a silver halide layer and a silver-receptive stratum superposed on and coextensive at least in part with said silver halide layer, said silver-receptive stratum comprising silver precipitating nuclei deposited on said layer by condensing a silver precipitating substance from the vapor phase onto said layer in a finely dispersed condition, said nuclei being present on said layer essentially free of protective colloid, said silver precipitating nuclei comprising a refractory and relatively water-insoluble substance.

11. The product of claim 10 wherein the silver precipitating nuclei are at least one substance from the class consisting of metallic sulfides and selenides and metals.

12. The product of claim 10 wherein the silver precipitating nuclei are a noble metal.

13. The product of claim 10 wherein the silver precipitating nuclei are gold.

14. The product of claim 10 wherein the silver precipitating nuclei are silver.

15. The product of claim 10 wherein the silver precipitating nuclei are mercury.

16. The product of claim 10 wherein the silver precipitating nuclei are copper.

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