PHOTOGRAPHIC SILVER HALIDE DIFFUSION TRANSFER PROCESS

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In the well-known silver halide diffusion transfer process of photography, an exposed emulsion layer is developed in the presence of a silver halide solvent, the emulsion layer being for at least a portion, or for the whole of the development period in effective contact with a receiving sheet, the surface of which generally carries a quantity of a silver precipitant which may comprise either physical development nuclei such as colloidal silver or silver sulfide or a chemical precipitant for silver ions, such as zinc sulfide. Development of the emulsion layer proceeds and is followed immediately by complexing of the precipitated silver halide with a silver halide solvent also present in the developer composition, and image-wise diffusion of the resulting silver complex to the receiving sheet where the silver precipitant causes the formation of an argentophil image.

In this process there is often appreciably more silver halide transferred to the receiving layer than is required, or may be desired, for forming the argentophil (silver-containing) image. Moreover, it may be desirable to control the sensitometric properties of the image independent of the amount or type of silver halide transferring. Also it may be desirable to assure a complete transfer of the undeveloped silver halide thereby leaving a useable silver image in the original sensitive element substantially free of silver halide.

We have discovered that we can obtain a satisfactory negative and also a satisfactory positive print by the diffusion transfer process by employing a special reception element which contains at least two silver precipitating layers. These precipitating layers may be separated by a light-colored permeable layer relatively opaque to light or the light-colored permeable layer may also be a silver precipitating layer. The light-colored permeable layer is used to isolate the silver image obtained in the underlying silver precipitating layer so that upon viewing the element, only the silver image in the other layer will be seen. Of course, if the support of the reception layer is transparent and the two silver precipitating layers are separated by a light-colored permeable layer relatively opaque to light, the image in the lower layer can also be viewed. Of the two silver precipitating layers, the one next to the support of the reception element contains substantially more silver precipitating agent than the other layer.

In one embodiment of our invention, a support such as paper carries a first hydrophilic layer such as gelatin containing from about 0.5—100 mg./ft.² of a silver precipitating agent such as colloidal silver or silver sulfide, useful about 5—25 mg./ft.² in the case of silver nuclei, and also sufficient, light colored, preferably white, pigment to render the coating relatively opaque to light. Titanium dioxide or similar pigment or even a substance becoming opaque during the process may be used. Upon the opaque layer is coated a second hydrophilic silver precipitating layer such as gelatin containing from about 0.03 to 5 mg./ft.² of the same or a different silver precipitating agent, useful about 0.1 to 2 mg./ft.² in the case of silver nuclei.

In another embodiment, a support such as paper carries a first hydrophilic layer such as gelatin containing from 0.5—100 mg./ft.² of a silver precipitating agent over which is coated a light colored, preferably white hydrophilic layer relatively opaque to light, such as a gelatin layer containing titanium dioxide or a similar pigment. Upon the relatively opaque layer is coated a second hydrophilic silver precipitating layer such as gelatin containing from about 0.03—5 mg./ft.² of the same or a different silver precipitating agent.

The above described receiving elements may be used in the process as a separate element for receiving silver halide transferring from a diversity of exposed and developed negative materials. Thus, a wide range of photographic films containing different quantities of silver halide may be used with the reception element. In a particularly useful embodiment, the receiving layers are coated on a polyester support and contacted against an exposed silver halide emulsion in the presence of a diffusion transfer processing solution containing a silver halide developer, a silver halide complexing agent, a silver precipitating agent, etc. After formation of the silver image in the receiving layers, the receiving support is separated from the negative material and a satisfactory negative image is obtained as well as a satisfactory print which is formed in the top receiving layer of the reception element. The receiving element may be separated from the exposure and contacted against the exposed negative material in a web processing system of particular usefulness when rapid processing is desired shortly after the negative material has been exposed.

It will be appreciated that whereas the reception element described herein is a light-insensitive element, that it can be over-coated with a light-sensitive silver halide emulsion, adapted to be removed by coating on a suitable stripping layer, exposed, developed using a diffusion transfer processing solution as described above and, the positive print obtained by then stripping off the silver halide emulsion. To facilitate removal of the emulsion layer from the surface of the reception element, the stripping layer under the silver halide may be one of those known in the art such as a gelatin-cellulose nitrate layer. During development with an alkaline developer solution, the negative image forms in the emulsion layer in contact with the undeveloped silver halide diffusing to and forming positive silver images in the two silver precipitating layers, after which the emulsion layer can be removed.

In using the reception elements described, it is possible to obtain a certain quality of print in the reception element with a given negative material such as a high-speed negative film, and also to leave a certain quality of negative silver image in the negative film for subsequent use in making additional prints by the usual contact printing methods. By selection of the appropriate amount, type and proportion of silver precipitating agent in the two layers of the reception element the desired result can be obtained as illustrated in Example 4 below.

In additional variations the desired positive image can be obtained in the silver precipitating layer next to the support and the auxiliary positive image in the outer silver precipitating layer. In this case the opaque layer can be dispensed with and by use of an alkali soluble vehicle such as cellulose ether phthalate in the outer layer, or by using a stripping layer, the outer layer can be removed following processing to leave a single positive silver image on the support.

The following examples are intended to illustrate our invention but not to limit it in any way:

EXAMPLE 1

A light insensitive reception element was prepared on a subbed polyester support which consisted of the following:

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Material: Coverage
Gelatin .......................... grams/ft.\(^2\)  - 1.32
Titanium dioxide .......................... grams/ft.\(^2\)  - 0.29
Nickel sulfide nuclei .......................... mg./ft.\(^2\)  - 0.7

On top of this layer was coated a thinner layer composed of:

Material: Coverage
Gelatin .......................... grams/ft.\(^2\)  - 0.50
Nickel sulfide nuclei .......................... mg./ft.\(^2\)  - 0.07

A spreading agent and hardener of the type well known in the art were included in the coatings. The dried sheet was then soaked for 10 minutes at 70° F. in a solution containing per liter of solution:

Diethylenedioctanol SO\(_4\) (20% by weight SO\(_4\)) .......................... 100.0
Diethylenedioctanol .......................... 10.0
Sodium sulfite .......................... 20.0
Hydroquinone .......................... 0.4
Sodium thiosulfate pentahydrate .......................... 2.0
Potassium iodide .......................... 0.1
2-methyl-1-phenyl-3-pyrazolidone .......................... 0.5
3-mercaptop-1,2,4-triazole .......................... 0.1

The surface solution was removed from the sheet and it was rolled into contact with a fine grain bromoiodide photographic film. After 10 minutes the film and sheet were separated. A high quality neutral toned reflection positive print was observed in the processing sheet. A fully developed and fixed negative image was produced in the photographic film.

A similar test was run with a processing sheet which did not contain any nickel sulfide nuclei in the titanium dioxide layer. The positive image produced in such a sheet was of very poor quality in that the image areas were "blocked-in" in medium and heavy density regions. There was a dichroic appearance to the entire image which appeared as an overall loss of contrast.

EXAMPLE 2

A 0.005" piece of subbed film base (non-fibrous cellulose acetate) material was coated on one side with a layer containing 0.65 gram/ft.\(^2\) of gelatin and 0.39 gram/ft.\(^2\) of titanium dioxide. The other side was coated with a 1300 mg./ft.\(^2\) of gelatin pad containing the following:

Barium sulfate .......................... mg./ft.\(^2\)  - 290
Zinc sulfide .......................... mg./ft.\(^2\)  - 0.7

On top of this layer a gelatin pad was coated which contained on each square foot:

Gelatin .......................... 500
Nickel sulfide nuclei .......................... 0.7

This layer was overcoated with a gelatin coating at a coverage of 150 mg. gelatin/ft.\(^2\).

A sheet prepared as above was soaked for 10 minutes at 70° F. in the solution described in Example 1. Following the procedure described in Example 1, the soaked sheet was used to process a medium speed silver bromoiodide photographic film. The positive image was of good contrast and free of any dichroic appearance. There was no surface "silvering" which degraded the image.

EXAMPLE 3

A reception element wherein a positive image can be formed by the diffusion transfer process is formed by preparing a subbed support having the following layers applied to it:

Layer 1:
Gelatin .......................... Mg./ft.\(^2\)  - 1320
Barium sulfate .......................... 290
Zinc sulfide .......................... 0.8

Layer 2:
Gelatin .......................... 500
Zinc sulfide .......................... 0.7

Such an element was treated for 8 minutes in a solvent containing developer as described in the earlier examples and rolled into contact with a high speed photographic film. After 10 minutes, they were separated to obtain a fully processed negative and a positive silver image on the reception element which was free of dichroic areas.

EXAMPLE 4

A subbed film support was coated with a dispersion of yellow colloidal silver in aqueous gelation solution so as to obtain 0.94 gram gelation and 20 mg. silver per square foot. Upon this layer was coated an interlayer from a dispersion of titanium dioxide in gelation solution so as to obtain 0.27 gram gelatin and 0.81 gram titanium dioxide per square foot. A final dispersion of zinc sulfide in gelatin solution was coated so as to obtain 0.36 gram gelatin and 1.32 cc. of 0.002 N (0.128 mg.) of zinc sulfide per square foot.

The resultant reception element was treated for two minutes in the following developer solution:

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2,2′-Iminodinitroso-SO\(_4\) addition product (13.8% SO\(_4\)) .......................... 200
2,2′-Iminodinitroso .......................... 50
4,4-dimethyl-1-phenyl-3-pyrazolidone .......................... 1.0
Hydroquinone .......................... 11.0
Hypo .......................... 8.0
Water to 1000.

Then squeezed and rolled into contact with an exposed silver chlorobromide film. The two sheets were maintained in contact for 10 minutes then stripped apart to obtain a negative silver image substantially free of silver halide on the film, and a positive silver image on the reception element which was clearly visible against the background of the titanium dioxide interlayer. As mentioned, in this process the proportions and type of nuclei in the two layers can be varied with the expectation that a change in the density, contrast and even tone of the silver images in the reception element will be obtained.

In carrying out the invention, the alkaline component of the developer solution may be varied and may include alkali metal hydroxide or carbonate. Other silver halide developing agents can be used and all or a part of the developing agent can be contained in the emulsion layer used in the process, and the silver halide solvents used to transport the undeveloped positive silver halide may include alkali metal and ammonium thiosulfates. All or a part of the required amount of silver halide solvent may be contained in one of the layers of the reception element of the invention.

The silver precipitating agents used in the silver precipitating layers of the reception element may include e.g. sulfides, selenides, polysulfides, polyselenides, thiourea, stannous halides, heavy metals, heavy metal salts and fogged silver halide. The heavy metals such as colloidal silver, gold, platinum, palladium and mercury, and metal sulfides, including heavy metal sulfides, such as lead, silver, nickel, zinc, antimony, cadmium and bismuth sulfides, and complex salts of these with thioacetamide, dithio-oxamide or dithio-biuret, are especially useful in the silver precipitating layers.

The silver halide emulsions used in the process to provide the silver halide image transferring to the reception layers, may be varied and, for example, silver bromide, silver chloride, silver iodide, silver chlorobromide, silver chloroiodide, silver chlorobromide and silver bromoiodide emulsions can be used.

The organic colloid component of the three layers of the reception element should be hydrophilic and is preferably gelatin although other hydrophilic organic colloids such as polyvinyl alcohol, partially hydrolyzed cellulose ester etc., permeable to the dissolved silver halide and developer solution can be used.

The opaque substance in the interlayer or second precipitating layer may be varied and includes inert light-
colored, preferably white, pigments such as titanium dioxide, zinc oxide, barium sulfate and similar materials opaque to visible light.

Alternatively, the opaque layer may be one wherein the opacity is formed as in vesicular material, or an opacity may be introduced by means of crystallization, or by blushing of the layer by a nonsolvent.

In a similar process an emulsion layer is exposed and developed with developer solution such as above, in contact with a reception element containing an opaque support, single silver precipitating layer thereon and underlying opaque layer, with the result that the silver image obtained in the reception element is intentionally obscured by the opaque layers and the desired image is the silver negative image obtained in the emulsion layer. Similarly, the undeveloped silver halide can be transferred to a single layer containing a mixture of a silver precipitating agent such as colloidal silver and fogged silver halide with the result that silver images obtained thereon are not readily visible and the desired image is that obtained in the emulsion layer.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and a defined in the appended claims.

We claim:

1. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer containing from about 0.5 - 100 mg. of silver precipitating agent per square foot, superimposed on the first layer an alkali permeable second layer relatively opaque to light, and superimposed over the second layer an alkali permeable third layer containing substantially only enough silver precipitating agent for the formation of an image of good contrast, said layers containing a hydrophilic colloid binder.

2. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 100 mg. of a silver precipitating agent per square foot and superimposed over the first layer an alkali permeable second layer containing substantially only enough silver precipitating agent for the formation of an image of good contrast, said layers containing a hydrophilic colloid binder.

3. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer containing from about 0.5 - 100 mg. of a silver precipitating agent per square foot, superimposed on the first layer an alkali permeable second layer relatively opaque to light containing a titanium dioxide pigment, and superimposed over the second layer an alkali permeable third layer containing substantially only enough silver precipitating agent for the formation of an image of good contrast, said layers containing a hydrophilic colloid binder.

4. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 25 mg. of a silver precipitating agent per square foot, and a light colored pigment, and superimposed on the first layer an alkali permeable second layer containing substantially only enough silver precipitating agent for the formation of an image of good contrast, said layers containing a hydrophilic colloid binder.

5. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 100 mg. of a silver precipitating agent per square foot, and superimposed on the first layer an alkali permeable second layer containing substantially only enough silver precipitating agent for the formation of an image of good contrast, said layers containing a hydrophilic colloid binder.

6. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 25 mg. of colloidal silver per square foot, and titanium dioxide pigment, and superimposed on the first layer an alkali permeable second layer containing substantially only enough zinc sulfide nuclei for the formation of an image of good contrast, said layers containing a hydrophilic colloid binder.

7. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 25 mg. of nickel sulfide nuclei per square foot, and titanium dioxide pigment, and superimposed on the first layer an alkali permeable second layer containing from about 0.1 - 5 mg. of zinc sulfide nuclei per square foot, said layers containing a hydrophilic colloid binder.

8. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 25 mg. of nickel sulfide nuclei per square foot, and barium sulfate pigment, and superimposed on the first layer an alkali permeable second layer containing from about 0.1 to 5 mg. of nickel sulfide nuclei per square foot, said layers containing a hydrophilic colloid binder.

9. A light-insensitive reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon in order, a first layer relatively opaque to light containing from about 0.5 - 25 mg. of zinc sulfide nuclei per square foot, and barium sulfate pigment, and superimposed on the first layer an alkali permeable second layer containing from about 0.1 to 5 mg. of zinc sulfide nuclei per square foot, said layers containing a hydrophilic colloid binder.

10. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contiguity with a silver halide solvent image-wise by diffusion to a light insensitive reception element, as described in claim 1 whereby a portion of the transferred silver halide forms a silver image in said third layer and a portion of the transferred silver halide penetrates said second and third layers and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and third layers.

11. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contiguity with a silver halide solvent image-wise by diffusion to a light insensitive reception element, as described in claim 2 whereby a portion of the transferred silver halide forms a silver image in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

12. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contiguity with a silver halide solvent image-wise by diffusion to a light insensitive reception element, as described in claim 3, whereby a portion of the transferred silver halide forms a silver image in said third layer and a portion of the transferred silver halide penetrates said second and third layers and is precipitated in said first layer, substantially all of the
transferred silver halide being precipitated in the said first and third layers.

13. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contingency with a silver halide solvent image-wise by diffusion to a reception element, as described in claim 4, whereby a portion of the transferred silver halide forms a silver image of good contrast in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

14. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contingency with a silver halide solvent image-wise by diffusion to a reception element, as described in claim 5, whereby a portion of the transferred silver halide forms a silver image of good contrast in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the first and second layers.

15. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contingency with a silver halide solvent image-wise by diffusion to a reception element, as described in claim 6, whereby a portion of the transferred silver halide forms a silver image of good contrast in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

16. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contingency with a silver halide solvent image-wise by diffusion to a reception element, as described in claim 7, whereby a portion of the transferred silver halide forms a silver image in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

17. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contingency with a silver halide solvent image-wise by diffusion to a reception element, as described in claim 8, whereby a portion of the transferred silver halide forms a silver image in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

18. A photographic silver halide diffusion transfer process which comprises developing an exposed silver halide emulsion layer, transferring the undeveloped silver halide of the emulsion layer in contingency with a silver halide solvent image-wise by diffusion to a light insensitive reception element, as described in claim 9, whereby a portion of the transferred silver halide forms a silver image in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

19. A photographic silver halide diffusion transfer process which comprises contacting an exposed light sensitive silver halide emulsion layer against a light insensitive reception element as described in claim 1, containing imbibed therein a solution containing a silver halide developing agent and a silver halide solvent, transferring the undeveloped silver halide of the emulsion layer image-wise by diffusion to the said light insensitive reception element, whereby a portion of the transferred silver halide forms a silver image in said third layer and a portion of the transferred silver halide penetrates said third layers and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and third layers.

20. A photographic silver halide diffusion transfer process which comprises contacting an exposed light sensitive silver halide emulsion layer against a light insensitive reception element as described in claim 2, containing imbibed therein a solution containing a silver halide developing agent and a silver halide solvent, transferring the undeveloped silver halide of the emulsion layer image-wise by diffusion to the said light insensitive reception element, whereby a portion of the transferred silver halide forms a silver image in said second layer and a portion of the transferred silver halide penetrates said second layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and second layers.

21. A photographic silver halide diffusion transfer process which comprises contacting an exposed light sensitive silver halide emulsion layer against a light insensitive reception element as described in claim 3, containing imbibed therein, a solution containing a silver halide developing agent and a silver halide solvent, transferring the undeveloped silver halide of the emulsion layer image-wise by diffusion to the said light insensitive reception element, whereby a portion of the transferred silver halide forms a silver image in said third layer and a portion of the transferred silver halide penetrates said third layer and is precipitated in said first layer, substantially all of the transferred silver halide being precipitated in the said first and third layers.

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