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PROCESS OF WASHING AND PROTECTING PHOTOGRAPHIC SILVER IMAGES

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This invention relates to the provision of a protective environment for a photographic silver image and, more particularly, to washing and protecting a photographic silver image by applying to at least one of its faces, in a layer, a composition containing water for dissolving residual water-soluble processing reagents from the image and material for producing a protective coating upon the image when the composition is dried.

Processes of the invention are particularly applicable to thin photographic silver images of the type described in the copending application of Edwin H. Land, Serial No. 302,746, now Patent No. 2,719,791 filed August 5, 1952. Such a thin photographic silver image, for example, may be produced by applying a photographic composition, which includes a silver halide developer and a silver halide solvent, to a photoexposed silver halide element and an image-receptive element which are in superposed relation. The composition acts to reduce exposed silver halide to silver, to react with unreduced silver halide to form a water-soluble, complex silver salt, and to transfer the salt to the image-receptive element where it is reduced to silver.

Objects of the present invention are: to provide as a novel product a photographic silver image of the foregoing type having a protective environment containing a low molecular weight compound selected from the class consisting of the polybasic alcohols and the sugars; to provide as a novel photographic product a silver image of the foregoing type having a protective environment containing, in addition to such a compound, a water-soluble heavy metal salt; to provide, in a novel process for washing and protecting a photographic silver image, the step of applying to at least one of its faces, in a layer, a composition comprising an aqueous solution of a low molecular weight compound selected from the class consisting of the polybasic alcohols and the sugars, and the step of drying the layer to produce a residue composed primarily of this compound; and to provide, in a novel process for washing and protecting a photographic silver image, the step of applying to at least one of its faces, in a layer, a composition comprising an aqueous solution of this compound and of a heavy metal salt, and the step of drying the layer to produce a residue composed primarily of this compound and this salt.

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.

A thin photographic silver image, formed in accordance with a process of the type described in the aforementioned copending patent application, ordinarily retains at least traces of the photographic reagents with which

it has been processed and the continued presence of which may adversely affect its stability. For example, silver may be oxidized by sulfur from the residue of sodium thiosulfate which has been employed as the solvent. Also, silver may be oxidized by such agents as hydrogen sulfide often present in the atmosphere. Furthermore, traces of unexhausted developer, if oxidized by atmospheric oxygen, may slightly discolor the highlights of the image.

A composition to be employed in the process of the present invention comprises water for dissolving such residual processing reagents from the image and a low molecular weight compound, selected from the class consisting of the polyhydric alcohols and the sugars, for producing a protective coating upon the image when the composition is dried. Preferred examples of such compounds are sorbitol, mannitol, inositol, dextrose, sucrose, sorbose, galactose, maltose, arabinose, raffinose, lactose, levulose, α-methyl-d-glucoside and α-methyl-d-mannoside.

It is often desirable to include in a composition to be employed in accordance with the present invention, in in addition to a compound of the foregoing type, an agent capable of protecting the image specifically from atmospheric sulfides. Examples of such agents are salts, preferably water soluble, containing heavy metal cations which form water-soluble sulfides. These salts, for example, are composed of: cations such as zinc, cadmium, lead, manganese, zirconium and tin; and anions such as acetate, sulfate, nitrate and formate. Heavy metal salts which are pale in appearance and which react to form pale sulfides are preferred. The salts of zinc, in particular, are preferred because they and their sulfides are white.

Specifically, compositions of the foregoing type may be prepared by dissolving one of the above-described, low molecular weight compounds in water at room temperature in the proportion of about 5–50 grams of compound to 100 grams of water. When desired, to such a solution 1–15 grams of heavy metal salt is added.

Photographic materials useful in the production of photographic silver images of the type referred to above are described in detail in Patent No. 2,543,181, which issued on February 27, 1951, in the name of Edwin H. Land. In a typical process employing such materials, a processing composition, containing a silver halide developer, a silver halide solvent and an alkali, is spread in a uniformly thin layer between the superposed surfaces of a photoexposed gelatino silver halide layer and an image-receptive element, for example by advancing the elements between a pair of pressure-applying rollers. The elements are maintained in superposed relation for a predetermined period during which exposed silver halide is reduced to silver and unreduced silver halides forms a water-soluble complex salt which diffuses through the layer of composition to the image-receptive element, there, upon being reduced to silver, to form a visible print composed of dense aggregates of silver distributed in a thin layer. At the end of this period, the silver halide element, preferably, together with the layer of processing composition, is stripped from the image-receptive element. Various techniques for causing the layer of processing composition to adhere to the silver halide element in preference to the image-receptive element are described in United States Letters Patent No. 2,647,056, issued to Edwin H. Land on July 28, 1953.

The gelatino silver halide element employed in the foregoing process, for example, is laminated to a conventional support composed of a suitable paper or a suitable plastic material such as cellulose nitrate or one of the organic acid cellulose esters including cellulose acetate, cellulose triacetate, cellulose propionate, cellulose butyrate and cellulose acetate butyrate. The image-receptive element, in the form of a layer upon a support of the

foregoing type, preferably includes certain materials the presence of which, during the transfer process, has a desirable effect on the amount and character of silver precipitated on the image-receptive element. As examples of silver precipitating materials, mention may be made of metallic sulfides and selenides, certain colloidal metals such as colloidal silver, thiooxalates and thioacetamides. These preferably are distributed in a macroscopically continuous film that consists of submacroscopic agglomerates of minute particles of a suitable water-insoluble, inorganic, preferably siliceous, material such as silica aerogel. Materials of the foregoing types are more specifically described in United States Letters Patents Nos. 2,698,237 and 2,698,245, both of which issued to Edwin H. Land on December 28, 1954.

Preferably, there is interposed between the image-receptive element and its support a water-impermeable layer capable of preventing the penetration of moisture from the processing composition into the support. This layer is responsible for the production of a substantially dry image as the photosensitive element is stripped from it. This layer cooperates with a protective coating of the type described above to completely envelop the image within a barrier against agents capable of harming the image. The water-impermeable layer, for example, may be composed of unplasticized polymethacrylic acid or one of the cellulosic esters such as cellulose nitrate, cellulose acetate, cellulose butyrate, cellulose propionate, celluose acetate butyrate or celulose acetate propionate. Preferred, however, are such rubbery polymers as polyvinyl butyral. If the support is water impermeable, of course, a discrete water-impermeable layer need not be provided.

Preferably, the composition is applied to one face of the image by means of an absorbent applicator composed, for example, of flannel, cotton batting or cellulose sponge which is charged with the composition. When the face of the image is swabbed with such an applicator, residual reagents of the image are dissolved in the composition and, for the most part, transferred into the applicator, and the image becomes coated with a thin layer of the composition. The composition layer is then dried to form a water-insoluble protective coating.

Example I

In a specific process of the foregoing type, the photosensitive stratum was an iodobromide emulsion of moderate speed, the silver-receptive stratum contained lead sulfides and selenides dispersed in silica aerogel, and the processing composition was of the following formulation:

Water	cc.	1860.0
Hydroquinone	g.	52.0
Sodium hydroxide	g.	74.6
Sodium sulfite	g.	78.0
Citric acid	g.	38.5
Sodium carboxymethyl cellulose	g.	93.0

This processing composition was spread between the silver halide stratum and the silver-receptive stratum in a layer from 1 to 6 thousandths of an inch thick. Approximately one minute thereafter, the silver halide stratum, together with the layer of processing composition, was stripped from the silver-receptive stratum to make the resulting print available for use. The free face of this silver print was washed with a cotton swab charged with a washing and protecting solution of the following formulation:

Sorbitol	g.	20.0
Zinc acetate	g.	3.0
Water	cc.	100.0

The print, when dried, was provided with a clear, unusually effective protective coating.

Example II

The print of Example I was swabbed with a washing and protecting solution of the following formulation with similarly excellent results:

Sucrose	g.	40.0
Zinc acetate	g.	5.0
Water	cc.	100.0

The present invention thus specifically contemplates providing the silver of a silver transfer-reversal print with a protective environment by the application of an aqueous solution of a low molecular weight compound selected from the class consisting of the polybasic alcohols and the sugars.

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. A method of producing a stable photographic print, said method comprising the steps of so permeating a silver-receptive stratum and an exposed gelatino silver halide stratum, which are in superposed relation, with a silver halide developer and a silver halide solvent in the presence of water, that exposed silver halide in the silver halide stratum is reduced to silver and unreduced silver halide from the silver halide stratum forms a water-soluble complex silver salt that diffuses to the image-receptive stratum where it is reduced to silver to form a visible print, stripping the silver-receptive stratum from the silver halide stratum whereby the print retains a residue of the solution, and swabbing the print with an absorbent applicator charged with a composition containing an aqueous solution of a compound, selected from the class consisting of the sugars and the six-membered carbonchain, cycloaliphatic and aliphatic polyhydric alcohols, in order to wash the residue substantially from the silver-receptive stratum into the applicator and to leave on the silver-receptive stratum a coating containing said compound.

2. A method of producing a stable photographic print, said method comprising the steps of so permeating a silver-receptive stratum and an exposed gelatino silver halide stratum which are contiguous, with a silver halide developer and a silver halide solvent in the presence of water, that exposed silver halide in the silver halide stratum is reduced to silver and unreduced silver halide from the silver halide stratum forms a water-soluble complex silver salt that diffuses to the image-receptive stratum where it is reduced to silver to form a visible print, stripping the silver-receptive stratum from the silver halide stratum whereby the print retains a residue of the solution, swabbing the print with an absorbent applicator charged with a composition containing an aqueous solution of a compound, selected from the class consisting of the sugars and the six-membered carbon-chain cycloaliphatic and aliphatic polyhydric alcohols, in order to wash the residue from the silver-receptive stratum into the applicator and to leave on the silver-receptive stratum a layer containing said compound, and drying said layer to produce a solid coating composed primarily of said compound.

3. The process of claim 2 wherein a heavy metal salt is incorporated in said solution.

4. The process of claim 3 wherein said heavy metal salt is a zinc salt.

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