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PROCESS OF WASHING AND PROTECTING PHOTOGRAPHIC SILVER IMAGES

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This invention relates to the protecting of photographic images by forming protective coatings therefor, to the washing and protecting of photographic silver images by removing residual processing reagents therefrom and forming protective coatings therefor, and to the photographic products of such processes.

Processes of the present 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, filed August 5, 1952, for Method of Improving the Stabilization of Finished Photopgraphic Prints by Applying a Liquid Composition Thereto, and the Product of Said Method (now Patent No. 2,719,791). 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.

Such a thin photographic silver image 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.

The processes describe below relate to the washing and protecting of a photographic silver image by applying to at least one of its faces a composition containing water and a salt of a heavy metal which forms a water insoluble sulfide. The water serves to wash residual processing reagents from the image. The composition contains a concentration of the salt sufficient to provide the residue, which is formed on the face of the image when the composition is dried, with a quantity of salt that is large relative to the quantity of silver in the image. Consequently, in accordance with the law of mass action, atmospheric sulfides which penetrate the coating react with the heavy metal salt in preference to the silver of the image.

Objects of the present invention are: to provide a process for protecting a photographic image by applying thereto a composition containing a salt of a heavy metal which forms a water insoluble sulfide; to provide a process for washing and protecting a photographic silver image by applying thereto a composition containing water and a salt of a heavy metal which forms a water insoluble sulfide; to provide in a process, for washing and protecting a photographic silver image, the step of applying to at least one face thereof, in a layer, a composition containing water and a salt of a heavy metal which forms a water insoluble sulfide, and the step of drying the layer to form a residue containing the salt; to provide in a process, for washing and protecting a photographic silver image, the step of applying to at least one face thereof, in a layer, a composition containing water, a coating material, and a salt of a heavy metal which forms a water insoluble sulfide, and the step of drying the layer to form a residue containing the coating material and the heavy metal salt; to provide a process of the foregoing type in which the heavy metal is zinc; to provide a process of the foregoing type in which the composition is applied by swabbing the image with an absorbent applicator; and to provide, as products, the protected photographic silver images resulting from the above processes.

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.

In accordance with the present invention, a composition of the foregoing type is applied to one face of a photographic silver 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 layer then is dried to form a protective coating which contains the heavy metal salt.

Heavy metal salts, preferably water-soluble, to be employed in accordance with the present invention contain: heavy metal cations such as zinc, cadium, lead, manganese, germanium, zirconium and tin; and anions such as acetate, sulfate, nitrate and formate. Preferably, the concentration of the heavy metal salt, by total weight of the composition, ranges approximately from 1% to 15%. A concentration of this order is such that the image is provided, when the composition is dried, with a quantity of salt large relative to the quantity of silver in the image. The latter quantity is of the order of 2 milligrams in an image having a 12 square inch face. The former quantity is so small that the salt and its sulfides do not appreciably affect the appearance of the image. 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.

A composition to be employed in accordance with the present invention, in one form, consists merely of an aqueous solution of a heavy metal salt. Alternatively, such a composition contains, in addition to water and a heavy metal salt, a material which is so constituted as to form, when the composition is dried, a solid protective coating of the following character: unaffected by fingerprints; stable throughout a wide temperature range, substantially unaffected by solar radiation; and optically clear. A composition may contain the water, the heavy metal salt and the coating in one of a variety of relationships.

In one form, the composition comprises an aqueous solution of a heavy metal salt of the above-described type and a coating material such as a protein, a gum, a carbohydrate or a resin. Examples of the latter material are polyvinylpyridine, polyvinyl alcohol, sodium carboxymethyl cellulose, hydroxyethyl cellulose, gelatin, gum

arabic, dimethyl hydantoin formaldehyde, dextrose, sucrose and sorbitol.

Example I

A composition of the foregoing type was prepared by dissolving 15 g. of hydroxyethyl cellulose and 5 g. of zinc acetate in 100 g. of water.

In order that the protective coating be water insensitive, it is preferred that a water-insoluble plastic material be employed. It is often desirable, therefore, to dissolve a heavy metal salt and a plastic material, which is insoluble in water itself, in a mixture of water and a water-miscible organic solvent. The plastic material, for example, is a polymer such as polyvinyl pyrrolidone or a polyvinyl butyral, the copolymerization product of acrylamide and maleic anhydride, or the interpolymerization product of hexamethylene adipamide, hexamethylene sebacamide and caprolactam, sold by DuPont under the trade name "Nylon FM 6501." Preferably, the organic solvent is volatile so that it imparts to the washing and protecting composition an over-all quick-drying character. As examples of suitable, water-miscible, organic solvents, mention may be made of lower alcohols such as ethanol, methanol and propanol, dioxane and the lower ketones such as acetone and a methylethyl ketone. If the organic solvent is of a type which is harmful to the photographic silver image to be washed and protected, the ratio of water to organic solvent must be so chosen that the harmful effect of the latter is obviated.

Example II

A composition of the foregoing type was prepared by stirring 5 g. of zinc acetate into a solution of 8 g. of a partially hydrolyzed polyvinyl butyral in a mixture of 60 cc. of water and 40 cc. of methanol.

In another form, the washing and protecting composition is prepared by dissolving, in a mixture of water and a water-miscible organic solvent, a heavy metal salt and the salt of a volatile weak electrolyte and a water-insoluble polymer having weak polar groups. It is apparent that in such a solution, the salt, the polymer, the electrolyte and their ions are in dynamic equilibrium. When a layer of such a composition is dried, volatilization of the electrolyte causes formation of the water-insoluble polymer from the salt to proceed to completion and consequent production of a protective coating of extreme water insensitivity. A water-insoluble polymer of the foregoing type, for example, is a vinylpyridine polymer such as poly-2-vinylpyridine, poly-3-vinylpyridine, poly-4-vinylpyridine, or a copolymer in which a vinylpyridine is the characteristic ingredient. As examples of suitable volatile weak electrolytes, mention may be made of acetic and propionic acids. The organic solvent, preferably volatile, for example, is a low molecular weight alcohol such as methanol, ethanol or propanol, dioxane or a low molecular weight ketone such as acetone or methylethyl ketone. This organic solvent cooperates in the dissolution of the polymer and imparts to the solution an over-all quick-drying character. Furthermore, as a consequence of the presence of the organic solvent, only a fraction of the stoichiometric quantity of electrolyte is required to render the polymer water-soluble and only this small quantity of electrolyte need volatilize to render the protective coating water-insoluble.

Example III

A sample of poly-2-vinylpyridine was prepared as follows. 105 g. (1 equivalent) of distilled 2-vinylpyridine was dissolved in a mixture of 138 ml. of water and 34.3 ml. of commercial sulfuric acid (96%). The temperature of the resulting solution being maintained at 25° C., 1 g. of ammonium persulfate, which had been dissolved in a minimum quantity of water, was added to the solution with stirring. The solution was heated in a nitrogen atmosphere at 15° C. for 18 hours. One part by volume of the reaction product was diluted with 19 parts by volume of water. A solution of 49.6 g. of sodium hydroxide in 500 cc. of water gradually added to the solution caused it to become slightly basic and caused granular poly-2-vinylpyridine to precipitate. The polymer was washed with cold water and dried under vacuum at a temperature of approximately 65° C.

A composition for washing and protecting photographic silver images was prepared as follows. 10 g. of poly-2-vinylpyridine prepared as above was mixed with 50 ml. of 60/40 water/ethanol by volume. 1.6 ml. of glacial acetic acid was added to the mixture. The mixture was heated gently with stirring until dissolution of the polymer occurred. Finally, 2.5 g. of zinc acetate dihydrate was dissolved in the solution.

In a further form, the washing and protecting composition is an emulsion comprising an aqueous internal phase containing a dissolved heavy metal salt and an external phase containing a hydrophobic organic liquid solution of a hydrophobic plastic material. The hydrophobic plastic material, for example, may be a phenol formaldehyde such as that sold by Rohm & Haas under the trade name "Amberol," a maleic rosin such as that sold by Rohm & Haas under the trade name "Amberlac," a polystyrene such as that sold by Dow under the trade name "PS3," paraffin wax, an ethyl cellulose such as that sold by Hercules under the trade name "Ethocel," a hydrogenated rosin ester such as that sold by Hercules under the trade name "Stabelite," a coumarone indene resin such as that sold by Neville under the trade name "Nevindene," a polymerized rosin ester such as that sold by Hercules under the trade name 'Poly-pale," and an acrylic resin such as that sold by Rohm & Haas under the trade name "Acryloid." As examples of the wide variety of hydrophobic organic solvents to be thus employed, mention may be made of aromatic hydrocarbons such as xylene, cumene, cymene, ethyl and diethyl benzene and aromatic-aliphatic hydrocarbon mixtures such as those obtained from petroleum fractionation. Preferably, these hydrophobic organic solvents having boiling points ranging from 120° C. to 200° C. by reason of which they are, in general, quick drying but not so volatile as to preclude their convenient storage for prolonged periods.

Example IV

A composition comprising a plastic material of the foregoing type is prepared as follows. 0.1 liter of an aqueous 25% solution by weight of cadmium acetate was mixed with 1 liter of a solution prepared by dissolving 500 g. of Rohm & Haas "Amberlac D-96" in 1 liter of xylene. A stable emulsion was formed by passing the mixture through a homogenizer.

Photographic materials useful in the production of thin photographic silver images, of the type specifically referred to above, to which the foregoing washing and protecting compositions are particularly applicable, are described in detail in Patent No. 2,543,181, which issued on February 27, 1951, in the name of Edwin H. Land, for Photographic Product Comprising A Rupturable Container Carrying A Photographic Processing Liquid. 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 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 halide forms a water-soluble complex salt which diffused through the layer of composition to the image-receptive element, there, upon being reduced to silver, to form a visible print. At the end of this period, the silver halide element, together with the layer of composition, is stripped

from the image-receptive element. The gelatino silver halide element employed in this process, for example, is laminated to a conventional support. The image-receptive element (also in the form of a layer upon a conventional support, 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. Materials of this type are specifically described in copending U. S. patent application Serial No. 727,385, filed by Edwin H. Land on February 8, 1947, for Photographic Product and Process (now U. S. Patent No. 2,698,245) and Serial No. 164,908, filed by Edwin H. Land on May 29, 1950, for Photographic Silver Halide Product and Process (now abandoned and replaced by Serial No. 449,995, filed August 16, 1954, and issued as Patent No. 2,698,237).

Preferably, there is interposed between the image-receptive element and the support a water-impermeable layer capable of preventing penetration of moisture from the processing composition into the support. This layer is designed to produce a water-impermeable layer capable of preventing penetration of moisture from the processing composition into the support. This layer is responsible for the production of a dry image immediately after the photosensive element is stripped from the image-receptive element. 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, cellulose acetate butyrate or cellulose acetate propionate. Preferred, however, are such rubbery polymers as polyvinyl butyral. The water-impermeable layer, in one form, contains a heavy metal salt of the above-described type and, consequently, cooperates with a protective coating, formed in accordance with the present invention, to protect an image from atmospheric sulfides. If the support is water impermeable, of course, a discrete water-impermeable layer need not be provided.

The water-impermeable layer permits traces of processing reagents to be washed from the silver image with a limited quantity of water. Therefore, in accordance with the present invention, only a small quantity of composition, such as that carried in an applicator of the type described above, need be employed to wash the silver image. The thin layer of composition thereafter remaining on the silver image may be dried rapidly to produce a protective coating. One of the products of the present invention, then, comprises, in sequence, a suitable support, a water-impermeable layer, a photographic silver image and a protective coating containing a salt of a heavy metal which forms an insoluble sulfide. In this product, the layers at opposite faces of the silver image completely envelop the image within a protective barrier.

In certain circumstances, as where harmful residual processing reagents are not present, a photographic silver image may be protected adequately by the application of a nonaqueous composition containing a heavy metal salt of the above-described type.

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 photographic process for producing a stable print, said photographic process comprising the steps of subjecting a silver halide stratum to an alkaline aqueous solution of a silver halide developer and a silver halide solvent while said silver halide stratum and a silver-receptive stratum are in superposition, transferring a soluble silver complex from said silver halide stratum to said silver-receptive stratum in order to form a print in said silver-receptive stratum, removing said silver halide stratum from said silver-receptive stratum, and thereafter applying to said silver-receptive stratum a composition containing an aqueous solution of a salt containing heavy metal cations selected from the class consisting of zinc, cadmium, lead, manganese, germanium, zirconium and tin, said cations having pale sulfides.

2. A photographic process for producing a stable print, said photographic process comprising the steps of subjecting a silver halide stratum and a silver-receptive stratum in superposition to an alkaline aqueous solution of a silver halide developer and a silver halide solvent in order to form a print in said silver-receptive stratum, removing said silver halide stratum from said silver-receptive stratum, and thereafter applying to said silver-receptive stratum an aqueous solution of an organic plastic and a pale salt containing heavy metal cations selected from the class consisting of zinc, cadmium, lead, manganese, germanium, zirconium and tin, said cations having pale sulfides.

3. A photographic proces for producing a stable print, said photographic process comprising the steps of subjecting a silver halide stratum and a silver-receptive stratum in superposition to an alkaline aqueous solution of a silver halide developer and a silver halide solvent in order to form a print in said silver-receptive stratum, removing said silver halide stratum from said silver-receptive stratum, and thereafter applying to said silver-receptive stratum an aqueous solution of an organic plastic and a pale salt containing heavy metal cations selected from the class consisting of zinc, cadmium, lead, manganese, germanium, zirconium and tin, and anions selected from the class consisting of acetate, sulfate, nitrate and formate, said cations having pale sulfides.

4. A photographic process for producing a stable print, said photographic process comprising the steps of subjecting a silver halide stratum and a silver-receptive stratum in superposition to an alkaline aqueous solution of a silver halide developer and a silver halide solvent in order to form a print in said silver-receptive stratum, removing said silver halide stratum from said silver-receptive stratum, and thereafter applying to said silver-receptive stratum a composition containing an aqueous solution of a zinc salt

5. A photographic process for producing a stable print, said photographic process comprising the steps of subjecting a silver halide stratum and a silver-receptive stratum in superposition to an alkaline aqueous solution of a silver halide developer and a silver halide solvent in order to form a print in said silver-receptive stratum, removing said silver halide stratum from said silver-receptive stratum, and thereafter applying to said silver-receptive stratum an aqueous solution of an organic plastic and a zinc salt.

6. A photographic process for producing a stable print, said process comprising treating a silver halide stratum and a silver-receptive stratum by reacting a silver halide developer with exposed silver halide in said silver halide stratum to reduce silver halide to silver, reacting a silver halide solvent with unreduced silver halide in said silver halide stratum to form a water-soluble complex silver salt, transferring said complex silver salt from said silver halide stratum to said silver-receptive stratum, reducing said complex silver salt to silver to form a visible print in said silver-receptive stratum, and thereafter applying to said silver-receptive stratum a composition containing an aqueous solution of a salt of a heavy metal which forms a water-insoluble sulfide, said composition being in sufficient quantity to provide, when dried, a residue containing a quantity of said heavy metal salt, said quantity of heavy metal salt in said residue being large relative to the quantity of silver in said print and being sufficiently small so that it and sulfides formed from it do not appreciably affect the appearance of said print.

7. A photographic process for producing a stable print, said process comprising treating a silver halide stratum and a silver-receptive stratum by reacting a silver halide developer with exposed silver halide in said silver halide

stratum to reduce silver halide to silver, reacting a silver halide solvent with unreduced silver halide in said silver halide stratum to form a water-soluble complex silver salt, transferring said complex silver salt from said silver halide stratum to said silver-receptive stratum, reducing said complex silver salt to silver to form a visible print in said silver-receptive stratum, and thereafter applying, in a thin layer to said silver-receptive stratum, a composition containing an aqueous dispersion of an organic polymer and a salt of a heavy metal which forms a water-insoluble sulfide, said composition being in sufficient quantity to provide, when dried, a residue containing a quantity of said heavy metal salt, said quantity of said heavy metal salt in said residue being large relative to the quantity of silver in said print and being sufficiently small so that it and sulfides formed from it do not appreciably adversely affect the appearance of said print, said heavy metal salt constituting from 1 to 15% by total weight of said composition.

8. A photographic process for producing a stable print, said process comprising treating a silver halide stratum and a silver-receptive stratum by reacting a silver halide devleoper with exposed silver halide in said silver halide stratum to reduce silver halide to silver, reacting a silver halide solvent with unreduced silver halide in said silver halide stratum to form a water-soluble complex silver salt, transferring said complex silver salt from said silver halide stratum to said silver-receptive stratum, reducing said complex salt to silver to form a visible print in said silver-

receptive stratum, and thereafter swabbing said print with an absorbent applicator, charged with a composition containing an aqueous dispersion of an organic polymer and a salt of a heavy metal which forms a water-insoluble sulfide, said composition being in sufficient quantity to provide, when dried, a residue containing a quantity of said heavy metal salt, said quantity of said heavy metal salt in said residue being large relative to the quantity of silver in said print and being sufficiently small so that it and sulfides formed from it do not appreciably adversely affect the appearance of said print, said salt constituting from 1 to 15% by total weight of said composition.

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