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PROCESS OF WASHING AND PROTECTING PHOTOGRAPHIC SILVER IMAGES, AND PHOTOGRAPHIC PRODUCTS THEREOF

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10 Claims. (Cl. 96—29)

This invention relates to the washing and protecting of a photographic silver image and, more particularly, to the washing and protecting of 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 a plastic material for producing a protective coating on the image when the composition is dried.

This application is a continuation-in-part of application Serial No. 359,438, filed on June 3, 1953, by Edwin H. Land et al., now abandoned, for Process of Washing and Protecting Photographic Silver Images.

Objects of the present invention are: 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 a solution in which both water and a water-insoluble, film-forming material are contained, and the step of drying the layer to produce a residue composed primarily of the water-insoluble polymer; to provide, for use in this process, an absorbent applicator charged with a composition of the foregoing type; and to provide, as novel products, protected photographic silver images produced by this process.

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 products 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.

The process of the present invention is particularly useful for washing and protecting thin photographic silver images of the type described in U.S. Patent No. 2,719,791, issued to Edwin H. Land on October 4, 1955. Such a photographic silver image ordinarily retains at least traces of photographic reagents with which it has been processed and the continued presence of which may adversely affect its stability. For example, some oxidized developers tend to oxidize silver and thus to cause the shadows of the image to fade. Or, silver may be oxidized by reaction products from residual sodium thiosulfate. Also, silver may be oxidized by such agents as hydrogen sulfide often present in the atmosphere. Furthermore, traces of unexhausted developer, oxidized by atmospheric oxygen, may slightly color the highlights of the image.

A composition, to be employed in the process of the present invention, comprises a solution prepared from

(1) a water-insoluble organic polymer having acidic groups, preferably weak, (2) water, (3) a water-miscible organic solvent, and (4) a base, preferably weak. The water, organic solvent and base cooperate to dissolve the polymer which is insoluble in water alone. It is believed that salt formation by a proportion of the base and a proportion of the acidic groups of the polymer is one of the driving forces for solution. This solution, because of its aqueous character, is readily adapted to dissolve residual, water-soluble, photographic processing reagents from a photographic silver image. The water-miscible, volatile, organic solvent imparts to the solution an over-all, quick-drying character. Examples of such a solvent are low molecular weight alcohols such as methanol, ethanol and propanol, dioxane, and low molecular weight ketones such as acetone and methylethyl ketone.

It is desirable that the solution contain an agent capable of becoming dispersed in the protective coating and of protecting the image by reacting with atmospheric sulfides that penetrate the protective coating. Preferred protective agents are salts, preferably water-soluble, containing heavy metal cations which form water-insoluble sulfides. These salts, for example, are composed of: cations such as zinc, cadmium, lead, manganese, germanium, zirconium and tin; and anions such as acetate, sulfate, nitrate and formate. Since these salts in small quantity are substantially invisible and form substantially invisible sulfides, they and their sulfides do not affect the optical clarity of the protective coating. A salt of zinc is preferred because zinc sulfide is white and does not tend to discolor the highlights of an image on which it is present.

As indicated above, the composition comprises a water-insoluble, organic polymer having acidic groups and a base. The polymer, for example, may be the controlled copolymerization product of an acidic vinyl monomer such as maleic anhydride, crotonic acid, acrylic or methacrylic acid and another suitable monomer such as a lower alkyl acrylate, methacrylate or vinyl acetate. Alternatively, the polymer may be an acidic vinyl homopolymer such as polystyrene carboxylic acid. Such acidic vinyl polymers also may be described as acidic polymers of a monomer containing a single carbon-to-carbon double bond as the sole carbon-to-carbon unsaturation and also containing groups selected from the class consisting of carboxylic acid and carboxylic acid anhydride groups. The initial product of the copolymerization of an equimolar mixture of maleic anhydride and methyl methacrylate gives excellent results. A discussion of the theoretical aspects of the copolymerization of maleic anhydride and alkyl methacrylates may be found in an article by M. C. De Wilde and G. Smets, Journal of Polymer Science, vol. V, No. 2, page 253 (1952). As examples of suitable bases, mention may be made of ammonia and pyridine.

Specifically, compositions of this type may be prepared by dissolving a maleic anhydride copolymer at room temperature in a mixture of water, a volatile, water-miscible, organic solvent and ammonia in the following proportions:

Polymer	g	10–25
Water	cc	50–70
Organic solvent	cc	30–50

Ammonia: Quantity sufficient to dissolve polymer.

Photographic materials useful in the production of thin

photographic silver images of the type referred to above are described in detail in Patent No. 2,543,181, which issued to Edwin H. Land on February 27, 1951. 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 halide 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 July 28, 1953, for One Step Photographic Transfer Process.

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 U.S. Patents Nos. 2,698,237 and 2,698,245, issued 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 only shortly after 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, cellulose acetate butyrate or cellulose 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.

The following nonlimiting examples further illustrate the present invention:

Example I

A copolymer of methyl methacrylate and maleic anhydride was prepared as follows. 54 ml. of methyl methacrylate and 49.4 g. of maleic anhydride were dissolved in 250 ml. of C.P. benzene containing .85 g. of azo-bis-isobutyronitrile. The mixture was polymerized at 70° C. in an atomsphere of carbon dioxide for approximately two hours. The resulting polymer, after being isolated by precipitation into methanol and purified by reprecipitation from benzene into methanol, was dried under vacuum at 50° C.

A composition for washing and protecting photographic silver images was prepared as follows. 20 g. of the above-described polymer was mixed with 100 ml. of 60/40 water/ethanol by volume. Concentrated ammonia was titrated into the mixture until the polymer dissolved, the final pH of the solution being approximately 7.

Example II

A copolymer of ethyl methacrylate and maleic anhydride was prepared as follows. 241 ml. of ethyl methacrylate and 281.5 g. of maleic anhydride were dissolved in 100 ml. of C.P. toluene. 12 g. of benzoyl peroxide was added to the solution. The solution was heated at 90° C. with stirring for a period of 8 minutes at the end of which the internal temperature of the reaction was 99° C. The reaction product was cooled in an ice bath and the resulting polymer was isolated by precipitation into methanol and purified by reprecipitation from acetone into methanol. 114 g. of dry polymer, corresponding to a conversion of 23% by weight, was obtained.

A composition for washing and protecting photographic silver images was prepared as follows. 20 g. of the above-described polymer was mixed with 100 ml. of 60/40 water/ethanol by volume. Concentrated ammonia was titrated into the mixture with stirring and heating until dissolution of the polymer occurred. The final pH of the solution was approximately 6 to 7.

The foregoing compositions, when applied to photographic silver images of the type hereinbefore specifically described, removed residual processing reagents therefrom and provided them with effective protective coatings as evidenced by the resulting remarkable stability of the images.

Since certain changes may be made in the above process and products 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 for producing a washed and protected silver-transfer reversal print from a photoexposed silver halide photosensitive material, said process comprising the steps of differentially reacting said silver halide material with a developer therefor in order to reduce photoexposed silver halide material to silver, differentially reacting reduced silver halide material with a solvent therefor in order to form a diffusible silver complex, transferring said diffusible silver complex to a print-receptive material, forming in said print-receptive material a print including silver from said complex, and applying to said print-receptive material a washing and protecting solution comprising (1) a polymer, (2) water, (3) a volatile, water-miscible, organic liquid that is a solvent for said polymer and (4) a weak base, said water, said organic solvent and said base cooperating to dissolve said polymer, said polymer being insoluble in water alone, said polymer being an acidic polymer of a monomer containing a single carbon-to-carbon double bond as the sole carbon-to-carbon unsaturation and also containing groups selected from the class consisting of carboxylic acid and

carboxylic acid anhydride groups, in order to wash the residue of said processing solution from said print-receptive material and to produce upon said print-receptive material a protective coating composed primarily of said polymer.

2. The process of claim 1 wherein said organic liquid is a low molecular weight alcohol.

3. The process of claim 1 wherein said organic liquid is a low molecular weight ketone.

4. The process of claim 1 wherein said base is ammonia.

5. A process for producing a washed and protected silver-transfer reversal print from a photoexposed silver halide photosensitive material, said process comprising the steps of differentially reacting said silver halide material with a developer therefor in order to reduce photoexposed silver halide material to silver, differentially reacting said unreduced silver halide material with a solvent therefor in order to form a diffusible silver complex, transferring said diffusible silver complex to a print-receptive material, forming in said print-receptive material a print including silver from said complex, and applying to said print-receptive material a washing and protecting solution comprising (1) a polymer, (2) water, (3) a volatile, water-miscible, organic liquid that is a solvent for said polymer and (4) a weak base, said water, said organic solvent and said base cooperating to dissolve said polymer, said polymer being insoluble in water alone, said polymer being an acidic polymer of a monomer containing a single carbon-to-carbon double bond as the sole carbon-to-carbon unsaturation and also containing groups selected from the class consisting of carboxylic acid and carboxylic acid anhydride groups, in order to wash the residue of said processing solution from said silver-receptive material and to produce upon said silver-receptive material a protective coating composed primarily of said polymer, said washing and protecting solution containing said polymer, said water, said organic solvent and said base in the following proportions:

Polymer	g—	10 to 25
Water	cc—	50 to 70
Organic solvent	cc—	30 to 50

Weak base: Quantity sufficient to dissolve polymer.

6. The process of producing a washed and protected silver-transfer reversal print, said process comprising the steps of applying an aqueous alkaline processing solution of a silver halide developer and a silver halide solvent to a silver halide material and a silver-receptive material that are in contiguity, reacting said silver halide developer with photoexposed silver halide in order to reduce said photoexposed silver halide to silver, reacting said silver halide solvent with unreduced silver halide to form a water-soluble silver complex, transferring said silver complex to said silver-receptive material, reducing said silver complex to silver at said silver-receptive material, and applying to said silver-receptive material a washing and protecting solution comprising (1) a polymer, (2) water, (3) a volatile, water-miscible, organic liquid that is a solvent for said polymer and (4) a weak base, said water, said organic solvent and said base cooperating to dissolve said polymer, said polymer being insoluble in water alone, said polymer being an acidic polymer of a monomer containing a single carbon-to-carbon double bond as the sole carbon-to-carbon unsaturation and also containing groups selected from the class consisting of carboxylic acid and carboxylic acid anhydride groups, in order to wash the residue of said processing solution from said silver-receptive material and to produce a protective coating upon said silver-receptive material composed primarily of said polymer, said solvent being selected from the class consisting of the low molecular weight alcohols and low molecular weight ketones, said polymer, said water, said

organic solvent and said base being in the following proportions:

Polymer	g—	10 to 25
Water	cc—	50 to 70
Organic solvent	cc—	30 to 50

Weak base: Quantity sufficient to dissolve polymer.

7. The process of claim 6 wherein said polymer is a copolymer of maleic anhydride and a compolymerizate reactive therewith.

8. The process of claim 6 wherein said polymer is polystyrene carboxylic acid.

9. The process of producing a washed and protected silver-transfer reversal print, said process comprising the steps of subjecting a silver halide material and a silver-receptive material that are in contiguity to an aqueous alkaline processing solution of a silver halide developer and a silver halide solvent, reacting said silver halide developer with photoexposed silver halide in order to reduce said photoexposed silver halide to silver, reacting said silver halide solvent with unreduced silver halide to form a water-soluble silver complex, transferring said silver complex to said silver-receptive material, reducing said silver complex to silver at said silver-receptive material, and applying to said silver-receptive material a washing and protecting solution prepared from (1) a polymer, (2) water, (3) a volatile, water-miscible, organic liquid that is a solvent for said polymer and (4) a weak base, said water, said organic solvent and said base cooperating to dissolve said polymer, said polymer being insoluble in water alone, in order to wash the residue of said processing solution from said silver-receptive material and to produce a protective coating upon said silver-receptive material composed primarily of said polymer, said solvent being selected from the class consisting of the low molecular weight alcohols and low molecular weight ketones, said polymer being a copolymer of a material selected from the class consisting of maleic anhydride, crotonic acid, acrylic acid and methacrylic acid, and a material selected from the class consisting of alkyl acrylate and vinyl acetate, said polymer, said water, said organic solvent and said base being in the following proportions:

Polymer	g—	10 to 25
Water	cc—	50 to 70
Organic solvent	cc—	30 to 50

Weak base: Quantity sufficient to dissolve polymer.

10. The process of producing a washed and protected silver-transfer reversal print, said process comprising the steps of applying an aqueous alkaline processing solution of a silver halide developer and a silver halide solvent to a silver halide material and a silver-receptive material that are in contiguity, reacting said silver halide developer with photoexposed silver halide in order to reduce said photoexposed silver halide to silver, reacting said silver halide solvent with unreduced silver halide to form a water-soluble silver complex, transferring said silver complex to said silver-receptive material, reducing said silver complex to silver at said silver-receptive material, and applying to said silver-receptive material a washing and protecting solution prepared from (1) a polymer, (2) water, (3) a volatile, water-miscible, organic liquid that is a solvent for said polymer and (4) a weak base, said water, said organic solvent and said base cooperating to dissolve said polymer, said polymer being insoluble in water alone, in order to wash the residue of said processing solution from said silver-receptive material and to produce a protective coating upon said silver-receptive material composed primarily of said polymer, said solvent being selected from the class consisting of the low molecular weight alcohols and low molecular weight ketones, said polymer being a copolymer produced by the copolymerization of an equimolar mixture of maleic anhydride and methyl methacrylate,

said polymer, said water, said organic solvent and said base being in the following proportions:

Polymer	g	10 to 25
Water	cc	59 to 70
Organic solvent	cc	30 to 50

Weak base: Quantity sufficient to dissolve polymer.

References Cited in the file of this patent

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Copolymers of Vinyl Compounds and Maleic Anhydride, Ind. and Eng. Chem., v. 41, No. 7, pages 1509–1513.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,956,877 October 18, 1960

Edwin H. Land et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 10, for "atomsphere" read -- atmosphere --; line 61, for "reduced" read -- unreduced --; column 6, line 9, for "compolymerizate" read -- copolymerizate --.

Signed and sealed this 16th day of January 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents