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

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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, now forfeited, filed on June 3, 1953, by Edwin H. Land et al. 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 polar groups, preferably weak, (2) water, (3) a water-miscible organic solvent, and (4) an electrolyte, preferably weak. The water, organic solvent and electrolyte cooperate to dissolve the polymer which is insoluble in water alone. It it believed that salt formation by a proportion of the

electrolyte and a proportion of the polar 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 propanal, 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 highlight of an image on which it is present.

The composition may comprise, as its water-insoluble organic polymer, one having basic groups and, as its electrolyte, an acid. The polymer, for example, is a vinylpyridine polymer prepared by polymerizing or copolymerizing vinylpyridine or some derivative thereof. Examples of such a vinylpyridine homopolymer are poly-2-vinylpyridine, poly-3-vinylpyridine, poly-4-vinylpyridine, poly-5-vinyl-2-methyl pyridine, poly-2-vinyl-5-ethyl pyridine and poly-2-vinyl-6-methyl pyridine. Examples of such a vinylpyridine copolymer in which a vinylpyridine is the characteristic ingredient may be prepared by copolymerizing vinylpyridine or some derivative thereof with a monomer of suitable reactivity and double bond charge such as methyl acrylate, acrylonitrile, styrene and ethyl methacrylate. Methods of preparing polyvinyl pyridines of the foregoing type are disclosed in U. S. Patent No. 2,491,472, entitled Polymerization of Vinyl Pyridines, issued in the name of J. Harmon, on December 20, 1949. As examples of suitable acids, mention may be made of acetic acid and propionic acid.

Specifically, compositions of this type may be prepared by dissolving a vinylpyridine polymer at room temperature in a mixture of water, a volatile, water-miscible, organic solvent and acetic acid in the following proportions:

Polymer	g—	10–25
Water	cc—	50–70
Organic solvent	cc—	30–50
Acetic acid	cc—	0.2–5

Alternatively, the composition may comprise, as its water-insoluble, organic polymer, one having acidic groups and, as it electrolyte, 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. 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. DeWilde 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	10–25 g.
Water	50–70 cc.
Organic solvent	30–50 cc.
Ammonia	Quantity sufficient to dissolve polymer.

In the washing and protecting of a thin photographic silver image of the type referred to above and now to be described in detail, a composition comprising an electrolyte such as acetic acid is preferred to a composition comprising an electrolyte such as ammonia for the reason that under some conditions the ammonia may be released in such a way as to be harmful to the image.

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, as described in 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 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 designed to produce 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 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 atomsphere 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. The mixture was heated gently with stirring until dissolution of the polymer occurred.

Example II

10 g. of poly-2-vinylpyridine prepared as in Example I was mixed with 50 ml. of 70/30 water/actone 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.

Example III

10 g. of poly-2-vinylpyridine prepared as in Example I was mixed with 50 ml. of 60/20/20 water/isopropyl alcohol/methanol by volume. 1.6 ml. of glacial acetic acid was added. 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.

Example IV

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 atmosphere 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 V

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. In a process for washing and protecting a photographic silver image, swabbing said image with an absorbent applicator charged with a composition comprising a solution prepared by dissolving a vinylpyridine polymer in a mixture of water, a water-miscible, volatile, organic solvent for said polymer and acetic acid in the following proportions:

Polymer	g.	10–25
Water	cc.	50–70
Organic solvent	cc.	30–50
Acetic acid	cc.	0.2–5

2. In a process for washing and protecting a photographic silver image: the step of spreading on one face thereof, in a thin layer, a composition comprising a solution prepared from (1) a vinylpyridine polymer, (2) water, (3) a volatile, water-miscible, organic liquid which is a solvent for said vinylpyridine polymer, and (4) a weak acid.

3. In a process for washing and protecting a photographic silver image: the step of spreading on one face thereof, in a thin layer, a composition comprising a solution prepared from (1) a vinylpyridine polymer, (2) water, (3) a volatile, water-miscible, organic liquid which is a solvent for said vinylpyridine polymer, and (4) a weak acid; and the step of drying said layer to produce a protective coating composed primarily of said vinylpyridine polymer.

4. The process of claim 2 wherein said solvent is a low molecular weight alcohol.

5. The process of claim 2 wherein said solvent is a low molecular weight ketone.

6. The process of claim 2 wherein said acid is acetic acid.

7. The process of claim 2 wherein said vinylpyridine polymer, said water, said organic solvent and said acid are in the following proportions:

Vinylpyridine polymer	g.	10–25
Water	cc.	50–70
Organic solvent	cc.	30–50
Acetic acid	cc.	0.2–5

8. A photographic product comprising, in sequence, a support, a water-impermeable layer, a photographic silver image and a layer composed of a vinylpyridine polymer and a salt containing heavy metal cations which form colorless, water-insoluble sulfides.

9. A photographic product comprising, in sequence, a support, a water-impermeable layer, a photographic silver image and a layer composed of a vinylpyridine polymer and a zinc salt.

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