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2,794,740

METHODS FOR WASHING AND PROTECTING PHOTOGRAPHIC SILVER IMAGES

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

The 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, filed August 5, 1952 for Method of Improving the Stabilization of Finished Photographic Prints by Applying a Liquid Composition Thereto (now Patent No. 2,719,791). Such a thin photographic print, 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 unexposed 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 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 sulphur 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 unexposed developer, if oxidized by atmospheric oxygen, may slightly discolor the highlights of the image.

Objects of this invention are: to provide a photographic silver image with a protective environment primarily containing hydrolyzed gelatin; to provide, in a novel process for washing and protecting a thin photographic silver image of the foregoing type, the step of applying to at least one of its faces in a layer a composition comprising an aqueous solution of hydrolyzed gelatin and the step of drying the layer to produce a residue composed primarily of hydrolyzed gelatin; and to provide, as novel products, protected photographic silver images produced by such a 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 which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

A preferred composition, to be employed in accordance with the present invention, is an aqueous solution of a hydrolyzed gelatin having polypeptide chains on the average of not less than 4 and not more than 12 amino acid units. Preferably, the hydrolyzed gelatin is not less than 15% and not more than 40% by total weight of the solu-

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tion. Such a solution, unlike a dispersion of ordinary gelatin, is fluid enough at ordinary temperatures to be readily spread upon an image of the foregoing type and, when dried, provides the image with a hydrolyzed gelatin environment unexpectedly possessing protective properties for silver similar to those of ordinary gelatin.

In general, such a solution may be prepared by hydrolyzing either alkali or acid extracted gelatin with a proteolytic enzyme such as papain, pepsin or trypsin and, when a desired degree of hydrolysis is reached, by stabilizing the solution with a preservative such as methyl p-hydroxy benzoate, cetyl pyridinium chloride or oxyquinoline.

Photographic materials useful in the production of photographic silver images of the general 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 for Photographic Product Comprising a Rupturable Container Carrying a Photographic Processing Liquid. In a typical process employing such materials, a viscous 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, ordinarily of the order of 40 to 120 seconds, during which exposed silver halide is reduced to silver and unexposed 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. 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 Patent No. 2,647,056, issued to Edwin H. Land on 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, of the order of 1 micron thick, 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. An image composed of dense aggregates of silver may be formed in this layer by the process described above. 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. A preferred image-receptive element in which these silver precipitating materials are distributed is a macroscopically continuous film consisting 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 copending U. S. patent application Serial No. 727,385, filed by Edwin H. Land on February 8, 1947 (now Patent No. 2,698,245) and Serial No. 164,908, now abandoned and replaced by application 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 its support a water-impermeable layer capable of preventing the penetration of moisture

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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 protective coating.

A specific example of a solution useful in accordance with the present invention follows:

To a dispersion of 44 pounds of 100 Bloom, alkali pre-treated gelatin in 19 gallons of water was added a dispersion of one-half pound of papain in one quart of water. The resulting mixture at 60° C. was stirred for a period of from 12 to 15 minutes during which hydrolysis of the gelatin occurred. At the end of this period, in order to halt the hydrolysis, one quart of 7% hydrogen peroxide was added and the temperature raised as rapidly as possible to 95° C. After the solution was filtered and cooled, one-half pound of methyl paracept was added as a preservative. The resulting solution contained, by total weight, approximately 22% of hydrolyzed gelatin having polypeptide chains on the average of approximately 7 amino acid units. This solution, after being swabbed by means of an absorbent applicator onto a thin photographic silver image of the above-described type, rapidly dried under ordinary atmospheric conditions to form a coating having excellent protective properties for the image.

Since certain changes may be made in the above 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 forming a stable photographic print, said method comprising the steps of spreading between a gelatin-free silver-receptive stratum and an exposed gelatino silver halide stratum, in a layer, an alkaline aqueous solution of a silver halide developer and a silver halide solvent whereby exposed silver halide is reduced to silver and un-reduced silver halide forms a water-soluble, complex silver salt which diffuses through the layer of solution to the silver-receptive stratum where, upon being reduced to silver, it forms a visible print, stripping said print from said gelatino silver halide stratum, said print containing a residue of said solution, swabbing said print with an absorbent applicator charged with an alkaline aqueous solution of hydrolyzed gelatin in order to

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wash said residue from said print into said applicator, and drying solution retained on said print in order to intimately associate said hydrolyzed gelatin with said silver in said print.

2. The method of claim 1 wherein said hydrolyzed gelatin has polypeptide chains on the average of not less than 4 and not more than 12 amino acid units.

3. The method of claim 1 wherein said solution, by total weight, contains not less than 15% and not more than 40% of said hydrolyzed gelatin.

4. The method of claim 1 wherein said hydrolyzed gelatin has polypeptide chains on the average of not less than 4 and not more than 12 amino acid units and by total weight is not less than 15% and not more than 40% of said solution.

5. A method of forming a stable photographic print, said method comprising the steps of subjecting a gelatin-free, silver-receptive stratum and an exposed gelatino silver halide stratum, in a layer, to an alkaline aqueous solution of a silver halide developer and a silver halide solvent whereby exposed silver halide is reduced to silver and un-reduced silver halide forms a water-soluble, complex silver salt which diffuses through the layer of solution to the silver-receptive stratum where, upon being reduced to silver, it forms a visible print, stripping said print from said gelatino silver halide stratum, said print containing a residue of said solution, swabbing said print with an absorbent applicator charged with an alkaline aqueous solution of hydrolyzed gelatin in order to wash said residue from said print into said applicator, and drying solution retained on said print in order to intimately associate said hydrolyzed gelatin with said silver in said print.

6. A method of forming a stable photographic print in a gelatin-free, silver-receptive stratum, said method comprising the steps of subjecting an exposed gelatino silver halide stratum to an alkaline aqueous solution of a silver halide developer and of a silver halide solvent, whereby exposed silver halide is reduced to silver and un-reduced silver halide forms a water-soluble silver complex, diffusing said complex from said silver halide stratum to said silver-receptive stratum where, upon being reduced to silver, it forms a visible print, separating said print from said gelatino silver halide stratum, said print containing a residue of said solution, and applying to said print an alkaline aqueous solution of hydrolyzed gelatin in order to wash said residue from said print and to intimately associate said hydrolyzed gelatin with said silver in said print.

7. The process of claim 6 wherein said silver-receptive stratum is siliceous.

8. The process of claim 6 wherein said hydrolyzed gelatin has polypeptide chains on the average of not less than 4 and not more than 12 amino acid units.

9. The process of claim 6 wherein said aqueous solution of hydrolyzed gelatin contains not less than 15% and not more than 40% of said hydrolyzed gelatin.

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