

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC RELIEF IMAGE

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This invention relates to photography and particularly to a method of forming photographic relief images.

It is known that relief images can be formed in silver halide emulsion layers by treating the developed silver halide layer with a hydrogen peroxide etch bath containing bromide ions and thereby removing the developed silver image together with the gelatin in the regions of the silver image. This method of forming a relief image is particularly useful where a positive relief image is to be formed from a positive color transparency since the positive relief image can be formed directly. It has been noted that the dissolution of the gelatin surrounding the silver grains takes place only when the hydrogen peroxide etch bath is strongly acid. If an etch bath is used which is not strongly acid, bleaching will take place but no dissolution of the gelatin will result.

I have found that if a hardened gelatino silver halide emulsion is used, a hydrogen peroxide bath of the proper degree of acidity will bleach the silver image to silver bromide and simultaneously soften the gelatin in the regions of the silver image. The gelatin in the areas of the residual silver halide is not seriously affected by this treatment. (Some small degree of softening takes place, but the gelatin remains mostly insoluble in hot water.) The softened negative gelatin, that is, the gelatin in the regions of the original silver image can then be washed off in hot water leaving a hard positive image. The residual silver halide of the positive image can be removed in the usual manner, or may be allowed to remain, or be developed after flashing, in a tanning developer to give the gelatin desirable dye transferring characteristics.

This method differs from the usual hydrogen peroxide etch process in that the gelatin is not removed by the etch bath but is only softened and is removed as a separate step by washing with hot water.

This method has the advantage that the resulting image is sharper than the image obtained by the usual hydrogen peroxide etch process. Furthermore, the etching solution does not become sludged with silver bromide and dissolved gelatin and can be reused many times. By washing off with hot water, the relief is left immediately clean and ready for drying. The usual etch method leaves a residue which washes off slowly. A further advantage is that the relief can be processed in a shorter time than is customary with the usual hydrogen peroxide etching process and by remaining in a hardened condition, a positive image is less subject to damage.

An average gelatino-silver halide emulsion which might be used according to my process could be hardened to a melting point of approximately 180° F. However, a change in balance of

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acidity can be made to accommodate emulsions of other degrees of hardness. The emulsion is coated on the usual support of cellulose acetate, cellulose nitrate or synthetic resin or may be coated on a paper support.

The emulsion may be blue-sensitive or panchromatic and is exposed in the usual way, for example, to a positive color transparency. Separation images may be made for use in the imbibition process by exposing through primary color filters if a panchromatic material is used. The emulsion is developed in the usual way to form a negative silver image leaving residual silver halide in the unexposed portions of the layer. The residual silver bromide may be removed by fixing at this stage or may remain in the layer for removal at a later stage.

After development of the silver image, the layer is treated with a hydrogen-peroxide-bromide bleach bath having a pH of approximately 2.6 to 3.0. The pH of the bleach bath is adjusted to the hardness of the particular emulsion which is used. If the emulsion is extremely hard, the pH would be low but if the emulsion is only moderately hard, the pH would be higher. The following formulas are suitable for use according to my invention.

Example 1

Copper sulfate	_____grams	33
Potassium bromide	_____do	10
Acetic acid (28% solution)	_____cc	13
Hydrogen peroxide (25% solution)	_____cc	105
Water to 1 liter.		

Example 2

Copper sulfate	_____grams	50
Potassium bromide	_____do	15
Acetic acid (28% solution)	_____cc	15
Potassium alum	_____grams	15
Water to 1 liter.		

For use, three parts of this formula are added to 1 part of 8% hydrogen peroxide solution.

With both of these formulas, softening of the emulsion in the region of the silver image takes place in approximately 1½ minutes at a temperature of 68° F.

In place of potassium bromide in the bleach bath, other bromides such as sodium or ammonium may be used. Acids other than acetic acid such as sulfuric acid or hydrochloric may be employed, the pH being adjusted within the range specified above.

After bleaching of the silver image, the emulsion is washed for 1 minute with water at a temperature of approximately 110° F. to wash off the gelatin in the region of the silver image. The positive relief image is then in a condition for use in an imbibition process or other process for which a relief image is suitable.

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The examples included herein are illustrative only and my invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. The method of forming a photographic relief image which comprises developing a gelatino-silver halide emulsion layer to form a silver image therein, bleaching the silver to silver bromide in a hydrogen peroxide-bromide bleach bath having a pH of approximately 2.6 to 3.0, without dissolving but with softening the gelatin in the region of the silver image, hardening said emulsion prior to said bleaching as a step in the process, washing off the gelatin softened by the bleach bath in warm water, to form a positive gelatino-silver halide relief image.

2. The method of forming a photographic relief image which comprises developing a gelatino-silver halide emulsion layer hardened to a melting point of approximately 180° F. to form a silver image therein, bleaching the silver to silver bromide in a hydrogen peroxide-bromide bleach bath having a pH of approximately 2.6 to 3.0, said bleach bath softening the gelatin in the region of the silver image without dissolving it, and washing off the gelatin softened by the bleach bath in warm water to form a positive gelatino silver halide relief image.

3. The method of forming a photographic relief image which comprises developing a gelatino-silver halide emulsion layer to form a silver image therein, bleaching the silver to silver bromide in a hydrogen peroxide bleach bath containing approximately 10 grams per liter of potassium bromide and having a pH of approxi-

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mately 2.6 to 3.0, hardening said emulsion to a melting point of approximately 180° F. prior to said bleaching as a step in the process, said bleach bath softening the gelatin in the region of the silver image without dissolving it, and washing off the gelatin softened by the bleach bath in warm water to form a positive gelatino-silver halide relief image.

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