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PHOTOGRAPHIC ETCH-BLEACH BATHS

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ABSTRACT OF THE DISCLOSURE

A process for gelatin relief images is described, comprising bathing the exposed and developed silver halide emulsion in an etch bleach bath. The etch bleach bath contains hydrogen peroxide, cupric ions, halide ions and at least 50 grams per liter of urea.

This invention relates to photography and particularly to a method of froming photographic relief images by the so called "etch-bleach" process.

It is known that gelatin relief images can be formed from gelatin layers containing a developed silver image by treating these layers with hydrogen peroxide and an activating compound. The silver is oxidised to a silver salt and the associated gelatin is degraded so that it may be washed away. This process is commonly called the "etch-bleach" process.

The etch-bleach process has been used for the formation of relief images which are dyed for colour photographic processes. The process is commonly used on developed but not fixed image bearing silver halide emulsion layers to remove the silver so that the remaining emulsion can be fogged and developed to form a reversal image. This process is particularly useful in the graphic arts field.

For many purposes the amount of gelatin removed by washing the gelatin layer after etch-bleach treatment is insufficient for subsequent use and it is necessary to augment the washing action with careful swabbing with cotton wool or a soft cloth to remove degraded gelatin adhering to the support. This latter step is both time consuming and laborious.

In recent years there has been a tendency for the manufacturers of the photographic materials used in the graphic arts field, such as lith type films, to increase the hardness of the gelatino-silver halide emlsion layers. This increased hardness improves the general handling facility of the materials allowing them to be processed at higher temperatures and improves their abrasion resistance. However, these materials are also frequently used in the etch-bleach process to provide reversed images and the increased hardness reduces their ability to respond to known etch-bleach baths.

It is an object of this invention to provide a novel etch-bleach bath which will remove silver images and adjacent gelatin from hardened photographic layers containing a silver image.

It is another object of this invention to provide an improved process for forming gelatin relief images.

It is a still further object of this invention to provide etch-bleach baths containing gelatin softening agents. It is likewise an object of this invention to provide an etch-bleach process using a single bath and avoiding subsequent washing.

These and further objects and advantages of this invention have been achieved by the discovery that the addition of urea to a hydrogen peroxide etch-bleach bath results in rapid bleaching of the silver and degradation of the associated gelatin with reduced adherence to the treated layer.

When the etch-bleach baths of my invention are applied to photographic layer by means of a spray, complete removal of the degraded gelatin formed by the action of the bath takes place. Immersion of a photographic layer into the bath without agitation requires a subsequent spray-wash with warm water to bring about complete removal of the degraded gelatin. In neither case is any swabbing or similar action required and the whole process may be carried out in automatic apparatus without supervision.

In the preferred embodiments of my invention the etch-bleach bath contains cupric and halide ions together with hydrogen peroxide and urea. The mixed bath rapidly loses its activity so that the hydrogen peroxide is normally added as an aqueous solution to the other constituents immediately before use.

EXAMPLE 1

Samples of a high contrast silver halide emulsion were exposed to a positive dot image and a positive line image and developed for high contrast silver halide emulsions supplied by Eastman Kodak Company in "Kodalith" Super Developer for 2¾ minutes at 20° C. the high contrast silver halide emulsion is a predominantly silver chloride, lith type emulsion as described in Yule et al. U.S. Pat. No. 2,691,586 and MacWilliam U.S. Pat. No. 2,691,-586 and carried by a biaxially oriented polyethylene terephthalate support. The developed film samples were immersed for 30 seconds in a stop bath contatining 5 percent by weight of acetic acid.

The samples were then immersed in either bath A, an etch bleach bath of known type, or bath B an etch-bleach bath according to the invention until the silver image was completely bleached. The samples were then rinsed.

Etch-bleach bath A:
- Copper sulphate, pentahydrate—120 gm.
- Citric acid, monohydrate—150 cm.
- Potassium bromide—7.5 gm.
- Water—to 1 litre
- pH—0.91

Etch-bleach bath B:
- Cupric chloride, dihydrate—10 gm.
- Citric acid, monohydrate—150 gm.
- Urea—150 gm.
- Water—to 1 litre
- pH—1.50

In use each bath is mixed with an equal quantity of 10 volume hydrogen peroxide solution (3 percent by weight H_2O_2). The resultant pH increased in each case to 1.11 for bath A and 150 for bath B.

It was found that the time for complete removal of silver in the bath A was 2 minutes whereas the time for bath B was only 1½ minutes.

After rinsing for 15 seconds in cold water to remove any adhering gelatin (in the case of samples bleached in bath A some swabbing with cotton wool was also required), the materials were exposed to light from 100 watt lamp on both sides to fog the remaining silver halide and developer in the developer for high contrast emulsions described above until the image was completely blackened. Finally the samples were rinsed in the stop bath and washed in running water.

The dot and line quality were particularly well retained in the samples bleached in bath B.

EXAMPLE 2

The procedure of Example 1 was repeated using the etch-bleach baths A and B which had been left unused in open dishes for 12, 24 and 48 hours respectively. The speed of bleaching was noted in each case.

BLEACHING TIMES IN MINUTES

Solution age	Fresh	12 hours	24 hours	48 hours
Bath A	2	3	3½	8
Bath B	1½	2	2½	6

It will be seen that the bleaching time in each case was less using the bath B according to my invention. The long times at 48 hours were due to extensive decomposition of the hydrogen peroxide and could be shortened by the addition of further peroxide.

EXAMPLE 3

The procedure of Example 1 was repeated using etch-bleach baths A and B which had been left partially used in open dishes for 12 and 24 hours respectively. The speed of bleaching was noted in each case.

BLEACHING TIME IN MINUTES

Partially used bath	12 hours	24 hours
Bath A	4	8
Bath B	3	4

It will be seen that the bleaching time in each case was less using bath B according to my invention even when partially exhausted.

The novel etch-bleach baths of my invention may be used for forming reversal images on gelatino-silver halide images as described herein. They may also be used for forming gelatin relief images for use as lithographic masters and in colour photography as imbibition dye matrices. The baths may also be used for the direct formation of colour images by the wash-off relief process.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A process for forming gelatin relief images comprising bathing a supported layer of gelatin containing a silver image obtained from exposure and development of a light sensitive silver halide emulsion in an etch bleach bath containing hydrogen peroxide, cupric ions, halide ions and at least 50 grams per liter urea.

2. A process for forming gelatin relief images according to claim 7 in which the etch bleach bath contains hydrogen peroxide, cupric chloride and between 50 grams and 250 grams per liter of urea.

3. A process for forming gelatin relief images comprising bathing a supported layer of gelatin containing a silver image obtained from exposure and development of a light sensitive silver halide emulsion in an etch bleach bath containing 1½ percent by weight hydrogen peroxide, 10 grams per liter cupric chloride, 150 grams per liter citric acid and 150 grams per liter urea.

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