

# UNITED STATES PATENT OFFICE

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## HYPO ELIMINATOR BATH

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This invention relates to a process for the elimination of thiosulfate mixing agents from photographic images and materials.

In the processing of photographic developing-out materials such as gelatino-silver halide emulsions coated on paper, film, or glass supports, if, after fixation, the hypo (usually sodium or ammonium thiosulfate) is not completely eliminated from the processed material by washing or other means, under suitable conditions of temperature and humidity during storage, the silver image will tend to "fade" or change color.

This fading is a result of the conversion of more or less of the silver image to silver sulfide by the sulfur present in the residual hypo, and is manifest by a change in hue of the image first to yellowish brown, then to yellow and, in most cases, the change is accompanied by a yellowing of the unexposed portions of the image. This yellowing of the highlights is a result either of (a) the use of an exhausted fixing bath, or (b) insufficient fixation whereby complex silver-sodium thiosulfates are retained and, under the proper conditions, decompose to give yellow silver sulfide.

In addition to attack of the silver image by hypo within the gelatin layer, many external agents are also effective, the most significant being hydrogen sulfide which is present in coal gas (illuminating gas). High humidity and temperature accelerate this reaction tremendously. Sulfur dioxide and other acid gases in the presence of the hypo of the image layer also accelerate the "fading" of the image.

The rate at which a silver image fades depends upon many factors, including (1) the concentration of hypo (or tetrathionate) in the image layer, (2) the concentration of hydrogen sulfide and other acid gases in the atmosphere, (3) the grain size of the silver image, and (4) the temperature and humidity of storage.

Tests have shown that the degree of fading in a given time is roughly proportional to the concentration of hypo up to a certain limit, and a content as low as 0.005 milligram per square inch may cause fading with fine-grained images, especially in the case of papers.

An increase in the humidity, temperature, or both, accelerates the rate of fading, and a combination of high humidity and high temperature, which conditions usually exist in tropical countries, is fatal to a photographic print containing hypo.

The presence of saline matter and acidic gases

in the atmosphere also tends to increase the rate of fading.

Since fading or sulfiding of the image must necessarily take place initially at the surface of the image grains, fine-grained emulsions will tend to fade much more rapidly than coarser-grained emulsions and, in practice, chloride paper emulsions give images which are much more susceptible to fading than bromide emulsions. Similarly, a fine-grained positive transparency is much more susceptible to fading than an image on a high-speed negative emulsion.

So-called hypo eliminators, which are oxidizing agents for sodium thiosulfate in photographic films, plates, and prints, such as the hypochlorites, iodine, potassium permanganate, and hydrogen peroxide, are well known in photography but all of them suffer from disadvantages. For example, the hypochlorites and potassium permanganate attack the images of fine-grain materials, such as prints and fine-grain films, when they are used in sufficient concentrations and acidities to rapidly oxidize hypo. The same is true with iodine, and, to a less extent, with hydrogen peroxide (in the absence of alkali). Both of these are open to the objection that they oxidize hypo principally to tetrathionate which can act as an agent in promoting image fading as is well known with hypo.

We have found that when a material such as sodium chlorite is used for the elimination of hypo, the principal product of the oxidation of the hypo is sulfate rather than tetrathionate, which is readily soluble and may be washed out easily.

Solutions of this chemical, 0.08 and 0.16 molar, with respect to sodium chlorite have been tried at pH values approximately 10.15 and 10.45 respectively and found to have slight effectiveness in eliminating hypo. When the product is employed with an acid or acid salt such as acetic or potassium acid phthalate, oxidation of thiosulfate to sulfate occurs, the rate increasing as the pH decreases.

In the presence of a buffer salt, or salt and an acid, to give a pH value in the approximate range of 3.0 to 7.0 but preferably 5.0 to 7.0, oxidation of thiosulfate to sulfate occurs with sufficient rapidity and the usual moderately washed print image is not appreciably attacked during the oxidation. The solution is sufficiently stable under these conditions for all practical purposes. Solutions with pH 3.0 to 5.0 may be used with more resistant photographic images and particularly if the prints are previously bathed in an



alkaline solution, e. g. 1% sodium carbonate, 2% sodium metaborate, or a solution containing 1% sodium carbonate and 1% sodium bicarbonate to decrease the hypo concentration.

Solutions of sodium chlorite at pH 4.5 to 12.0 may also be used as single treating solutions or with two-bath treatments in conjunction with dilute acid solutions (e. g. 1 per cent acetic acid) used either before or after the sodium chlorite treatment. Either the sodium chlorite or the acid solution or both may be buffered or not as required.

Acidified solutions of sodium chlorites may also be used for oxidizing thiosulfates and other oxidizable sulfur compounds in solutions. The use of buffer combinations enables the control of rate of oxidation of the sulfur compounds and prevents too rapid decomposition of the sodium chlorite since acid is generated in the reaction with sulfur compounds.

The source of sodium chlorite preferably used in our invention, is the commercial material "Textone" containing about 77 to over 86 per cent of sodium chlorite, and small quantities of chlorate, chloride and carbonate, believed to have little if any effect in the process of the present invention. In place of sodium chlorite, chlorites having suitable cation, such as other alkali metal, may be used.

#### EXAMPLE 1

Textone (80 per cent sodium chlorite)-----grams-- 9.0  
Acetic acid or mono, di, or trisodium phosphate to give pH-----grams-- 3.0 to 12.0  
Water to-----liter-- 1

Prints, negatives, etc., are treated for one to thirty minutes with the above solution and washed five to ten minutes to eliminate hypo, in the manner of our invention.

#### EXAMPLE 2

##### Solution A

Textone (80 per cent sodium chlorite) 9.0 grams dissolved in 600 cc. of water is adjusted to an approximate pH of 5.0 with acetic acid.

##### Solution B

About 23.8 cubic cm. of 0.1 N sodium hydroxide are added to 50 cc. of 0.1 M potassium acid phthalate solution to give pH 5.0.

In use solutions A and B are mixed and diluted to 750 cc. This mixed solution buffered at pH 5.0 and containing some free acid, was more active in oxidizing thiosulfate than a solution adjusted by acid alone. Partially washed prints (20-30 minutes) need be treated only five minutes and washed for five minutes to free them of hypo.

#### EXAMPLE 3

Textone-----grams-- 10  
Borax-----do----- 28  
Succinic acid-----do----- 15  
Water to-----liter-- 1

This mixture buffered at an approximate pH of 5.0 was used to treat partially washed prints (e. g. washed 20 to 30 minutes) treating for 5 minutes, followed by a final wash of 5 minutes. Prints partially washed and leached in dilute alkali and then partially washed may also be treated 5 minutes with the above solution and washed 5 minutes to rid them of hypo. This leaching treatment is of value to avoid concentrations of hypo in the vicinity of the image which

can cause reduction of the image with especially fine grained images.

#### EXAMPLE 4

Textone-----grams-- 10.0  
Borax-----do----- 32.0  
Succinic acid-----do----- 13.4  
Water to-----liter-- 1.0

This mixture is buffered at an approximate pH of 5.5. Instructions for use are as for Example 3.

#### EXAMPLE 5

Textone-----grams-- 5 to 10  
Sodium acetate (anhydrous)-----do----- 32  
Acetic acid (glacial)-----cc----- 24  
Water to-----liter-- 1

For use: Wash prints 20 to 30 minutes, leach for 5 minutes in one of the following solutions:

- (a) 1% sodium bicarbonate
- (b) 2% sodium metaborate ( $\text{Na}_2\text{B}_2\text{O}_7 \cdot 8\text{H}_2\text{O}$ )
- (c) 1% sodium carbonate and 1% sodium bicarbonate.

Then treat for 5 minutes in the hypo eliminator solution and wash 5 minutes.

#### EXAMPLE 6

A 0.16 molar solution of Textone (80 per cent sodium chlorite) may be used as a first or second bath in conjunction with a 1 per cent acetic acid solution, treating the print for five minutes in each solution. Thereafter, the prints are washed five minutes.

#### EXAMPLE 7

In case it is desired to package a dry mixture of chemicals for use in hypo elimination baths in the manner of our invention, a mixture of the following composition may be used.

In separate parts of a two-compartment package:

##### Part A

Textone-----grams-- 10

##### Part B

Borax-----grams-- 32  
Succinic acid-----do----- 14

Dissolve the chemicals of Part B in 1 liter of water followed by the chemicals of Part A. For use refer to instructions for Example 4.

Treatment of prints having excessive content of hypo will cause photographic reduction of the image. For this reason it is essential that the prints be washed 20 to 30 minutes in running water or partially washed and the hypo content further lowered by leaching in a dilute alkali bath as previously indicated.

Introduction of excessive quantities of hypo into the hypo eliminator solution will result in the formation of more or less chlorine dioxide giving a bright yellow color to the solution. To avoid the formation of chlorine dioxide in the solution add (to any of the Examples 3, 4, and 5) precipitated silver or finely divided silver powder or filings, for example 1 to 2 grams per liter, which acts as an acceptor to free the solution of chlorine dioxide.

It is to be understood that the disclosure herein is by way of example and that we consider as included in our invention all modifications and equivalents falling within the scope of the appended claims.

What we claim is:

1. A hypo eliminator bath for use in the elimi-



nation of hypo from photographic silver images comprising alkali metal chlorite.

2. A hypo eliminator bath for use in the elimination of hypo from photographic silver images comprising a buffered solution of alkali metal chlorite.

3. A hypo eliminator bath for use in the elimination of hypo from photographic silver images comprising a solution of alkali metal chlorite buffered to a pH within the range of 3 to 12.

4. A hypo eliminator bath for use in the elimination of hypo from photographic silver images comprising a solution of sodium chlorite buffered to a pH within the range of 3 to 5.0.

5. A hypo eliminator bath for use in the elimination of hypo from photographic silver images comprising a solution of sodium chlorite buffered to a pH within the range of 5.0 to 7.

6. A hypo eliminator bath for use in the elimination of hypo from photographic silver images comprising a solution of sodium chlorite buffered to a pH within the range of 3 to 5.0 with acetic acid.

7. A hypo eliminator bath for use in the elimination of hypo from photographic silver images comprising a solution of sodium chlorite buffered to a pH of 5 with a salt and an acid.

8. The method for the elimination of hypo from photographic silver images, which comprises

treating the images with alkali metal chlorite solution.

9. The dry chemicals packaged for use in making a hypo eliminator bath by dissolving in water for use in the elimination of hypo from photographic silver images, comprising alkali metal chlorite.

10. The dry chemicals packaged for use in making a hypo eliminator bath by dissolving in water for use in the elimination of hypo from photographic silver images, comprising alkali metal chlorite and a buffering compound.

11. The method of eliminating hypo from photographic silver images in a gelatin layer, which comprises treating the layer, after exposure, development, and fixing with hypo, with a solution of an alkali metal chlorite.

12. The method of eliminating hypo from photographic silver images in a gelatin layer, which comprises treating the layer, after exposure, development, and fixing with hypo, with a solution of an alkali metal chlorite buffered to a pH of 3 to 7 with a weak organic acid.

13. A hypo eliminator bath for use in the elimination of hypo from photographic silver images, comprising a solution of a dilute acid and sodium chlorite buffered to a pH within the range of 5.0 to 12.

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