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COMPOSITION FOR TREATING PHOTOGRAPHIC FILM TO ELIMINATE HYPO

Henry L. Scott, Beuchel, and William F. Hyatt,
Louisville, Ky., and James M. Carter, New
Albany, Ind., assignors to Brown-Forman Dis-
tillers Corporation, Louisville, Ky., a corpora-
tion of Delaware

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This invention relates to a composition for processing silver halide photosensitive emulsions in film form and relates in particular to a composition and method for treating developed film which reduces the washing time required for eliminating residual hypo.

In the processing of photosensitive silver halide emulsion films, including negatives and prints, etc., after the image of the exposed film is developed and fixed a residue of the hypo (usually sodium thiosulfate) remains in the emulsion. Heretofore it has been proposed to eliminate the residual hypo by treatment with various reagents, but so far as we are aware, no such reagents have received commercial acceptance. Reagents are available which can be made up into a treating solution but the reagents are not stable in storage, nor are the solutions made from them stable, and at best, only a limited number of prints or films can be treated before the solution becomes exhausted or inert. For example, an alkaline solution of hydrogen peroxide and potassium bromide has been proposed, but such solution decomposes rapidly and can treat only a small number of prints before it becomes exhausted. It has also been proposed to employ solutions of sodium hypochlorite in combination with sodium chloride to eliminate hypo from film. Although some retardation of bleaching is effected by this combination, the number of prints that can be treated by such a mixture is quite limited. It is therefore the present common practice to wash the film in running water for a long time to remove the residual hypo.

According to the present invention, a fixed photographic emulsion in the form of a negative film or plate, or a print, is treated with a solution of hypochlorous acid (which acid may be present as the alkali metal salt) containing an amount of a soluble metal halide in excess of the stoichiometrical proportion, and a magnesium salt. Although, in some cases, particularly where the soluble metal halide is an alkali metal bromide, the magnesium salt may be omitted, the presence of the magnesium salt is generally preferred because it greatly prolongs the useful life of the solution and increases the number of prints that can be treated with the solution. Preferably the magnesium salt is employed in the ratio of about four valences of magnesium to one of the halide.

In treating prints in this way according to the invention, it is not necessary to first wash out the hypo with water, but the print may be transferred from the fixing bath to the hypo-elimination bath, where it is retained for a few minutes,

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then removed, washed with water for a few minutes, and then dried. This treatment greatly reduces the time required to eliminate residual hypo, results in a finer grain structure in the finished print, and reduces greatly the quantity of water required for washing. The common practice of washing with running water for several hours fails to achieve the degree of elimination of hypo accomplished by treatment of the prints with the composition of the present invention. In communities where water is metered the saving of water alone, because of the reduction in washing time, is an important consideration.

We are unable to explain the manner in which the magnesium ion or the halide ion function in the preparation. A solution of .18 per cent sodium hypochlorite will cause a distinct bleaching of a print within about eight minutes. If sodium chloride is present, bleaching is retarded, but will take place in about thirty to forty minutes. If potassium bromide is present no bleaching is evident even after overnight exposure, so it is apparent that the potassium halide reduces the bleaching action. The action of the bromide ions in extending the useful life of the solution is even more pronounced. One gallon of a solution of .3 per cent hypochlorite containing ten per cent sodium chloride, when properly diluted, can treat about 112 to 150 prints 8 x 10 inches before it is exhausted, whereas a hypochlorite solution containing ten per cent potassium bromide will treat more than 500 such prints.

Experiment shows that the presence of the magnesium ion greatly extends the life of the chlorite solution in the presence of bromide ions or of an alkali metal chloride. Of these latter, the combination of magnesium ion and bromide ion gives the longer lived solution and is preferred. Sodium bromide or other soluble bromide may be used in place of potassium bromide; and magnesium ions may be used in the form of sulfate, bromide, chloride or other non-oxidizing soluble salt, the sulfate, however, being preferred.

We prefer to prepare a concentrated mixture of the alkali metal bromide and hypochlorite salt in water, with or without the addition of a magnesium salt. Such a concentrate has a long shelf life so that it can be stored or shipped, and need only be diluted with water for use. The concentration of hypochlorite in the concentrate may be varied, depending on the intended use, desired dilution of the concentrate, and desired duration of treatment of the film. The concentration of the halide and magnesium

ions also may be varied. However, the preferred ratio is substantially two parts by weight of magnesium compound to one part by weight of alkali metal halide, and in all cases, the amount of alkali metal halide is maintained in excess of the stoichiometrical equivalent of the hypochlorite, preferably in such ratio that upon dilution of the concentrate for use, the diluted solution will contain no less than one per cent alkali metal halide.

Where the concentrate is made up into predetermined quantity units, and is to be used a little at a time, the solubility of the mixed magnesium and alkali metal halide compounds in the concentrate and the desired degree of dilution limit the maximum permissible amount of hypochlorite that may be present in the concentrate. However, where the whole predetermined quantity is to be used at one time, magnesium and alkali metal halide compounds in excess of saturation may be present, because these compounds are readily dissolved in the diluent water, and the degree of dilution of the hypochlorite desired becomes the limiting factor, on the maximum hypochlorite that may be present in the concentrate. In turn, the desired time of contact of the photographic film in the dilute solution determines the concentration in the dilute solution, and thus determines the maximum hypochlorite in the concentrate and the degree of dilution to be employed. For the machine treatment of emulsion paper, or for treatment of X-ray plates, where the time of treatment is controlled by the machine, the higher concentrates of hypochlorite are preferred, whereas, a solution designed for use by an amateur or professional in a hand tank preferably will contain a lower concentration of hypochlorite so that time of treatment is not too critical. The concentrate may be diluted with from five to ten parts water, depending on the strength of treating solution desired. The treating solution will keep for about a week, so that it is not necessary to make up a fresh solution each day. If desired, ethyl alcohol or any other water soluble lower alcohol or any other compatible substance that reduces the surface tension of water, may be added to the dilute solution to further reduce the time of treatment.

The invention will be described in greater detail in connection with the following specific example:

EXAMPLE 1

A concentrated solution in water is prepared containing about 20 per cent magnesium sulfate, 10 per cent potassium bromide and .3 per cent sodium hypochlorite (NaOCl), the balance being water. Such a solution is stable and can be stored indefinitely. To use the concentrated solution it is diluted with about five to ten times its volume of water, and the diluted solution is employed for removing residual hypo from photographic prints. One gallon of such a concentrated solution, from which the magnesium sulfate has been omitted, will treat approximately five hundred 8 x 10-inch prints before exhaustion, and the dilute treating solution is stable enough to keep for about a week. The addition of the magnesium sulfate to the concentrated solution extends the solution so that more than one thousand prints can be treated from a gallon of concentrate before the solution is spent.

It should be pointed out that it is unnecessary to wash the prints with water before using our

hypo-eliminator solution. It is only necessary to transfer the wet print from the fixing bath to our prepared hypo eliminator bath, allow the prints to remain about five minutes in the hypo-eliminator bath, then transfer the print to a water tank and wash with water for about ten to fifteen minutes to remove all traces of the hypo. If desired, about 20 per cent ethyl alcohol may be added to the treating bath to reduce the time of treatment.

EXAMPLE 2

1424 grams magnesium sulfate ($MgSO_4$) and 712 grams potassium bromide are dissolved in hot water (nearly one gallon), and 92.5 cc. of six per cent sodium hypochlorite solution is added to the hot solution and the solution is made up to one gallon. This solution is approximately a saturated solution of the mixed magnesium sulfate and potassium bromide salts, and contains approximately 5.55 grams NaOCl per gallon and corresponds to a 1.3% solution. Upon cooling, some of the mixed salts may crystallize out, but the crystals readily dissolve upon dilution of the solution for use. This solution, diluted with six volumes of water is employed for washing machine processed paper emulsion where the washing time may vary from about 1 to 1½ minutes. In use with X-ray film, the washing time may vary from about 1½ to 4 minutes. With paper emulsions, an area in excess of four hundred thousand square inches can be processed by one gallon of concentrate; or over 360 double coated X-ray film size 14 x 17; or over 500 screen type film of the same size can be treated.

EXAMPLE 3

Two concentrated solutions were prepared as follows:

Solution A

.3% sodium hypochlorite
10% sodium chloride

Solution B

.3% sodium hypochlorite
10% sodium chloride
20% magnesium sulfate

These solutions were diluted for use with six volumes of water, and were used for treating 8" x 10" single weight "Kodabromide" glossy prints. The prints were prepared by the usual method, developed, treated with acetic acid short stop and fixed. The prints then were soaked for ten minutes in the test solutions, and then were washed with water for 15 minutes and dried. The prints then were tested for residual hypo. The exhaustion point was taken as the number of prints that could be passed through 1000 cc. of the concentrated solution (diluted as above) until the residual hypo content exceeded .02 mg. per square inch of emulsion as measured by the silver nitrate staining technique.

Solution A failed after passing about 30 to 40 prints, and based on this data, one gallon of concentrate would treat about 112 to 150 prints.

Solution B failed after passing about 55 prints, which represents about 206 prints per gallon of concentrate. Thus, the magnesium sulfate extended the life of the solution about 37% to 84%. This compared with Example 1 wherein about five hundred prints can be treated with the potassium bromide mixture, and more than one thousand prints can be treated if magnesium sulfate is present.

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By the term silver halide emulsion photographic film, we intend to include the film, whether or not applied to a backing, and therefore include what the art commonly calls a "print," which is a layer of emulsion on paper.

This application is in part a continuation of our application for Letters Patent Serial No. 240,045 filed August 2, 1951 for Composition and Method for Eliminating Hypo from Photographs.

We claim as our invention:

1. A composition for treatment of photographic films for removal of residual hypo comprising: an alkali metal halide; a hypochlorite salt; and a magnesium salt.

2. A composition as specified in claim 1 wherein the alkali metal halide is a bromide.

3. A composition as specified in claim 2 wherein the magnesium salt is the sulfate.

4. A composition as specified in claim 1 wherein the metal halide is potassium bromide.

5. A concentrated composition as specified in claim 1 wherein the ratio of magnesium salt to alkali metal halide is about two to one on a weight basis.

6. A concentrated aqueous solution for the treatment of photographic films for removal of residual hypo comprising: a hypochlorite; and an alkali metal bromide in an amount greater than about thirty three times the weight of the hypochlorite.

7. A composition as specified in claim 1 comprising up to about 1.3 per cent hypochlorite in the form of a salt.

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8. An aqueous concentrate for the treatment of photographic film to eliminate hypo comprising in a gallon of water up to about 5.5 grams hypochlorite in the form of a salt; alkali metal bromide in a ratio more than thirty-three times the weight of hypochlorite salt; and a magnesium salt in about twice the ratio by weight of the alkali metal bromide.

9. The composition as specified in claim 1 in aqueous solution.

10. An aqueous composition for treatment of photographic films for removal of residual hypo comprising: an alkali metal halide, hypochlorous acid, and a water soluble magnesium salt the ratio of magnesium salt to halide being in the proportion of about four magnesium valences to one of halide.

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