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PHOTOGRAPHIC WASHING ACCELERATORS

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1 Claim. (Cl. 96—61)

This invention relates to photography and more particularly to a process for accelerating the removal of sodium thiosulfate and silver salts from fixed photographic materials by the use of aqueous soluble sulfite washing solutions.

A common method of washing the fixed photographic image to remove the fixing chemicals is to employ running water from one-half hour to an hour. This removal of the fixing chemicals and the soluble by-products of the fixing operation is required in order to prevent deterioration of the print, film or plate.

Heretofore numerous "hypo eliminators" and "washing accelerators" have been described in the literature which are designed to lessen the washing time. Many of these have been tabulated by Crabtree, Eaton and Muehler in a paper printed in PSA J. 6:6–14, 1940, and they include oxidizing agents, alkalies and common salt. The latter substance, sodium chloride was presumed by Eaton and Crabtree, J. Soc. Mot. Pict. Eng., June 1, 1943, 380–391, to be the active ingredient in the accelerated washing obtained with sea water.

The washing accelerators described in the above literature while operable have a number of disadvantages. The oxidizing agents are inconvenient to use, unstable, and often cause excessive softening of the emulsion, as do the alkalies. Further, they tend to remove the soluble sodium thiosulfates but not the less soluble silver thiosulfates. In fact, the action of such washing accelerators is not as intense as desired particularly with photographic papers.

It is the principal object of the present invention to provide an improved method of accelerating the removal of hypo and silver salts from fixed photographic materials.

Another object is to remove these thiosulfates more rapidly and with less inconvenience than occasioned by previous methods.

Still another object is to remove the residual hypo concentration and to stabilize the hypo compounds which are not removed so that the tendency toward fading and staining is greatly reduced.

A further object of the invention is to improve the stability of the treated photographic material.

Another object is to provide an improved washing solution for washing fixed photographic images.

Other objects will appear hereinafter.

In accordance with the present invention these and other objects are attained by employing as a washing medium for washing fixed photographic images an aqueous solution containing one or more soluble sulfites. The sulfite ion employed may be the sodium salt as well as soluble sulfites of alkali metals and amines. Acid sulfites and neutral sulfites may be employed and the pH adjusted if desired by the addition of appropriate alkalies or alkaline or acidic substances. The preferable pH range for such a preparation is between pH values of 4 and 10, and a neutral solution, of substantially pH=7, has proved particularly useful. The sulfite may be precipitated from the solution by certain metals including calcium which is usually present in water from ordinary sources, as well as the aluminum salts carried over from the fixing bath. In order to prevent this precipitation an appropriate sequestering agent may be added such as sodium hexameta phosphate, sodium tetraphosphate or other polyphosphate, ethylene diamine tetracetic acid, citric acid or others of the well known sequestering agents.

Our invention is further illustrated in the following examples:

Example 1

Following fixation in a fixing bath which contains silver from previous use, Kodak Velox F–3 single weight paper was bathed for 5 minutes in (*a*) water, (*b*) a 2% solution of sodium bisulfite, and (*c*) a 2% solution of sodium sulfite. The prints were then washed for 15 minutes in cold water. Measurement of silver residual in sample prints after each washing showed that both the sulfite and bisulfite were effective in aiding its removal, the concentration being reduced from 0.017 mg. per square inch to 0.002 mg. per square inch. The residual hypo concentrations were 0.22 mg. per square inch (water only), 0.12 mg. per square inch (bisulfite treated), and 0.03 mg. per square inch (sulfite treated).

Example 2

Kodak Microcard paper, which is difficult to free from hypo in short washing periods, was fixed in a fresh fixing bath of standard composition, washed 3 minutes, and bathed for 1 minute in (*a*) a 2% solution of sodium sulfite, and (*b*) a mixture containing 10% sodium sulfite and 2% sodium bicarbonate. The washing was then continued for 2 more minutes. The hypo content of paper washed only for 6 minutes was found to be 0.19 mg. per square inch, and these prints faded rapidly on moist incubation at 110° F., PSA J. 238:8–17, 1948, Method for Predicting the Permanence of the Silver Images of Processed Film, Plates and Papers. Bathing in the sodium sulfite bath reduced the hypo concentration only slightly (to 0.15 mg. per square inch), but so stabilized the prints that the fading during incubation became insignificant. The sulfite-bicarbonate mixture reduced the hypo content to 0.099 mg. per square inch, and also stabilized the image so that no fading occurred. A number of other mixtures of sulfite and bicarbonate were tried with generally similar results.

Example 3

A bath containing sodium sulfite (2%) and sodium bicarbonate (1%) was employed with a series of fixed photographic papers, of fixing baths (both fresh and exhausted), and of washing cycles. This solution was compared with the prior art employed in removing hypo including the use of (1) an alkali (sodium metaborate), (2) a neutral salt (sodium sulfate), and (3) the powerful peroxide-ammonia hypo eliminator, PSA J. 6:6–14, 1940. The papers employed included single weight, double weight, and extra thin bases, with and without baryta coatings, and in one case, a water resistant base was employed. The hypo content obtained in these tests was in every case comparable to the lowest hypo content achieved by prior art methods (usually obtained with the HE–2, peroxide-ammonia eliminator), while the stability of the resultant image was in general superior to that obtained by any other method. The silver content of the treated prints was particularly low and less than that obtained with alkali treatment or with peroxide-ammonia.

Example 4

Mixtures of sodium bisulfite with tetra sodium pyro-

phosphate, sodium bisulfite with disodium hydrogen phosphate, and sodium sulfite with sodium bisulfite were all found effective in removing hypo from Kodak Opal G paper and in stabilizing the image.

Example 5

A 2% solution of sodium sulfite containing, in addition, an antiplumming agent was found to assist in the removal of hypo and the stabilization of prints in a Kodak Continuous Paper Processor, Model II. Papers employed included Kodak Opal G, Kodak Medalist, and Kodak Ektalure. Mixtures of sodium bisulfite with sodium bicarbonate also proved effective.

Example 6

In place of the sodium sulfite employed in Examples 1 to 5, we have repeated these examples employing lithium, potassium and ammonium sulfites and have found all of them are fully as effective as the sodium sulfite for hypo elimination from fixed photographic materials. Amine sulfites, such as triethanolamine sulfite, and the sulfite salts of ethylene diamine would also be entirely suitable.

Example 7

We have found that the following washing solution is particularly suited for washing fixed photographic materials.

	Grams per liter
Sodium sulfite	20.0
Sodium bisulfite	5.0
Sequestrene Na-4 (tetrasodium salt of ethylene diamine tetracetic acid)	0.5

This solution has been found to be highly effective for both films and papers and has been particularly beneficial in obtaining archival levels when washing microfilms. It has been found possible to greatly dilute this formula and still obtain effective hypo elimination when film is immersed in the bath for a long period and in one application the bath has been beneficially employed at $\frac{1}{30}$ of the above concentration.

It appears that the effectiveness of the sulfite solutions may be due to the following mechanisms: (*a*) Upon immersion in the sodium sulfite solution the thiosulfate ions absorbed to the gelatin, are displaced by sulfite ions from the solution until equilibrium is reached; (*b*) if alkaline, the solution also tends to displace the alum, which has a marked mordanting action for thiosulfate ions, and (*c*) the sulfite ions, left in the print, stabilize any residual hypo by causing the reaction

$$Na_2SO_3+S=Na_2S_2O_3$$

to shift to the right.

It has also been proposed to employ as a washing aid a solution containing both a soluble salt of a polyvalent anion and an alkaline substance. Suitable anions include sulfate, phosphate, pyrophosphate, tetraphosphate and citrate, which may be employed as sodium, potassium, ammonium, lithium and magnesium salts. These salts may be employed in concentrations of 0.5 to 10% but the preferred range is 1 to 2%. Suitable alkalies include sodium metaborate, sodium tetraborate, sodium bicarbonate, sodium sesquicarbonate, sodium carbonate, ammonium hydroxide, sodium hydroxide, dibasic and tribasic phosphates, and organic amines. Potassium, ammonium, and lithium salts may, of course, be substituted for the sodium salts provided the alkalinity is suitable. These alkalies may be used in concentrations of from 0.25% to 10% depending on the specific alkali and the effect desired.

The following is an example of the use of these washing aids.

Example 8

Kodak Velox F–3 (single weight) and Platino G–3 (double weight) papers were developed, rinsed and fixed in a bath of Kodak F–5 containing silver to simulate use. The F–5 acid hardening fixing bath is for general use with films and plates as disclosed on page 15 in the "Book of Formulas" published by Eastman Kodak Company, 1936. The bath contains sodium thiosulfate 960.0 grams, sodium sulfite 60 grams, acetic acid 190 cc., boric acid crystals 30 grams, potassium alum 60 grams and water 6.5 liters. They were then immersed in one of the following solutions for 5 minutes and washed for 20 minutes. The hypo and silver concentrations were estimated with the Kodak HT–2 solution. The HT–2 solution contains water 1750 cc., acetic acid 125.0 cc., silver nitrate 7.5 grams. In addition, strips were given moist incubation for 2 weeks at 110° F. While the sodium thiosulfate alone produced a significant reduction in silver and hypo, particularly on the single weight paper, the further addition of the alkali caused a more complete elimination of hypo and silver, and further, greatly improved the stability towards moist incubation. For example, whereas prints treated only in water faded severely in 2 days, and those in sodium sulfate faded in 7 days, those bathed in solutions containing sodium sulfite and an alkali faded only slightly in 14 days.

The above solutions efficiently cause the elimination of hypo and greatly reduce the danger of fading from this source. However, another cause of impermanence is the reaction of the image with gaseous vapors, particularly paint vapors and other sources of peroxide. We have found that we can protect against this type of fading, as well as that due to residual thiosulfate, by adding a reactive selenium compound to the sulfite washing accelerator. Another benefit of the addition of this type of selenium compound is that the image is also protected against the change of image tone on hot drying known as plumming. In accomplishing this protection the image is very lightly reacted with the selenium compound but to a small enough extent that it need not necessarily be visibly affected.

Compounds containing a labile selenium atom suitable for this purpose are the selenosulfates, selenocyanates and the selenides. Of these the selenosulfates are particularly effective. The selenosulfates may be readily formed by dissolving metallic selenium in a solution of an alkali metal sulfite.

The following examples illustrate the preparation of such a selenosulfate and its incorporation in a washing aid.

Example 9

Ten grams of metallic selenium and 90 grams of potassium sulfite were mixed and 200 cc. of warm water were added slowly with stirring. Stirring was continued for 5 minutes and the solution then filtered leaving a residue of 0.05 gram of unreacted selenium or impurity. The solution was evaporated to dryness and yielded approximately 100 grams of a pure white powder comprising a mixture of potassium selenosulfate with excess potassium sulfite. The above preparation containing 10% selenium by weight was blended with various sulfite and bisulfite mixtures. It was found to be completely stable when blended with sodium sulfite, potassium sulfite or potassium metabisulfite but visible discoloration occurred when sodium bisulfite was present in the mixture. The preferred mixture contained 10 grams of the above potassium selenosulfate-potassium sulfite mixture, 200 grams of sodium sulfite and 5 grams of tetra-sodium salt of ethylene diamine tetracetic acid. A solution of 21 grams of this powder in 1000 cc. water was used to treat processed prints after fixing and found effective in preventing peroxide fading.

Example 10

To a sulfite washing accelerator containing, per liter of working strength bath, 20 grams of sodium sulfite and 5 grams of sodium bisulfite, quantities of selenium varying from 1.0 to 0.02 gram per liter were added by

heating in a more concentrated form and then diluting for use. Kodak Platino paper was processed normally, bathed in this solution for 3 minutes, and washed for 20 minutes. The hypo content was low (about 0.05 mg. per square inch) but when the prints were exposed to an atmosphere of vapors from a hydrogen peroxide solution the control prints (bathed in the unmodified sulfite solution or washed only) became very brown in hue and lost density, while those treated with the solutions containing the selenium, even at the lowest concentration employed, were almost completely unaffected. Some change in image tone was produced by the highest concentration of selenium, but not by the lower concentrations.

Example 11

The above experiment was repeated with Kodak Athena and Medalist papers, using the unmodified sulfite solution and one containing 0.05 gram of selenium per liter. Again, on exposure to peroxide vapors, the prints processed through the unmodified sulfite solution faded badly, while those processed in the solution containing selenium proved entirely stable. Also, the Athena control print, on strong exposure to paint vapors faded in a similar manner, while that slightly selenided proved entirely stable.

Example 12

Yet another type of image instability is the shift in hue and density which may occur on the hot drying of a print. The prints of Example 11 were subjected to a standard "plumming" test by immersing a portion in water at 190° F. for 30 seconds. The Athena print which had been treated in the solution containing selenium showed little plumming tendency whereas the control print strongly showed the development of a strong "plum" color. The same qualitative difference was noted for the Medalist print, although the plumming of the control was here less evident.

We claim:

In the method of exposing, developing, fixing, water washing and drying a gelatin-silver halide emulsion layer, the improvement residing in the step which consists in rinsing said emulsion layer intermediate the said fixing and water washing steps with a solution consisting of about 20.0 grams sodium sulfite, 5.0 grams sodium bisulfite and 0.5 gram tetrasodium salt of ethylene diamine tetraacetic acid per liter of solution, whereby the time of the duration of said water washing step is materially reduced.

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