Formation of Silver Sulfide in the Photographic Image During Fixation

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A photographic silver image is made permanent (fixed) after development by bathing it in a solution containing thiosulfate which forms a soluble thiosulfate complex with the residual silver halide. Some of the silver in the image is sulfided by the thiosulfate during fixation. The purpose of this study was to determine the amount of sulfiding of the silver in the image during fixation of film and paper. The amount of the silver reacting depends on the type of the light-sensitive layer. Also, during bleaching, the residual thiosulfate in the film or paper reacts with silver in a potassium dichromate-sulfuric acid bleach bath to form silver sulfide. For one paper, it was shown that the amount of silver sulfide which was formed in the bleach bath increased with the increase of the concentration of the residual thiosulfate in the paper. A procedure was developed for the reduction of silver sulfide in an emulsion layer to silver so that the silver sulfide may be determined in terms of the optical density of the silver deposit. The use of hypo eliminators was investigated and a test procedure was found for testing the effectiveness of hypo eliminators. A small amount of potassium iodide added to the fixing bath was found effective in preventing most of the sulfiding of the silver image during fixation.

1. Introduction

A photographic silver image is made permanent (fixed) after development by bathing it in a solution containing thiosulfate which forms a soluble thiosulfate complex with the residual silver halide. Some of the silver in the image is sulfided by the thiosulfate during fixation. The permanence of the silver image in processed film and paper is related to the degree of sulfiding of the silver in the image which takes place during fixation and the amount of silver thiosulfate complex and thiosulfate which remain after the washing process. The purpose of this study was to determine the amount of sulfiding of the silver in the image during fixation of film and paper. A brown stain or "ghost" image remains when the silver in an image is removed by most bleaching solutions [1, 5, 6, 7, 8, 9, 11].[1] This stain has been identified as silver sulfide [1, 2, 3].

The silver sulfide residue which remains when a silver image is bleached may have three sources. The first is the reaction of the silver in the image with the thiosulfate during fixation. The amount of this sulfiding of the silver depends on the type of the sensitized emulsion. This silver sulfide is present before and after the silver has been bleached. The second source of silver sulfide is the residual silver thiosulfate complex and thiosulfate which have not been removed in the washing process and have not yet reacted with the silver in the image to form silver sulfide but do react in the bleach bath. This reaction was used to study the effect of different residual thiosulfate concentrations on the amount of

silver sulfide formed in the bleach bath for one paper. A third source of silver sulfide may be traced to the residual silver thiosulfate complex and thiosulfate which have not been removed in the washing process but have reacted during storage to form silver sulfide. This silver sulfide is present before and after the silver has been bleached. The silver thiosulfate complex eventually decomposes to form silver sulfide. The residual thiosulfate, because of its labile sulfur, reacts with the silver in the image to form silver sulfide, especially at high relative humidities. The effect of excessive sulfiding of the silver image first appears in the areas of low silver density, the highlights, causing the image tone to become brownish. Eventually silver sulfide, itself, may bleach, particularly at high relative humidities and in the presence of excess salts which have not been removed during the washing process [4].

Levenson and Sharpe [11] made an intensive study of the role of thiosulfate in the formation of silver sulfide stains in a bromide emulsion during the bleaching process. They found that the stain was produced after the silver image had been in contact with thiosulfate either in the developer or after fixing in a sodium thiosulfate fixing bath. They exposed their samples to a step wedge and plotted the silver density and the stain density against relative values of the logarithm of exposure to show the amount of stain produced by the corresponding silver densities for a bromide fine-grain emulsion. They concluded that a certain amount of thiosulfate was strongly absorbed on the silver of the image as thiosulfate or as a thiosulfate complex and that it reacted with silver ions in the bleach to form silver sulfide. This subject is discussed further in section 6.

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[1] Figures in brackets indicate the literature references at the end of this paper.

2. Processing Procedures

Samples of the photographic film and paper were cut to 1⅜ in. by 10 in. and exposed to a step wedge. Not more than eight samples were processed or treated at one time. About 2 liters of fresh solution were used in each processing operation employing nominal 8- by 10-in. enameled trays. The samples were continuously agitated by hand during processing and washed in running tap water. The processing solutions are listed in the appendix, section 8. The temperature of the processing solutions were at room temperature (22° to 28° C).

2.1. Developing and Fixing the Silver Image

The samples were developed 3 min, treated 1 min in the short stop bath, and fixed 10 min in two baths (5 min in each bath). Next the samples were rinsed 1 min in tap water, treated 10 min in the hydrogen peroxide eliminator No. 1, bathed 2 min in a 1-percent solution of sodium sulfite, washed 30 min, and hung to dry at room temperature. Two fixing baths were used to facilitate the removal of the silver thiosulfate complex. Tests showed that the amount of silver sulfide formed in the silver image during fixation reached a maximum in about 3 min in the acid-hardening fixing bath.

2.2. Bleaching the Silver Image

The samples were treated 5 min in the dichromate bleach bath, washed 30 min in tap water at 25° ± 2° C, treated 5 min in the clearing bath, treated 3 min in the thiosulfate eliminator No. 3, and washed 30 min in tap water. The operation was performed in daylight but not in direct sunlight. The bleach removed the silver, leaving the silver sulfide which formed during fixation. Additional silver sulfide was formed when the silver thiosulfate complex or residual thiosulfate was present. The potassium dichromate-sulfuric acid bleach oxidized the silver in the image in 1 to 2 min. The bleach did not dissolve the silver-sulfide residue when the bleaching time was extended to 15 min. The clearing bath, which was used to remove the residual dichromate, was the one employed by Levenson and Sharpe [11] and proved to be quite satisfactory for both films and papers. It was found necessary to fix the samples after clearing to remove the last traces of silver salts which, when present, increased the density of the silver sulfide residue slightly.

2.3. Reduction of the Silver Sulfide to Silver

The samples were treated 2 to 3 min in the permanganate bleach bath, rinsed 10 sec in running tap water, treated 5 min in the clearing bath, washed 30 min in running tap water, blotted to remove surface water, and dried in the dark. The samples were then exposed for 10 min to a 100-w tungsten lamp at a distance of 12 in., developed 5 min in running tap water, and hung to dry. With the exception of the drying of the samples before exposure the operations were performed in daylight but not in direct sunlight.

The permanganate bleach converted the silver sulfide to silver chloride. The potassium bromide in the clearing bath prevented the loss of silver in the gelatin layer because silver chloride is more soluble than silver bromide. There was a partial solution of the silver chloride when sodium chloride was used in the clearing bath. Unfortunately, the gelatin layer was quite soft after treatment in the clearing bath and the high alkalinity of most developers caused the gelatin to break loose from the support. The amidol developer was found to be satisfactory for papers and most films. However, films with a normally soft gelatin layer should be washed 5 min after treatment in the clearing bath, treated 5 min in a 2-percent solution of formaldehyde, and washed 10 min before drying.

The reduction of silver sulfide in the gelatin layer to silver appeared to be quantitative. When this reduced silver was sulfided the original silver sulfide densities were again obtained. The silver was sulfided in an atmosphere of hydrogen sulfide. The sample of film or paper was soaked in water for 5 min and, after removing the surface water with a blotter, it was suspended for 1 hr in a ½-gallon bottle above a solution containing 50 g of sodium sulfide ($Na_2S \cdot 9H_2O$), 35 g of citric acid ($H_3C_6H_5O_7 \cdot H_2O$), and 500 ml of water. After this treatment the sample was washed for 30 min in running tap water.

3. Removal of the Thiosulfate During the Washing Process

The thiosulfate must be removed from processed films and papers when investigating the reaction of thiosulfate with the silver of the image during fixation. Solutions which remove the thiosulfate from the gelatin layer and paper base are generally known as "hypo eliminators." Crabtree et al. [13] showed that hydrogen peroxide in an ammoniacal solution eliminates thiosulfate from photographic materials. The hydrogen peroxide oxidizes the thiosulfate to sulfate. This hypo eliminator was used in the experimental work reported in this paper and is listed as formula No. 1 in the appendix, section 8.1. It is the same hypo eliminator used in an American Standards Association photographic standard [16].

Salt solutions have proved effective in removing the thiosulfate from films and papers [12, 13, 14, 15]. Such solutions are convenient because they can be prepared and stored before use and no temperature control is necessary. In the course of this study two salt solutions were developed which proved to be quite efficient in removing the thiosulfate. One solution contained sodium sulfate and ammonium hydroxide and the other sodium sulfate and sodium sulfite. The sodium sulfate helps to prevent undue swelling of the gelatin caused by the alkalinity of the salt solutions. The formulas for these solutions are listed as No. 2 and 3 in the appendix, section 8.1. The two salt solutions have been used in experimental studies only and have not been evaluated for use in large-scale production. The sodium

thiosulfate content of single-weight samples of photo-copy, contact, and enlarging papers was reduced to 0.005 mg or less per square inch when treated in these solutions. When the hydrogen peroxide hypo eliminator No. 1 was used no sodium thiosulfate could be found in films or papers. The residual thiosulfate in photographic papers was determined by the method of Crabtree et al. [17] and in photographic films by the method of Crabtree and Ross [22].

4. Results and Discussion

4.1. Silver Sulfide Formed in Photographic Papers During Fixation

The paper sample was exposed to a step wedge, processed and treated in the hydrogen peroxide hypo eliminator No. 1 after fixation. The silver image was removed by the potassium dichromate-sulfuric acid bleach leaving the silver sulfide image or residue which in turn was reduced to silver. During the above procedure reflection density [2] measurements were made of the original silver image, the silver sulfide image remaining after the bleach, and the silver image obtained by reducing the silver sulfide to silver. No filter was used in measuring the densities of the silver sulfide. The density of the paper base was subtracted from the density readings. The densities for the three images obtained from a single sample were plotted against relative values of the logarithm of exposure and the three characteristic curves are shown in figures 1, 2, and 3, respectively, for a photocopy paper, a contact paper, and an enlarging paper. The papers were all single weight. The lowest curve in figures 1, 2, and 3 shows the density of the silver sulfide formed in the image during fixation. The middle curve shows the density of the silver which is obtained by reducing the silver sulfide to silver. The percentage of the original image silver sulfided during fixation may be determined from the density reading in the middle curve and the corresponding density reading in the highest curve which is that for the original silver image. In the region of high-silver densities or full exposure the amount of sulfiding of the silver image is about 25 percent for the photocopy paper, about 17 percent for the contact paper, and about 28 percent for the enlarging paper. At lower silver densities the amount of sulfiding of the silver image is about 20 percent for a density of 0.6 for the photocopy paper, about 9 percent for a silver density of 1.0 for the contact paper, and about 14 percent for a silver density of 1.0 for the enlarging paper. The percentage of the silver sulfided increases as the silver density in the image increases up to the high densities. The amount of silver sulfide formed reaches a maximum in the high densities and levels off as shown by the curve for silver sulfide in figures 1, 2, and 3.

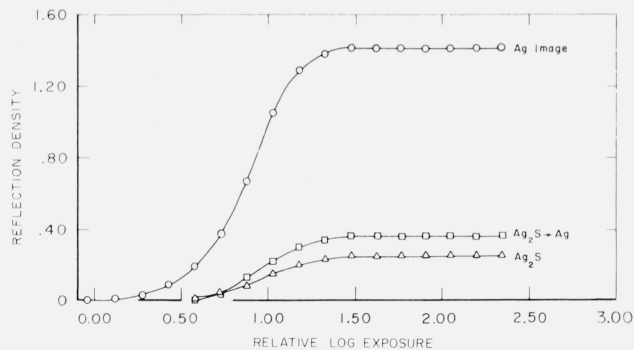[2] The reflection density was measured by the American Standards Association method [10].

FIGURE 1. *Reflection density versus relative logarithm of exposure for the silver image, the silver sulfide residue, and the silver obtained by the reduction of the silver sulfide, for one sample of a single-weight photocopy paper.*
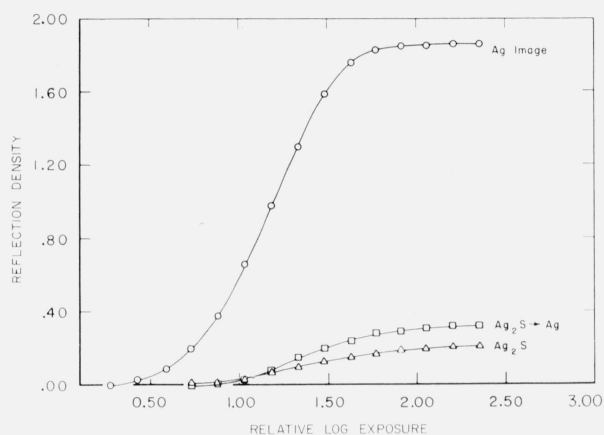

FIGURE 2. *Reflection density versus relative logarithm of exposure for the silver image, the silver sulfide residue, and the silver obtained by the reduction of the silver sulfide, for one sample of a single-weight contact paper.*
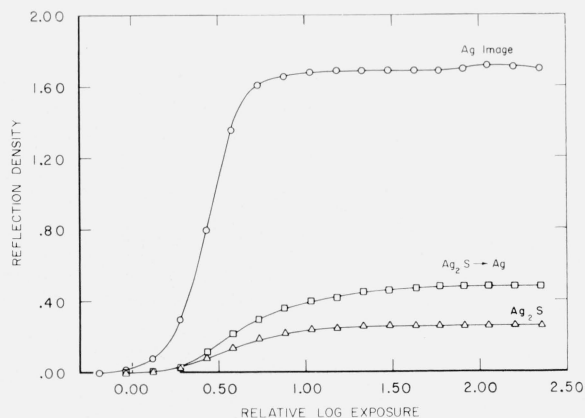

FIGURE 3. *Reflection density versus relative logarithm of exposure for the silver image, the silver sulfide residue, and the silver obtained by the reduction of the silver sulfide, for one sample of a single-weight enlarging paper.*

The above results demonstrate that an appreciable amount of the silver in the image of photographic papers is sulfided during fixation. The silver sulfide cannot be removed by washing or the use of hypo eliminators. If photographic papers are to be used for permanent records the thiosulfate must be removed or reduced to the lowest possible concentration during the washing process to prevent the formation of additional silver sulfide. Residual thiosulfate in the processed paper reacts with the silver in the image to form more silver sulfide. This reaction is slow at low relative humidities but quite rapid at high relative humidities. Further sulfiding of the silver image would be especially objectionable in areas of low silver densities corresponding to the highlights of pictures. The amount of the sulfiding of the silver in films and papers depends on the type of emulsion.

Transmission density measurements were also made of the silver and silver sulfide in this study on the sulfiding of the silver image in papers during fixation. The transmission density of a paper base depends on the optical system of the transmission densitometer; however, if the same densitometer is used in a series of tests useful relative data are obtained. For example, transmission density measurements were made of the same sample of photocopy paper which was used for figure 1. The densities were plotted against relative values of the logarithm of exposure and the three characteristic curves are shown in figure 4. The density of the paper base has been subtracted from the density readings. The curves in figure 4 show approximately the same percentage of sulfiding of the silver image for the highest silver densities as those in figure 1 but in the lower silver densities the transmission density measurements show a higher percentage of silver sulfided than the reflection density measurements. This was found to be true also for contact and enlarging papers.
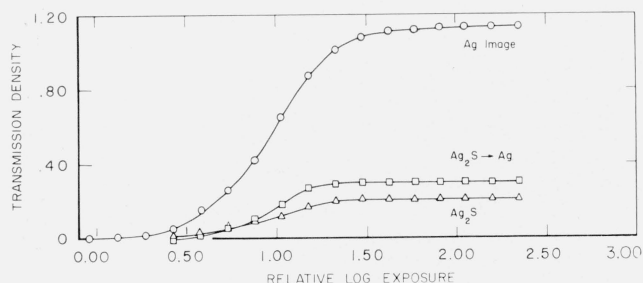
4.2. Silver Sulfide Formed in Photographic Films During Fixation

The amount of sulfiding of the silver image during fixation was determined for two microfilms, a photomechanical film, and an X-ray film by the same procedure as that described for photographic papers except that the densities were measured by transmitted light. No filter was used in measuring the densities of the silver sulfide. The transmission densities were plotted against relative values of the logarithm of exposure. From the characteristic curves obtained for each film the density of the silver sulfide and silver obtained when the silver sulfide was reduced to silver were determined for various densities of the original silver image. The results are tabulated in table 1. The characteristic curves for microfilm A are shown in figure 5. The results in table 1 show that the amount of sulfiding of the silver image in the high densities is about 7 percent for microfilm A and 5 percent for microfilm B. These values compare well with the 5 percent found by Levenson and Sharpe [11] for a bromide fine-grain emulsion. This amount of sulfiding of the silver image during fixation should have a negligible effect on the permanency of the image in microfilm. However, the residual thiosulfate must be removed in the washing process to prevent further sulfiding of the silver image.

As in the case of photographic papers, the amount of sulfiding of the silver image in films depends on the type of emulsion. The values for the photo-

FIGURE 4. *Transmission density versus relative logarithm of exposure for the silver image, the silver sulfide residue, and the silver obtained by the reduction of the silver sulfide, for the same sample of single-weight photocopy paper shown in figure 1.*
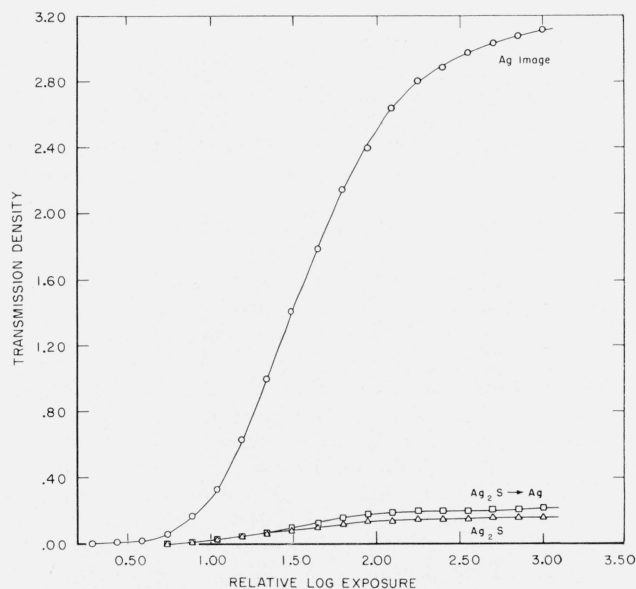

FIGURE 5. *Transmission density versus relative logarithm of exposure for the silver image, the silver sulfide residue, and the silver obtained by the reduction of the silver sulfide, for one sample of microfilm A.*

mechanical and X-ray films are given in table 1 to show the difference in types of emulsions in films. A silver sulfide density of 0.02 was obtained for a silver density of 1.8 for one ciné fine-grain film not shown in the table.

TABLE 1. *Densities of the silver image in films and the corresponding densities of the silver sulfide residue and the silver obtained by the reduction of the silver sulfide*

Density of the silver image	Density of silver sulfide after bleach	Density of the silver obtained by the reduction of the silver sulfide
Microfilm A		
0.50	0.05	0.05
1.00	.07	.07
1.50	.08	.10
2.00	.11	.14
2.50	.13	.18
3.00	.15	.20
Microfilm B		
0.50	0.02	0.03
1.00	.03	.05
1.50	.04	.06
2.00	.06	.08
2.50	.08	.11
3.00	.10	.14
Photomechanical film		
0.50	0.03	0.08
1.00	.06	.12
1.50	.09	.18
2.00	.12	.22
2.50	.14	.26
3.00	.17	.28
3.50	.19	.30
4.00	.20	.31
X-ray film (2 light-sensitive emulsions)		
0.50	0.04	0.05
1.00	.06	.08
1.50	.08	.12
2.00	.10	.14
2.50	.12	.17
3.00	.13	.19
4.00	.16	.23

4.3. A Test for Hypo Eliminators

The potassium dichromate-sulfuric acid bleach which was used in this investigation removes the silver from the photographic image, leaving the silver sulfide formed during fixation by the reaction of thiosulfate with the silver image. Also, any residual thiosulfate reacts with silver ions in the bleach bath to form additional silver sulfide. It seemed feasible to use the latter reaction to determine the effect of different thiosulfate concentrations on the silver image by measuring the increase in the silver sulfide density above that found when the residual thiosulfate is completely eliminated by the hydrogen peroxide hypo eliminator No. 1. A concentration of 0.005 mg of sodium thiosulfate ($Na_2S_2O_3$) per square inch in photographic papers gave a measurable increase in the silver sulfide density above that

normally formed during fixation. This type of test for residual thiosulfate in papers and films shows the direct effect of the residual thiosulfate on the silver in the image and should simulate the reaction of residual thiosulfate with the silver in the image during storage. The Crabtree et al. [17] method for determining thiosulfate in paper measures the thiosulfate concentration in a clear area of the paper.

If residual thiosulfate is present when papers are bleached, some silver sulfide may be precipitated in the paper base. Reflection density measures only the density of silver and silver sulfide in the gelatin layer. For this reason, transmission density is recommended instead of reflection density for measuring the silver sulfide in papers as a test procedure for evaluating hypo eliminators.

The effect of different residual thiosulfate concentrations in paper on the increase of the density of the silver sulfide is shown in figure 6. Samples of a
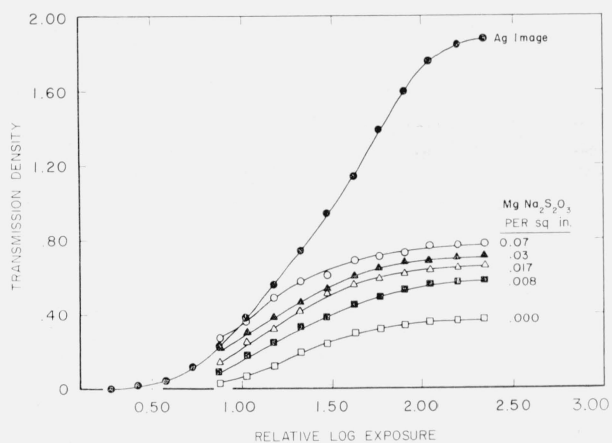

FIGURE 6. *The effect of the residual sodium thiosulfate concentration on the amount of silver sulfide formed in the bleach bath is shown for a single-weight contact paper.*

Characteristic curves are given for the original silver image and for the silver obtained by the reduction of the silver sulfide formed with varying concentrations of residual sodium thiosulfate. The concentration of the residual sodium thiosulfate is shown at the end of the curves.

single weight contact paper were given the same exposure to a step wedge and processed in the same manner and at the same time except that, after fixation, one sample was treated in the hydrogen peroxide hypo eliminator No. 1 and one sample was washed in tap water for each of the following washing times: 120, 60, 30, and 10 min. The samples were bleached and the silver sulfide was reduced to silver. The transmission densities of the silver image and the silver of the silver sulfide reduced to silver were plotted against relative values of the logarithm of exposure. The density of the paper base was subtracted from the density readings. The lowest curve shows the silver of the image sulfided during fixation, where all of the residual thiosulfate had been removed by the hydrogen peroxide hypo eliminator No. 1. The curve for the original silver

image was obtained from the sample which had been treated in the hydrogen peroxide hypo eliminator No. 1. The other curves fall in order of their residual thiosulfate concentrations which are given in milligrams of sodium thiosulfate ($Na_2S_2O_3$) per square inch at the end of the curves. The curves show that the silver sulfide increases appreciably as the residual thiosulfate increases. For a silver image density of about 1.9 the sample containing 0.008 mg of sodium thiosulfate per square inch shows a 57 percent increase in the sulfiding of the silver above that taking place during fixation and the sample containing 0.07 mg of sodium thiosulfate per square inch shows 111 percent increase.

The above results show that the efficiency of a hypo eliminator may be evaluated by testing it against the hydrogen peroxide hypo eliminator No. 1 used as a standard. This test may be made by giving samples of film or paper from the same roll or box the same exposure to a step wedge and processing them at the same time in the same solutions except that, after fixation, one set of samples is treated in the hypo eliminator to be tested and the other in the hydrogen peroxide hypo eliminator No. 1. The samples are then bleached and the transmission densities of the silver sulfide are measured and plotted against relative values of the logarithm of exposure. For greater sensitivity the silver sulfide may be reduced to silver. The characteristic curve for the hydrogen peroxide hypo eliminator No. 1 shows the silver sulfide formed during fixation. The characteristic curve for the hypo eliminator being tested will be the same if all of the residual thiosulfate has been eliminated but will be higher if residual thiosulfate is present. Its height will depend on the concentration of the residual thiosulfate as shown in figure 6.

5. Effect of Potassium Iodide on the Formation of Silver Sulfide During Fixation

The addition of potassium iodide to the fixing bath has been found to prevent the formation of the brown silver sulfide stain which interferes in reversal and reduction operations [7, 18, 19]. Murray [18] added three-fourths of an ounce of potassium iodide to one gallon of the fixing bath. Crabtree et al. [7] found that 0.1 to 1.0 percent of potassium iodide in the fixing bath eliminated the brown stain in positive film.

The effect of potassium iodide in the acid fixing bath on the sulfiding of the silver image was investigated. One gram of potassium iodide was added to each liter of the fixing bath. The samples were given a full exposure, developed, fixed, treated in the hydrogen peroxide hypo eliminator No. 1, and bleached. The density of the silver sulfide ranged from 0.02 to 0.04 for contact and enlarging papers which normally yielded a silver sulfide density of 0.2 to 0.25. The density of the silver sulfide was about 0.005 for two microfilms which normally yielded a silver sulfide density of 0.10 to 0.15. The densities were measured by transmission without a filter. These results show

that a small amount of the iodide ion in the fixing bath is quite effective in preventing most of the normal sulfiding of the silver. When processed samples of film or paper, which had been fixed in the acid fixing bath containing potassium iodide, were again treated in the acid fixing bath containing no iodide ion, the amount of sulfiding of the silver was almost as great as that normally obtained.

The effect of the iodide ion in preventing the formation of silver sulfide in the silver image would suggest that silver ions were present in the fixing bath. Silver iodide instead of silver sulfide would be formed because it is less soluble than silver sulfide. It is not known what effect any residual silver iodide or potassium iodide might have on the stability of the silver image. Small concentrations of the iodide ion in the fixing bath retards the rate of fixation [20] and decreases its fixing capacity.

6. Silver Sulfide Formed During Fixation in a Thiosulfate Fixing Bath

Reindorp [1] postulated that the silver sulfide was formed during fixation by the decomposition of a silver thiosulfate complex. Levenson and Sharpe [11] concluded that the thiosulfate was absorbed as a simple ion or a complex ion on the silver in the image during fixing and that the silver sulfide was formed in the bleach bath by the reaction of silver ions with the absorbed thiosulfate. If the thiosulfate is absorbed as a simple ion or as a complex ion on the surface of the silver grains it might be possible to eliminate it and prevent the formation of silver sulfide. But, if the silver sulfide is formed during fixation it could not be removed and would be an integral part of the image. This problem was investigated and the experimental results gave strong evidence that the silver sulfide is formed during fixation.

6.1. Experimental Results

a. Removal of the Silver Sulfide From the Silver Image

An investigation was made to determine if the silver sulfide, which formed during fixation, could be removed from the silver image before it was bleached. A solution containing 30 g of silver nitrate and 180 g of anhydrous sodium sulfite per liter was found capable of removing all of the silver sulfide from a sulfided silver strip. A similar solution was used by Hickman and Weyerts [21] in their studies on optical intensification of silver sulfide images.

A brown coating of silver sulfide was formed on silver strips, ¾-in. by 5-in. and 0.01-in. in thickness, by exposing them to an atmosphere of hydrogen sulfide gas for 1 to 4 hr. The strips were first cleaned in glacial acetic acid, washed, and then suspended in an atmosphere of hydrogen sulfide. The silver nitrate-sodium sulfite solution removed the silver sulfide layer from the silver in 2 to 6 hr at room temperature and in diffuse daylight. The time required for the removal of the silver sulfide layer depended on its thickness and the intensity of the

light. This test shows that the silver nitrate-sodium sulfite solution dissolves silver sulfide.

Processed samples of 2 microfilms, a contact paper, and an enlarging paper were treated for 2 hr in the silver nitrate-sodium sulfite solution in diffuse daylight at 25° C, washed for 30 min in tap water, and bleached. The densities were measured by transmission without a filter. These samples had been treated in the hydrogen peroxide hypo eliminator No. 1 during processing. For areas of high silver density of almost full exposure the silver sulfide density in microfilm A was reduced from 0.10 to 0.00; microfilm B, 0.15 to 0.005; a contact paper, 0.20 to 0.07; and an enlarging paper, 0.26 to 0.09. The first value in each case was the normal silver-sulfide density obtained when the silver image was bleached.

The silver sulfide image or residue, left in the gelatin layer of papers after the removal of the silver by the bleach bath, was only slightly dissolved by the silver nitrate-sodium sulfite solution under the above experimental conditions but, when exposed to direct sunlight during treatment for 4 hr at 28° C, most of the silver sulfide was removed. Densities of 0.2 to 0.3 of silver sulfide residue in papers were reduced to a density of 0.04. It was necessary to rebleach the samples to remove the silver deposited by the silver nitrate-sodium sulfite solution in the gelatin layer and paper base.

The above results indicate that silver sulfide was formed on the silver image during fixation.

b. Staining Effect of the Fixing Bath on a Silver Surface

Glass plates, 3-in. by 4-in., were coated with silver by the Rochelle salts process. The silver coated plates were partially immersed in an acid or neutral fixing bath for 1 min and washed. A brown stain was clearly visible on the surface of the silver in that area treated in the fixing bath. The brown stain was more pronounced when wet but still visible when dry.

Silver strips, ¾-in. by 5-in. and 0.01-in. in thickness, were treated in a solution containing 60 ml of distilled water and 40 ml of concentrated nitric acid, and washed. This operation produced a fine white, mat surface on the silver strip. The silver strips, wet or dry, were partially immersed in an acid or neutral fixing bath for 10 sec and washed. In each case a brown stain was clearly visible on that portion of the strip treated in the fixing bath. The brown stain was assumed to be silver sulfide. These tests show that the thiosulfate in the fixing bath reacts rapidly to stain mirror and fine mat silver surfaces and it would be expected that the silver in a photographic image would react in a like manner with thiosulfate in the fixing bath to form silver sulfide during fixation.

c. Conversion of Absorbed Thiosulfate to Silver Sulfide

It should be possible to increase the density of the silver in the image by converting any thiosulfate absorbed on the silver to silver sulfide. Contact and enlarging papers were subjected to the Crabtree et al. [17] hypo test used for determining residual thio-sulfate in papers. The solution used in this test contains silver nitrate and sulfuric acid and reacts quantitatively with thiosulfate to form silver sulfide. Several tests were made on paper samples with high silver densities (full exposure) but no increase in the density of the silver image could be detected. This indicated that no thiosulfate was present in an absorbed state on the surface of the silver in the image. These same paper samples yielded a silver sulfide residue with a density of 0.20 to 0.25 when the silver was removed by the bleach bath. These results indicated that the silver sulfide obtained after bleaching was formed during fixation and not in the bleach bath by the reaction of silver ions with absorbed thiosulfate.

6.2. Formation of the Silver Sulfide

It is well known that thiosulfate in a fixing bath attacks the silver in a photographic image and the rate of attack depends on several factors such as the composition of the bath, acidity of the bath, temperature, and agitation [23]. The silver ion reacts with the thiosulfate anion to form silver sulfide. Experimental evidence indicates that the silver in the image is oxidized in the fixing bath in the presence of oxygen [3, 23] and this reaction would be a source of silver ions. Reindorp [1] suggested that silver ions may be formed in the fixing bath by a secondary dissociation of the anions of a silver thiosulfate complex. More information is necessary to establish the exact mechanism of the formation of silver sulfide in the silver image during fixation.

It is to be noted that no silver sulfide residue is obtained when the silver image is bleached if fixation takes place in a 2-percent solution of potassium cyanide but, if a silver image which has been fixed in potassium cyanide is exposed to an atmosphere of hydrogen sulfide gas for a few minutes, a silver sulfide residue is obtained when the silver is removed in the bleach bath.

7. Summary and Conclusions

Silver sulfide forms in the silver image of photographic materials during fixation. The percentage of the silver sulfide in the image is small in microfilms but is quite large in photographic papers as shown in section 4. The thiosulfate which is not removed by the washing process causes further sulfiding of the image. The extent of the sulfiding depends chiefly on the concentration of the residual thiosulfate and the storage conditions. If the photographic image is to be used for permanent or archival records, the thiosulfate must be removed as completely as possible during the washing process. If the thiosulfate is not sufficiently removed by the wash water, it may be necessary to use a hypo eliminator.

Hypo eliminators may be evaluated for their efficiency by comparing them with the hydrogen peroxide hypo eliminator No. 1. A solution of sodium sulfate together with either sodium sulfite or ammonium hydroxide will reduce the hypo (sodium thiosulfate, $Na_2S_2O_3$) content of single-weight papers to 0.005 mg or less per square inch.

The effect of different residual thiosulfate concentrations on the sulfiding of the silver image can be determined by measuring the density of the silver sulfide formed when the image is bleached. The thiosulfate reacts with the silver ion in the bleach bath to yield silver sulfide and the density of the silver sulfide increases as the residual thiosulfate concentration increases. This method would be more rapid than the oven aging tests used by Crabtree and Ross [22] and in an American Standards Association specification [16] to determine the effect of residual thiosulfate on the silver image.

Silver sulfide, which remains in the gelatin layer after the silver is bleached, may be reduced to silver by the procedure outlined in section 2.3. The percentage of silver sulfide is calculated from the densities of the reduced silver and the silver in the original image.

The addition of potassium iodide to the fixing bath will prevent most of the sulfiding of the silver image which takes place during fixation. The iodide ion increases the fixing time and decreases the fixing potential of the bath.

Experimental evidence is presented to show that silver sulfide is formed in the silver image during fixation. However, more information is necessary to establish the exact mechanism of its formation.

8. Appendix

8.1. Formulas for Developing and Fixing the Silver Image in Films and Papers

Developer

Monomethyl p-aminophenol sulfate	3.1 g.
Sodium sulfite, anhydrous	45.0 g.
Hydroquinone	12.0 g.
Sodium carbonate, anhydrous	67.5 g.
Potassium bromide	1.9 g.
Water to make	1 liter.

Dilute 1 to 1 before use.

Stop Bath

Acetic acid, glacial	12 ml.
Water to make	1 liter.

Fixing Bath

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$	240.0 g.
Sodium sulfite, anhydrous	15.0 g.
Acetic acid (28%)	48 ml.
Boric acid	7.5 g.
Potassium aluminum sulfate, $KAl(SO_4)_2$ $\cdot 12H_2O$	15.0 g.
Water to make	1 liter.

Hypo eliminators

No. 1

Water	300 ml.
Hydrogen peroxide (30%)	50 ml.
Ammonium hydroxide (28%)	10 ml.
Potassium bromide	1.0 g.
Water to make	1 liter.

After fixation the sample of film or paper is rinsed 1 min in running tap water, treated for 10 min in the above solution, bathed for 2 min in a 1 percent solution of sodium sulfite to remove the excess hydrogen peroxide, and washed 30 min in running tap water.

No. 2

Sodium sulfate, anhydrous	140 g.
Ammonium hydroxide (28%)	2 ml.
Water to make	1 liter.

No. 3

Sodium sulfate, anhydrous	71 g.
Sodium sulfite, anhydrous	63 g.
Water to make	1 liter.

When hypo eliminators No. 2 and 3 are used, the sample of film or paper, after fixation, is rinsed 1 min in running tap water, treated for 10 min in the hypo eliminator, and washed 30 min in running tap water.

8.2. Formulas for the Bleaching Process in Which the Silver of the Photographic Image Is Removed and the Silver Sulfide Is Left as a Residue in the Emulsion Layer

Bleach Bath

Potassium dichromate	5.0 g.
Sulfuric acid (95%)	5.0 ml.
Water to make	1 liter.

Clearing Bath

Sodium sulfite, anhydrous	50.0 g.
Sodium hydroxide	1.0 g.
Water to make	1 liter.

Fixing Bath

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$	240 g.
Sodium sulfite, anhydrous	15 g.
Water to make	1 liter.

Hypo eliminator

Use hypo eliminator No. 3 which is listed in section 8.1.

8.3. Formulas for Reducing the Silver Sulfide Residue in the Gelatin Layer to Silver

Bleach Bath

Potassium permanganate	5.0 g.
Sodium chloride	10.0 g.
Acetic acid, glacial	50 ml.
Water to make	1 liter.

Clearing Bath

Sodium bisulfite	50. 0 g.
Potassium bromide	12. 0 g.
Water to make	1 liter.

Developer

Amidol, 2,4-Diaminophenol Dihydrochloride	5. 0 g.
Sodium sulfite, anhydrous	30. 0 g.
Water to make	1 liter.

Stop Bath

Citric acid, $H_3C_6H_5O_7 \cdot H_2O$	35 g.
Water to make	1 liter.

8.4. Quality of the Chemicals Used for the Formulas Listed in This Appendix

All of the solutions were made up with distilled water. The following chemicals were of reagent quality meeting ACS specifications: sodium sulfite, sodium sulfate, acetic acid, boric acid, potassium bromide, sodium carbonate, citric acid, sodium chloride, potassium permanganate, sodium hydroxide potassium dichromate, ammonium hydroxide, and sulfuric acid. The monomethyl p-aminophenol sulfate, hydroquinone, sodium thiosulfate, and potassium aluminum sulfate conformed to American Standard Specifications for Photographic Grade Chemicals. The Amidol was Eastman Kodak Cat. No. P–614. The sodium bisulfite was Mallinckrodt analytical reagent grade.

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