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Fixation and Washing Techniques for

Increasing Image Stability in

Photographic Papers

by

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Submitted in Partial Fulfillment
of the Requirements for the Degree
Bachelor of Science

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OUTLINE

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Fixation and Washing Techniques for Increasing Image Stability in Photographic Papers.

Factors Affecting Image Stability

When photographic prints coated with emulsions of the silver salt type are processed by developing, fixing, washing, and drying, the processed prints usually contain some sodium thiosulfate, together with considerably smaller quantities of complex silver thiosulfate ions in amounts depending on the thoroughness of the fixing and washing operations. The impurities if allowed to remain in the emulsion tend to impair the permanence of the print by the formation of silver sulfide resulting in fading of the image or an overall brown stain or both.¹

Residual silver compounds due to incomplete fixation are primarily responsible for the overall staining of processed photographic material often encountered under conditions of high temperature and humidity or on exposure to actinic light or to other radiation which causes the light sensitive substance to photolize. The presence of labile sulfur either in the atmosphere

¹ American Standard Association, "Residual Thiosulfate and Tetrathionate in Processed Photographic Papers", p. 5.

or as the product of decomposition of sulfur compounds in the materials will also cause the conversion of these silver compounds to silver sulfide, even when the temperatures and humidity are not extreme.²

The fixation of a photographic material involves three main phases; 1) diffusion of the thiosulfate ion into the gelatin of the emulsion, 2) the chemical reaction with the silver halides to form soluble complexes, and 3) the partial diffusion of the complexes and alkali halide out of the emulsion into the solution.

The chemical reaction is thought to be relatively rapid and that most of the fixation time is occupied by the diffusion process. When photographic materials are left undisturbed during processing operations, a stagnant layer of partially exhausted solution remains near the surface, acting as a barrier to rapid diffusion. In fixation, agitation prevents the collection of this layer of exhausted hypo near the surface of the emulsion and reduces fixation time.

In general chloride emulsions will fix more rapidly than chlorobromides, which in turn fix more rapidly than diiodobromides. Another emulsion factor affecting fixation rate is grain size. Smaller grains present a

² American Standard Association, "The stability of the Images of Processed Black and White Films, Plates, and Papers", pp. 7-8.

much larger surface area per weight of silver halide than larger grains and therefore will fix more rapidly. The hardness of an emulsion layer within limits, has comparatively little effect, due in part to the fact that any hindrance to diffusion is largely offset by the reduced swelling of the hardened layer giving a shorter diffusion path.³

At low thiosulfate ions concentrations the clearing time was found to be fairly long. It decrease rapidly with an increase in thiosulfate ions concentration up to a certain optimum value beyond which the clearing time begin to increase. Figure #1 shows clearing time verses grams per liter of hypo relations for both ammonium and sodium thiosulfate.

The temperature of the fixing solution has a decided effect on the clearing time. The magnitude of the effect is a pronounce function of the concentration, being a minimum for the most rapid-working concentrations and becoming much greater for concentrations much above or below the optimim. An increase of temperature has evidently a double influence, increasing the swelling

³ Baines, H. The Science of Photography, p. 121.

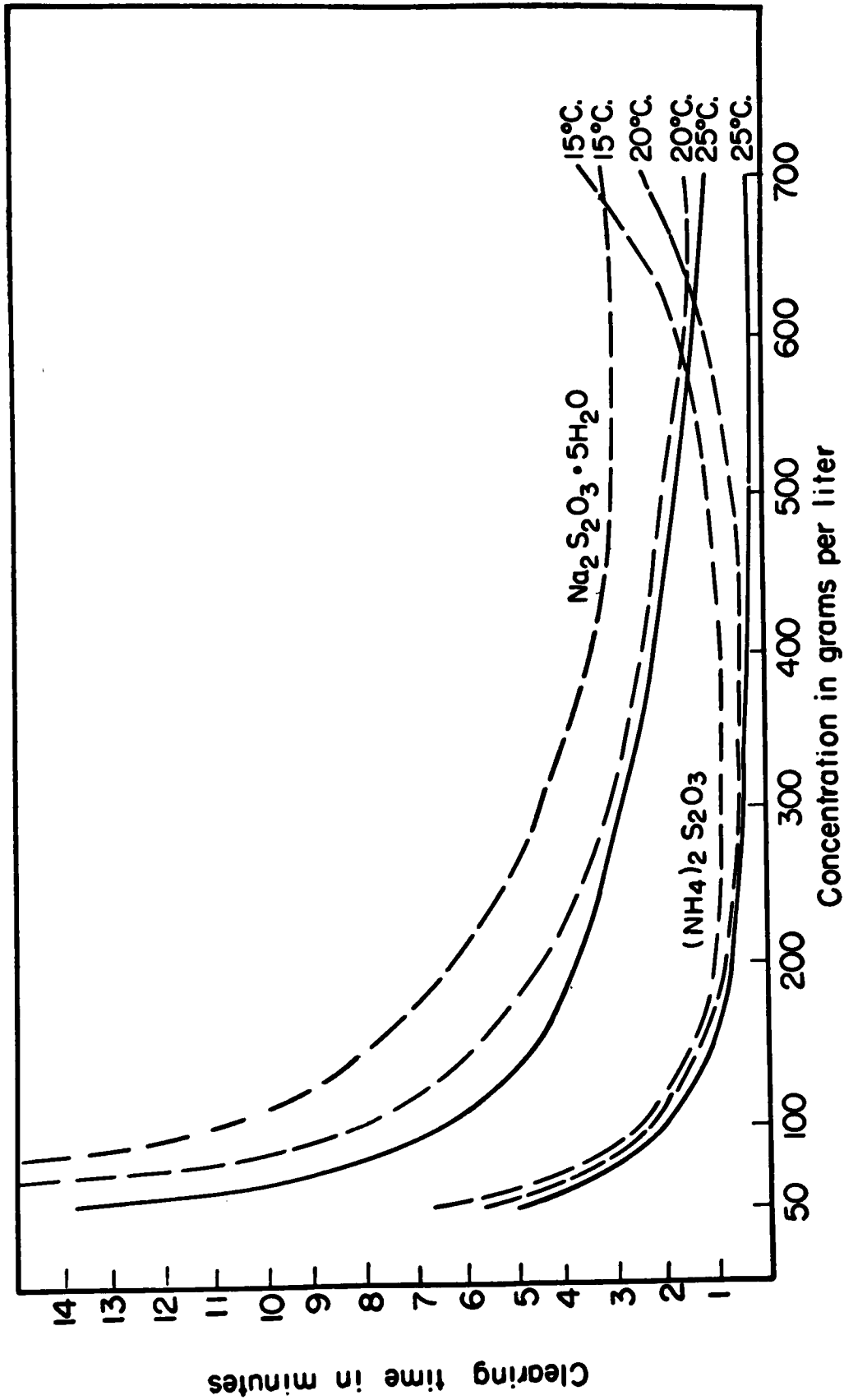


Fig. 1 Clearing times of film at various concentrations of both sodium and ammonium thiosulfates.

of the gelatin and increasing the rate of diffusion. The optimum working temperature appears to lie between 65° and 75° F. Below this range, the action is too slow, while above it the swelling of the gelatin may be excessive. Where temperatures above 75° F. are unavoidable, it is desirable to add some agent to repress the swelling of the gelatin.⁴

There are three main chemical changes which occur in a fixing bath during use: (1) a decrease in concentration of hypo, (2) an increase in concentration of silver thiosulfate complexes, and (3) an increase in concentration of soluble halides. These all tend to slow down the reactions occurring during fixation to a greater or lesser extent. The third factor is not important in a bath used solely for fixing chloride emulsion, but the accumulation of soluble iodide in a fixing bath used for iodobromide emulsions has a marked depressing effect on silver ion concentration, and seriously slows down fixation.⁵ As the fixing bath becomes exhausted, the complexity of the silver thiosulfate ions increases. It is probable that double and triple silver thiosulfate

⁴ O. E. Mees, The Theory of the Photographic Process, p. 721.

⁵ H. Baines, The Science of Photography, p. 124.

complexes are formed that are extremely large and can not be removed from the emulsion by normal washing procedures.⁶ Should the emulsion not be fixed to completion the undissolved silver halides will remain in the emulsion after washing. This is due to the low solubility of silver halides.

Removal of Thiosulfate and Silver
Thiosulfate Complexes From Paper

Photographic paper prints, even after careful processing, are more susceptible to deterioration than film negatives or positives. Two factors influence this apparent susceptibility are: (1) the high degree of reflection of the print reveals very slight changes in the silver image, and (2) the structure of the print is such that more hypo is retained per unit area than by an equivalent area of film following the same fixing and washing procedure. In general these papers consist of a paper base, a baryta coating, and an emulsion coating, all of which retain hypo and silver. In a plain hypo solution the baryta coating retains hypo which is not readily removed by washing. When a potassium alum fixing bath is used, a much greater amount of hypo is retained by the baryta which can not be removed by prolonged

⁶ A. Lumiere, A. Seyewetz, British Journal of Photography, p. 873.

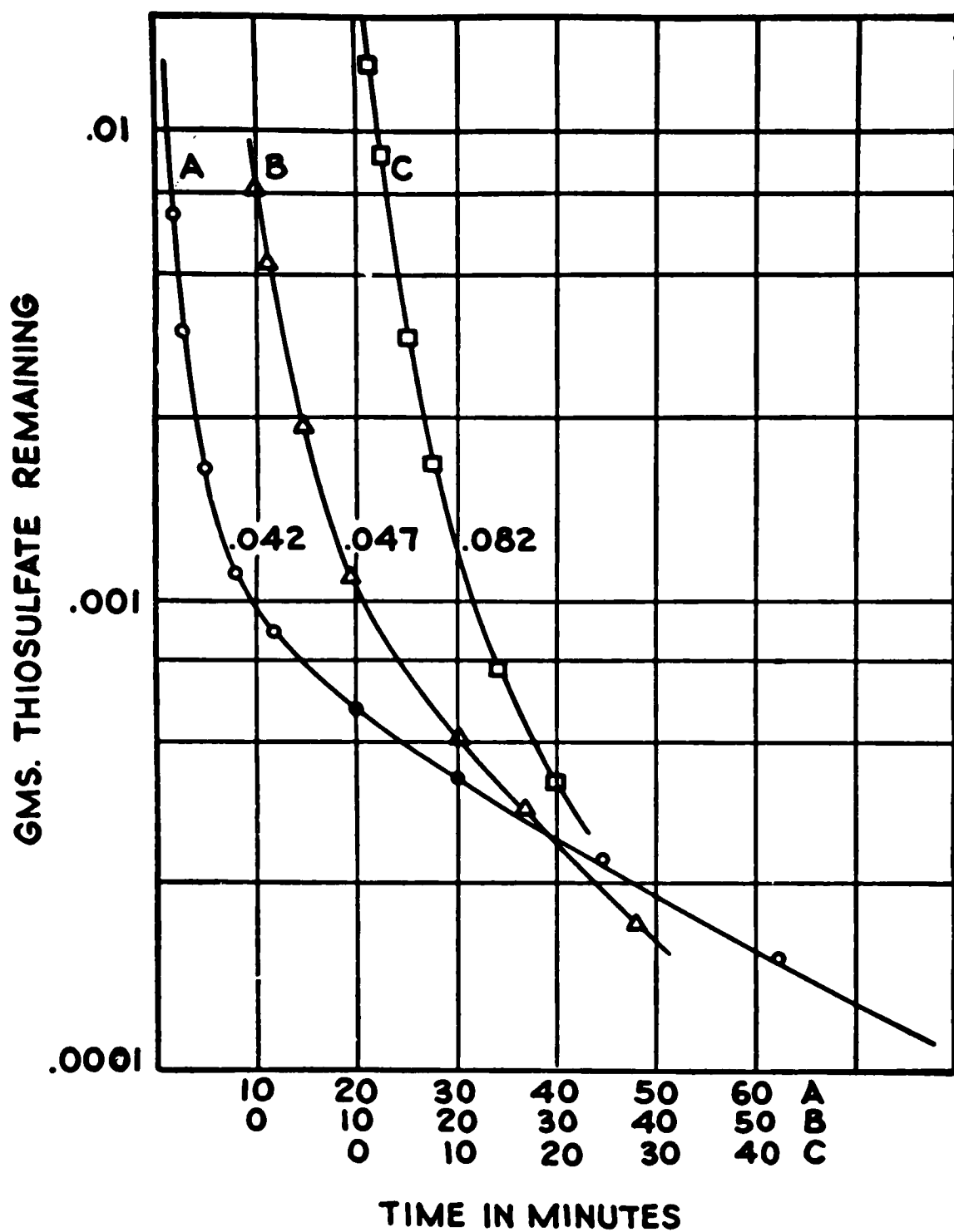


Fig. 2 Elimination curves for (A) paper base; (B) baryta-coated paper; (C) emulsion-coated paper.

washing.⁷ Figure #2 shows the elimination curves for paper base, baryta coated paper and emulsion coated paper.

The adsorption of thiosulfate ions into the wash water is governed by many factors. Washing efficiency is one of the most important factors in that the more rapid the change of water during washing the less time required for washing. Washing is more rapid if nonhardening or chrome alum baths are used than with fixing baths containing potassium alum. The washing time varies with the pH of the fixing bath when potassium alum is used hypo leaves the gelatin layer more rapidly at pH above 4.9 and more rapidly when fixed in fresh rather than in partly exhausted baths. The time of washing for emulsions which have been properly hardened decreases slightly with the decrease of the wash water.⁸ Curves for single and double weight papers washed at various temperatures are shown in Fig. 3.

Hypo Elimination

To shorten washing times and to insure archival quality it may be advisable to use hypo elimination. Eliminations

⁷ J. I. Crabtree, "The Removal of Hypo and Silver Salts From Photographic Materials as Affected by the Composition of the Processing Solutions," p. 38.

⁸ C. B. Neblette, Photography Its Materials and Processes, p. 231.

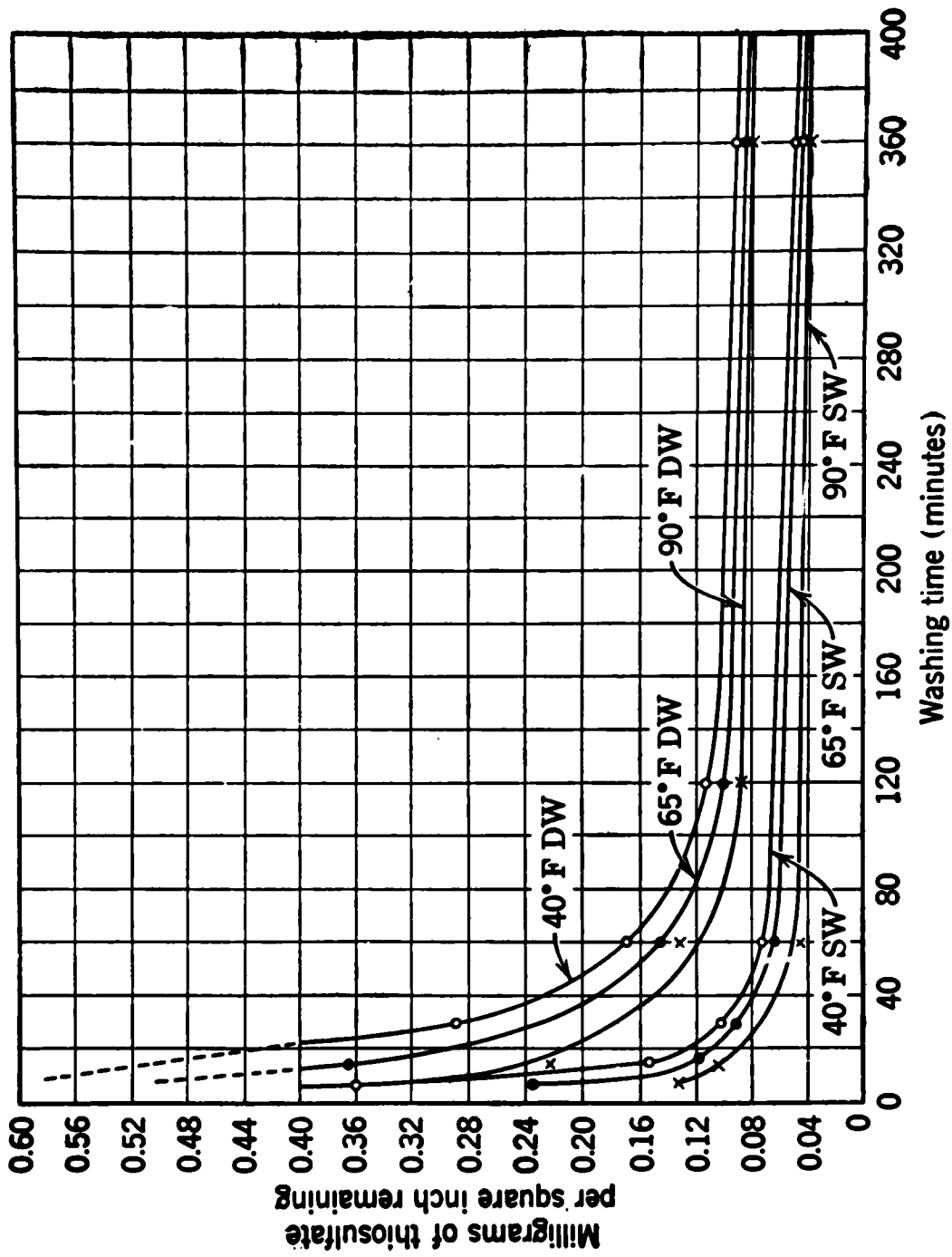


Fig. 3 Washing curves for typical single-weight (SW) and double-weight (DW) photographic papers. (Crabtree, Eaton, and Muehler.)

may be classified into two types, physical and chemical. The physical types such as Kodalk or sodium sulfide merely swell the gelatin allowing the large complexes to diffuse out into the wash water. The chemical types such as the alkaline hydrogen peroxide (ie. hydrogen peroxide and ammonia) will completely oxidize sodium thiosulfate to sulfate which is not absorbed to the paper fibers and baryta and unlike the thiosulfate is removable completely by washing in water.⁹

Tests for Residual Silver Ion and
Residual Silver Thiosulfate

In order to obtain archival quality certain tests should be performed to check for residual silver ions and silver thiosulfate complex ions. According to the American Standard Association the following tests are prescribed.

For silver ion choose a portion of a sheet or strip which has received representative processing treatment, blot dry, if necessary, and spot a clear area of the image side using an 0.2-percent freshly prepared solution of pure fused sodium sulfide. In the case of papers, spot

⁹ Ibid., pp. 232-233.

both sides. Wash away or blot up the reagent after 3 minutes. If the spot-treated areas show no more than a just perceptible tint, the photographic material may be considered stable in respect to susceptibility to staining arising from the action of sulfide on residual silver compounds.¹⁰

The residual silver thiosulfate ions test depends on the production of an insoluble brown silver sulfide stain in the print itself by the quantitative reaction between the thiosulfate or tetrathionate and silver nitrate occurring when the print is bathed for four minutes in an acid solution containing an excess of this soluble silver salt. To prevent possible subsequent darkening of the treated area the treatment is followed by bathing in a solution of sodium chloride to completely convert the excess silver nitrate into insoluble white silver chloride, removing the silver chloride in a suitable fixing solution, and finally washing and drying. The transmission density of the treated area is then read,

The transmission density of the untreated area is read and subtracted from that of the treated area. The resulting

¹⁰ American Standard Association, "The Stability of the Images of Processed Black-and-White Films, Plates, and Papers," p. 9.

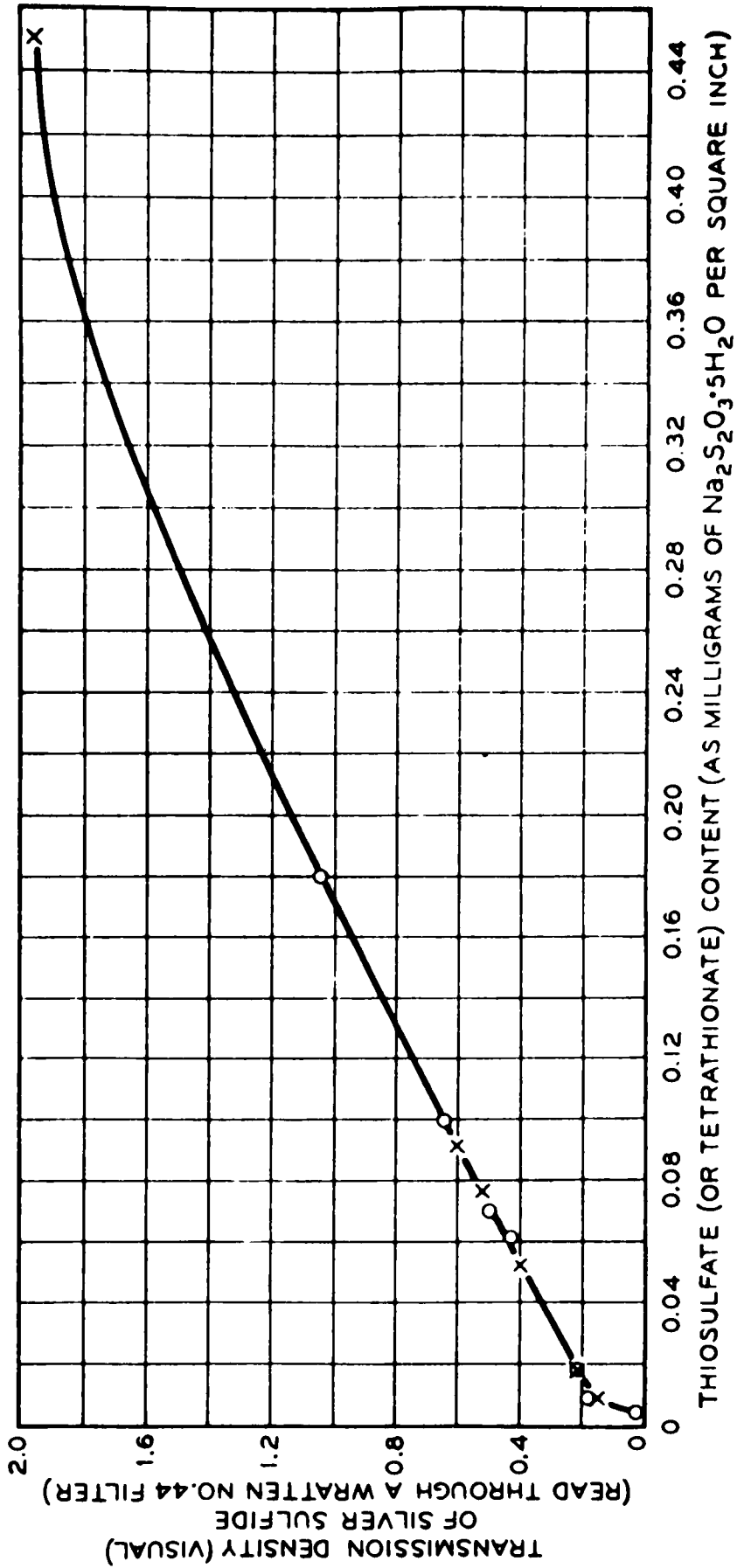


FIG. 4

value representing the transmission density of the silver sulfide is compared with the standard curve of Fig. 4, from which the corresponding equivalent content of thiosulfate or tetrathionate as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in mg per square inch is found.

With ordinary care it is possible to determine quantities of thiosulfate in photographic prints as low as 0.005 mg per square inch as $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The visual threshold of the test appears to be about 0.003 mg per square inch. Quantities up to 0.4 mg per square inch are indicated in the standard curve of Fig. 4.

The following solutions are required. In stoppered bottles they keep for at least six months at 68 F. (20°C). Unused solutions should be employed for each set of tests.

Solution A

Water	750.0 cc
Acetic acid (glacial)	30.0 cc
Silver nitrate	10.0 g
Water to make	1.0 liter

Store in a brown or blackened glass-stoppered bottle away from strong light.

Solution B

Water	750.0 cc
Sodium Chloride	45.0 g
Water to make	1.0 liter

Solution C

Solution C

Water	750.0 cc
Sodium chloride	15.0 g
Sodium thiosulfate, crystalline	45.0 g
Water to make	1.0 liter

To determine th thiosulfate in the paper, a non-image portion at least $\frac{1}{4}$ x 1 inch in size is removed and approximately one-half of it dipped and allowed to remain submerged, with occasional agitation, in an excess of solution A for four minutes, then totally immersed with treatment sucessively in Solution B for four minutes, and Solution C for four minutes, washed five to ten minutes, and dried. In tests of batch washing, unexposed paper of the same weight and general size processed with the lot can be used to give representative tests, provided the agitation is uniform.

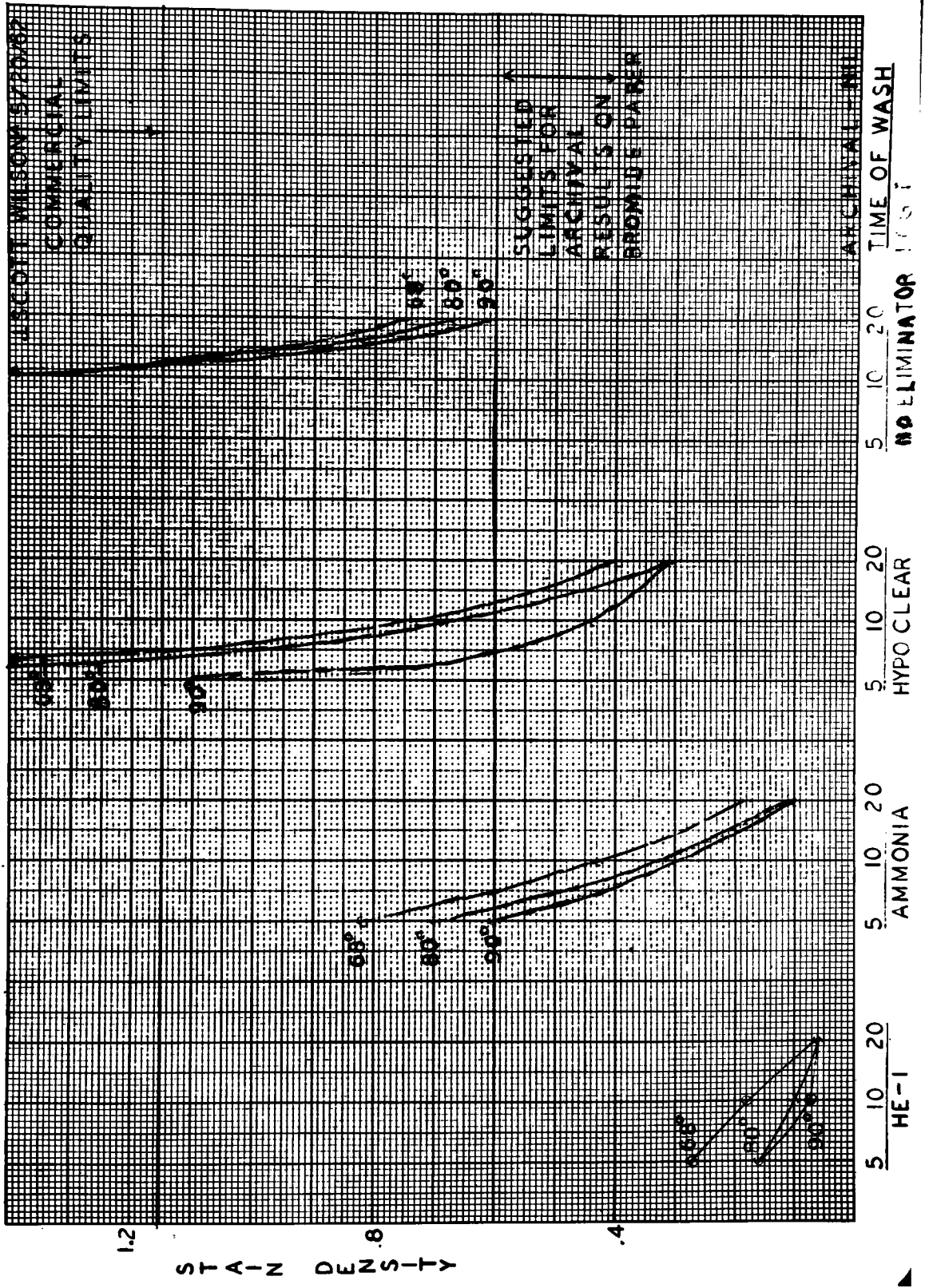
Following the preparation of the ~~the~~ print samples for indication of thiosulfate, the transmission densities of corresponding treated and untreated samples are determined by means of a visual transmission densitometer. All readings for the purpose of this standard are made using a Wratten No. 44 filter placed over the eyepiece of the densitometer. If other types, such as photoelectric densitometers, are employed, specific calibration curves must be determined.

The difference between the density readings of the treated and the untreated areas is the visual transmission density of the silver sulfide produced by the thiosulfate in the paper and is a quantitative measure of the residual thiosulfate which the paper contained. The corresponding thiosulfate content in terms of crystalline sodium thiosulfate in mg per square inch is obtained by reference to the standard curve in Fig. 4.¹¹

In an experiment conducted by Wilson and Eynard on the use of hypo clearing agents in the reduction of wash time, it was found that short washing times producing archival quality could be achieved by the use of hypo clearing agents. Various hypo clearing agents and eliminators were tested, such as: Kodak's Hypo Clearing Agent, Kodak's HE - 1, and house hold ammonia. A control with no eliminator was also run. The results of these tests can be seen in Fig. 5. Kodak's HE - 1 or alkaline hydrogen peroxide produced archival quality on double weight paper when washed in a tray with a flow of about 1.5 gallons per minute after only 5 minutes of wash at 68° F. This was the most effective eliminator since it produced results all well within the suggested archival limits for bromide paper.

¹¹ American Standard Association, Residual Thiosulfate and Tetrathionate in Processed Photographic Papers, pp. 5-6.

COMPARISON OF HYPO ELIMINATORS VS. WASH TIME AND TEMPERATURE



This was also the only eliminator that approached the nil point for residual thiosulfate ion.

The next most effective eliminator was the plain household ammonia. It produced acceptable results with 10 minutes wash time at all temperatures. The Hypo Clearing Agent produced acceptable results only after 20 minutes of wash.

The above two eliminators are more of the physical type since they are alkaline and thus swell the gelatin to let the large complexes diffuse out into the wash water. The HE - 1 on the other hand contains hydrogen peroxide that will oxidize the thiosulfates to sulfates.

There are many factors influencing the image stability of paper prints as can be seen from the above, but the three most important in order of importance are: 1) state of hypo, 2) type of elimination and 3) time and temperature of wash.

For best results two baths are suggested where silver thiosulfate complexes do not exceed $.30$ g. per liter for the first bath and 0.05 g. per liter for the second. This will insure that the complexes left in the paper before washing will be small enough to diffuse out into the wash water and also that all the undeveloped silver halides will have dissolved.

HE - 1 seems to be the best type of eliminator as suggested by the experiment. This eliminator will work most effectively on the small complexes formed by the "fresh" hypo, making the wash the least critical of the factors.

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