

The Washing of Thiosulphate from Gelatin Layers

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ABSTRACT. The transport of fixer salts from a gelatin layer during washing proceeds via a fast stage of exponential loss followed by a slower stage during which thiosulphate appears to be lost by exchange for anions from the wash water. The conductance of the layer falls to a minimum value at the point where the second stage of washing becomes dominant. At this point the fixer residue, determined as silver sulphide, may be high or low in concentration depending on the pH of the fixing bath. The presence of alum in the fixer is equivalent to a large drop in pH value in its effect on thiosulphate retention. Inasmuch as the residual thiosulphate at the second stage does not significantly contribute to the conductivity of the wet layer it may be considered to be bound to the gelatin.

INTRODUCTION

In a previous paper¹ it was shown that the salt concentration of the water used for washing fixed emulsions had an important bearing on the rate of washing. Distilled water was less efficient as a washing medium than tap water of moderate hardness. This finding was, of course, consistent with the earlier work on the effect of a neutral salt bath as a washing aid^{2,3} and with the finding that additions of neutral salt to the fixer would speed washing.⁴

Further study of the curve of residual thiosulphate against time, obtained when hardened emulsions were washed in demineralized water, suggested that the loss of thiosulphate from the emulsion to the water took part in two stages. In stage 1 there was a rapid loss of thiosulphate from the layer presumably following Fick's Law, the rate being proportional to the concentration gradient, or to the concentration in the film if the concentration in the water was considered low and constant. In stage 2 the rate of washing was much lower and on a plot of log residual thiosulphate against time there were two substantially linear parts, the steep slope of stage 1, changing to the low slope of stage 2.

Fig. 1 shows results typical of this phenomenon. A fast, negative emulsion was bathed for 4 minutes in a dummy developer bath, rinsed for $\frac{1}{2}$ minute in demineralized water and fixed for 5 minutes in a conventional ammonium-thiosulphate fixer, with (Fig. 1a) and without (Fig. 1b) aluminium hardener, the pH in both instances being made the same at 4.35. Washing was carried out in demineralized water and in solutions of M/250 and M/25 sodium bicarbonate. The initial rate of loss of thiosulphate was much the same in all cases. In the case of the hardening fixer, stage 2 was very slow when

demineralized water was used and was speeded up by the presence of bicarbonate. In the absence of aluminium hardening, stage 2 was entered at a lower residual thiosulphate level and washing was faster in this stage.

The same two-stage phenomenon can be deduced from the data of the early work of Hickman and Spencer.⁵ It seems likely that the first stage is a purely physical, mass-transport process and if this were to hold throughout the entire course

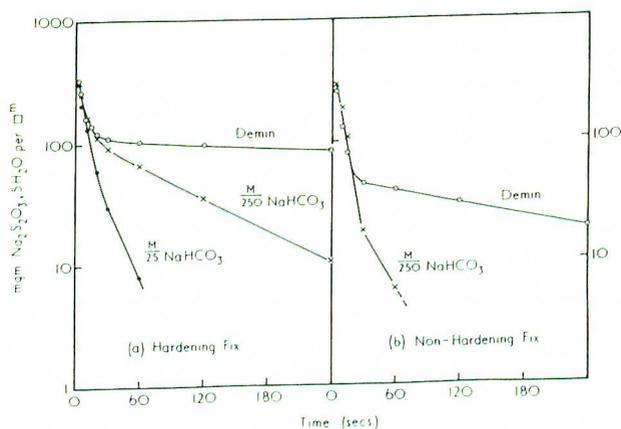


Fig. 1. The concentration of residual thiosulphate after fixing in (a) hardening fixer (b) non-hardening fixer and then washing in demineralized water or dilute solutions of sodium bicarbonate.

of washing the process would be rapid. In Fig. 1, a level of 50mg hypo would correspond to satisfactory washing of the negative film. As Hickman and Spencer pointed out, the photographic plate should need less washing than the vessel in which it is treated.

It seems that in the second stage we are dealing with an ion-exchange process in which thiosulphate can be released only in exchange for suitable anions from the washing medium. The purpose of the present paper is to show that the hypo present in the gelatin in Stage 2 is not free to contribute to ionic transport and is presumably bound to the colloid.

EXPERIMENTAL

Methods of *post-facto* determination of thiosulphate in film emulsions are too slow to follow the rapid initial stages of washing. Hickman and Spencer were able to follow conductimetrically the concentration of thiosulphate in the wash water. For the purposes of the present work we have attempted to follow the conductance of the salts in the layer during the course of washing. The apparatus used to carry out this work employs the well-known method of high-frequency sensing with external electrodes out of contact with the electrolyte being measured (Fig. 2a).⁶

The film was held by suction, emulsion up, to an inclined block so that its surface could be sluiced by solution or water from a juxtaposed jet. Cemented to the face of the block were two parallel strips of metal foil 28 × 5mm in dimensions and about 6mm apart. To these foil strips, which were in contact with the dry support side of the sample under test, was fed a 15 MHz signal. The equivalent circuit, shown in Fig. 2b, amounted to two capacitors joined by a variable resistor, the capacitors being formed by the electrodes and the emulsion, and the resistor being principally the wet emulsion, the conductance of which fell with the salt concentration. The voltage across the rectifier was recorded by a high impedance Y-time recorder.

The recorded voltage from the instrument was some complex function of the conductance of the solution within the layer under test. Fig. 3 shows the results for a film coated with gelatin at a thickness of 9μm which was soaked in solutions of potassium chloride of various concentrations. The molecular conductivity of potassium chloride falls about 25 per cent between 0.01 M and 1 M, which is much less

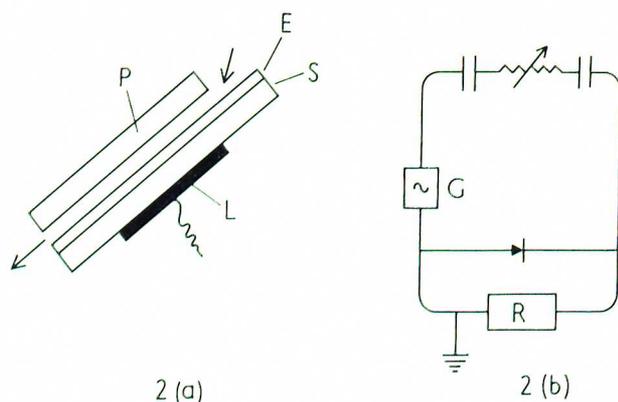


Fig. 2. (a) The wash water runs through a gap between the emulsion E and a spacing plate P which fixes the depth of the aqueous layer. (b) The diagrammatic circuit of the apparatus used. Key: E, emulsion; S, film support; L, electrode (one of pair); P, spacing plate for sluice; G, wave generator; R, recorder.

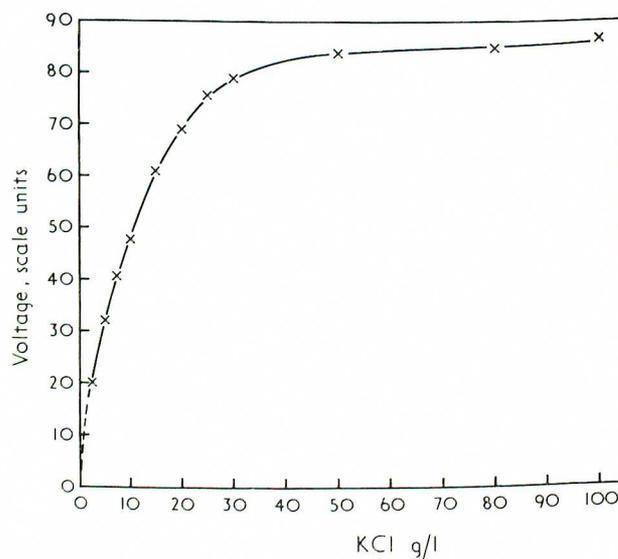


Fig. 3. The change of recorded voltage against concentration of potassium chloride.

than the deviation in recorded voltage given by the equipment over the range. However, at the lower concentrations the response was good enough for the present purposes. The data of Watkins and Jones⁸ for the molecular conductivity of sodium thiosulphate shows a fall of about 25 per cent from infinite dilution to 0.125 M which is over twice as large as that for potassium chloride over the same range but is still small enough not to need consideration here.

The special gelatin-coated film was soaked in solutions of fixer, for 4 minutes at 20°C, wiped carefully on the support side, and washed in the above apparatus using, in separate runs, tap water and demineralized water at 230 ml per minute, at 20°C. The runs were continued until the recorded voltage had fallen to a steady value. In a second series of runs, the Matthey and Henn⁷ stain test was applied to samples that had been washed to the conductivity end-point and to such shorter times as could be managed without serious error on account of manipulation time.

Four fixers were used, based on plain 1.0 M sodium thiosulphate:—(a) no addenda, (b) with 50g per litre sodium sulphite and adjusted with acetic acid to pH 4.5, (c) as (b) and with sodium hydroxide added to reach pH 11.9, and (d) with 50g per litre sodium sulphite, 15g per litre potassium alum and adjusted with acetic acid to pH 4.5.

RESULTS

The set of curves in Fig. 4 shows the change in output from the conductivity apparatus with time and Table 1 summarizes the data by giving the time taken to reach the level of constant, low conductance.

TABLE I
Time to reach a constant conductance (seconds)

Fixer	Time to reach a constant conductance (seconds)	
	Demineralized water	Tap water
(a) 1 M sodium thiosulphate	27	40
(b) pH 4.5	18	25
(c) pH 11.9	20	55
(d) With hardener, pH 4.5	15	20

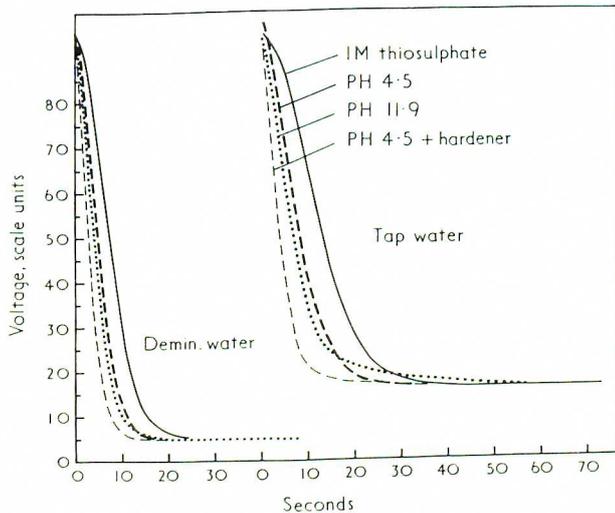


Fig. 4. Typical recordings of the voltage from the conductivity apparatus against time.

When demineralized water was used, the end signal was substantially constant. When tap water was used, the end signal was greater because of the water solutes and there was a very slow drift downwards amounting to 1 per cent of full scale per minute. Therefore, the times were measured to the point where the descending curves joined the line of drift.

In Fig. 5 are shown the residual thiosulphate concentrations given by the Matthey and Henn test in the later stages of the runs with the three fixer solutions and with plain thiosulphate and on each curve is marked the time at which the conductance became constant. In one instance, in which films were fixed at high pH and washed in tap water the conductance did not become steady in time to be meaningfully indicated in Fig. 5. Apart from this, the arrows showing the point of steadying correspond reasonably well to the point at which stage 2 washing becomes dominant.

DISCUSSION

When thiosulphate is washed from a gelatin layer by pure water, a point is rapidly reached at which the conductance of the layer reaches a low and constant value. At this point there may be a considerable amount of thiosulphate in the layer available for estimation as silver sulphide. This residual thiosulphate may be said to be bound to the gelatin. The logarithm of the concentration of the thiosulphate T bound to the gelatin at the conductance endpoint falls with pH roughly according to the expression:

$$\log \text{conc } T \propto K - 0.2 \text{ pH.}$$

The effect of the alum in the fixer at pH 4.5 was, accordingly, equivalent in terms of thiosulphate retention to a drop in the pH of this fixer of about 3 units.

If the washing continues in pure water, loss of thiosulphate will be a slow reaction depending on some re-arrangement of the gelatin because only H^+ and OH^- are available for ion exchange.

The tap water used in these experiments was moderately hard, equivalent to 200 ppm $CaCO_3$, and bicarbonate ion, the principal among others, was available for exchange. The exchange equivalence of thiosulphate for bicarbonate or

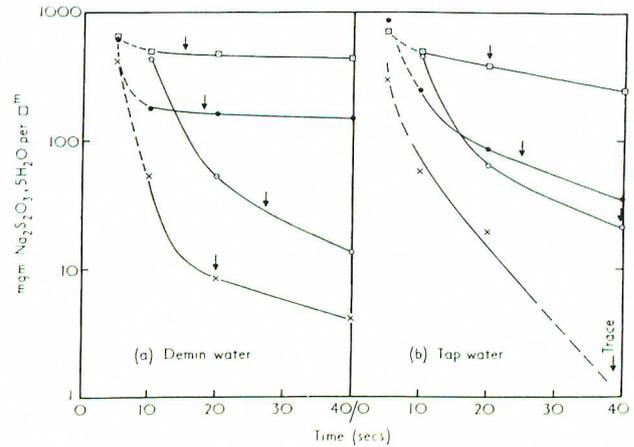


Fig. 5. The later course of washing after fixing in hardening fixer at pH 4.5 \square — \square , non-hardening fixer at pH 4.5 \bullet — \bullet , plain thiosulphate \odot — \odot , and fixer at pH 11.9 \times — \times .

gelatin is not known. The International Critical Tables⁹ give the molecular conductivity for $Na_2S_2O_3$ at 0.001 M and 25°C as 254 while that for $NaHCO_3$ is given as 93.5, and Na_2CO_3 (by extrapolation) is 224. Whether the exchange for $S_2O_3^{2-}$ is HCO_3^- or $2HCO_3^-$ or CO_3^{2-} , there will be a greater or smaller increase in the conductance within the emulsion as thiosulphate is mobilized, and a minimum will be reached at a lower concentration of residual thiosulphate than corresponds to the conductance minimum when pure water is used. This is shown in Fig. 5 and the slopes in the stage 2 washing shown in Fig. 5 are steeper when tap water is used. The recordings of conductance, as mentioned above, showed a slight downwards drift in this stage 2 perhaps as further exchange of bound thiosulphate for bicarbonate or carbonate caused a drop in the conductance of the wet gelatin itself.

The wash-out of plain thiosulphate from gelatin is somewhat irregular compared with the wash-out of fixer solutions containing sulphite. This is seen in Fig. 5. The important feature to note is that the rate of washing in tap water is not greater than that for demineralized water. This result was obtained on several occasions and appears to be real. It implies that in the absence of sulphite the thiosulphate ion is not available for ion exchange; or that without the stabilizing effect of sulphite the thiosulphate has undergone some degradation. The level of residue at the conductance endpoint after plain thiosulphate is roughly where it would be expected to be on account of the pH of the solution.

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