

## ROLE PLAYED BY AMMONIUM SALTS IN THE CLEARING OF NUCLEAR EMULSIONS

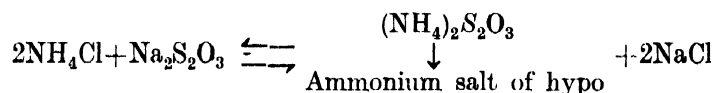
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**ABSTRACT.** The effect of the addition of various ammonium salts (ammonium chloride, ammonium sulphate, and ammonium acetate) to the usual hypo solution on the clearing time of nuclear emulsions and also their influence on the grain size and the shrinkage factor, have been investigated in view of some contradictory results reported by various authors in recent years. The addition of the ammonium salts has been found to cause a decrease in the clearing time, and then a slight increase after attainment of the optimum concentration. The addition of ammonium salts, however, has been found to have no effect on the grain size or the shrinkage factor of nuclear emulsions. Results obtained have also been explained on the basis of the current theory.

Thick emulsions necessitate longer clearing times, and this prolonged fixation leads to severe distortions in nuclear emulsions. As such, the methods for decreasing the clearing time have been studied by various authors, and it has been found that the addition of ammonium salts to hypo decreases the fixation time considerably, because the ammonium salts of hypo are better complex forming salts with silver halides than the sodium salts of hypo.



Piper worked on this problem, and investigated the change in the clearing time of thin plates with a change in the concentration of ammonium salts. He reported a fall in the clearing time with an increase in the concentration of the ammonium salt, till an optimum concentration is attained, after which, the clearing time has been reported to increase again. Also, according to him the  $\ll\text{Cl}\gg$  ion in ammonium chloride is responsible for eating up the developed grains, near the surface of the emulsion.

Prakash *et al.* (1958) reported a contradiction to the observations made by Piper. According to them, the clearing time decreases up to an optimum concentration of the ammonium salt, after which it remains more or less constant, and does not have an appreciable rise as reported by Piper.

In view of the above contradictions the author found it useful to take up some work in this direction. The observations and the results thus arrived at are reported in this paper.

EXPERIMENTAL PROCEDURE

The ammonium salts selected were ammonium chloride, ammonium acetate and ammonium sulphate. The first salt was selected, because in addition to ammonium thiosulphate the chlorine ion concentration affects the diffusion rate of the fixer, and therefore, may suppress the reaction and also because it offers a direct verification of the observations made by Piper and those due to Prakash *et al.* Ammonium sulphate and acetate were selected so as to study the effect due of any other two suitable ammonium salts, not tried so far.

For this work Ilford K<sub>2</sub> plates of 100, 200, and 400 microns, and also K<sub>0</sub> and G<sub>5</sub> plates of 200 micron thickness were used, so as to study the effect on the clearing time by a change in the thickness and type of the emulsion. Further, the experiments were conducted in the following stages :

1) Effect of the change in the concentration of ammonium chloride on the clearing time of K<sub>2</sub> Ilford 100 micron plates K<sub>2</sub> and G<sub>5</sub> was studied, using different concentrations of hypo. Plates were directly put in the fixing solution maintained at 17°C. Care was taken to see that the level of the fixing solution is same in all the three cases. The results are plotted as shown in Fig. 1.

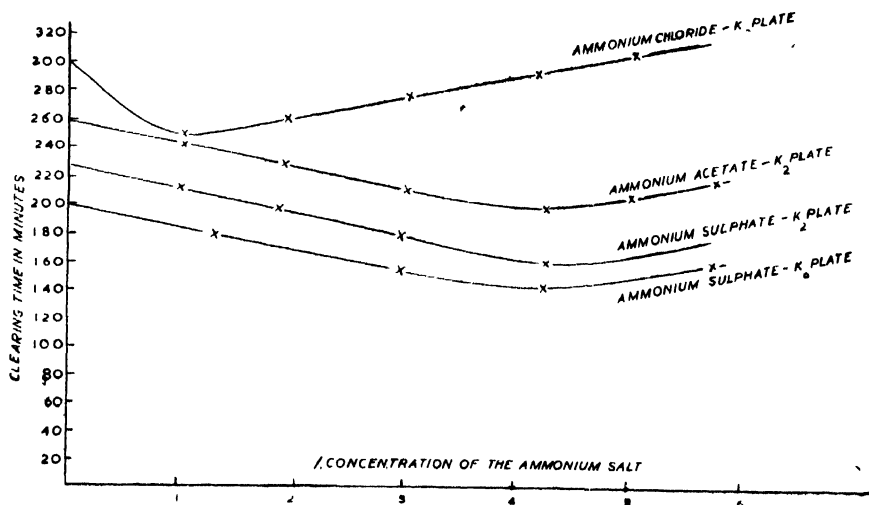


Fig. 1. The percentage concentration of NH<sub>4</sub>Cl against the clearing time in minutes for different concentrations of hypo for 100 plates K<sub>2</sub> & G<sub>5</sub> (temperature 17°C).

The curves show a fall upto an optimum value of concentration, and then a rise, although the rise is not as pronounced as reported by Piper. Moreover, a shift in the position of optimum concentration was observed with a change in the hypo concentration, as shown in Fig. 1. Change in the type of emulsion, however, has been found to have no effect on the clearing time of the emulsion.

2) Secondly, the change in the clearing time of K<sub>2</sub> and K<sub>0</sub> 200 micron plates with a change in the concentration of the three ammonium salts was studied. A

fall, and then a rise has been observed in the case of all the three curves, for ammonium chloride, ammonium sulphate and ammonium acetate. The rise is more pronounced in the case of ammonium chloride than in the case of other two ammonium salts. Results, which have further been found to be independent of the type of emulsion used, are represented in Fig. 2.

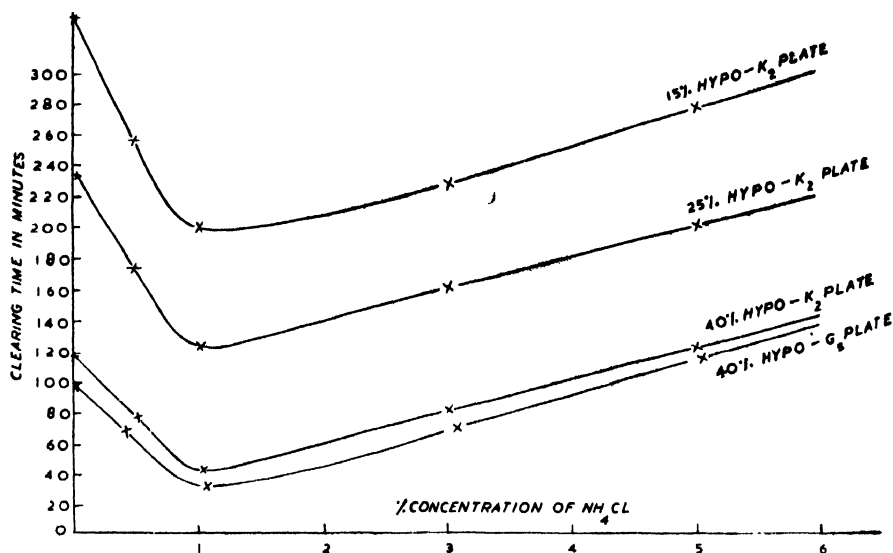


Fig. 2. Percentage concentration of various ammonium salts clearing time in minutes for 200 Ilford K<sub>2</sub> & K<sub>0</sub> plates temperature during clearing 17°C hypo concentration in each solution 40%

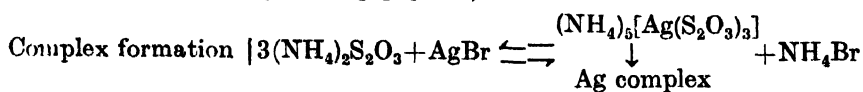
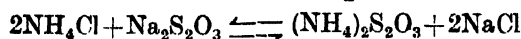
3) Thirdly, the effect of the emulsion thickness over the percentage reduction in the clearing time was investigated in the case of K<sub>2</sub> plates for all the three ammonium salts. The curves were found to have a fall up to 200 microns in all the cases excepting for ammonium chloride where the fall persists beyond 200 microns. These results are plotted as shown in Fig. 3.

#### RESULTS AND DISCUSSION

The results may be discussed in light of the three stages of observations mentioned above.

1. The rise and fall of curves shown in Fig. 1 can be accounted for as follows :

Ammonium salts of hypo being better complex forming salts with silver halides, as compared to sodium salts of hypo, any increase in the concentration of the ammonium salts should decrease the clearing time.



The optimum concentration can be explained on the basis of the reversible nature of the reaction, and so also the shift in the position of the optimum with respect to different hypo concentrations. The rise in the curves may be explained as being due to the fact that higher complexes of ammonium thiosulphate and silver halides are unstable as compared to the higher complexes of sodium thiosulphate, and silver halides. The clearing time, however, is independent of the type of the emulsion as is expected.

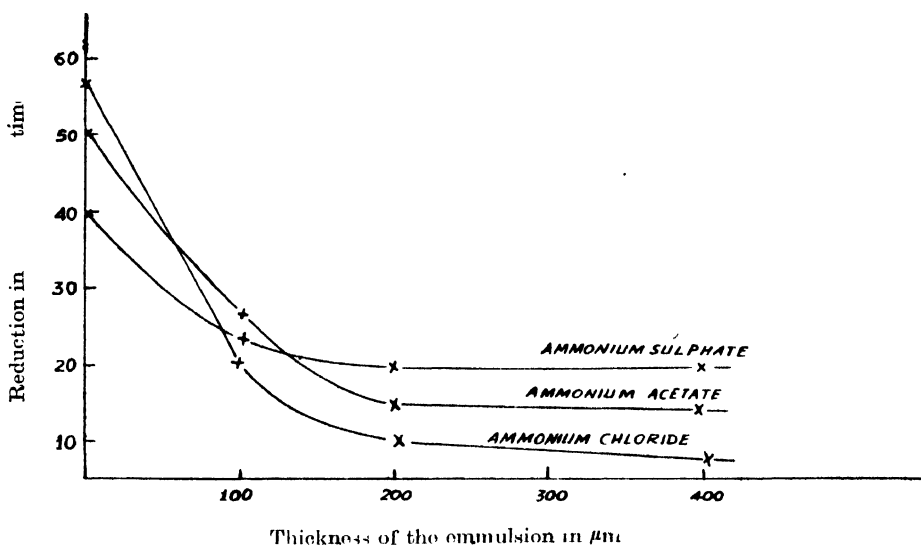


Fig. 3. Emulsion thickness Vs % reduction in the clearing time.

2) A fall, and then a rise in the curves is obtained in case of all the three ammonical salts, as is explained on the basis of the explanations given above. The more pronounced rise observed in the case of ammonium chloride can be explained as being due to the presence of  $\ll\text{Cl}\gg$  ion which effects the rate of diffusion, as chlorine harden the gelatine of the emulsion, thereby increasing the clearing time by effecting the diffusion rate. As this factor is absent in the case of other two ammonium salts, the rise is not as pronounced in their case,

3) The percentage fall goes on decreasing in the case of higher thicknesses for  $\text{NH}_4\text{Cl}$ , whereas for other salts it remains constant after 200 microns. The reason for this is that upto 200 microns the diffusion velocity of the fixing solution decreases with an increase in the thickness, and hence a fall in the curve. In case of ammonium chloride this effect persists beyond 200 microns, because of the contribution of the  $\ll\text{Cl}\gg$  ion, which, however, is not the case with other ammonium salts. Also, the diffusion velocity becomes independent of emulsion thickness beyond  $200\mu\text{m}$ , which explains the flatness of the curves beyond  $200\mu\text{m}$ .

*Effect on the shrinkage factor and the grain size:*

Effect on the grain size was investigated so as to find out whether or not the chlorine eats away the developed grains at the surface as reported by Piper.

For this, the grain size at the top and the bottom of the plate was found in case of pure hypo, and hypo with each of the other ammonium salts. (The optimum concentration being used in each case). The plates of the same type were simultaneously put in the four different baths and the fixing carried out under the same experimental conditions. The observations regarding the shrinkage factor and the grain size are shown in Tables I and II

TABLE I  
Observations regarding the shrinkage factor

Plate thickness in $\mu\text{m}$	Shrinkage factor			
	Pure hypo	Hypo with optimum concentration of $\text{NH}_4\text{Cl}$	$(\text{NH}_4)_2\text{SO}_4$	$\text{NH}_4\text{C}_2\text{O}_4\text{H}_3$
100	2.00	2.16	2.05	2.04
200	2.50	2.60	2.4	2.72
400	2.75	2.50	2.50	2.75

TABLE II  
Observations regarding the grain size

Thickness of the plate in $\mu\text{m}$	Surface of emulsion	Grain size			
		Free hypo	Hypo having optimum concentration of $\text{NH}_4\text{Cl}$	$(\text{NH}_4)_2\text{SO}_4$	$\text{NH}_4\text{C}_2\text{O}_4\text{H}_3$
100	Bottom	0.5	0.75	0.5	0.5
	Top	0.5	0.50	0.5	0.5
200	Bottom	0.75	0.75	0.5	0.75
	Top	0.75	0.75	0.75	0.75
400	Bottom	0.5	0.75	0.5	0.50
	Top	0.75	0.75	0.75	0.50

The study of the shrinkage factor, and the grain size reveals that within the allowed statistics, the shrinkage and the grain size is in no way affected by the addition of the ammonium salts. It also contradicts the hypothesis that chlorine is responsible for eating away the emulsion at the surface. The optimum concentration of the various ammonium salts used by the author are 1.5% for ammonium chloride, 2.5% for ammonium sulphate and 2.5% for ammonium acetate. Relative study of the suitability of these salts as regards the clearing of thick plates :

For thick plates the clearing time depends predominantly upon the diffusion velocity of the fixing solution, as against the thin plates. Consequently then

pH value of the fixing solution becomes an important factor. To make a relative study of the usefulness of these salts as regards the clearing of thick plates, pH values of the various concentrations of these solutions were calculated by the usual formulae, Vogel (1958). The results are shown in Table III:

TABLE III  
Observations regarding clearing time

Conc. of the amm. salt %	.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
pH-of $(\text{NH}_4)_2 \text{SO}_4$ - (optm. conc.)+ hypo (40%)	5.3	5.6	5.8	6.2	5.7	5.6	5.3	5.0
pH of $\text{NH}_4\text{C}_2\text{O}_4\text{H}_7$ - (optm. conc.)+ hypo (40%)	6.3	6.8	6.9	6.0	7.4	7.8	7.9	8.1
pH-of $\text{NH}_4\text{Cl}$ (optm. conc.)+ hypo (40%)	6.1	6.5	6.7	6.8	6.2	5.7	5.4	5.2

The table clearly shows that the pH value of hypo+amm. sulphate and also hypo+amm. chloride solution is well within the zeid region, thus ensuring a high diffusion velocity, and the pH value of amm. acetate being in the basic region, it does not have a high diffusion velocity. Therefore, amm. acetate + hypo is not as suitable for clearing as the other two salts. Amm. sulphate, however, has been found to be most suitable for this purpose.

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