

CYCLIC VOLTAMMETRIC STUDIES OF THE PHOTOGRAPHIC FIXER SOLUTION

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During the processing of photographic films, X-ray films and motion pictures, effluents are generated at various stages of film developments. Due to the rapid rise in price of silver and fixer chemicals and increasing pressure with respect to environmental discharge requirements, it is imperative to recover silver besides the regeneration of fixer chemicals. In B/W films processing, nearly 75% of silver in the film is dissolved whereas essentially all the silver is removed from colour processing. Eventhough several methods are available for the recovery of silver, the electrochemical route is well suited in that it not only yields a silver of high purity from fixing baths, but also the regenerated fixer solution could be recycled in the process. When the potential is cycled between -50 mv and -1350 mv, four peaks, two on the cathodic scan and two on the anodic scan are observed. The effect of potential cycling between different potentials and the effect of scan rate on the various electrochemical reactions have been studied.

Keywords: Cyclic voltammetry, fixer solution and motion picture.

INTRODUCTION

During the processing of photographs, X-ray films and Cine films, the silver present in the film is dissolved in the sodium thiosulphate fixer solution. Reduction of environmental pollution and saving of chemicals and money by way of reusing the processing baths are two important reasons which made it imperative to recover silver [1]. Several methods are available for the recovery of silver from photographic process wastes such as chemicals, cementation [2], ion-exchange [3], electrolysis [4] etc. The electrochemistry of photographic fixer solution is rather complex because of the fact that sulphur compounds present may undergo a variety of redox reactions, which interact with the starting material or themselves to yield a number of related products. These reactions not only affect the current efficiency of silver deposition but also drastically affect the purity of the deposit. Cyclic Voltammetry is best suited to identify the various products that may be formed.

EXPERIMENTAL

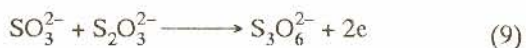
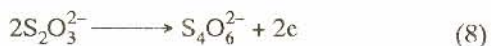
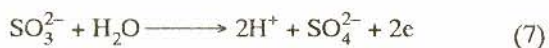
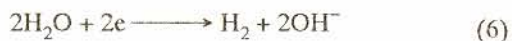
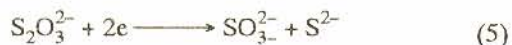
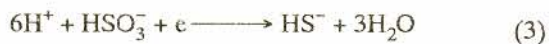
A glass cell employed is provided with inlet and outlet for deaeration with platinum disc (0.28cm²) as working

electrode, platinum black or large surface as counter electrode and Saturated Calomel Electrode (SCE) as reference electrode separated by a salt bridge. A Wenking potentiostat (model POS73) and X-Y recorder (Rikadenki Model RW-201T) are used. Emery papers down to 4/0 grade are employed in succession to polish the working electrode, degreased with acetone and finally washed with double distilled water. The synthetic fixer solution (catholyte) consists in a mixture of silver as silver-thiosulphate complex : 1-8 g.dm⁻³; sodium thiosulphate (hypo):240 g.dmm⁻³ and sodium sulphite: 15.0 g.dm⁻³. All investigations are carried out at 303±1 K. The range of potential scan is from -50 to -1350 mv vs SCE. All measurements are made and represented with respect to SCE unless otherwise stated.

RESULTS AND DISCUSSION

During electrolysis, the following cathodic and anodic reactions may be envisaged.





In Fig. 1 it may be observed from the cyclic voltammogram of sodium thiosulphate and sodium sulphite that there is a steep increase in current at -1100 mv which may be due to the various simultaneous reactions involving the reductions of thiosulphate, sulphite as well as the evolution of hydrogen.

When silver is present in the fixer solution, a cathodic peak is observed at -450 mv in both pH 4.9 and 8 solutions (Fig. 2). It may also be seen that while the low pH solution exhibits another peak at -620 mv, the same is absent in the alkaline solution. This is followed by steep increase in current at high potentials in both cases. In the reverse direction also two peaks are observed in both cases. Although the first anodic peak occurs at different potentials (-450 mv in case of pH 4.9 and -750 mv in case of pH 8.0, the second anodic peak occurs at -160 mv. The first cathodic peak at -450 mv may be ascribed to the deposition of silver and the second peak is due to the sulphide formation. The rise in current may be due to the simultaneous reactions involving

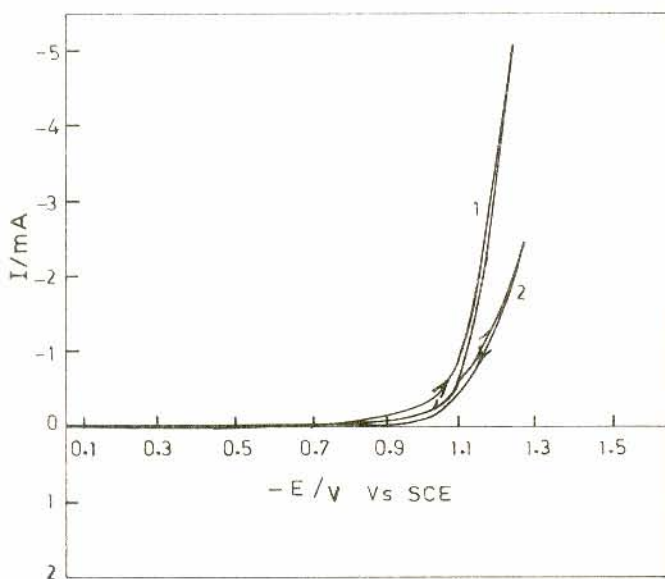


Fig. 1: Cyclic voltammograms of 1) sodium thiosulphate solution: 240 G/L and 2) sodium sulphite: 15 G/L; Scan range: -50 to -1300 mV; Scan rate: 20 mV/sec

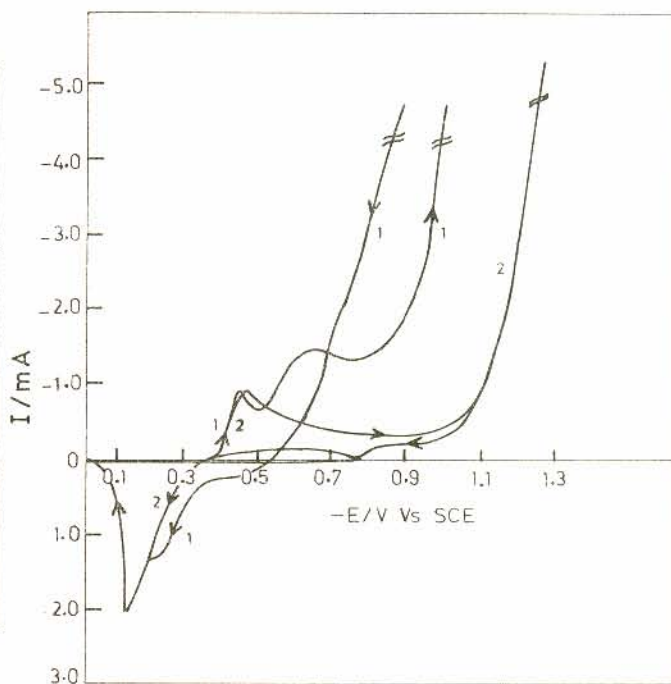


Fig. 2: Cyclic voltammograms of synthetic fixer solution with different pH containing silver: 6 G/L 1) pH 4.9 and 2) pH 8 Scan range: -50 to -1350 mV; Scan rate: 20 mV/sec

hydrogen evolution and the complex sulphur compound reactions. The first reverse peak in the reverse scan at -620 mv is due to the oxidation of sulphur compounds of silver. In the absence of silver, no peak is observed with either sulphite or thiosulphate. The second peak at -720 mv is due to the dissolution of silver deposited.

The sulphide formation is shifted to more negative values in case of alkaline solutions. This may be useful for the deposition of silver even at high potential without deterioration in purity of silver but the effect current density is reduced in alkaline solution as observed by Degenkolb [5].

CONCLUSION

From the cyclic voltammograms, it may be concluded that for efficient recovery and good quality of the silver deposit,

the electrolytic cell has to be operated below -600 mV. Also, this technique can be gainfully utilised as a tool for the quick analysis of silver in photographic fixer solution.

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