COST EFFECTIVE POTENTIOSTATIC CONTROL UNIT FOR RECOVERY OF SILVER FROM PHOTOGRAPHIC FIXER SOLUTION

N SATHAIYAN, M PANDIAMMAL, S VINCENT, P ADAIKKALAM
K V VENKATESWARAN AND Y MAHADEVA IYER

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

Photographic fixer solution originates from the processing of black and white photographic films and the silver concentration in the fixer is around 2 to 8 gl^{-1}. Due to ever increasing cost of silver and very stringent pollution regulations, it makes one to recover silver from the fixer solution which is a good secondary source for silver. Normally during the silver recovery from fixer in galvanostatic mode, current has to be decreased with respect to silver concentration in fixer for avoiding sulphide formation. In order to achieve this a cost effective potentiostatic control unit is employed for silver recovery which will make the current to decrease due to decreasing silver concentration in the fixer solution. In this paper the effect of cathode potential and the effect of silver concentration on silver recovery from fixer solution using the cost effective potentiostatic control unit are studied and the results are reported.

INTRODUCTION

In India the availability of primary silver ore is very negligible and hence the silver demand is met mainly through various secondary sources of which photographic solution is an example. The processing of X-ray films in hospitals and the photographic industries like still film studios, cine film studios etc generate large volume of silver containing effluents (fixer solution) which have a high material value and potential for reuse. The treatment of these photographic solutions emanating from the processing of still films, cine films, X-ray films etc has become a must for recovering silver. Abatement of very stringent environmental pollution and savings of chemicals and money through recycling are the important reasons for the recovery of silver. The recovery of silver to a reasonably low level is a must for recycling the fixer with good efficiency. They are generally treated chemically or electrochemically to recover the silver. Several techniques are available to recover silver from photographic processing liquors [1-5]. The electrolytic route is suitable since it produces high pure silver in a single step.

This paper describes the potentiostatic mode of operation with cost effective potentiostatic control unit which gives high pure silver from fixer solution without any contamination because this unit reduces the current during the electrolysis due to the decreasing silver concentration in the fixer. The effect of cathode potential and the silver concentration in fixer on the silver recovery have been attempted in this paper for getting pure silver along with regenerated fixer solution for possible recycling.

EXPERIMENTAL

As shown in the functional block diagram of the instrument in Fig. 1, the low cost potentiostatic control unit comprises of operational amplifier based functional blocks such as a potentiostat, voltage follower, calibration amplifier, comparator, low pass filter, an high power metal oxide semiconductor field effect transistor (MOSFET) switches and display units[6] to monitor the cell potential and cell current which can operate in the potential range of +5 V to -5 V with maximum current of 1 ampere. Through a voltage

follower, a suitably selected cathode potential is applied to the low cost potentiostat which maintains the electrochemical cell potential constant throughout the silver recovery process. Under controlled potential condition initially the maximum cell current is limited to one ampere and it slowly tends to decrease exponentially towards zero over a period of 1-2 hours. The comparator enables electrolytic silver recovery process by driving both MOSFET switch S1 and high power MOSFET switch S2 into on condition as long as the cell current is greater than the low electrolytic cell current level of 50 mA. As soon as the current level in its exponential decay path reaches the value of 50 mA the comparator switches off the electrolytic silver recovery process by disabling the MOSFET switch S1 which brings down the input potential of the low cost potentiostatic control unit to zero. With appropriate range selecting hardware such as a decimal point selector switch and an amplifier selector switch incorporated in the cell current display circuits high current range selection enables one to read the current ranging from 0 to 1000 mA.

Experiments were carried out in a divided cylindrical cell made of PVC with a cation exchange membrane as separator [7]. The cathode, rotating cylindrical electrode (RCE) consisted of a solid PVC rod of 2.7 cm diameter covered with a suitable stainless steel sleeve. Nickel coated mild steel sheet, bent in the form of a cylinder served as anode. Synthetic fixer solution (silver: 2-10 gl^{-1} as sodium thiosulphate complex; free sodium thiosulphate: 225 gl^{-1}, sodium sulphite: 20 gl^{-1}, pH: 5.0) served as catholyte. The catholyte was 350 ml of fixer solution and the anolyte was 350 ml of 1M sodium hydroxide. The solution temperature was maintained at 303 ± 1 K. Prior to each silver deposition , the surface of RCE was polished with 600 grade silicon carbide paper, washed with deionised water. The cathode potential of the working electrode was maintained constant by the developed cost effective potentiostatic control unit. Current and cell voltage were monitored using a 3 1/2 digit multimeter. Hand tachometer was used to control the RPM of the RCE. The peripheral velocity of the cathode is 60 cm/sec. Silver analysis was carried out by volumetric method. Saturated calomel electrode was used as reference electrode. All potentials were quoted with respect to it.
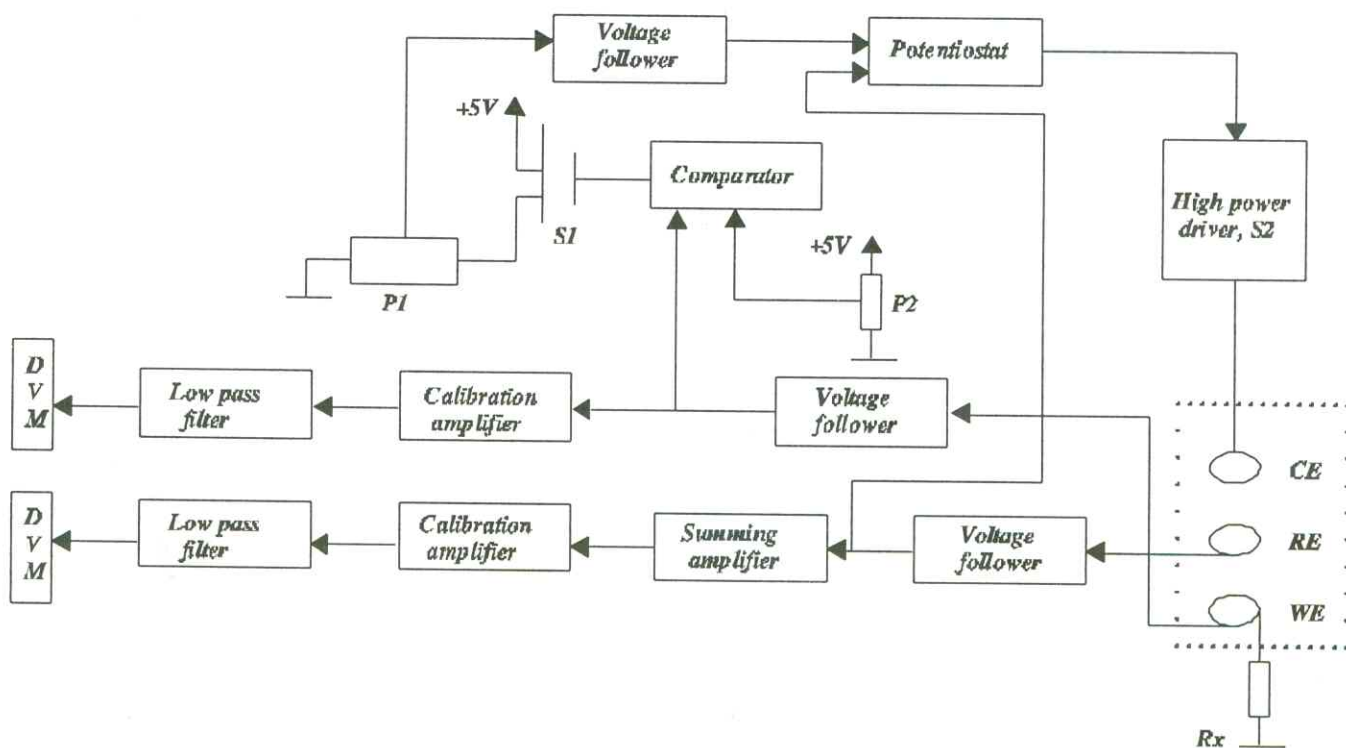

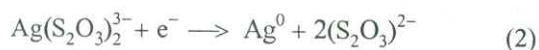Fig. 1: Block diagram of low cost potentiostatic control unit

RESULTS AND DISCUSSION

Effect of cathode potential

The minimum cathode potential which is necessary for silver deposition was found to be -0.35 V and if the potential is kept below this value no appreciable current passed and the maximum value tolerable for this system was determined in this study. Optimum cathode potential was determined [7] employing cyclic voltammetric technique on recovery of silver from fixer to avoid the sulphide formation. During the fixation, the unexposed silver halide in the film is changed into a soluble thiosulphate complex as

$$Ag^+ + 2(S_2O_3)^{2-} \longrightarrow Ag(S_2O_3)_2^{3-} \qquad (1)$$

The main cathodic reaction is

$$Ag(S_2O_3)_2^{3-} + e^- \longrightarrow Ag^0 + 2(S_2O_3)^{2-} \qquad (2)$$

At more negative potentials silver sulphide is formed as

$$2Ag^+ + S^{2-} \longrightarrow Ag_2S \qquad (3)$$

The effect of cathode potential was carried out keeping other variables at constant value for optimizing the cathode potential without sulphide deposit. Table I shows the effect of cathode potential (0.4-0.60 V) on silver recovery from synthetic fixer solution. As the cathode potential

was increased the duration decreased due to passing of more current. The current was made to decrease and the unit was cut off at 50 mA employing the cost effective potentiostatic control unit with decreasing silver concentration to avoid sulphiding. The recovery of silver was 90%. With increase of cathode potential to -0.60 V , there was little decrease in current efficiency indicating absence of side reactions. The deposit nature changed from shiny silver foils into powdery form .The energy consumption for the silver recovery was found to be more due to rise in cell voltage. Hence for efficient silver recovery the cathode potential of -0.6 V was found to be optimum. Beyond this potential, a quick dark grey deposit was obtained with the formation of sulphide leading to impure silver deposit [8-9]. At cathode potentials of -0.90V and above the liberation of hydrogen sulphide, a toxic gas is possible.

Effect of silver concentration

The effect of silver concentration in synthetically prepared fixer solution on silver recovery was carried out with the silver concentration ranging from 2 to 10 gl^{-1} in the fixer and the data was given in Table II. As the silver concentration in the fixer was increased the cathode current also increased and hence electrolysis with more ampere hour was feasible. The recovery of silver from fixer also increased from 77~100% with increase in silver concentration in the fixer solutions. The

TABLE I: Effect of cathode potential on silver recovery from fixer solution of 5 gl^{-1} silver

Parameters	Cathode potential (V)			
	0.400	0.450	0.500	0.600
Duration (min)	175	130	80	63
Ampere hour passed	0.461	0.548	0.508	0.46
Cathode current density (A/m^2)	31-6	63-8	106-38	106-11
Weight of silver deposit (gm)	1.604	1.577	1.433	1.433
Nature of silver deposit	shiny foils	foils & powders	foils & powders	****
Recovery of silver (%)	91.7	90.1	81.9	81.7
Current efficiency (%)	86.9	78.6	70.3	79.0
Energy consumption (KWh/Kg of silver)	0.283	0.390	0.464	0.453

**** More powders and less foils

TABLE II: Effect of silver concentration on silver recovery from fixer solution at -0.60 V as cathode potential

Parameters	Silver concentration in fixer (gl^{-1})		
	2.0	5.0	10.0
Duration (min)	50	63	54
Ampere hour passed	0.189	0.460	0.923
Cathode current density (A/m^2)	31-19	106-11	238-13
Weight of silver deposit (gm)	0.540	1.430	3.480
Nature of silver deposit	foils & powders	powders & foils	shiny foils & powders
Recovery of silver (%)	77.2	81.7	99.7
Current efficiency (%)	71.4	79.0	93.3
Energy consumption (KWh/Kg of silver)	0.491	0.453	0.436

current efficiency also increased when silver concentration was increased due to the presence of more silver complex ions near the cathode. From this table it was revealed that the fixer solution of higher silver content was able to deposit silver and yielded higher current efficiency (93.3%) when compared with fixer solution of lower silver content. The low current efficiency for the latter may be attributed to the possible redissolution of silver deposit via corrosion or contact with anode [9].

CONCLUSION

¤ In the electrowinning of silver from synthetic fixer solution the effect of cathode potential and silver concentration in the fixer solution was studied employing the cost effective potentiostatic control unit.

¤ The optimum cathode potential was found to be -0.6 V.

¤ Current efficiency for deposition of silver from high silver containing fixer solution was found to be high when compared with low silver containing fixer solution (71.4%). The low current efficiency for the latter case may be attributed to side reactions/possible redissolution of silver deposit via corrosion or contact with anode.

REFERENCES

1. Rami Mina, *J SMPTE*, **90** (1981) 754
2. Anon,*Method recovering silver from photoprocessing*, Chemical Engineering News, **60** (1982) 7
3. M L Schreiber, *J SMPTE*, **74** (1965) 505
4. N Sathaiyan, P Adaikkalam and S Visvanathan, *Proc "Hydrotech 93" Sym held at RRL, Bhubaneswar,* 5-6 Oct (1993) 266
5. M Frank, *Radiography,* **29** (1963) 351
6. A K Sawhney and P Sawhney, *A course in electrical and electronic measurements and instrumentation,* Pub: Dhampat Rai & sons, Delhi (1996)
7. N Sathaiyan, P Adaikkalam and S Visvanathan, *J Photogr Sci,* **41** (1993) 143
8. F C Walsh, *"The performance of electrochemical reactors for removal of silver from photographic process liquors" in Proc "Electrochemical Engineering" (ed) N A Hampson, Pub: Institution of Chemical Engineers, held at Loughborough, London,* 21-23 April (1986) 137
9. F C Walsh and D E Saunders, *J Photogr Sci,* 31 (1983) 35