Reutilisation of Exhausted Fixer Solution by Electrolysis Process

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ELECTROLYTIC recovery of silver from the exhausted fixer solution (photographic/radiographic) finds not only high yield in terms of cost return but also offers silver-extracted solution to be re-used in cyclic order without being wasted. In order to make the process more attractive and economically acceptable to radiographic and photo industrial complexes, authors in this paper provide some experimental basis on the behaviour of silver extracted fixer solution as regards its pH value, silver content, thio-sulphate concentration and fixing performance along with a brief outline of chemistry of fixation and silver recovery process.

INDUSTRIAL and Medical X-ray units, Motion Picture Laboratories and various other large scale processors of photographic films require every year an enormous quantity of fixer solution for processing purpose. During the course of film processing silver salts are partially dissolved in the fixer solution and the balance remain in the exposed film. Depending on the length of time and the degree of processing, the fixer solution gradually loses its fixing power and eventually gets exhausted with consequent enrichment of silver salt in solution. A high yield of pure silver can thus be obtained economically from the exhausted fixer solution by various methods of which electrolytic process of silver recovery has been known for many years.

In the process of reclaiming silver, financial return can be further augmented by controlling the variables in the electrolytic bath and thus re-utilising silver extracted fixer solution instead of allowing it to run to waste. In the light of this background, the authors undertook systematic studies on the chemical aspects of electrolytically silver extracted fixer solution in order to establish the conditions for re-using the same as that of a freshly prepared fixer solution.

Chemistry of fixation : The chemistry of fixation, perhaps in the field of film processing is rather complex and needs elaborate studies for complete understanding. However, factors[1,2] more or less involved in controlling the efficiency of a fixing bath are :

i) It must dissolve the unexposed silver halides completely.

ii) It must form salts with the dissolved silver halides that are soluble in the fixing bath.

iii) It must not destroy the gelation/emulsion support of the film.

iv) It must not affect seriously the silver grains of the developed image.

Fixing is achieved by immersing the film after development in a solution of sodium/ammonium thio-sulphate which forms a soluble compound with silver halides without affecting the silver image and reduces the concentration of free silver ions in solution. Several types of these complex silver-thio-sulphate compounds are formed during the active period of fixation. The reaction that takes place during fixation is represented by the following equation :

$$2\,Ag\,Br + Na_2\,S_2\,O_3 + H_2O = Ag_2\,SO_3 + 2Na\,Br + H_2O$$

Fixing process occurs mainly by (i) diffusion of the fixing agent in-to the gelation emulsion, (ii) dissolution of the unexposed silver halide grains and (iii) diffusion of silver-thio-sulphate complex ions from the gelation emulsion in to the solution. With increasing use of fixing bath, formation of complex compounds increases resulting in further complexity of the system. In the process a different type of silver-thio-sulphate complex is developed as soon as total quantity of dissolved silver reaches a certain level and becomes difficult to be removed by washing. At this point, the fixing bath ceases its power of fixing and is termed exhausted. Beyond this, chemistry of fixing virtually stops.

Silver recovery : There are two primary recovery processes namely, electrolysis and metallic replacement. Although metallic replacement method is fast and least expensive for the average film processing plant, electrolysis process is abundantly used for obtaining high purity of silver with consequent increase in the efficiency of the regenerated fixer solution.

The process of silver recovery from the used X-ray fixer solution by means of electrolysis, as well as production of silver ingot as carried out in the Central Laboratory is shown in the flow sheet (Fig. 1) below.

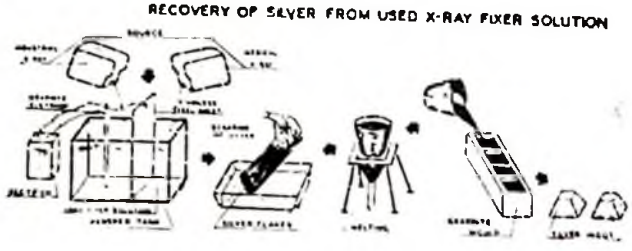


Fig. 1 Flow sheet for recovery of Silver from used X-ray fixer solution

Principle of electrolysis involves in passing on electric current of specified current density through a solution of exhausted fixer through two electrodes (cathode and anode) depositing a high purity silver on the cathode. By suitably controlling the conditions of electrolysis, formation of impurities which contaminates the bath as well as interferes with efficient utilisation of the process, can be avoided.

Reactions that take place during electrolysis may be represented in three stages by the following equations :

1) $Ag_2S_2O_3 \longrightarrow Ag^+ + (S_2O_3)^{--}$
$\downarrow e^-$
S_2O_3

2) $NaBr \longrightarrow Na^+ + Br^-$
$\downarrow e^-$
Br

3) $2Na^+ + S_2O_3 = Na_2S_2O_3$

(Pure Ag^+ deposits in the form of metallic silver on the cathode while, $Na_2S_2O_3$ goes in-to solution as soluble salts liberating hydrogen and bromine at the anode).

Experimental Procedure : A number of experiments involving low current density method were conducted to determine the fixing properties of the exhausted fixer (obtained from radiographic film processing) after silver extraction by electrolysis process. Characteristics/conditions followed in the experiment are given in Table 1.

Electrolysis was carried out in a non-conducting plastic tank using 50 mm dia. split graphite cylinder as anode and polished stainless steel sheet as cathode with optimum current density in the range of 0.22 – 0.33 mA/sq. cm. Working principle of the electrolysis employed in this investigation is schematically shown in Fig. 1.

Current and voltage during the period of electrolysis, were checked by avometer and

TABLE 1

Characteristics of exhausted as well as fixer solutions

Sl. No.	Characteristics	Exhausted fixer solution	Fresh fixer solution
1.	Volume of fixer solution taken for electrolysis	5 gallons or 22.5 litres	—
2.	Condition	Free from sediment or suspended impurities like dust etc. and carry over of developer solution	—
3.	Location	Electrolysis carried out in semi dark room free from effect of dust.	—
4.	Colour	Light yellow	Colourless to light brown
5.	pH	5.8	4.5
6.	Silver content	12.80 g/l	—
7.	Thiosulphate content	—	240 g/l
8.	Clearing time	Abnormally long time	5 mts.

adjusted accordingly. pH value as well as silver content of the exhausted fixer solution were progressively determined at regular interval-s of time during electrolysis by chemical method. Thiosulphate concentrations of the silver extracted as well as original fixer solutions were determined along with their respective fixing capabilities. Total amount of silver recovered by way of electrode-position were also measured.

RESULTS

1. Determination of pH, silver content and colour: Effectiveness fixing property of a fixer solution was found to depend not only on its pH value but also on the inter-related relationship between pH and silver content. pH of the freshly prepared solution is generally around 4.5. During the course of usage pH value rises and at pH 6.0, the solution is considered to be exhausted. Silver content also to a large extent affects the fixing ability. Results of experiments conducted to determine pH value, silver content at different intervals of time during the period of electrolysis till pH value reached around 4.5, are given in Table 2 and Fig. 2. Colours of the solution observed at various stages of electrolysis are also shown in the Table against the corresponding pH values.

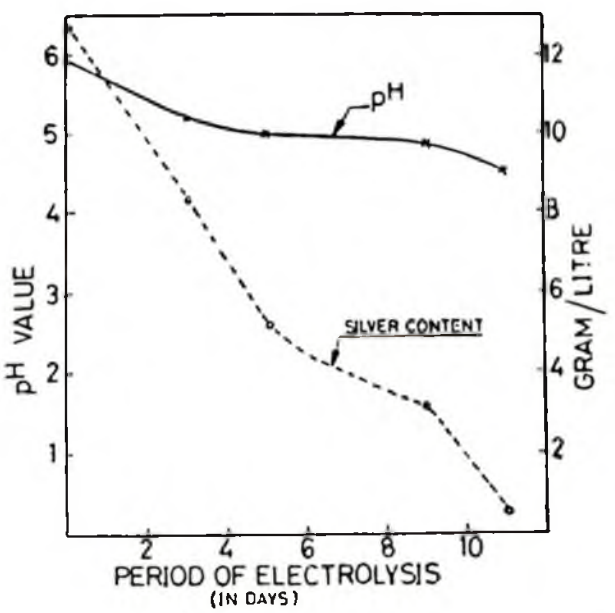


Fig. 2 Shows the relationship between pH value and silver content against the period of electrolysis

2. Estimation of thiosulphate concentration; Respective thiosulphate concentration of silver extracted fixer solution (at 4.6 pH) as well as original fixer solution were chemically estimated as $(NH4)_2 S_2O_3, 5H_2O$ and the values are given in Table 3.

TABLE 2

Results of pH value, silver content and colour at various stages during electrolysis of exhausted fixer solution

Sl. No.	Period of Electrolysis (days)	pH: Exhausted fixer solution	Colour	pH: Original fixer solution	Silver content gm/litre
1.	—	5.8	Light Yellow		12.80
2.	3	5.2	,,		8.40
3.	5	5.0	,,	4.5	5.20
4.	9	4.9	Light Brown		3.20
5.	11	4.6	,,		0.5

TABLE 3

Results of thiosulphate concentration

Thiosulphate concentration (gm/litre)	Silver extracted fixer solution (at 4.6 pH)	Original fixer solution (at 4.5 pH)
—	235.60	240.40

3. Assessment of fixing capability : Both radiographic and photographic films after usual exposure and development were fixed with silver extracted fixer solution of pH 4.6 and compared with that of original fixer solution. The results are given in Table 4.

TABLE 4

Showing results of fixing performance

Type of film	Fixing Rate (in mts.): Silver extracted fixer solution	Fixing Rate (in mts.): Original fixer solution
Agfa Geveart (for X-ray)	5	5
Forte pan (for photography)	5	5

4. Recovery of silver: On completion of electrolysis of 22.5 litres of exhausted solution

with pH value reduced to a range of 4 6, silver was recovered by scrapping out the light yellowish deposits from the stainless steel sheet cathode and melting them in a graphite crucible with suitable fluxes into a half a kg weight ingot of 97% purity silver.

5. Cost evaluation : For 5 gallons of fixer solutions, cost benefit was arrived at the following, calculating on the basis of silver recovery as well as re-utilisation of the exhausted fixer solution.

Cost of fixer solution per gallon	Rs. 20/-
Loss of solution due to drag out by the films, spilage, etc.	around 20%
Saving per cyclic electrolysis (5—1) × 20 Rs. 80/- (Cost of electrolysis involving labour, equipment, etc., taken as negligible).	
Cost of silver (97% purity) for ½ kg at the present rate of Rs. 2,300/- per kg	Rs. 1,150/-
Total cost benefit per electrolysis	Rs. (1,150 + 80) = 1,230/-

DISCUSSION

From the above tests and results, it is very clear that the possibility of re-utilising the exhausted fixer solution after silver extraction (under proper control) not only holds good in terms of performance but also from cost benefit point of view, with an added advantage of being a cyclic method for recovery and regeneration process.

From Table 1 and Fig. 2 it is evident that pH value of the order 4.6 (equivalent to that of original fixer solution) was obtained after 11 days of electrolysis of 22.5 litres of exhausted fixer solution (pH 5.8) under the conditions stipulated in the experimental procedure. pH value was found gradually decreasing with increase in the duration of electrolysis and remained almost consistent with the results obtained at regular interval of time. It is recognised that pH value is one of the major factors that leads to achieving efficiency of the fixing bath. Although the fixer solution after silver extraction might show a 4 4– 4 6 pH value but it may not retain the same fixing extraction process is deviated from the conditions achieved in this investigation, largely because or bath contaminations due to precipitations/accumulation of impurities (from electrolysis) impeding the fixing ability of the extracted fixer soluion. This serves an explanation for the longer time involved in the electrolysis process to achieve pH value equivalent to that of the original fixer solution. It is also further recognised that other parameters namely, silver concentration, thio-sulphate content, also responsible for attaining satisfactory level of fixing ability of the fixer may vary widely and bring about unsatisfactory results if extreme cares are not taken in controlling the bath under proper condition of electrolysis.

As already stated amount of silver content present in the fixer after electrolysis to pH value of the original fixer also determines the efficiency of the fixing bath. It is observed from Table 1 and Fig. 2 that silver concentration in the electrolyte found diminished with the gradual decrease of pH value. The rate ot decrease in silver concentration was rather slow upto 5.2 pH and thereafter sufficiently rapid till 4.5 pH was reached where a minimum silver content amounting to 0.5 gm/litre (about 4% of the original silver concentration) was achieved. With minimum concentration of silver (left out in the electrolyte) maximum is the fixing capability of the silver extracted fixer solution. On a literature survey[1,2] it is found that a minimum coneentration of silver of the order 0.3 gms/litre is suitable for silver extracted fixer solution to be used for fixing purpose.

This suggests that a relationship between pH value and amount of silver concentration seem to be interrelated but generally betrays such condition under improper control of the bath. Therefore, a close control of silver content and pH is an important step towards achieving an optimum level of performance. Last but not the least major fixing agent that fixes the image is the amount of thio-sulphate concentration of silver extracted solution was comparable with that of original fixer solution. This thio-sulphate reacts with silver forming silver halide along with complex thio-sulphate compounds (during fixing) which get dissociated on electrolysis freeing thio-sulphate in its original form.

As a result of proper combination among the various factors (achieved in the investigation) responsible for fixing performance, the merit of the

exhausted fixer solution after silver extraction was found to be same as that of original fixer solution as evidenced in Table 3 as regards its fixing ability.

CONCLUSION

In the light of the forgoing discussion, it is concluded that re-utilisation of exhausted fixer solution by electrolysis process is feasible and that the fixing capability of the exhausted fixer solution after silver extraction is comparable with that of original fixer and can be re-used advantageously with a benefit of economical saving as determined by the amount and purity of silver recovered in the process as well as numbers of cycles the same fixer is subjected to re-use.

Following are the summary of the investigation :

1. pH value of the order 4.6 equivalent to that of original fixer solution (4.5) is obtained by subjecting the exhausted fixer solution (pH 5.8) to electrolysis.

2. Silver concentration of the order 0.5 gms/litre after silver extraction to a pH value of 4.6 is found satisfactory in retaining the characteristic fixing capability of the original fixer.

3. Thiosulphate concentration of the silver extracted fixer solution is found comparable with that of the original fixer solution.

4. Fixer characteristics (rate & performance) are found to be same for both silver extracted as well as original fixer solutions.

5. Significant saving is envisaged by adopting electrolysis process which is continuous and nvolves simple inexpensive equipment, negligible manpower for carrying out the operation and at the same time yielding substantial amount of pure silver.

REFERENCES

1. Kodak Publication No. 229 *"Practical Processing in Black and White Photography"*.
2. *High Speed Fixation Booklet*, May and Baker Ltd.