Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Jdid, E. A. , Hakkou, R. , Blazy, P. and Elamari, K.(1995) 'Silver Recycling from Photographic Bleach-Fix Baths by Ionic Flotation and Thermal Decomposition and Reuse of the Baths', Separation Science and Technology, 30: 10, 2211 — 2221

To link to this Article: DOI: 10.1080/01496399508013902

URL: http://dx.doi.org/10.1080/01496399508013902

SEPARATION SCIENCE AND TECHNOLOGY, **30**(10), pp. 2211–2221, 1995

Silver Recycling from Photographic Bleach-Fix Baths by Ionic Flotation and Thermal Decomposition and Reuse of the Baths

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ABSTRACT

Silver was recovered selectively by ionic flotation from photographic bleach-fix solutions containing Fe-EDTA. The collector chosen was sodium di-isobutyldithiophosphinate (Aerophine 3418A), which gives a well flocculated precipitate containing 34% Ag and floats in less than 5 minutes. For a collector concentration ranging between once and twice the silver concentration, the recovery rates reach 99% and they are not significantly affected by a pH variation from 4 to 8 and a temperature increase between 20 and 40°C. The desilvered solutions can be recycled in photographic processing, and pure metallic silver at 99.9% Ag is easily obtained from the precipitate phase by thermal decomposition at 900°C.

INTRODUCTION

Silver sources in the photographic industry are the processing solutions, scrap film, and paper. The majority of the products processed by photofinishers are color films and photographic papers. Therefore, most of the recoverable silver is present in the photographic solutions, i.e., fixer, conventional bleach-fix, and final washwaters. Depending upon the operating conditions, the silver content in these solutions is generally in the 0.5–10 g/L range (1), and the iron concentration varies between 4 and 15 g/L (2).

The recovery of silver from photographic bleach-fix solutions is desirable due to economical and environmental reasons:

The silver ultimately recovered may be recycled
After correcting the composition, if necessary, the desilvered fixer or bleach-fix solution may be recycled
Recent legislation has imposed low allowable concentrations (<1 mg/L) for residual silver in the effluents

Many techniques have been reported for silver recovery from photographic solutions, but those used in the photographic industry are electrolysis, metallic replacement (cementation), precipitation, and ion-exchange resins. Comparison of them shows that the use of each technique depends on the silver concentration, the specific needs, and the size of a given photofinisher (3–6). However, to achieve a silver concentration below 1 mg/L in the effluent, it is often necessary to combine two of these techniques.

In this paper, ionic flotation is investigated as an alternative technique for silver recovery from bleach-fix media. The goals are:

The treatment of photographic solutions with a wide range of silver concentrations
The achievement of a residual silver concentration below 1 mg/L
The recycling of the bleach-fix

This technique has been studied by Amaryan et al. (7) for spent fixer solutions which do not contain ferric ions. These authors used xanthate collectors, and they recommended the use of higher fatty alcohols in order to modulate frothing. However, it was necessary to operate in three electroflotation stages to reach a recovery rate of 98%.

EXPERIMENTAL PROCEDURE

Synthetic Solutions. These were prepared by using silver acetate (Fluka), acetic acid (Fluka), ammonium thiosulfate (Prolabo), sodium sulfite anhydrous (Fluka), ethylenediaminetetraacetic acid–ammonium iron(III) salt (Fluka), and sodium chloride (Prolabo).

Industrial Bleach-Fix Solutions. Two bleach-fix solutions, Kodak Ektachrome R3 and Kodak Ektacolor RA 4, were supplied, respectively, by Euro Labo Service (ELS) and SEPIA Laboratory. Solution Kodak Ektachrome R3 was subjected to electrolysis in an electrochemical reactor using a rotating cylindrical electrode.

Ionic Flotation. The flotation apparatus was a glass column, 30 cm in height and 3 cm in internal diameter, which was fitted with a sintered glass disk of porosity 4 through which nitrogen was injected (8). Before beginning the flotation operation, the required volume of the collector was added to 300 mL of a solution containing silver (concentration C_0) and then stirred. Upon introduction of the collector, precipitation of Ag occurred immediately. Then the solution containing the precipitate was transferred to the flotation cell and nitrogen gas was passed through it at a flow rate of 2 L/h.

The recovery rate (R) was calculated as follows:

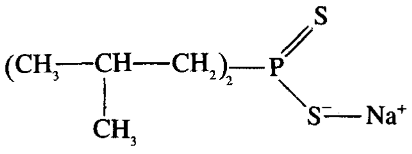
$$R\ (\%) = (1 - C_r/C_0) \times 100$$

where C_0 is the initial silver concentration in solution, mg/L, and C_r is the residual silver concentration in solution after precipitation and flotation, mg/L.

In order to control selectivity, the iron, sulfite, and thiosulfate concentrations were also determined.

RESULTS AND DISCUSSION

Tests were first run in synthetic solutions in order to study the concentration effects of collector and silver as well as the influences of pH and temperature. Thereafter, industrial media containing Fe-EDTA were studied. The chosen collector is sodium di-isobutyldithiophosphinate, commercialized by Cyanamid under the proprietary name Aerophine 3418A Promoter. Its molecular formula is



The collector Aerophine gives a well-flocculated precipitate with Ag^+. Depending on the silver concentration, this precipitate floats in 3 to 5 minutes and the liquid content of the froth (the ratio of volume of liquid in the froth to the initial volume of solution) varies between 5 and 10%.

Ionic Flotation

Synthetic Media

Solubility Product of the Sublate "Silver-Aerophine." Chemical analysis of the precipitate "silver-Aerophine" gives Ag 34%, C 30%, S 20% and P 9.5%. This composition corresponds to a stoichiometry of Aerophine/Ag = 1/1, and the precipitation reaction should then be written:

$$Ag(S_2O_3)_n^{(2n-1)^-} + X^- \longrightarrow AgX + nS_2O_3^{2-} \qquad (1)$$

where X^- = Aerophine and n = 1 to 3. In bleach-fix solutions, at pH

6.5, only the silver trithiosulfate and dithiosulfate species predominate with molar fractions ranging, respectively, from 0.82 to 0.8 and 0.18 to 0.2 for Ag concentration of 10^{-7} to 10^{-2} M.

The equilibrium concentrations of ionic species are only controlled by the solubility product K_s, which is given by

$$K_s = [Ag^+][X^-] = [Ag^+]_0^2(1 - R)(\Phi - R) \qquad (2)$$

where Φ is the ratio of collector concentration to silver concentration and $[Ag^+]_0$ is the initial concentration of silver (C_0).

The pK_s of Reaction (1) is equal to 8.4, and because all the precipitate floats, the flotation recoveries can be determined by using Eq. (2).

Effect of Collector and Silver Concentrations. The experiments were carried out with solutions of pH 6.35 ± 0.05 containing:

Variable concentration of Aerophine (Φ = 1, 2, 4, 6); Ag^+, 1.85×10^{-3} M (212.8 mg/L); $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M; NaCl, 2×10^{-3} M; CH_3COOH, 0.07 M

Variable concentration of Ag^+, 4.8×10^{-4} M (51.4 mg/L) to 4.8×10^{-3} M (523 mg/L); $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M; NaCl, 2×10^{-3} M; CH_3COOH, 0.07 M; Φ = 1.5

It can be seen from the results of Tables 1 and 2 that the recovery rates of silver increase with the Φ value and the initial silver concentration, reaching a maximum of ~99% at Φ = 2 and $[Ag^+] \approx 100$ mg/L, respectively. Furthermore, for Φ = 1 (equal to the stoichiometry of the reaction), the removal obtained is ~95% (Table 1), which indicates that the reaction is very quantitative. Therefore, it is necessary to use an excess of collector in order to achieve a low residual concentration of silver (<1 mg/L) in the solution. After silver recovery, the physicochemical characteristics

TABLE 1

Effect of Collector Concentration (Φ) on Silver Recovery and Characteristics of the Solution. Synthetic Solutions: Ag, 212.8 mg/L; $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M. pH 6.35. Temperature = 20°C

	Desilvered solution				
Collector Φ	$S_2O_3^{2-}$ (M)	SO_3^{2-} (M)	pH	Ag (mg/L)	Silver recovery (%)
1	0.65	0.10	6.32	11.2	94.7
2	0.65	0.10	6.31	0.14	99.9
4	0.63	0.09	6.30	0.44	99.8
6	0.63	0.10	6.32	0.21	99.9

TABLE 2
Effect of Silver Concentration on Recovery and Characteristics of the Solutions. Synthetic Solutions: $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M. pH 6.35. Φ = 1.5. Temperature = 20°C

Initial silver concentration (mg/L)	Desilvered solutions				Silver recovery (%)
	$S_2O_3^{2-}$ (M)	SO_3^{2-} (M)	pH	Ag (mg/L)	
523.0	0.65	0.10	6.35	0.50	99.9
206.5	0.65	0.10	6.30	0.93	99.5
100.1	0.65	0.09	6.41	1.40	98.7
51.4	0.65	0.09	6.37	3.70	92.8

of the medium are not affected, as shown in Tables 1 and 2 which give the pH values and the thiosulfate and sulfite concentrations.

Equilibrium potential measurements, Table 3, show that E_{eq} decreases linearly with an increasing concentration of collector. At $\Phi = 1.5$ the potential of Ag electrode is about −485 mV/SCE, and this value is close to that of an electrolyte free of silver. It can be deduced that it is possible by means of potential measurements to estimate the silver concentration in fixer solutions free of iron, before and after ionic flotation of silver.

Effects of Temperature and pH. Tables 4 and 5 show the results obtained by varying the pH between 4 and 8.5 and the temperature between 20 and 40°C. The recovery rates of silver are not significantly affected by increasing the temperature but they vary slightly with pH variation. In fact, at acidic pH (<6) the protonation of the collector occurs whereas at basic pH (>7) the species $Ag(S_2O_3)_n^{(2n-1)^-}$ becomes more

TABLE 3
Evolution of the Equilibrium Potential of the Solution as a Function of the Ratio Φ during Silver Ionic Flotation. Synthetic Solution: Ag, 200 mg/L; $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M. pH 6.5. Temperature = 20°C

Φ	Ag (mg/L)	E_{eq} (mV/SCE)
0.0	200	−369
0.5	102	−392
1.0	3	−465
1.5	1	−485
$S_2O_3^{2-}$ + SO_3^{2-} + CH_3COOH + Aerophine (Φ = 1.5)	0	−490

TABLE 4
Effect of pH on Silver Recovery. Synthetic Solution: Ag, 200 mg/L; $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M. $\Phi = 1.5$. Temperature = 20°C

pH	4.0	6.5	8.3
Silver recovery, %	94.2	99.5	88.5

stable. Then, for both cases the precipitation of silver is less quantitative. Nevertheless, high silver recoveries could be reached by increasing the ratio Φ, i.e., the collector consumption.

Industrial Media

The characteristics of industrial solutions are given in Table 6.

Ektachrome R3 Bleach-Fix. The Kodak Ektachrome R3 solution which had been subjected to electrolysis in an electrochemical reactor employing a rotating cylinder cathode still contained 212.6 mg/L Ag and 3.68 g/L Fe_{total}. In this medium the quasi-totality of iron is present as Fe(III), consequently there is anodic oxidation of Fe(II) during electrolysis.

As shown in Table 7, the recovery of silver increases with collector concentration in the same manner as in synthetic solutions. The reaction remains quantitative and the selectivity toward iron is satisfactory.

Kodak Ektacolor RA 4. The Kodak Ektacolor RA 4 solution obtained from an industrial photographic processing is highly concentrated in silver and iron, containing 3.21 g/L Ag and 7.51 g/L Fe_{total}, with a ratio Fe(II)/Fe(III) ≈ 4.5.

The results shown in Table 8 were obtained for silver recovery as a function of collector concentration. It appears that the removal rate reaches 99.9% as early as $\Phi = 1$ in this silver concentrated medium. This result is expected according to Reaction (1). Therefore, the precipitation reaction is selective even in the presence of a high iron-EDTA concentration.

TABLE 5
Effect of Temperature on Silver Recovery. Synthetic Solution: Ag, 200 mg/L; $S_2O_3^{2-}$, 0.65 M; SO_3^{2-}, 0.1 M. $\Phi = 1.5$. pH 6.5

Temperature, °C	20	25	30	40
Silver recovery, %	99.5	99.4	99.2	99.2

TABLE 6
Chemical Composition of the Industrial Bleach-Fix Solutions Kodak Ektachrome R3 and Kodak Ektacolor RA 4

Elements	Ektachrome R3	Ektacolor RA 4
Ag^+, g/L	0.2–0.5	3.21
$Cl^- + Br^-$, M	10^{-2}	3×10^{-2}
Fe_{total}, g/L	3.71	7.51
$S_2O_3^{2-}$, g/L	56	60
SO_3^{2-}, g/L	4.8	5
$CH_3CO_2^-$, g/L	4.13	5
NH_4^+, g/L	28	18
Na^+, g/L	6	3
Al^{3+}, mg/L	—	3
pH	7	6.5

TABLE 7
Effect of Collector Concentration on Ag Recovery in Industrial Ektachrome R3 Solution

Collector	Desilvered bleach-fix			Ag recovery	Precipitate content (%)	
Φ	Ag (mg/L)	Fe (g/L)	pH	(%)	Ag	Fe
1	8.8	3.56	7.00	95.8	32.05	0.16
2	1.7	3.57	7.01	99.2	31.03	0.21
4	0.3	3.45	7.05	99.9	31.74	0.14
6	0.2	3.24	7.07	99.9	31.58	0.15

TABLE 8
Effect of Collector Concentration (Φ) on Silver Recovery in Industrial Solution Kodak Ektacolor RA 4. Temperature = 20°C

Collector	Desilvered bleach-fix			Ag recovery	Precipitate content (%)	
Φ	Ag (mg/L)	Fe (g/L)	pH	(%)	Ag	Fe
1	0.3	7.51	6.49	99.9	33.94	0.05
2	0.3	7.51	6.46	99.9	33.75	0.05

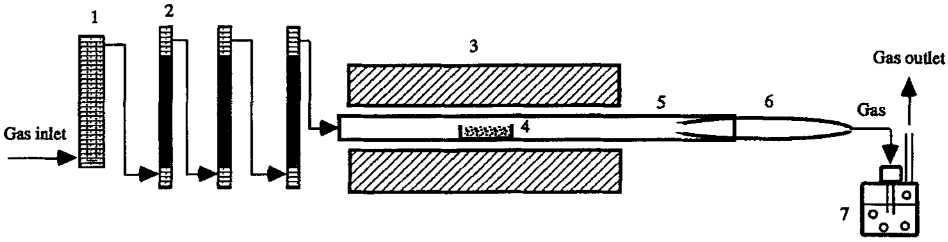


FIG. 1 Schematic drawing of thermal decomposition apparatus. (1) Flowmeter, (2) P_2O_5 column, (3) horizontal furnace, (4) combustion boat, (5) quartz reactor tube, (6) condensation tube, (7) NaOH vessel, (O) gas bubbles.

Recovery of Silver Contained in the Ionic Flotation Precipitate

The method adopted to recover silver contained in the Ag-Aerophine precipitate is thermal treatment. A horizontal experimental setup was used for isothermal tests (Fig. 1). The furnace's temperature was regulated automatically with a precision of ±2°C. Residues were weighted and chemical analyses were used to determination their compositions. The temperature effect was studied in the 350 to 900°C range for a reaction time of 1/2 hour at a gas flow rate maintained at 3 L/h. The weight of precipitate used in each run was 100 mg in all tests.

The results are summarized in Table 9. According to the chemical analysis, carbon, phosphorus, and sulfur contents decrease with an increase of temperature. After heating the sample in the presence of air during isothermal conditions at 900°C, metallic silver of 99.9% grade is produced. The weight loss is about 65%, equal to the theoretical value calculated from the molecular formula. It seems that the oxygen is indispensable for

TABLE 9
Composition of the Metallic Residues after Thermal Treatment of the Organometallic Precipitate at Different Temperatures

	Metallic residues content (%)			
Temperature (°C)	Ag	S	C	P
350	68.99	9.78	2.74	9.46
500	77.45	7.49	0.55	7.24
800	91.27	8.73	0	0
900	99.9	0	0	0

TABLE 10
Chemical Composition of the Spent Fixing Solution Before and After Silver Recovery by Ionic Flotation

	Before silver recovery	After silver recovery
Ag, mg/L	250.8	0.49
$S_2O_3^{2-}$, M	1.25	1.24
HSO_3^-, M	0.055	0.050
pH	5.50	5.54

obtaining pure metallic silver; indeed, the residue obtained from a test made under nitrogen atmosphere still contains sulfur and carbon.

Recycling of Fixing Bath after Silver Recovery

For the purpose of testing the efficiency of photographic baths after recovery of silver by ionic flotation, tests were carried out by comparison of photographs obtained by black and white photographic printing on paper by using the fresh fixing bath and the raffinate recycle after ionic flotation operation at the stoichiometric Φ ratio. The chemical compositions before and after silver recovery are given in Table 10.

The physicochemical characteristics of the solution are not altered, but a white precipitate is formed in the fixing tank and the gloss of the early three photographs is decreased during reuse of the desilvered bath. This is due to the residual collector which reacts with the dissolved silver. In fact, once the residual collector is eliminated by precipitation, the contrast and gloss of the secondary photographs are identical to those obtained with a fresh fixing solution. Thus, the value of Φ must be adjusted to a value just below the stoichiometric one.

This test enabled us to confirm that:

The physicochemical properties of photographic baths are not altered by the recovery of silver by ionic flotation
The photographic solution can be reused after silver recovery
In order to avoid affecting picture quality, it is better to remove any collector excess

CONCLUSION

In the light of the results obtained, it appears that the ionic flotation technique is well adapted to the selective recovery of silver from photographic media. This method enables a silver concentrate containing

31–34% Ag to be produced. The recovery rate reaches 99% at Φ values ranging from one to two times the stoichiometry of the precipitation reaction, depending on the initial Ag concentration.

The interaction between silver and the collector Aerophine 3418A is very selective, even in presence of high concentrations in Fe(III)-EDTA/Fe(II)-EDTA, which allows use of the ionic flotation technique both in black and white and in color photographic solutions. Furthermore, the desilvered bath can be reused and pure metallic silver containing 99.9%

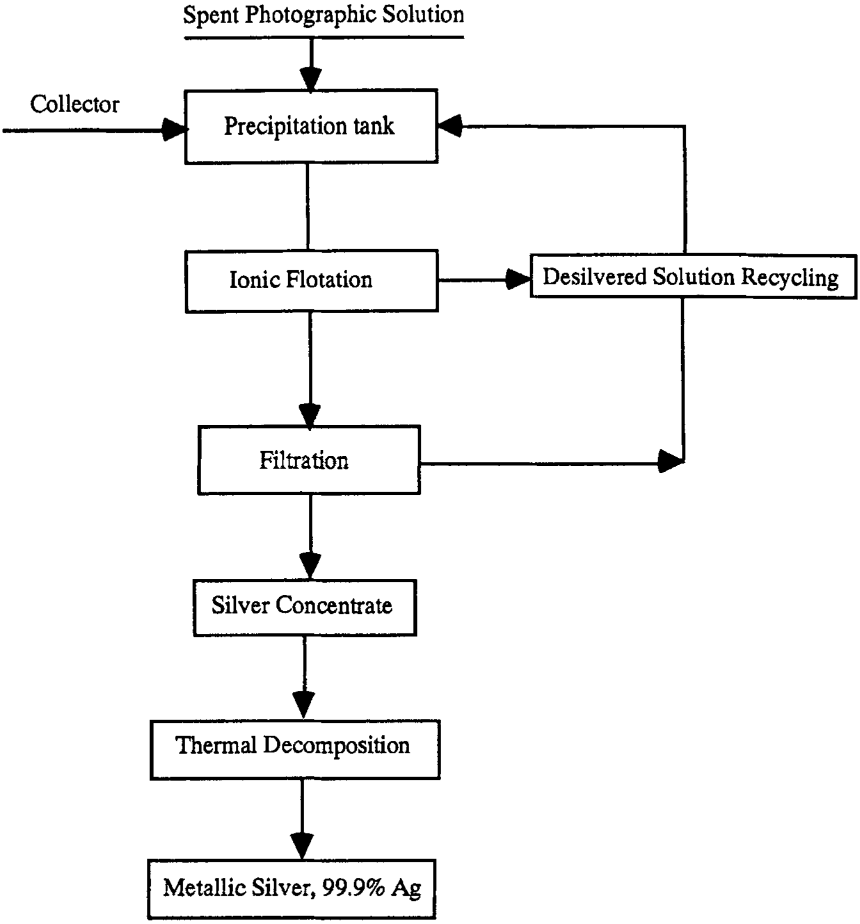


FIG. 2 Schematic block diagram of ionic flotation of silver from spent photographic solutions, bath recycling, and metallic silver collection.

Ag can be obtained by thermal decomposition at 900°C from the floated precipitate. The scheme of the proposed ionic flotation process for silver recovery is given in Fig. 2.

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Received by editor June 9, 1994