TREATMENT AND RECYCLE OF PHOTOGRAPHIC BLEACH SOLUTIONS USING ELECTROLYTIC REGENERATION

DIRECTORATE OF ENVIRONICS TYNDALL AIR FORCE BASE, FLORIDA 32401

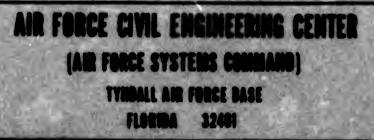
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UNCLASSIFIED SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered) **READ INSTRUCTIONS REPORT DOCUMENTATION PAGE** BEFORE COMPLETING FORM REPORT NUMBER 2. GOVT ACCESSION NO. 3_RECIPIENT'S CATALOG NUMBER AFCEC-TR-76-6 TITLE (and Subtitle) YPE OF REPORT & REPION COVER Final Report. Treatment and Recycle of Photographic Apr 73-Dece Bleach Solutions Using Electrolytic 75. Regeneration . 7. AUTHOR(a) CONTRACT OR GRANT NUMBER(+) 16 Capt, USAF, BSC Brian D. Bennett PERFORMING ORGANIZATION NAME AND ADDRESS 10. PROGRAM ELEMENT PROJECT, TASK Air Force Civil Engineering Center 64308F 2054 3005 Tyndall Air Force Base, FL 32401 11. CONTROLLING OFFICE NAME AND ADDRESS 12. REPORT DATE Air Force Civil Engineering Center 976 Jan I Trl A Tyndall Air Force Base, FL 32401 26 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. SECURITY CLASS. (of this report) Unclassified ISA. DECLASSIFICATION DOWNGRADING 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. 17. DISTRIBUTION STATEMENT (of the obstract entered in Block 20, If different from Report) 18. SUPPLEMENTARY NOTES Available in DDC 19. KEY NORDS (Continue on reverse side if necessary and identify by block number) Ferricyanide Bleach Photowaste Environics 10. ABSTRACT (Continue on reverse olde il necessary and identify by block number) The use of the Mead Ferricyanide Solution Management System, TE7207C for batch mode regeneration of all spent ME-4 ferricyanide bleach used at the Aerospace Audio Visual Service, Norton Air Force Base, CA was investigated. Installation of the system was modified to process the effluents from multiple processors in order to increase the cost benefit of the system. Problems associated with maintaining proper bleach feed pressures and

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replenisher flow were encountered. Results indicated that the system did regenerate ferricyanide bleach to standards required for photoprocessing. Chemical costs using the electrolytic process were less than one half that previously associated with persulfate regeneration.

PREFACE

This report was prepared by the Air Force Civil Engineering Center, Tyndall Air Force Base, FL resulting from research performed under Program Element 64708F Project 2054.

The inclusive dates of this effort were April 1973 to December 1975. This report was submitted in January 1976 by the Air Force Civil Engineering Project Officer, Captain Brian D. Bennett. The former project officer was Captain Dean D. Nelson.

The author wishes to extend appreciation to Mr. Joe Robinson and Mr. Carl Robinson of Aerospace Audiovisual Service for their support on this project.

This report has been reviewed by the Information Officer and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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TABLE OF CONTENTS

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Section	Title	Page
I	INTRODUCTION	1
	A. Background	1
	B. Statement of Problem Situation	2
	C. Objective and Scope	3
II	SYSTEM OPERATION	4
III	INSTALLATION AND EVALUATION	12
IV	CONCLUSIONS AND RECOMMENDATIONS	19

LIST OF ILLUSTRATIONS

Figure	Title	Page
1	Mead Ferricyanide Solution Management System Fe 7207	5
2	Typical Replenishment Control System	6
3	The LNP Process Controller (Cross Section)	8
4	Bleach Circulation Flow Schematic	13

SECTION I

INTRODUCTION

A. Background

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The Environmental Protection Agency's draft development document for effluent limitations guidelines and standards of performance, February 1975, for the miscellaneous chemicals industry includes photofinishing laboratories and the developing and printing of commercial motion picture film (Reference 1). The effluent limitation guidelines set forth the quality of effluent attainable from photoprocessing operations applying the best practicable control technology currently available (BPCTCA). The document further identifies the effluent reduction to be achieved by July 1, 1983 by applying the best available technology economically achievable (BATEA).

Limitations have been proposed for biochemical oxygen demand, chemical oxygen demand, total suspended solids, silver thiosulfate and ferrocyanide. In-plant measures to reduce discharges as well as end-of-pipe methods are included as recommended treatment technologies. Recommendations for 1977 effluent limitations (BPCTCA) limit the average of daily values for 30 consecutive days to 3.5 milligrams/liter (mg/l) ferrocyanide or less. Similar standards are recommended for 1983 with an allowable maximum for any one day of 6.8 mg/l ferrocyanide.

Present state-of-the-art in-plant pollution abatement techniques can effectively reduce many of the problems associated with photographic-processing effluents. The most advantageous systems, both environmentally and economically, regenerate and reuse the processing effluents to reduce end-of-pipe treatment requirements and overall operating costs. Various methods for regeneration and reuse of ferricyanide bleaches have been developed and are in use today including the use of persulfate, ozone and hydrogen peroxide oxidation techniques. Another method which has been used is electrolytic oxidation. It is this process which is the basis of operation for the Mead Ferricyanide Solution Management System, Model Fe 7207 currently installed at the Aerospace Audio Visual Service (AAVS) at Norton Air Force Buse CA.

B. Statement of Problem Situation

The AAVS, located at Norton Air Force Base, San Bernadino, California operates a substantial motion picture processing laboratory. The bulk of the films processed in this facility are color ma-The color reversal materials are processed terial. using the Eastman Kodak ME-4 chemical formulations in an EH-88B 16 and 35mm motion picture processor. The effluent from these processors and others in the laboratory is diverted to holding tanks. The wash waters go to the storm sewer, while the fixing bath overflow from the ferricyanide bleach goes to another, the developers go to yet another, and all other effluents go into a tank identified as miscellaneous. The tanks are emptied periodically and trucked to a municipal sewage treatment plant.

The ferricyanide bleach consists principally of potassium or sodium ferricyanide, sodium ferrocyanide, sodium bromide, alkaline borates and a small amount of polyethylene glycol. During the photographic processing operation ferricyanide bleach converts the metailic silver on a photographic film to silver halide as shown by the following reaction:

 $Fe(CN)_{6}^{-3} + Ag^{\circ} + Br^{-} \rightarrow AgBr + Fe(CN)_{6}^{-4}$

This process consumes bromine and reduces the ferricyanide to ferrocyanide. Bleach replenishment is therefore required to continue process operations.

Historically, many processors discharged the overflow from the bleaching operation untreated to the sewer. In addition to economic advantages, recent water pollution control standards have made bleach regeneration and reuse even more desirable. Ferricyanide bleach is non-biodegradable and will generally pass through municipal treatment plants untreated. Additionally, ferricyanide bleach is considered one of the more serious potential pollutants from photographic processes. In the presence of sunlight and air it has been found that ferrocyanide is oxidized to ferricyanide, which is hydrolyzed to iron hydroxide and a mixture of soluble cyanide and hydrogen cyanide (Reference 2). The reactions for this process are: $4Fe(CN)_{6}^{-4} + 0_{2} + 2H_{2} \rightarrow 4Fe(CN)_{6}^{-3} + 4(OH)^{-1}$ $4Fe(CN)_{6}^{-3} + 12H_{2}O \xrightarrow{UV} 4Fe(OH)_{3} + 12HCN + 12(CN)^{-1}$

Studies by Burdick and Lipschietz (Reference 3) have shown the decomposition products of ferricyanide and ferrocyanide to be toxic to fish and wildlife at concentrations as low as 2 mg/l ferro-ferricyanide.

A number of alternative methods of regeneration exist. One of the most simple methods utilizes liquid bromine to oxidize the ferrocyanide back to ferricyanide while at the same time replacing the bromine ions removed by the film as it passes through the bleach. This process is carried out as shown by the following chemical reaction:

$$2Fe(CN)_{6}^{-4} + B_{2} \xrightarrow{2} 2Fe(CN)_{6}^{-3} + 2Br^{-1}$$

Probably the most common method and the one previously used at AAVS uses persulfate to oxidize the ferrocyanide as shown:

$$2Fe(CN)_{6}^{-4} + S_{2}O_{8}^{-2} \longrightarrow 2Fe(CN)_{6}^{-3} + 2SO_{4}^{-2}$$

This technique is simple to use, involves minimal capital expenditures and utilizes comparatively safe and stable chemicals. However, this method of regeneration results in a buildup of sulfate ions which slow the rate of bleaching thus reducing the amount of bleach which can be recycled. Additionally, ozone and electrolytic methods of regeneration can be used to accomplish bleach recycle.

C. Objective and Scope

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Sec. 1

The Mead Ferricyanide Solution Management System, Model Fe 7207 was adapted to a batch mode of operation in order to handle ferrocyanide bleach from a number of automatic processors. The system previously installed on one EH-88B processor was relocated and replumbed to regenerate all of the ME-4 bleach used at AAVS. The system was evaluated to determine its ability to produce a bleach solution which could be reused in photoprocessing and operate automatically and reliably under batch mode conditions.

SECTION II

SYSTEM CPERATION

The Mead Ferricyanide Solution Management System, Fe 7207, Figure 1, consists of three components. The LNP Process Controller, PC 7104, provides the sensing and servocontrol for the system; the Electro-MOXY® Ferri Regenerator, EM 7207, provides for on-line regeneration of the ferricyanide bleach and the Control and Mounting Module CM 7204 provides the interface between the system and the machine and operator.

The LNP Process Controller is the key to automation of the system. The controller senses bromide ion activity in the bleach and compares this level against a known bleach solution as a reference. A deviation of the bromide activity from the norm causes a control signal to be sent out for replenisher addition and regeneration of the ferricyanide bleach by the Electro-MOXY[®] unit.

A typical replenishment control system is shown schematically in Figure 2 as installed on a typical continuous film processor. The normal configuration utilizes a recirculation and tempering system consisting of a pump, filter, and heater that provides uniform mixing and temperature control of the process solution in the sump tank of the processor. The LNP Process Controller is installed directly in the recirculation loop downstream of the tempering unit. The process solution is continuously analyzed by the LNP Process Controller and is compared with a standard process When the analysis indicates the need for solution. replenishment, the LNP Process Controller actuates the solenoid valve, permitting the replenisher solution to be pumped into the system at the injection point. The flow rate of the replenisher solution is regulated by the flow meter. When the continuous analysis indicates that the process solution is properly replenished, the LNP Process Controller turns off the replenisher pump and closes the solenoid valve, preventing replenisher flow. This cycle continues as long as film is being processed. As a result, the on-line replenishment control system maintains the process solution at nominal working strength on a real-time basis.

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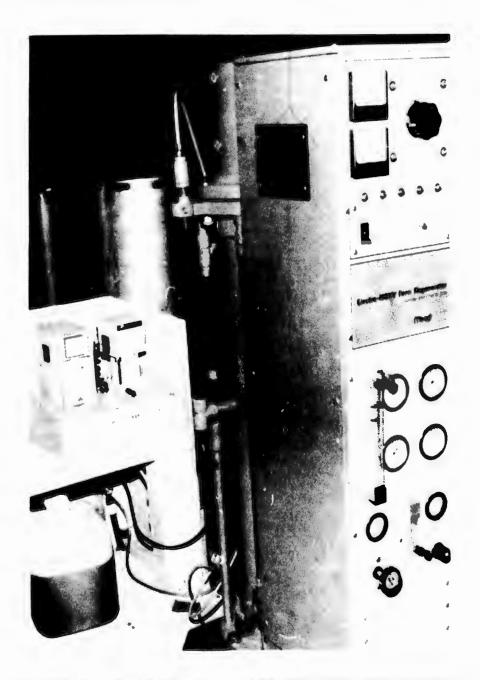
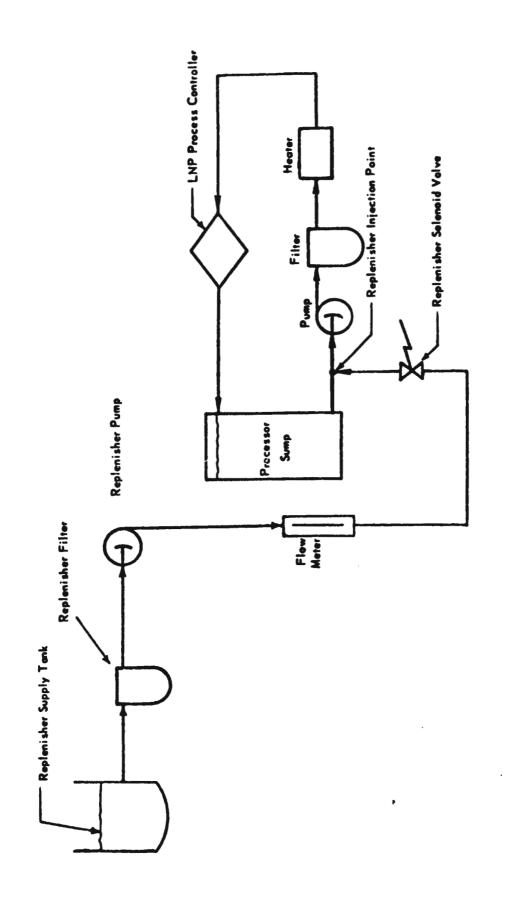


Figure 1. Mead Ferricyanide Solution Management System Fe 7207





The LNP Process Controller applies the concept of a symmetrical cell to continuous process-stream analysis and control. By virtue of symmetry, most of the errors normally associated with potentiometric analysis of process streams are eliminated, and the operation and calibration procedures are simplified.

A cross-sectional view of the LNP Process Controller is shown in Figure 3. The upper portion houses the control electronics, and the lower portion comprises the flow cell. The two portions of the controller are held together by two side latches and are sealed by an O-ring (A).

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The LNP Process Controller is plumbed directly into the process stream by means of 1/2 inch NPT female connections at the rear base of the unit. Within the flow cell a sample of the process stream is diverted to the sample chamber in a closed side-stream fashion. The sample flow rate is regulated by means of a needle valve and is monitored by a flow meter tube (not shown). The sample enters the sample chamber through the sample inlet where it mixes with a constant volume of sample solution. The sample leaves the chamber through the sample return tube and flows to the process stream outlet after merging with the main process stream. Α coarse adjustment of the sample flow rate is accomplished by a valve (not shown) at the base of the flow cell; the fine adjustment is made with the needle valve.

Within the flow cell the reference reservoir contains the standard reference solution, which is chemically identical to the conditions desired in the process stream. A continuously changing solution sample of the process stream surrounds the reference The reservoir is held in place by means of reservoir. a locking taper which forms a liquid junction between the standard reference and sample solutions. liquid junction provides an electrical connection between the standard reference and sample solutions, but prevents significant mixing of the two. Heat transfer through the reference reservoir wall insures that the standard reference solution temperature is maintained at the sample solution temperature.

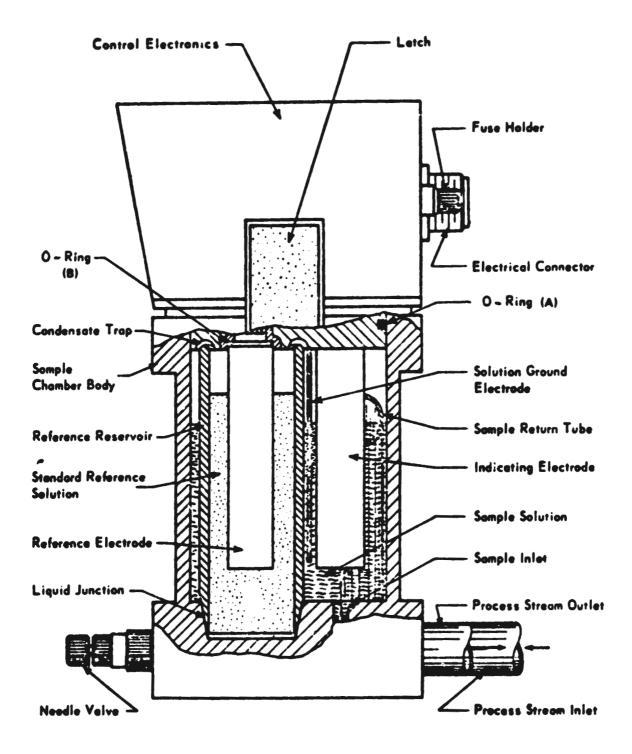


Figure 3. The LNP Process Controller (Cross Section)

The ionic activities of the standard reference and sample solutions are continually analyzed by two identical specific ion electrodes (reference and indicating, respectively). The solution ground electrode provides an isolated ground for the electronics. The electrodes are threaded into the bottom of the electronics housing. An O-ring(B) seals the connection between the electrodes and electronics, preventing the sample solution from entering the electronics housing. The electronics compare the signals of the reference and indicating electrodes and, when the sample solution differs significantly from the standard reference solution, the controller operates the solenoid valves (not shown) permitting flow of the replenisher solution(s) into the process stream. When the process stream returns to its desired composition (identical to the composition of the standard reference solution), the controller closes the solenoid valves preventing flow of replenisher.

The Electro-MOXY[®] Ferri Regenerator is a compact, fully automatic, high-current density, flow-through electrolytic cell which effectively oxidizes ferrocyanide to ferricyanide in photographic bleach solutions. Concentric anode and cathode compartments are housed in a single column. The bleach flows through the anode compartment and is separated from the catholyte by a cation-permeable membrane. When the LNP Process Controller signals for replenisher to be added, electrolysis at a preset current level occurs with the ferrocyanide being oxidized to ferricyahide at the anode.

Unlike chemical oxidizers which yield a by-product due to the oxidation of ferrocyanide, electrolysis has no by-product buildup. Nor is there an increase in potassium or sodium cation activity as has been experienced with ozonation. The Electro-MOXY[®] cell utilizes a cation-permeable membrane which allows the voltage-carrying cations to migrate from the bleach to the cathode. Hence, electrolysis provides regeneration of ferrocyanide bleach without increasing the cation activity or formation of by-products detrimental to recycling the solution. Other bleach rejuvenating oxidizers liberate bromine, or like ozone are toxic allotropic gases. The Electro-MOXY[®] unit can be operated safely without hydrogen gas hazard in any plant. During conventional electrolysis, due to decomposition of water, oxygen is liberated at the anode and hydrogen is formed at the cathode. The cathode of the Electro-MOXY is packed with MOXY Contacogen (catalyst) and aerated so that any hydrogen formed at the cathode/catalyst/bleach interfaces is rapidly oxidized by air to form hydroxide and water. The cation migrating from the anode associates with the hydroxide to maintain ionic equilibrium.

The Electro-MOXY® Ferri Regenerator System employs interlocked operating features to provide reliable performance. Since aeration of the MOXY® Contacogen is required, a flow sensor shuts off electrolysis if insufficient air is flowing through the cathode chamber. The system is also interlocked to prevent electrolysis if the bleach recirculation rate drops below a prescribed level, thereby eliminating the potential for over-oxidation of the bleach solution. The system is also operated in conjunction with an LNP Process Controller which monitors and controls the electro-oxidation process, thereby ensuring optimum performance.

The control and mounting module of the Ferricyanide System electronically links the LNP Process Controller ON-OFF output control signal with the Electro-MOXY unit and the replenisher control system. Addition of a concentrated bleach replenisher replaces bromide lost due to the film and other bleach chemicals lost due to dilution. A relationship exists between the amount of bromide consumed in rehalogenation of the film and the amount of ferricyanide reduced to ferrocyanide. This relationship can be expressed as follows:

Ag°	+	KFe (CN) 6	Ag+	+	K_4 Fe(CN) ₆
silver image		pot assium ferricyanide	silver ion		potarsium ferrocyanide
Ag+	+	NaBr	AgBr	+	Na ⁺
silver ion		sodium bromide (insoluble)	silver bromide		sodium ion

This equation shows that there is a one-for-one molar relationship between bromide, ferricyanide, and ferrocyanide. Hence, during a replenishment ON cycle, the amount of bromide in the replenisher being added per minute to the bleach recirculation system is equivalent to the amount of ferrocyanide being oxidized at the anode of the Electro-MOXY[®] unit.

The control and mounting module contains the concentrated replenisher control system. The replenisher is filtered external to the module, then feeds a metering pump. The pump discharge flows through a flow rater, through the solenoid, and then into a lowsuction venturi on the bleach recirculation line, prior to the LNP Process Controller. Sufficient mixing of the replenisher with the recirculated process stream occurs in the line so that the LNP Process Controller senses the average tank solution activity. Due to the variable flow lag network built into the LNP Process Controller, no over-replenishment or oscillation about a mean is experienced. (Reference 4.)

SECTION III

INSTALLATION AND EVALUATION

The AAVS motion picture processing area is located on two floors. The EH-88B processors are located on the second floor with the mixing and chemical distribution area located on the first floor.

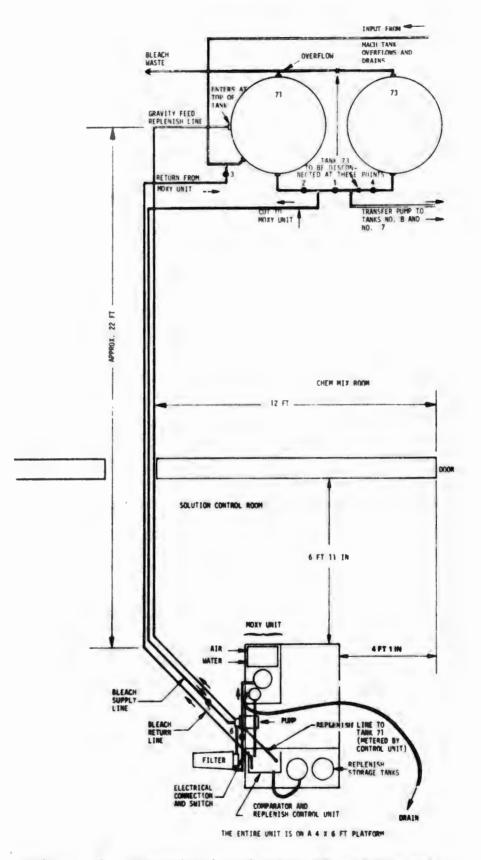
For this evaluation the system was relocated outside the chemical mix room at AAVS. Figure 4 is a schematic of the bleach circulation flow as processed by the regeneration system. All spent bleach from the processing machines was collected in tank number 71 located in the chemical mix room on the first floor for periodic regeneration. Normal operation consisted of collecting approximately 150 gallons of bleach prior to regeneration. The bleach was then pumped through a 1/2-inch PVC pipe to the Electro-MOXY unit and through the comparator and control unit. Concentrated replenisher was fed directly to tank number 71 where it was mixed with the bleach. This circulation pattern continued with concentrated replenisher being added until the quality of the bleach reached the standard maintained in the LNP process/controller. During the_addition of concentrated replenisher, the Electro-MOXY® Ferri Regenerator oxidized the ferrocyanide to ferricyanide. When the concentrations had come to the desired standard the controller deactivated the unit automatically.

Installation of the bleach regeneration system is subject to a number of plumbing constraints in order to obtain maximum operating efficiency. These limitations include:

1. Bleach feed pressure to the Electro-MOXY® should be in the range 18-28 psig to provide for proper pressure balancing with the system maximizing cathode and anode reactions.

2. Bleach flow rate through the Electro-MOXY[®] should be greater than 2 gallons per minute to insure interlocking mechanisms are operative.

3. Concentrated replenisher addition cannot be made into the recirculation line ahead of the





Electro-MOXY[®] because of possible localized ferrocyanide dilution.

The desired regeneration goal was to obtain bleach with the following chemical standards:

Sodium	bromide	43.0 +5.0 g/l
Sodium	ferricyanide	140.0 ^{+5.0} g/1
рH	-	8.70 + 0 .15
	ferrocyanide	15-20 ⁻ g/1

using the system with concentrated replenisher consisting of the following formulation:

TABLE 1. BLEACH STANDARDS

Component

Sodium bromide	134.8 g/l
Sodium ferricyanide	188.0 g/1
Sodium nitrate	40.0 g/l
Carbowax 1540	4.42 g/l
Borax decahydrate	15.0 g/l
10N NaOH	5.0 ml/l
pH to 10.8 20°C	

Initial performance runs of the system utilizing batch mode operation commenced during November 1974. Operational problems were encountered with a leaking pump within the unit and insufficient bleach feed pressure to the system. The feed pump installed was capable of developing 6-10 psig as compared to the recommended 18-28 psig. The data as shown in Table 2 were obtained during runs made at these reduced feed pressures. Operation under these conditions was inefficient with long regeneration times and large quantities of concentrated replenisher required to bring the bleach to standard. The regenerated bleach obtained was, however, of satisfactory quality to permit AAVS personnel to recycle it for use in their photoprocessing. No detrimental effects were reported on the quality of material processed using this regenerated bleach.

The bleach feed system was then modified in an attempt to increase the feed pressure to the recommended 18-28 psig range. The 1/2-inch ID PVC pipe

	TABLE	2.	INITIAL PERFORMANCE TESTING RESULTS	MANCE TE	STING RESI	OLTS
	Ferro- cyanide (g/l)	Ferri- cyanide (g/l)	Bromide (g/l)	ΡH	Time (hrs)	Volume of Replenisher (gallons)
Run No 1						
Initial	34.8	114.6	40.5	8.54	*	4
Final	8.3	134	40	#		
Run No 2						
Initial	33.4	112	41.8	8.33	*	äC
Final	24.7	114	47	8.72		0
Run No 3						
Initial	28.6	126.4	39.5	8.40	0 2	C L
Final	16.0	133.7	43.2	¢	n . 0 t	71
* No data available	vailable					

TABLE 2. INITIAL PERFORMANCE TESTING RESULTS

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was replaced with 1-inch ID piping and a 1/2-horsepower pump installed. This increased the bleach feed pressure to 18-20 psig at a flow rate of 2.5 to 3 gallons per minute.

Regeneration runs were performed at this increased bleach feed pressure, an air inlet pressure of 16 psig and a current setting of 60 amps. The system was started up on 28 October 1975 with an initial volume of 125 gallons of bleach to be regenerated. Manual addition of replenisher chemicals to the holding tank was performed during this run due to problems in the liquid replenisher feed system. The unit was operated daily during normal duty hours from 28 October to 7 November 1975 except for maintenance and backflushing performed during 3-4 November 1975.

The data obtained during this regeneration run are shown in Table 3. On 7 November 1975, 250 gallons of regenerated bleach were withdrawn and used as new bleach makeup for photoprocessing. Comparison of the end product obtained during the regeneration with the desired chemical goal shows good agreement and as anticipated, no detrimental effects were experienced using this regenerated bleach for processing. The periodic addition of overflow from the processing machines contributed to the large amount of bleach This addition also contributed to finally regenerated. the variability of the bleach being regenerated because the ferricyanide and ferrocyanide concentrations in the overflow are known to vary between 116-99.4 g/1 and 30.0-25.6 g/l, respectively.

Chemical costs for regeneration during this time are significantly less than similar costs associated with persulfate regeneration. Based on data supplied by AAVS, the following chemical cost of regeneration can be derived for the MOXY[®] unit:

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Date	Time	Ferri- cyanide (g/l)	Ferro- cyanide (g/l)	Bromide (g/l)	рH	Sodium Hydrox- ide	Volume (gal)	Ferro- cyanide added	Sodium Bromide added	Oper- ation (hrs)
28 Oct	0900 1445	115.0 116.8	28.6 21.3	38.9 37.0	8.04 7.0	* +4 oz		*	-14	* 9
29 Oct	0815 1600	118.0 124.2	18.4	39.1 39.3	7.86 8.03	+5 oz	140			8.5
30 Oct	0730 1500	123.6 124.7	11.1 15.5	37.04 43.2	7.65 8.35	+4 oz +3 oz	165	+13 lb	+8 1b	ŝ
31 Oct	0745 1500	123.6 135.9	17.9 23.2	43.2 45.0	8.3 8.7	+10 oz	190	41 81+	+4 1b 8 oz	8.5
3 Nov	0745 1245	124.2 123.4	22.3 23.7	44.2 42.7	8.37 8.75	+8 oz	220			2
5 Nov	0800	125.6	20.8	44.2	8.46		240			6.5
6 Nov	0930	133.1 140.4	16.8 19.8	44.2 48.7	8.56 8.4		200 220			3.5
7 NOV	1000	1:2.2	14.0	41.7	8.19				5 1b 9 oz	6.5
	TOTAL					34 oz	260	31 Ib	18 1b 1 oz	49.5
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TABLE 3. EXTENDED TEST DATA

The total volume of bleach regenerated was 260 gallons. Therefore the chemical cost of regeneration is approximately \$0.31 per gallon of bleach.

A survey of past regenerating chemical costs based on the same unit price indicates a favorable cost benefit using the MOXY[®] system. Cost estimates based on previous regenerations utilizing the persulfate method result in a price of \$0.69 per gallon.

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Once the problem of supplying bleach at an adequate feed pressure was resolved, the system effectively regenerated spent bleach. However, problems were encountered with clogging at the internal valves resulting in loss of bleach flow and automatic shutdown. Backwashing with fresh water was required to correct the problem and restore the unit to normal operation. Although not a serious problem, this did result in frequent maintenance attention. Future operation would require flushing with water after each regeneration run in order to mitigate this problem.

The rate of regeneration during these batch tests was below that achieved during previous continuous flow. This was most probably caused by the reduced bleach temperatures during the batch runs which were in the range 20-22°F less than during the continuous mode of operation due to storage prior to regeneration. Operating at a current setting of 60 amps and a bleach feed temperature of 70-72°F, it is estimated that 10 grams per minute of bleach were being regenerated as extrapolated from manufacturer's data.

18

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

The results of this study have shown the Mead Ferricyanide Solution Management System Fe7207 to be an effective method of regenerating ferricyanide bleach from photographic developing processors. An improved cost of regeneration over the persulfate method was demonstrated which reduces the volume of cyanide discharged. This not only contributes to a decrease in operating costs associated with bleach makeup but also provides for reduced waste treatment costs.

The production rights for the regeneration system have been sold by the Mead Corporation. At present, the system as installed at AAVS is unavailable on the commercial market and is no longer in production. Redesign of a similar type system is being undertaken for operation at atmospheric pressures, thus overcoming the problems associated with operation at the elevated feed pressures which were encountered during the previous testing of the system.

The principles of bleach regeneration and recycle are economically and environmentally sound and should continue to be applied at Air Force photofinishing laboratories. The method of regeneration, i.e., electrolytic, ozonation or chemical, should be evaluated as to its intended use for a particular installation based on cost-benefit analysis. Since there are a number of commercially available systems using different methods of regeneration, selection of the proper system becomes a unique problem associated with a particular application.

REFERENCES

1. Draft Development Document for Effluent Limitations Guidelines and Standards of Performance, Miscellaneous Chemicals Industry, EPA, February 1975.

2. Bober, Thomas W. and Dagon, Thomas J., "The Regeneration of Ferricyanide Bleach using Ozone," Kodak publication J-42.

3. Burdick, G. E. and Lipschietz, M., "Toxicity of Ferro and Ferricyanide Solutions to Fish and Determination of the Cause of Mortality." Trans American Fisheries Society, 78,192 (1950).

4. Erb, Deith, and Parsonage, Harry, "Evaluation of a Ferricyanide Bleach Recycling System." AFWL-TR-72-205, November 1973.

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TAC/DEEV	î		
		USAF Rgn Civ Engrg (Atlanta)	1
TAC/SGPB	1	USAF Rgn Civ Engrg (San Fran)	1
USAFSS/DEMM	1	USAF Rgn Civ Engrg (Dallas)	1
CINCUSAFE/Surgeon	1	SAMMA/MAGCB	1
CINCUSAFE/DEPV	2	USAFSO/DEE	1
AFISC/SGMS	1	1 Med Service Wg/SGB	1
AFISC/SES	2	4 Med Service Sq	ī
AFRES/DEEE	1	AFCEC/WE	î
USAFA/DEV	1	DDC/TCA	12
3800 ABW/DEE	1	ARPA	1
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