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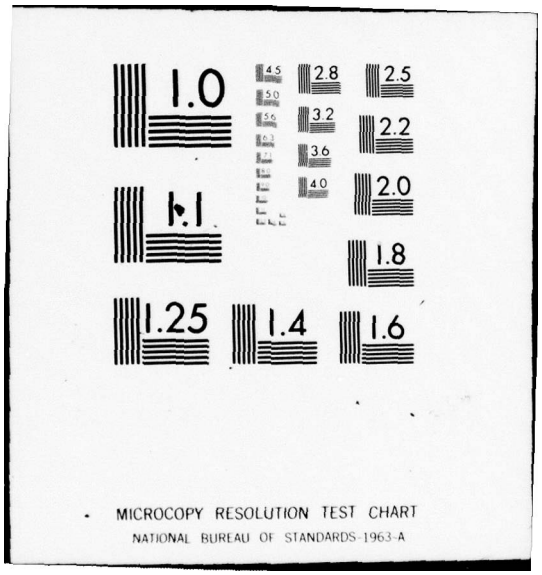
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REPORT NUMBER 4

ANNUAL REPORT

FEASIBILITY STUDY ON A PROCESS FOR ELECTROLESS METAL DEPOSITION IN PITS AND FISSURES OF TEETH FOR USE IN PREVENTIVE DENTISTRY

THOMAS J. O'KEEFE

July 1977

SUPPORTED BY

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
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Advances during the past year include the development of an alternate reduction system which would exclude the use of → next page

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20. ABSTRACT (Continued)

hydrazine, the futher characterization of this alternate system, and a comparison of it to the hydrazine-based system by means of resistance measurements, rate studies, tensile testing, ESCA, and scanning electron microscopy. Animal tests were also made at the USAIDR Laboratories to further test the suitability of the new chemical system.

ABSTRACT

Further examinations have been conducted which test the feasibility of using metal films, deposited by electroless or chemical methods, for use in various areas of the military dental program.

Advances during the past year include the development of an alternate reduction system which would exclude the use of hydrazine, the further characterization of this alternate system, and a comparison of it to the hydrazine-based system by means of resistance measurements, rate studies, tensile testing, ESCA, and scanning electron microscopy. Animal tests were also made at the USAIDR Laboratories to further test the suitability of the new chemical system.

TABLE OF CONTENTS

I. INTRODUCTION

During the first year of this project, it was demonstrated that thin metal films could be successfully deposited on extracted human teeth. The research was extended during the second year to include in vivo animal studies at the USAIDR Laboratories through the efforts of Col. Cutright and Lt. Col's Hoffman and Woody. The third year was spent in chemical and physical characterization of the deposits, in an attempt to better understand the mechanisms involved in the deposition and adherence of the metal to the enamel. At this stage of the research, it became obvious that the development of an alternate system, which used a reducing agent other than hydrazine, was desirable. This was due primarily to the possible toxicity problems which might be encountered with its use.

Therefore, the goals for the work during the past year became very obvious. An alternate chemical reducing agent which produced the desirable results obtained when hydrazine was used, but which was less toxic, was to be sought. Another goal was to have the system operate in a more neutral pH range to minimize any undesirable chemical side reactions. It was found that under certain conditions the ferrous ion could serve as a satisfactory reducing agent. After numerous in vitro trials it was decided to attempt to use the new system in vivo. Further animal studies were therefore

conducted at the USAIDR Laboratories through the efforts of Col. Cutright and Lt. Col's Posey and Woody. Characterization of both the hydrazine—based system and the iron system were continued, including extensive rate studies and morphological examinations, among others. The methods used were similar to those used in previous studies.

II. EXPERIMENTAL RESULTS

A. Resistance Measurements

After rather extensive testing it was found that ferrous sulfate worked satisfactorily as a reducing agent when used with silver fluoride. Addition agents (SnF_2 and $NaKC_4H_4O_6$) were also added to the system, to determine what effects these materials might have.

The results of the resistance tests are given in Plates I through III on metal films made using this system. In each case, the substrates were human molar enamel, etched for one minute with 42.5% H_3PO_4, then rinsed. Plate I shows that, as expected, resistances decreased with increased concentrations of silver fluoride and/or ferrous sulfate. Plates II and III demonstrate the effects of ferrous sulfate solution pH, as well as addition agent concentration, on the electrical resistances of the deposits formed for silver fluoride systems. For both addition agents examined, the resistances decreased with increased reduction solution pH over the pH range examined. When SnF_2 was used as the additive, deposit resistances decreased with decreased addition agent concentration. Results were not the same when Rochelle Salt was used as the additive. Here the resistances maximized and then dropped again with increased Rochelle Salt concentration.

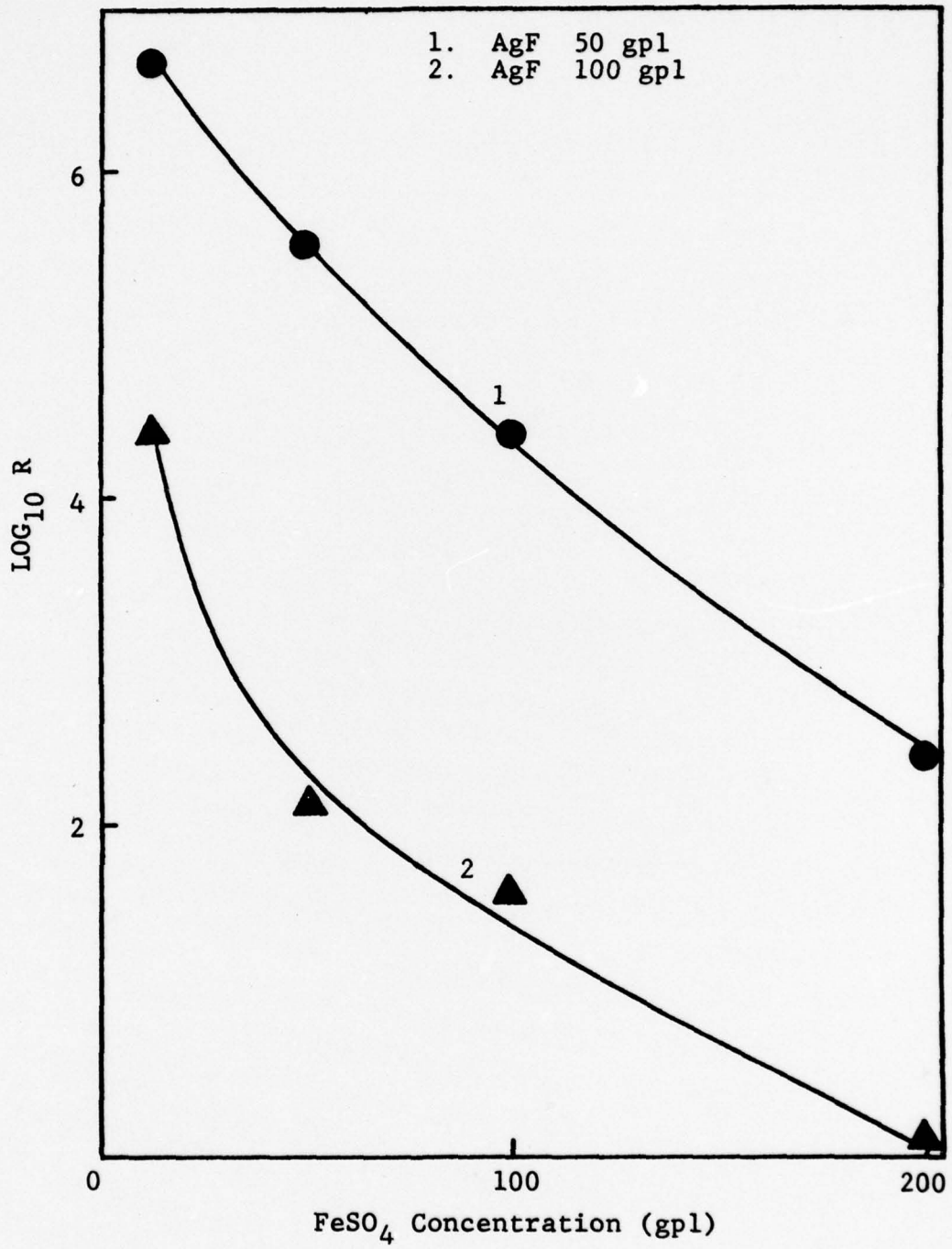

Plate I. Log_{10} of the electrical resistance R of silver deposits on tooth enamel as a function of $FeSO_4$ concentration for the plating sequence [AgF, pH 6.5 - $FeSO_4$, pH 3.5] 10 repetitions. The enamel had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

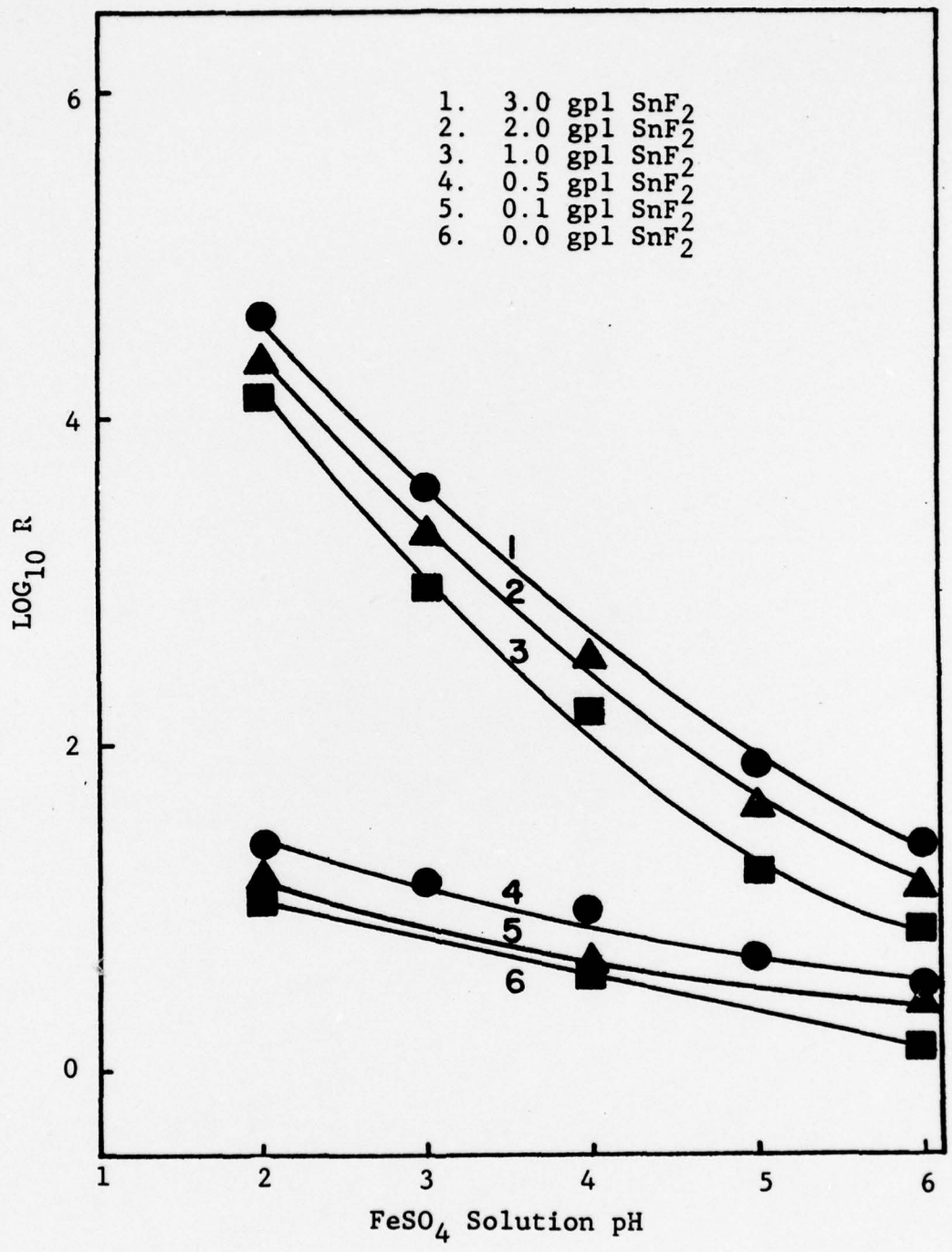

Plate II. Log_{10} of the electrical resistance R of silver deposits on tooth enamel as a function of $FeSO_4$ solution pH for the plating sequence [AgF 100 gpl, pH 6.5 - $FeSO_4$ saturated solution + $XSnF_2$] 10 repetitions. The enamel had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

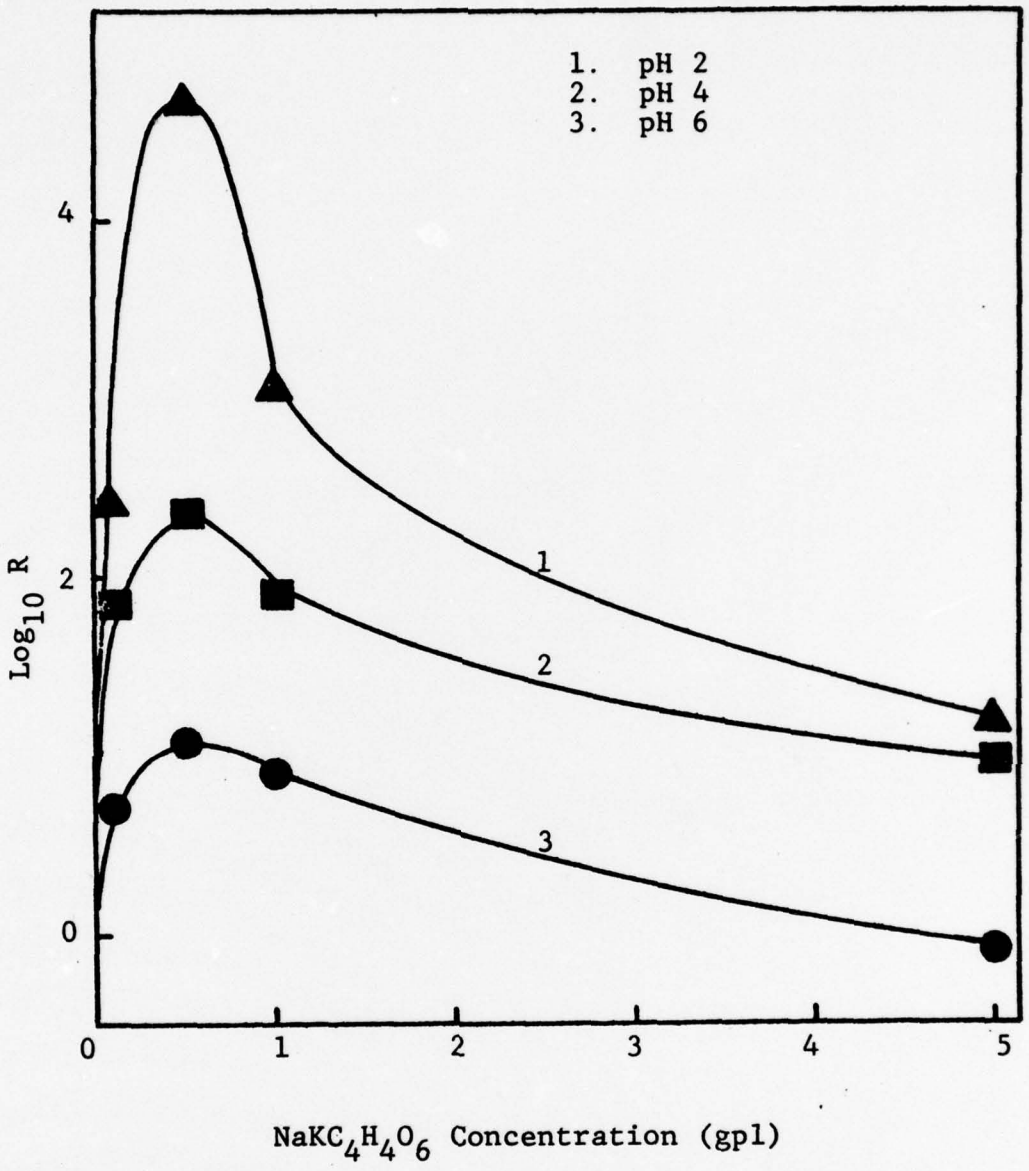

PLATE III. - Log_{10} of the electrical resistance R of silver deposits on tooth enamel as a function of $NaKC_4H_4O_6$ concentration for the plating sequence [AgF^1 100 gpl, pH 6.5 - $FeSO_4$ saturated solution + X $NaKC_4H_4O_6$] 10 repetitions. [1]The enamel had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

Further resistance testing of hydrazine-based systems was not attempted, as substantial resistance data for these have already been reported in past annual reports.

B. Rate Studies

In an attempt to find the quantity of silver that was deposited during a particular plating sequence, rate studies were undertaken. The amount of silver deposited on hydroxyapatite substrates was examined by masking all but a known area of the substrate, and then applying the desired number of repetitions to produce the metal film. The masking was then removed, and the film dissolved in nitric acid. After proper dilution, the samples were analyzed by atomic absorption (AA) techniques. All results are in grams of silver per square centimeter of substrate. Plates IV through VIII show the correlation between the number of grams of silver per square centimeter and the number of repetitions of a plating sequence for silver fluoride and silver nitrate solutions reduced with ferrous sulfate or hydrazine. In each case, the greater the number of repetitions of the sequence, the greater the amount of silver present.

The rates obtained for either ivory or human molar enamel were very comparable, as shown in Plate IV. Hydrazine systems seemed capable of depositing more silver on the substrates than did their ferrous sulfate counterparts, as can be seen by comparing Plates IV and V with Plates VI-VIII. In comparing Plates VI and VII, the system [AgF, 80 gpl, pH

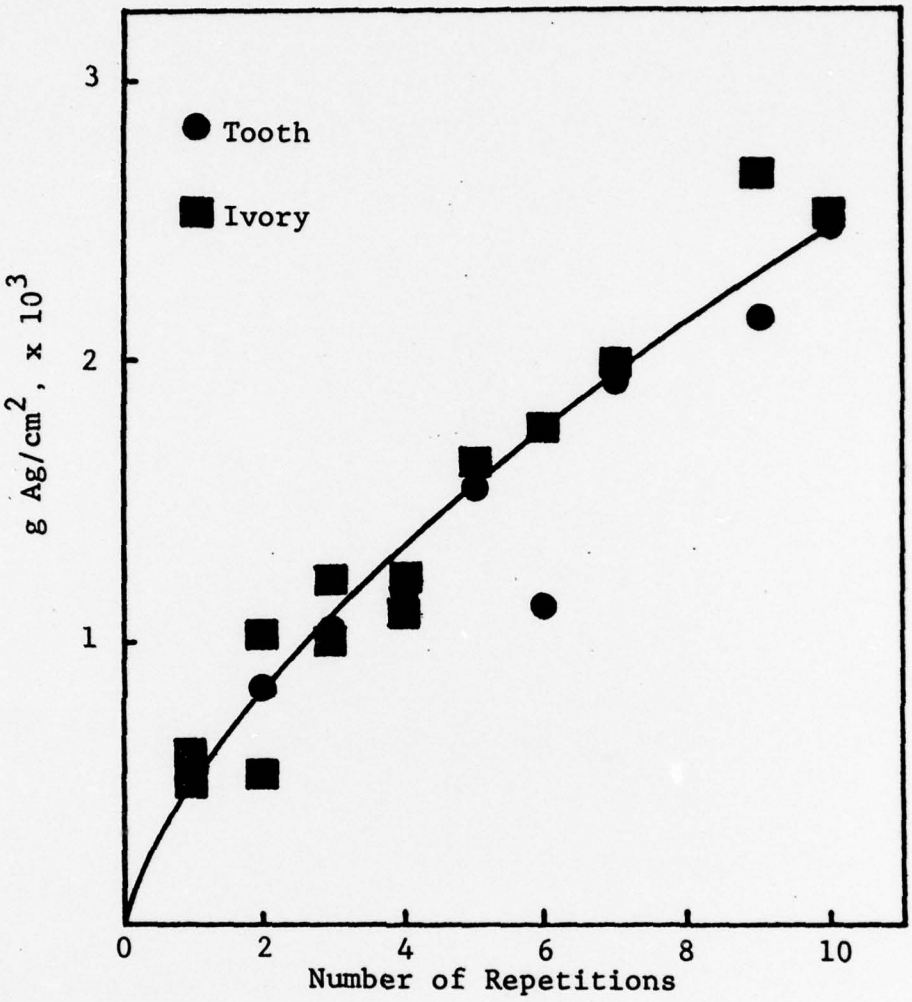

PLATE IV. - Grams of silver deposited per square centimeter of substrate as a function of the number of repetitions of a sequence for the sequence AgF 100gpl, pH6.5 - $FeSO_4$ saturated solution, pH 3.5. The substrate had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

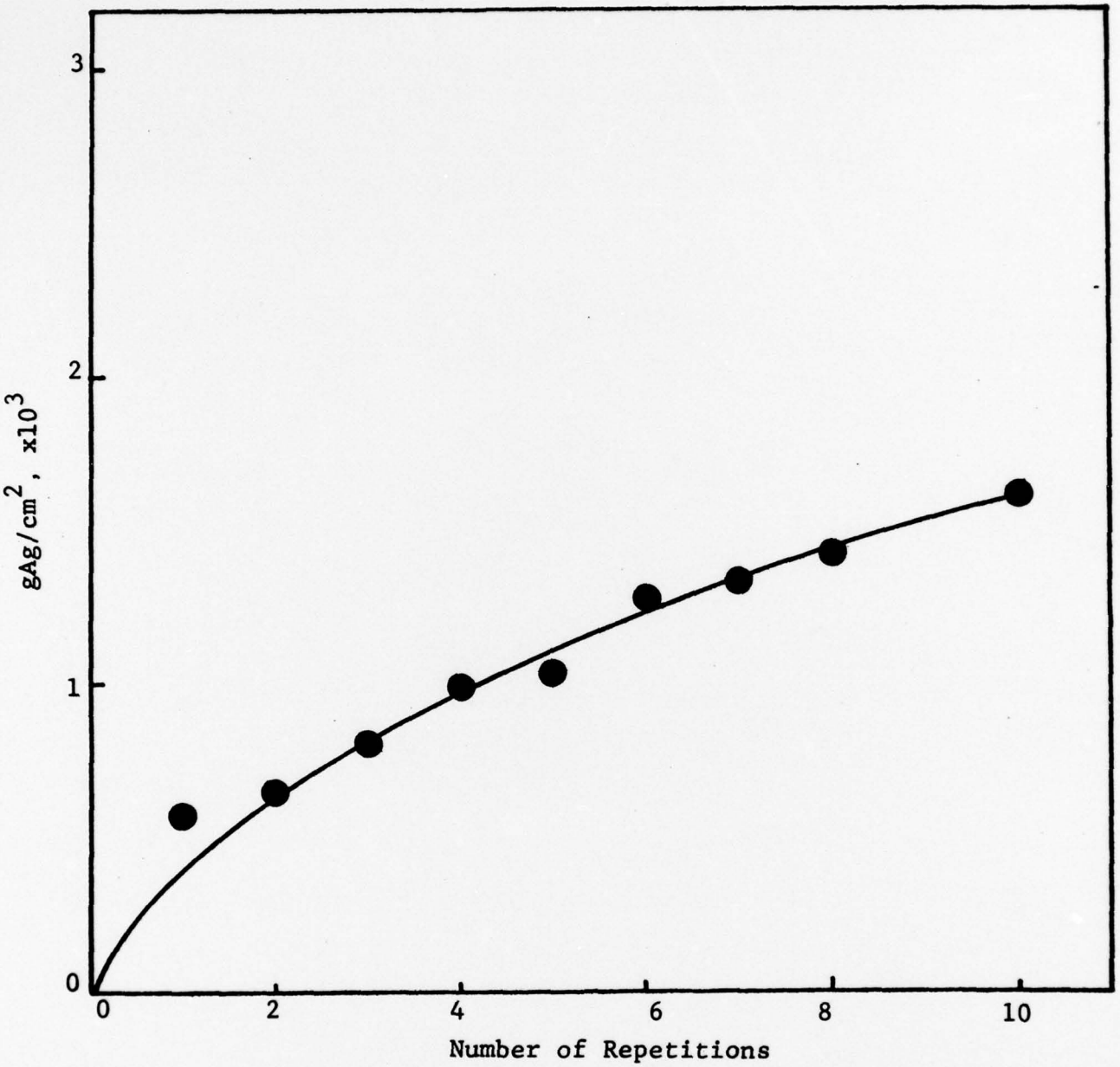

PLATE V. - Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [$AgNO_3$ 120gpl, pH4.0 - $FeSO_4$ 200gpl, pH3.5] The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

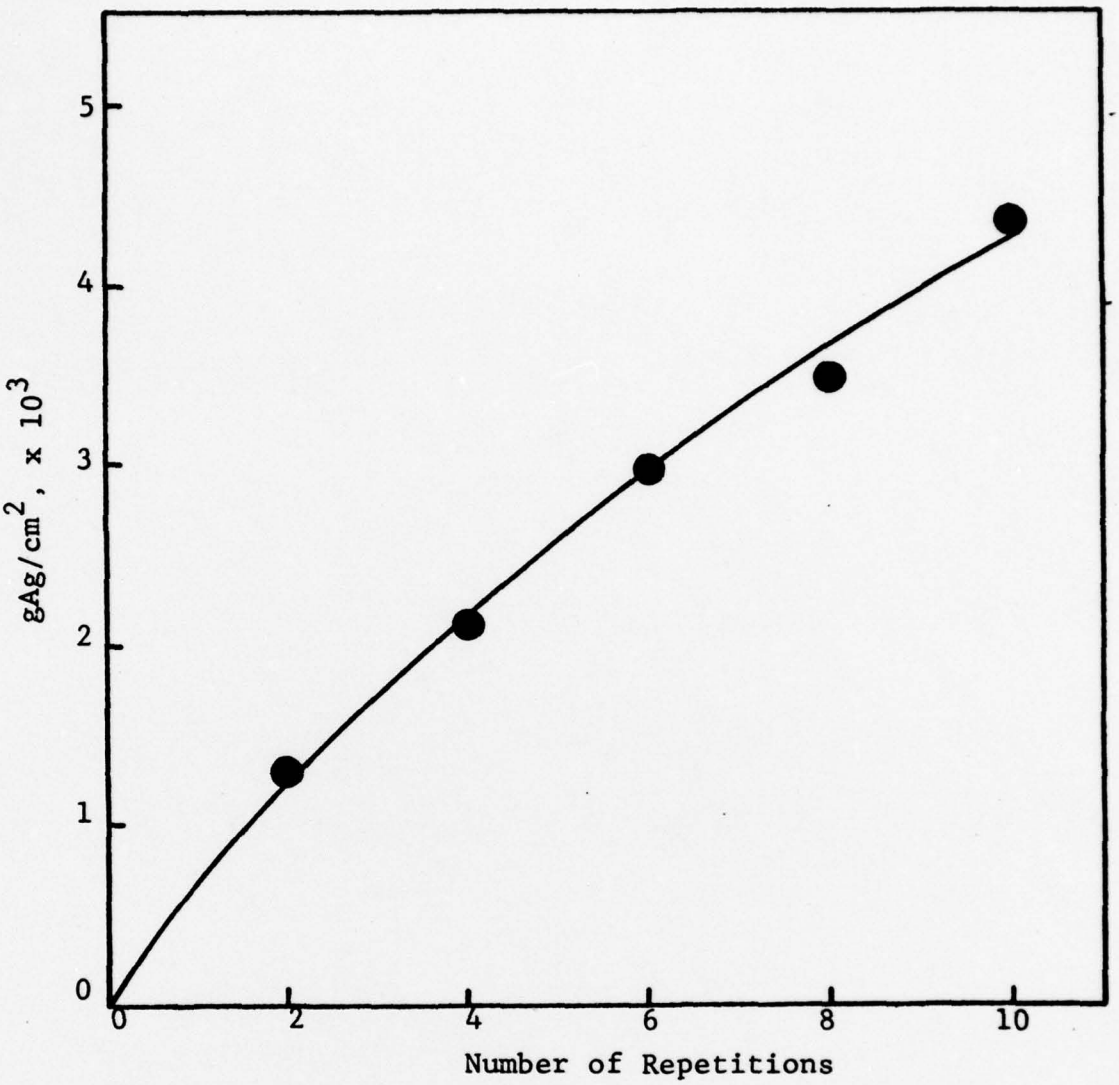

PLATE VI. - Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [AgF 80gpl, pH 8.75 with NH_4OH - N_2H_4 10 ml/l, pH 9.0]. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

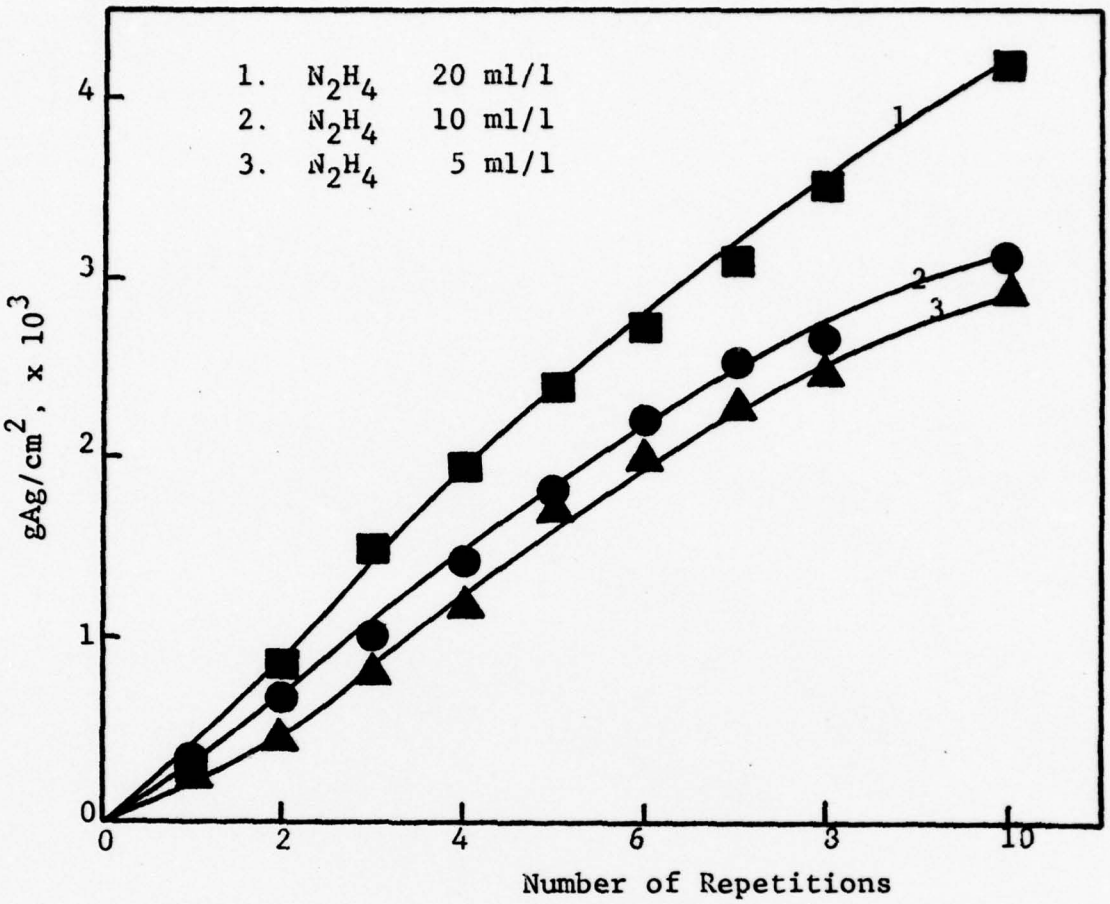

PLATE VII. - Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [$AgNO_3$ 120gpl, pH 8.75 with NH_4OH - N_2H_4, pH 9.0]. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

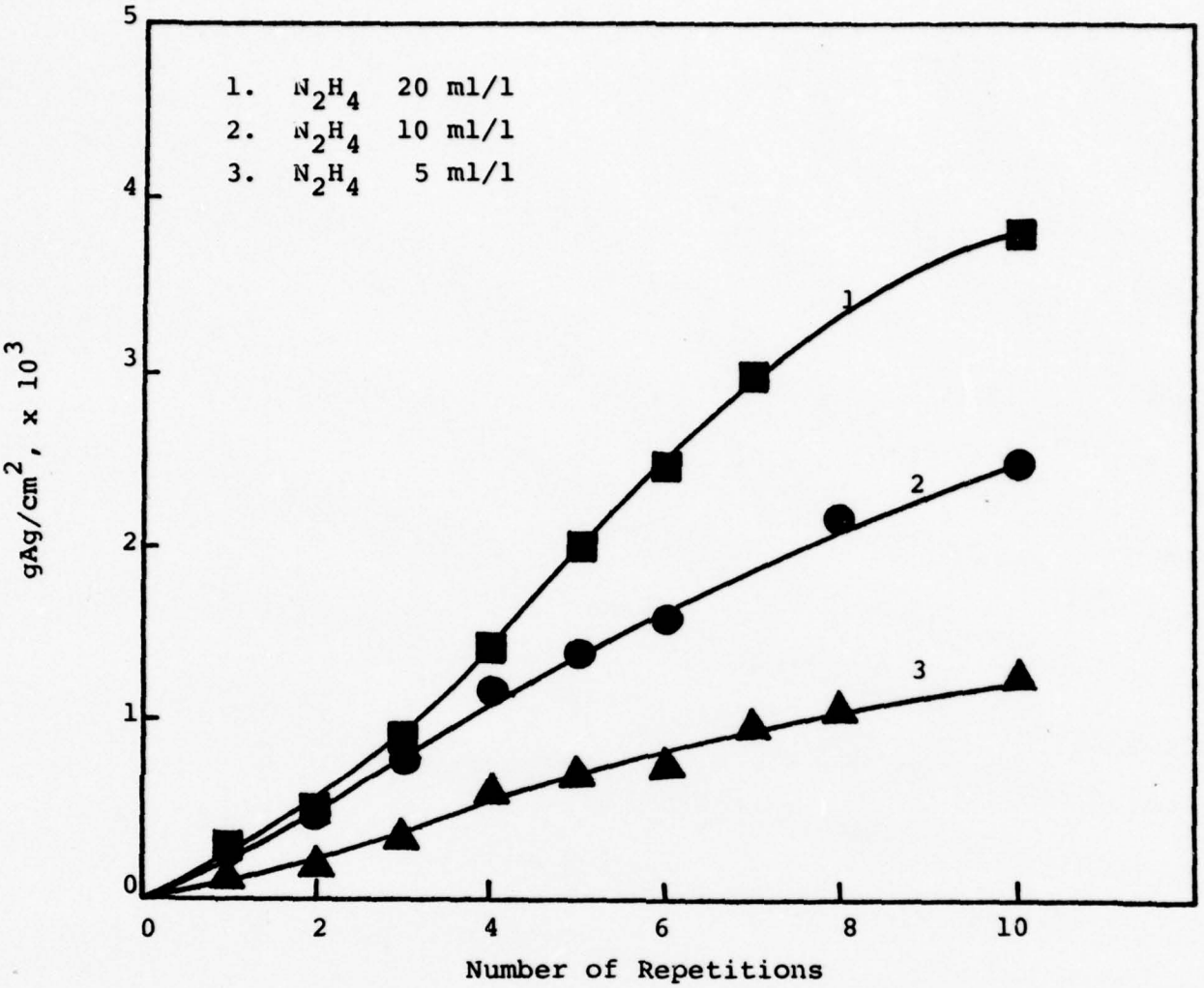

PLATE VIII. - Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [$AgNO_3$ 60gpl, pH 8.75 with NH_4OH - N_2H_4, pH 9.0]. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

8.75 with NH_4OH-N_2H_4, 10 ml/l, pH 9] was capable of depositing roughly the same amount of silver as the system [$AgNO_3$ 120 gpl, pH 8.75 with NH_4OH-N_2H_4 20 ml/l pH 10]. Plates VII through X show the effect of increased silver concentration and increased reduction solution concentration on the amount of silver deposited, again for silver nitrate and silver fluoride solutions reduced with either ferrous sulfate or hydrazine. The trend is as expected, with higher concentrations providing greater amounts of silver per square centimeter of substrate.

Plates XI and XII depict the effects that certain addition agents can have on silver deposition rates for silver fluoride-ferrous sulfate systems. Often, small concentrations of certain additives are apparently more detrimental than higher levels of the same additive. In certain cases, the addition agent caused a decrease in deposition rates. When Rochelle Salt additions were made, as seen in Plate XII, rates first dropped slightly then increased slightly with increasing addition agent concentration.

C. Tensile Testing

Several tensile tests were performed, with the results being listed in Table I. All tensile strengths were greater than 2500 psi, with all failures in the epoxy.

D. ESCA Analyses

ESCA surface analyses were performed on several samples

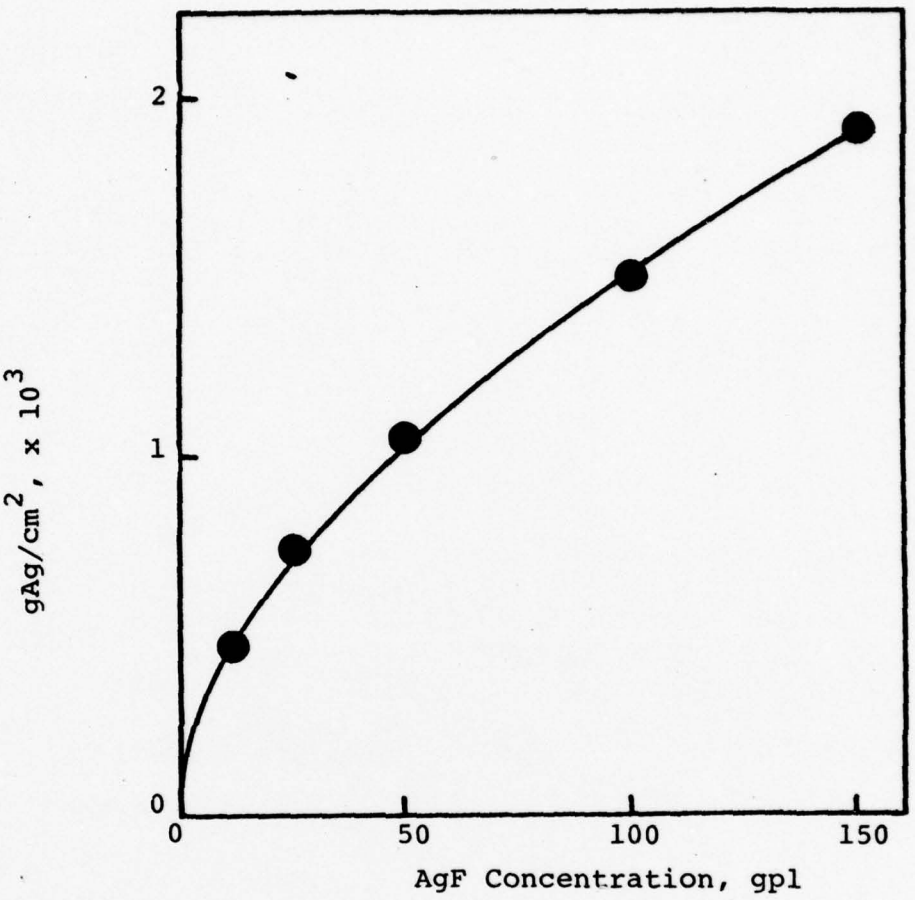

PLATE IX. - Grams of silver deposited per square centimeter of ivory as a function of AgF concentration for the plating system [AgF, pH 6.5 - $FeSO_4$, saturated solution, pH 3.5] 5 repetitions. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

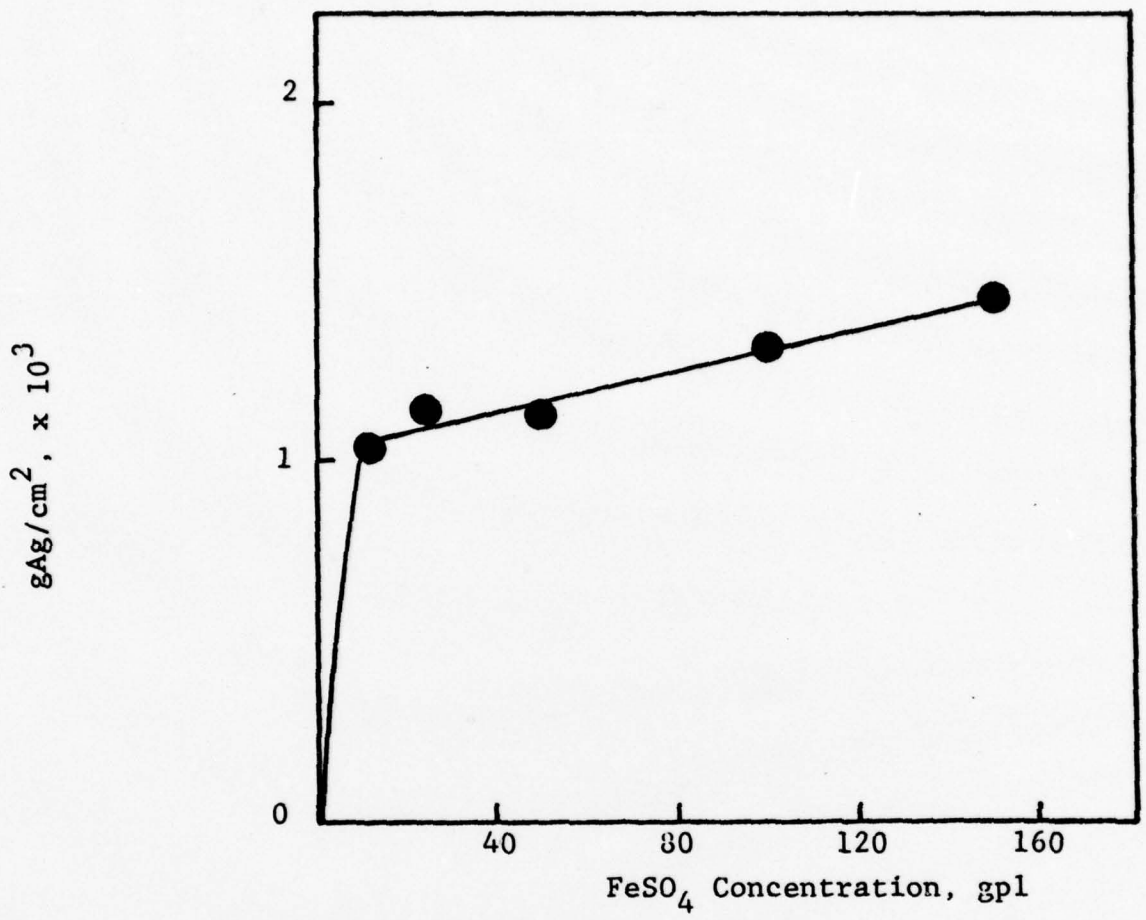

PLATE X. - Grams of silver deposited per square centimeter of ivory as a function of $FeSO_4$ concentration for the plating system [AgF 100 gpl, pH 6.5 - $FeSO_4$ pH 3.5] 5 repetitions. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was rinsed prior to plating.

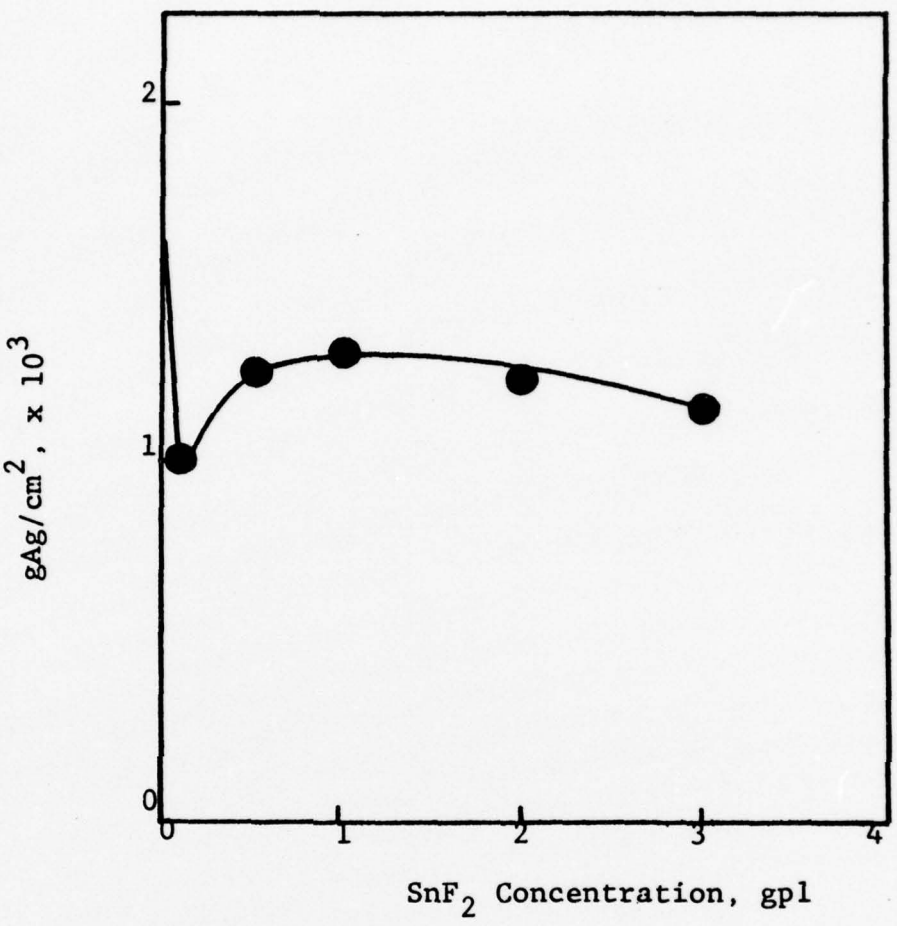

PLATE XI. - Grams of silver deposited per square centimeter of ivory as a function of the concentration of SnF_2 in the $FeSO_4$ solution, for the plating system [AgF 100 gpl, pH 6.5 - $FeSO_4$ saturated solution, + X SnF_2, pH 6.0]. 5 repetitions. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was rinsed prior to plating.

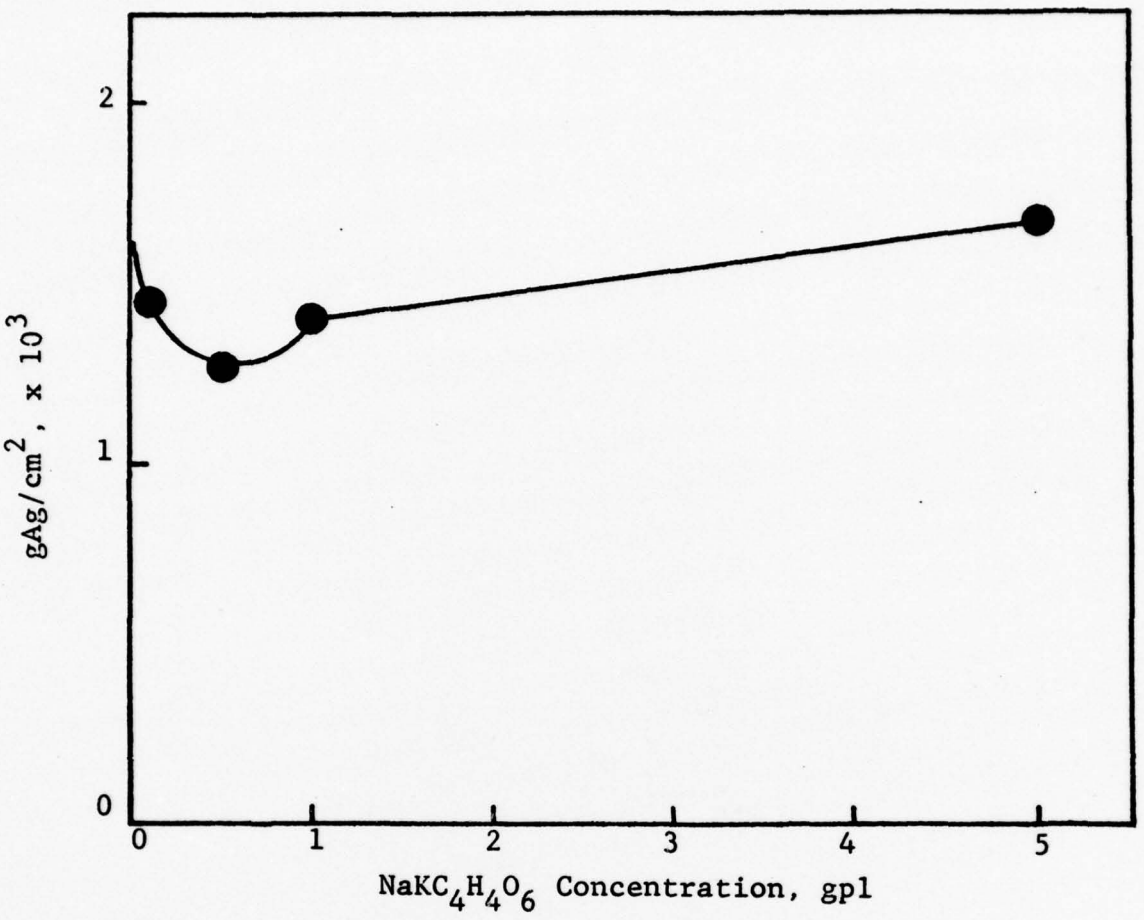

PLATE XII. - Grams of silver deposited per square centimeter of ivory as a function of the concentration of $NaKC_4H_4O_6$ in the $FeSO_4$ solution, for the plating system [AgF 100 gpl, pH 6.5 - $FeSO_4$ saturated solution + X $NaKC_4H_4O_6$, pH 6]. 5 repetitions. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was rinsed prior to plating.

TABLE I

Tensile Tests on Ivory

	Plating Sequence	Tensile Strength	% Silver Film Removed
(1)	Etch 1.0 minute 42.5% H_3PO_4, rinse.	2517 p.s.i.	0
	(a) $AgNO_3$ 100 gpl, no NH_4OH		
	(b) {$FeSO_4$ saturated - 30 ml / NaF - 50 gpl - 30 ml} mixed 10X		
(2)	Etch 1.0 minute 42.5% H_3PO_4, rinse.	2680 p.s.i.	0
	{$AgNO_3$ 100 gpl, no NH_4OH / $FeSO_4$ saturated} 10X		
(3)	Etch 1.0 minute 42.5% H_3PO_4, rinse.	3423 p.s.i.	0
	{$AgNO_3$ 100 gpl, with NH_4OH / N_2H_4 10 ml/l} 10X		

which were prepared by plating with silver nitrate-ferrous sulfate systems varying in pH and in amounts of additives. Approximately 150 Å of material were removed prior to sample analysis. The results indicated that the silver-to-calcium ratios were better at higher pH levels (6 or so) of the $FeSO_4$ solution. NaF additions to low pH $FeSO_4$ solutions resulted in lower silver-to-calcium ratios. NaF additions to higher pH $FeSO_4$ solutions resulted in silver-to-calcium ratios which were better than when no NaF was used. Further additions of 0.1 gpl SnF_2 altered the silver-to-calcium ratio, and for two repetitions of the plating sequence, decreased the silver present. With additions of 50 gpl NaF and 0.1 gpl SnF_2 to the $FeSO_4$ solution, after six repetitions of the plating sequence, the calcium and oxygen peaks were almost nonexistent. The silver count was very high. As with all samples, no iron or tin was detected.

E. In Vivo Studies

During February, 1977, the second series of in vivo tests were conducted at the USAIDR Laboratories, Walter Reed Army Hospital, Washington, D.C. The major objective of this test was to evaluate the new ferrous sulfate reducing agent and to compare it to previous successful tests in which hydrazine had been used. A total of five monkeys and eight rats had certain teeth plated with silver. An amalgam filling material was also applied on top of

several selected silver films. The deposition process seemed to perform satisfactorily, and the results were quite similar to those which had been seen in the in vitro studies. Additions of stannous fluoride to the reduction solution were detrimental to initial amalgam adherence to the silver film. More detailed information of the protocol is in Table II.

F. Scanning Electron Microscopy

The SEM has been an invaluable aid in studying the morphologies of the deposits using various metal reduction processes, particularly where dealing with changes in concentrations of the solutions and the use of addition agents. Figures 1 through 4 show the effects of silver concentration changes and ferrous sulfate concentration changes on the resulting deposits for silver fluoride systems. Figures 1 and 3 show quite clearly the underlying hydroxyapatite substrate. Figures 5 through 8 show the effects of pH and addition agents on a silver nitrate-ferrous sulfate plating system. As can be seen, deposits ranging from non-continuous and nonadherent to continuous and adherent are possible, depending on the additives and the solution pH. Figures 9 and 10 are examples of the morphologies seen with silver fluoride-ferrous sulfate systems with no addition agents, while the remaining micrographs are of silver fluoride-ferrous sulfate systems with various additive concentrations.

TABLE II

Summary of Protocol on Plating of
Animals at Walter Reed Army Hospital

A. Monkeys

M-397

Quadrants plated - upper right, lower left.

Etch - 1.0 minute 42.5% H_3PO_4, rinse.

Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution +.1 gpl, SnF_2, pH6] 10X

Incline planes etched well, but not bottom of fissures.

Large amount of yellow phosphate formed before first Fe^{++} reduction.

10Ω/cm after 5 applications.

On incline planes, white appearance with start of 8th application.

.7 Ω/cm to 30Ω/cm between 2 incline planes after 10 repetitions. Less than 1Ω/cm over rest of teeth after 10 repetitions.

First molars then covered with amalgam.

Applied by R. Christie

P-483

Quadrants plated - upper right, lower left.

Etch - 1.0 minute 42.5% H_3PO_4, rinse

Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH6] 10X.

Incline planes etched well, but not bottom of fissures.

Yellow phosphate again formed before 1st Fe^{++} reduction.

15-150Ω/cm after 5 repetitions. White color after 10th application. 0.5-7.0Ω/cm.
2nd molars covered with amalgam.
Applied by R. Christie.

P-512

Quadrants plated - upper right, lower left.

Etch - 1.0 minute 42.5% H_3PO_4, rinse.

Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH6] 10X.
Incline planes etched well, but not bottom of fissures.
Yellow phosphate again formed before 1st Fe^{++} reduction.
(Light on right, heavy on left.) Upper right 1-10Ω/cm after 10 repetitions. Lower left - heavy reduction, 1st application 0.5Ω/cm. .1-.3Ω/cm after 10 repetitions.
Upper right applied by T. O'Keefe
Lower left applied by R. Christie

H-395

Quadrants plated - upper right, lower left.

Etch - 1.0 minute 42.5% H_3PO_4, rinse.

Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH6] 10X.
Incline planes etched well, but not bottom of fissues.
Yellow phosphate again formed before 1st Fe^{++} reduction.
Upper right 1.5-200Ω/cm after 10 repetitions. Lower left 7-150Ω/cm after 10 repetitions.
2nd molars received amalgam.
Applied by Lt. Col. R. Woody

H-336

Quadrants plated - upper right lower left

Etch - 1.0 minute 42.5% H_3PO_4, rinse.

Deposition - [AgF 100 gpl - N_2H_4 10 ml/l] 10X.

Etch good.

Upper right - medium yellow phosphate, rate of reduction high. 4-7Ω/cm after 3rd repetition.

0.2-0.5Ω/cm after 10th repetition.

Electroplated 1st & 2nd bicuspids, 1st molar.

0Ω/cm after electroplate.

Lower left - loose, medium yellow phosphate.

0-0.1Ω/cm after 10 repetitions.

Applied by R. Christie.

B. Rats

All plated with following sequence.

Etch - 1.0 minute 42.5% H_3PO_4, rinse.

Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH6] 10X

#1m Right side, upper and lower quadrants. Yellow phosphate appeared before 1st Fe^{++} reduction. No resistance data taken. Optalloy applied to both upper and lower. Applications made by R. Christie.

#2m Left side, upper and lower quadrants. Etch judged to be good. Yellow phosphate appeared before 1st Fe^{++} reduction. No resistance data taken. Optalloy applied to both quadrants. Applied by R. Christie.

#3m Right side, upper and lower quadrants. Etch appeared good, light yellow phosphate. Optalloy applied to both quadrants. Applied by T. O'Keefe.

#4m Left side, upper and lower quadrants. Etch good. Yellow phosphate appeared. Good first coat after 1 application. No amalgam. Applied by T. O'Keefe.

#5m Right side, upper and lower quadrants. Yellow phosphate light. No amalgam. Applied by T. Planje.

#6m Left side, upper and lower quadrants. Good yellow phosphate. Applied by R. Christie.

#7m Right side, upper and lower quadrants. Yellow phosphate appeared. Good plate. Applied by Lt. Col. R. Woody.

#8m Left side, upper and lower quadrants. Good yellow phosphate formation. Applied by Lt. Col. R. Woody.

Figure 1. SEM micrograph of human molar enamel partially covered with silver. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4, and then rinsed. Plating sequence [Ag 25 gpl, pH6.5-$FeSO_4$, saturated solution, pH 3.5] 10 repetitions. Magnification 1000X

Figure 2. SEM micrograph of a silver metal deposit human molar enamel. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4, then rinsed. Plating sequence [AgF 100 gpl, pH6.5-$FeSO_4$ saturated solution, pH 3.5] 10 repetitions. Magnification 1000X.

Figure 3. SEM micrograph of human molar enamel partially covered with silver. The enamel had been etched for 1.0 minute, then rinsed. Plating sequence [AgF 100gpl, pH 6.5-$FeSO_4$ 50 gpl, pH 3.5] 10 repetitions. Magnification 1000X.

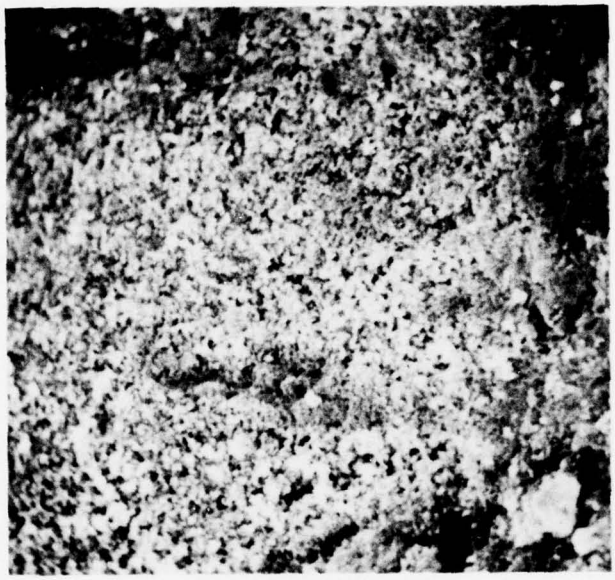

Figure 4. SEM micrograph of a silver metal deposit on human molar enamel. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4, then rinsed. Plating sequence [AgF 100 gpl pH6.5-$FeSO_4$ 150gpl, pH3.5] 10 repetitions. Magnification 1000X.

Figure 5. SEM micrograph of human molar enamel partially covered with silver. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4. Plating sequence [$AgNO_3$ 100gpl, pH4-$FeSO_4$ 300gpl, pH 2] 10 repetitions. The very light areas are nonadherent silver particles. Magnification 1000X.

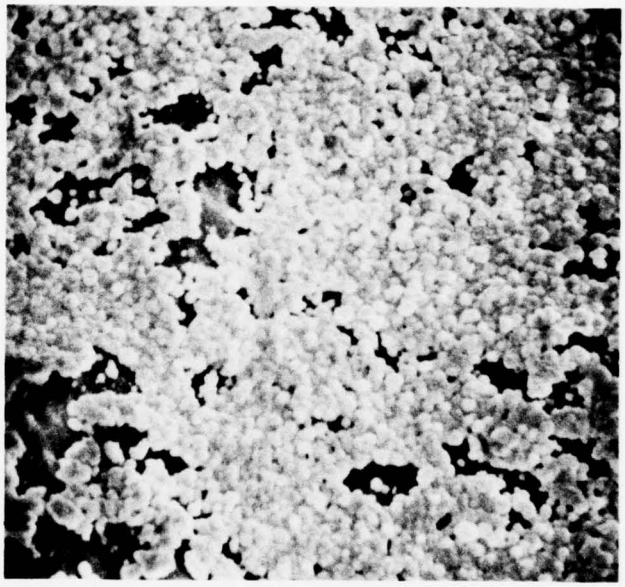

Figure 6. SEM micrograph of human molar enamel partially covered with silver. Conditions for plating were the same as for figure 5, except that the $FeSO_4$ solution pH was 6.5. Magnification 1000X.

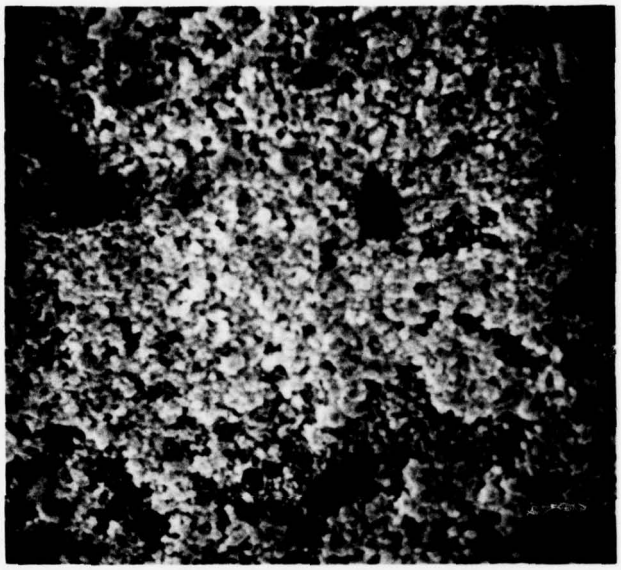

Figure 7. SEM micrograph of a silver metal deposit on human molar enamel. Conditions for plating were the same as for Figure 6, except that the $FeSO_4$ solution also contained 50 gpl NaF. 1 to 20 Ω/cm resistance. Magnification 1000X.

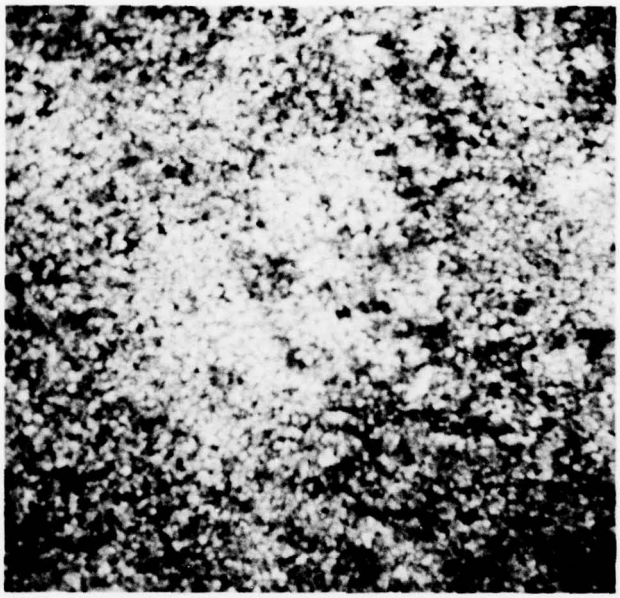

Figure 8. SEM micrograph of a silver metal deposit on human molar enamel. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4, then rinsed. Plating sequence [$AgNO_3$ 100 gpl, pH 4 - $FeSO_4$ 300 gpl, + NaF 50 gpl, + SnF_2 0.1 gpl, pH6.5] 10 repetitions. Very good, shiny deposit, 0.5-1.0Ω/cm resistance. Magnification 1000X.

Figure 9. SEM micrograph of a silver deposit on human molar enamel. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4, then rinsed. Plating sequence [AgF 100gpl, pH 6.5 - $FeSO_4$ saturated solution, pH 2] 10 repetitions. Magnification 1000X.

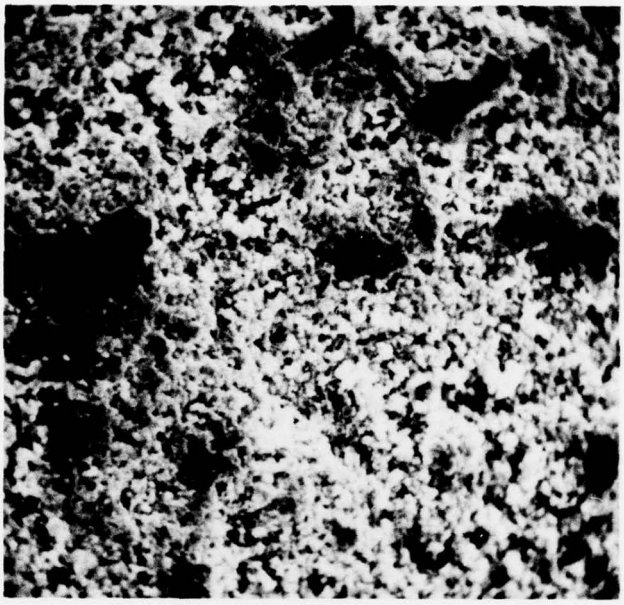

Figure 10. SEM micrograph of a silver deposit on human molar enamel. Conditions were the same as for Figure 9, except that $FeSO_4$ solution pH was 6. Magnification 1000X.

Figures 11 and 12 are of systems with SnF_2 as the addition agent, while Figures 13 through 15 are of systems which have Rochelle Salt as the additive.

G. Transmission Electron Microscopy

Figures 16 and 17 are double replica transmission electron micrographs of human molar enamel surfaces which have received treatments with silver fluoride and ferrous sulfate. Figure 16 shows several dark spheroidal areas which appear to be silver particles pulled from the enamel surface during replication. The particles apparently grow with increasing repetitions, as seen in Figure 17.

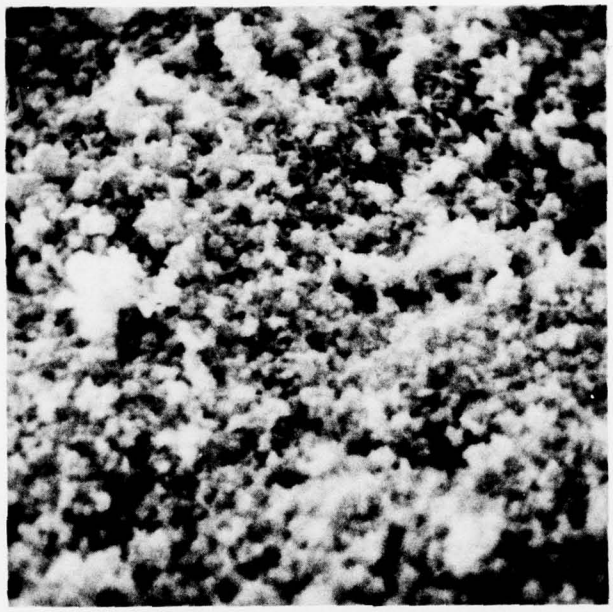

Figure 11. SEM micrograph of a silver metal deposit on human molar enamel. The enamel had been etched for 1.0 minute with 42.5% H_3PO_4, then rinsed. Plating sequence [AgF 100 gpl, pH 6.5 - $FeSO_4$ saturated solution + .1 gpl SnF_2, pH6.] 10 repetitions. Magnification 3000X.

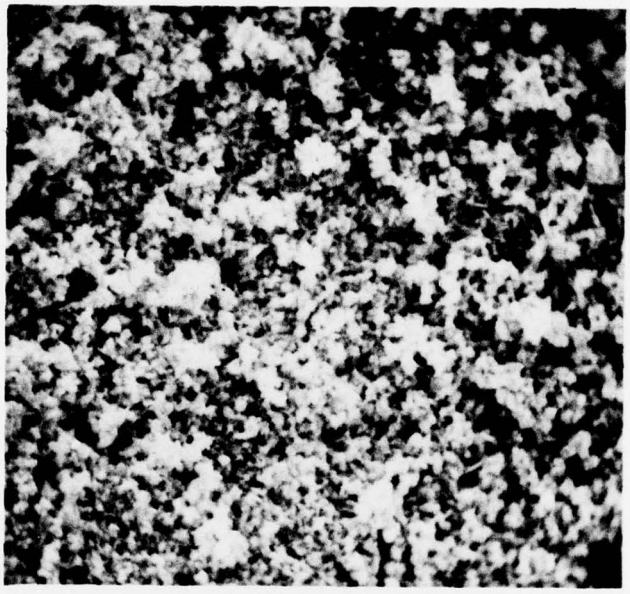

Figure 12. SEM micrograph of a silver metal deposit on human molar enamel. Conditions were the same as for Figure 11, only the SnF_2 concentration was 1.0 gpl. Magnification 1000X.

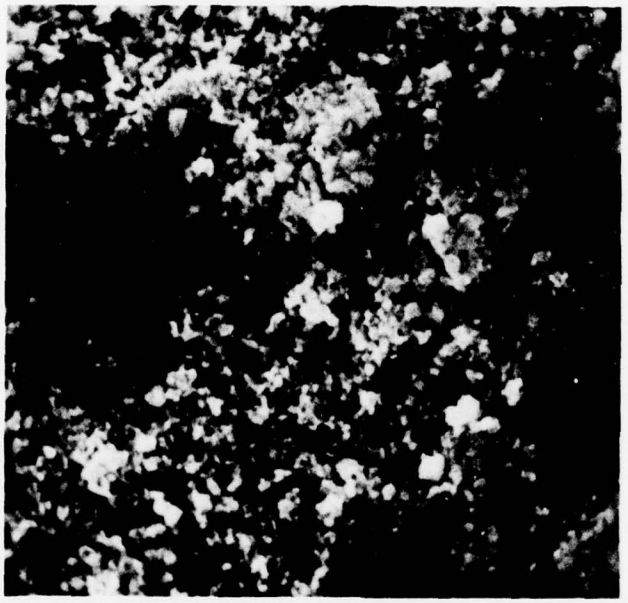

Figure 13. SEM micrograph of a silver metal deposit on human molar enamel.
Plating conditions were the same as for Figure 11, only .1 gpl Rochelle Salt was the additive instead of .1 gpl SnF_2.
Magnification 3000X.

Figure 14. SEM micrograph of a silver metal deposit on human molar enamel. Plating conditions were the same as for Figure 13, only the Rochelle Salt concentration was 1.0 gpl. Magnification 3000X.

Figure 15. SEM micrograph of a silver metal deposit on human molar enamel. Plating conditions were the same as for Figure 13, only the Rochelle Salt concentration was 5.0 gpl. Magnification 3000X.

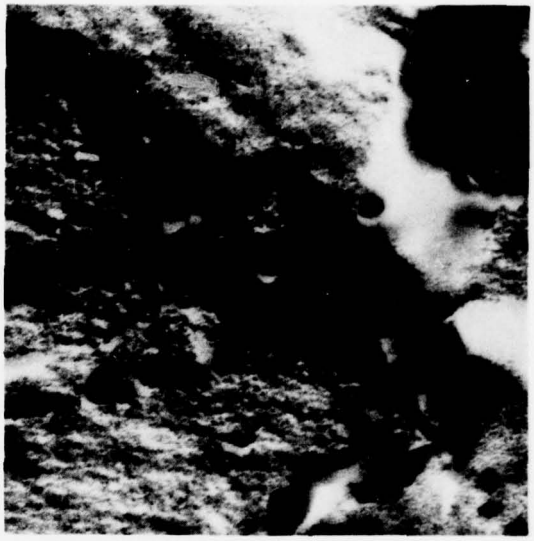

Figure 16. TEM double replica micrograph of human molar enamel which had been etched for 1.0 minute with 10% $HC_2H_3O_2$, then rinsed and given one repetition of an AgF-$FeSO_4$ plating sequence. AgF solution - 100 gpl, pH 6.5. $FeSO_4$ solution - saturated, pH 3.5.
The dark spheroidal areas are believed to be silver particles pulled from the enamel surface during replication. Average particle size was approximately .04 micron. Magnification 67,500X.

Figure 17. TEM double replica micrograph of human molar enamel which had been etched for one minute with 10% $HC_2H_3O_2$, then rinsed and given two repetitions of an AgF-$FeSO_4$ plating sequence. The solutions were the same as those used in Figure 16. The dark spheroidal areas are believed to be silver particles pulled from the enamel surface during replication. Average particle size was approximately .15 micron. Magnification 67,500X.

III. CONCLUSIONS

Definite progress has been made in certain specific areas of the research this year. An alternate system which utilizes solutions of nearly neutral pH, and which uses ferrous sulfate in place of hydrazine, has been developed. This should prove to be a vast improvement in helping to minimize any difficulties with the chemical toxicity of the system. Results of characterization studies on deposits produced by the new system are very encouraging and compare favorably with those made using hydrazine. Good deposits can be formed from both the ferrous sulfate systems and the hydrazine systems. Silver fluoride seemed to work better than silver nitrate with the ferrous sulfate systems, although additions of stannous fluoride and sodium fluoride did help produce better deposits than when no additions were made. Additions of stannous fluoride or Rochelle Salt to silver fluoride-ferrous sulfate systems did not greatly affect the amount of metal deposited, but did affect the deposit resistances. All ferrous sulfate systems produced deposits of lower resistances at a ferrous sulfate solution pH of 6 than at lower pH levels. Both silver fluoride and silver nitrate worked adequately with hydrazine systems. The results to date are quite promising. Technically, the process now appears to be definitely feasible. As always, this does not mean that there are not a few problems

which must be answered. There are areas in which optimization studies can be initiated, to allow for further refinements of the existing system. One of the most promising features of the process is its flexibility. Even though the metal deposition system is complex, the boundary conditions do not seem to be too rigid; thus variations in the chemistry can be attempted without completely nullifying the results. It would appear, therefore, that as specific problems arise or new applications need to be addressed, the system is capable of undergoing alterations which might allow the difficulties to be solved.

Finally, we would like to acknowledge the major contributions of Col. Cutright, Lt. Col's Posey and Woody, and the USAIDR Laboratory staff in this research effort. Their constructive criticism, suggestions, and direct and active assistance has been substantial and is greatly appreciated.

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