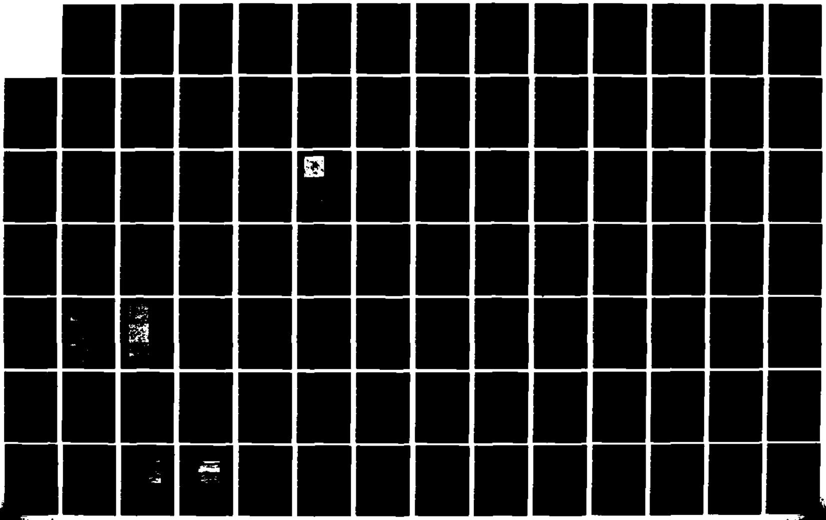
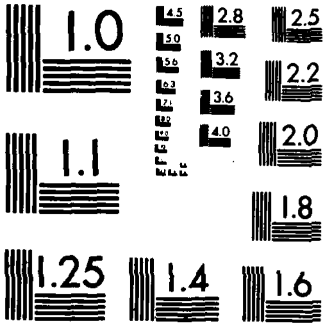
AD-A134 475 FEASIBILITY STUDY ON A PROCESS FOR ELECTROLESS METAL DEPOSITION IN PITS A..(U) MISSOURI UNIV-ROLLA T J O'KEEFE AUG 80 DADA17-73-C-3087 1/2

UNCLASSIFIED F/G 6/5 NL




1.0
4.5
5.0
5.6
6.3
7.1
8.0
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

AD-A134 475

(1)

Report Number 7

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

August 1980

Supported by

U.S. Army Medical Research and Development Command
Fort Detrick, Frederick, Maryland 21701

Contract No. DADA 17-73-C-3087

University of Missouri-Rolla
Rolla, Missouri 65401

83 11 07 047

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A134	3. RECIPIENT'S CATALOG NUMBER 475
4. TITLE (and Subtitle) Feasibility Study on a Process for Electroless Metal Deposition in Pits and Fissures of Teeth for Use in Preventive Dentistry		5. TYPE OF REPORT & PERIOD COVERED Annual Report July 1979 - August 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Thomas J. O'Keefe, Ph.D.		8. CONTRACT OR GRANT NUMBER(s) DADA-17-73-C-3087
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Missouri-Rolla Rolla, MO 65401		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102A 3S161103BS06.00.047
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Medical Research & Development Command Fort Detrick, Federick, MD 21701		12. REPORT DATE August 1980
		13. NUMBER OF PAGES 107 pages
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

electroless
plating
silver
additives
enamel
ivory

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Further studies were undertaken to test the feasibility of using metal films, deposited by electroless or chemical means, for use in the military dental program.

The research effort during the past year was concentrated in the following areas: preparing for and conducting the in vivo tests, testing alternate additives, evaluating the effects of pretreatment on the silver deposit, deposition rate study of metallic Ag on ivory and enamel and application of brush plating to dental materials.

I. INTRODUCTION

Major emphasis during the first quarter was placed on preparation for the in vivo studies conducted at the end of October 1979 at USAIDR, WRAH, Washington, D.C. The objective of the study was to determine the utility of the electroless silver films in reducing decay in caries susceptible rats, and to test the efficacy of the new plating system. These new systems included the use of organic additives (such as thiourea) in the ferrous sulfate reducing solution as well as brush plating an additional silver layer onto the electroless film.

A "Standard Operating Procedure" has been compiled, as it was felt that this was needed to define the methods applied at the various critical points in process. It should also be easier now to obtain a more uniform experimental procedure among the labs using the electroless process.

Much of the research effort was concentrated on improving the ferrous sulfate solution as a reducing agent. It has been found that low concentration additions of thiourea to the $FeSO_4$ produced significantly improved silver deposits. Other organic additives were tried, all of which were non-toxic and had a high complex stability constant with silver ions. This preliminary study gave some very promising results.

The research during the last quarter involved investigations on the initial layer formed during etching and prereduction. It has been found that the silver solution forms silver phosphate when it reacts with hydroxyapatite. The $FeSO_4$ solution does not reduce all the porous Ag_3PO_4 to metallic silver. This porous layer may cause the adherence of amalgam to decrease. Efforts were made to eliminate the formation of Ag_3PO_4, which was possible by using SnF_2 as a pretreatment.

A complete study on the deposition rate of metallic Ag on ivory and enamel is included as an entity in section A. It is planned to publish part of the rate study in the technical literature.

The series of experiments involving brush electroplating were completed and the results are included in this report in thesis form in section B. Part of the brush electroplating study will also be published.

II. IN VIVO STUDY

Solution Preparation:

Demineralized water was used to make up the solutions; however, distilled water could be substituted for demineralized water.

Silver Solutions:

#1: 100 gpl AgF + NH_4OH; (7.8 pH)

Constituents: 10 g AgF + (60 + 5 + 5.5) ml H_2O + (10 + 10 + 9.5) ml of 25 volume percent NH_4OH.

10 g AgF powder was dissolved in 60 ml of dimineralized water initially. The final pH was adjusted to 7.8 by trial and error approach with the addition of 25% NH_4OH in installments. The solution was continuously stirred when the additions were being made. When the pH approached the desired value (and this usually took about 3-4 days, especially for AgF solutions), the final volume adjustment was done by adding the necessary amount of water. AgF powder (98% purity) was supplied by PCR, Inc., P. O. Box 1466, Gainesville, Florida, 32602. All the AgF solutions had some undissolved residue. All the Ag solutions were prepared and stored in amber colored bottles.

#2: 100 gpl AgF + HNO_3; (5.5 pH)

Constitutents: 10 g AgF + (80 + 5 + 4.6) ml H_2O + (5 + 4 + 1.4) ml of 5 M HNO_3.

Procedure similar to that of solution #1.

#3: 100 gpl $AgNO_3$ + HNO_3; (2.2 pH)

Constituents: 10 g $AgNO_3$ + (95 + 5) ml H_2O + (0.10 + 0.05) ml of 5 M HNO_3.

Procedure similar to that of solution #1.

#4: 50 gpl AgF + 300 gpl KSCN + HNO_3; (5.3 pH)

Constituents: 50 ml of 100 gpl AgF + 50 ml of 600 gpl KSCN + (4 + 4 + 2 + 2) drops of 1 M HNO_3.

Procedure similar to that of solution #1.

Reducing Solutions:

These are prepared fresh. They are not used if more than one day old.

#1: 10 ml/l N_2H_4

1 ml of 95% N_2H_4 was dissolved in about 100 ml H_2O.

#2: Sat. $FeSO_4$ + H_2SO_4 + 0.3 gpl thiourea; (pH 2)

A certain amount of demineralized (or distilled) water was taken in a container and its pH was adjusted to about 2 by the addition of a few drops of 50% H_2SO_4. This helps in reducing the air oxidation of Fe^{+2} to Fe^{+3}, and also reduces the time required for saturation. Besides it simplifies the calculations and the procedure for thiourea addition since the volume of the solution increases as more and more $FeSO_4 \cdot 7H_2O$ dissolves due to the water of hydration. To speed up the process of saturation further, the container is kept in a water bath at 25°C. After the initial pH adjustment, $FeSO_4 \cdot 7H_2O$ crystals are added and the solution stirred until it saturates. After saturation the pH is adjusted again if necessary, and stirred again to make sure it remains saturated. From this stock solution a predetermined quantity (say 48.5 ml) of the sat. $FeSO_4$ (pH 2) solution is taken and 1.5 ml of 10 gpl thiourea stock solution is added to give the final solution of sat. $FeSO_4$ + H_2SO_4 + 0.3 gpl thiourea (pH 2).

When the solution is fresh it is green in color and as it ages (or oxidizes) it turns yellow.

#3: Sat. $FeSO_4$ + H_2SO_4 + 1.0 gpl thiourea; (pH 2)

Procedure similar to that of solution #2.

#4: Sat. $FeSO_4$ + NH_4OH; (pH 5.5)

In this case a saturated solution of $FeSO_4$ is prepared in plain demineralized water. The natural pH of this solution is about 3.3. The supernatant solution is transferred to another container and the pH is adjusted by trial and error method with a few drops of 25 volume percent NH_4OH. The solution is stirred when the additions are made. As the additions are being made the solution turns cloudy with some precipitation.

Other Solutions:

#1: 10 gpl thiourea stock solution

10 g of thiourea powder is dissolved in 100 ml demineralized water. If this stock solution is more than a week old, it is not used.

#2: H_3PO_4 etching solution

50 ml of demineralized H_2O and 50 ml of concentrated H_3PO_4 (85 weight percent) were mixed together at room temperature. Solutions were stored in glass bottles with no obvious deleterious effects noted with storage times in excess of one month.

Plating Procedure:

The following procedure was used to plate the rats and the monkeys. A single swab was used to apply the solutions to both the upper quadrants in the case of the rats and to one quadrant in the case of the monkeys.

Etching:

The teeth were etched with 42.5 weight percent H_3PO_4 for 1 minute and washed and dried twice. Washing and drying consisted of washing with a wet swab and blotting with a dry swab. For monkeys an additional squirt of water was used which was removed by the suction pump.

Pre-reduction:

Ag solution was applied for $\sim$30 seconds. It is common for a yellow coloration to appear, possibly due to silver phosphate formation. It was washed and reducing solution was applied for $\sim$30 seconds. It was washed again. The tooth tends to darken at this point, with variations in amount and intensity of darkening that is probably a function of the substrate and plating parameters. This is called the "pre-reduction step". The tooth may appear spotty at this point and is not always completely covered.

For further applications, from 2-10 X, the Ag solution-reducing agent-Ag solution sequence was used, and washing was done after every other application. After the last application the teeth were washed and dried twice. Again an additional water wash was used for monkeys. In general, the tooth should have a metallic appearance over its entire surface after 3 X.

Plating:

Plating was done at Walter Reed Army Hospital, Washington, D.C., on live rats and monkeys.

Rats:

White adult rats, both male and female, were used. Only upper quadrants were plated.

Protocol 1: Date - 10/25/79, 100 gpl AgF + NH_4OH; (7.8 pH) - 10 ml/l N_2H_4, 10X

Technician	Number of Rats Plated
Thomas O'Keefe	1
Ram Narasagoudar	1
Fred Chen	1
Lucy Anderson	1
Total Number of Rats Plated	4

Chesebrough-Ponds cotton swab Q-tips were used to apply the solution. Hydrazine solution was prepared fresh on the same day. Two of the rats died during the night.

Protocol 2: Date - 10/26/79, 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + H_2SO_4 + 0.3 gpl thiourea (2.1 pH), 10X

The reducing solution was prepared from a one day old stock solution of sat. $FeSO_4$ + H_2SO_4 (pH 2.1), but thiourea addition was done on 10/26/79.

Technician	Number of Rats Plated
Thomas O'Keefe	1
Ram Narasagoudar	1
Fred Chen	1
Lucy Anderson	1
Total Number of Rats Plated	4

Nasopharyngeal wool tipped Calgiswabs were used to apply the solutions. Inadvertently, saline solution was used for washing, causing poor plating because of AgCl precipitation.

Protocol 3: Date - 10/26/79, 100 gpl $AgNO_3$ + HNO_3 (2.2 pH) - sat. $FeSO_4$ + H_2SO_4 + 1.0 gpl thiourea (2.1 pH), 10X

The reducing solution was prepared from a one day old stock solution of sat. $FeSO_4$ + H_2SO_4 (pH 2.1), but thiourea addition was done on 10/26/79.

Technician	Number of Rats Plated
Thomas O'Keefe	1
Ram Narasagoudar	1
Fred Chen	1
Lucy Anderson	1
Total Number of Rats Plated	4

Nasopharyngeal wool tipped Calgiswabs were used to apply the solutions. Inadvertently, saline solution instead of distilled water was used for washing, causing poor plating because of AgCl precipitation.

Protocol 4: Date - 10/26/79, 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + NH_4OH (5.5 pH), 10X

$FeSO_4$ solution was prepared fresh on the same day.

Technician	Number of Rats Plated
Ram Narasagoudar	2
Lucy Anderson	2
Total Number of Rats Plated	4

Cotton swabs with wooden sticks were used to apply the solutions.

Protocol 5: Date - 10/26/79, 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + H_2SO_4 + 0.3 gpl thiourea (2.1 pH), 10X

The reducing solution was prepared from a one day old stock solution of sat. $FeSO_4$ + H_2SO_4 (2.1 pH), but the thiourea addition was done on 10/26/79. Calgiswabs had contaminated this solution during plating under protocol 2.

Technician	Number of Rats Plated
Thomas O'Keefe	2
Fred Chen	1
Total Number of Rats Plated	3

Cotton swabs with wooden sticks were used to apply the solutions.

Protocol 6: Date - 10/26/79, 100 gpl $AgNO_3$ + HNO_3 (2.2 pH) - sat. $FeSO_4$ + H_2SO_4 + 1.0 gpl thiourea (2.1 pH), 10X

The reducing solution was prepared from a one day old stock solution of sat. $FeSO_4$ + H_2SO_4 (2.1 pH), but the thiourea addition was made on 10/26/79. Calgiswabs had contaminated this solution during plating under protocol 3.

Technician	Number of Rats Plated	
Thomas O'Keefe	1	
Fred Chen	1	
Lucy Anderson	1	This one was not etched with H_3PO_4. It is tagged with picric acid on the head.
Total Number of Rats Plated	3	

Cotton swabs with wooden sticks were used to apply the solution

Monkeys:

Two monkeys were plated. Four systems were used for plating tl [illegible] r quadrants of each monkey on the basis of one system per quadrant. After all the four quadrants were plated, some selected teeth were brush plated (by Fred Chen) or amalgamated (by Thomas O'Keefe). During brush plating emphasis was given to the occlusal surface. For amalgamation Oralloy disposable capsule was triturated for 20 seconds on a Wig-1-Bug unit. One tooth each from the upper right and upper left were amalgamated in that order from one capsule. Similarly, one tooth each from the lower left and lower right were amalgamated in that order from the second capsule.

Monkey #1: Date - 10/25/79, Female

All the reducing agent solutions were prepared fresh on 10/25/79. Chesebrough-Ponds cotton swab Q-tips were used to apply the solutions.

Quadrant: upper right

Protocol 1: 100 gpl AgF + NH_4OH (7.8 pH) - 10 ml/1 N_2H_4, 10X

Technician: Fred Chen

Good yellow coloration with the application of AgF solution. With pre-reduction the darkening was faster than that of protocol 5.

Second tooth from the back was amalgamated with Oralloy.

Quadrant: upper left

Protocol 5: 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + H_2SO_4 + 0.3 gpl thiourea (2.1 pH), 10X

Technician: Thomas O'Keefe

Good yellow coloration with the application of AgF solution. With pre-reduction the darkening was slower and less than that of protocol 1.

Second tooth from back was amalgamated with Oralloy.

Quadrant: lower right

Protocol 4: 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + NH_4OH (5.5 pH), 10X

Technician: Lucy Anderson

With pre-reduction the darkening was faster than that of protocol 6. Also the plating was less chalky and more metallic than its usual in-vitro appearance.

Second tooth from the back was amalgamated with Oralloy.

Third tooth from the back was brush plated with 50 gpl AgF + 300 gpl KSCN (5.6 pH) at ∿20 mA and ∿1-1.5 V for 5 minutes. The brush plated tooth looked more shiny than that of lower left quadrant (protocol 6).

Quadrant: lower left

Protocol 6: 100 gpl $AgNO_3$ + HNO_3 (2.2 pH) - sat. $FeSO_4$ + H_2SO_4 + 1.0 gpl thiourea (2.1 pH), 10X

Technician: Ram Narasagoudar

With pre-reduction the darkening was slower than that of protocol 4.

Second tooth from the back was amalgamated with Oralloy.

Third tooth from the back was brush plated with 50 gpl AgF + 300 gpl KSCN (5.6 pH) at ∿20 mA and ∿1-2 V for 5 minutes. The brush plated tooth looked less shiny and more chalky than that of lower right quadrant (protocol 4). The fissures appeared to have plated better than the cusps.

Monkey #2: Date - 10/26/79, Male

Cotton swabs with wooden sticks were used to apply the solutions. The protocols were switched (4 and 6 to upper quadrants, 1 and 5 to lower quadrants).

Quadrant: upper right

Protocol 4: 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + NH_4OH (5.5 pH), 10X

The reducing solution was prepared fresh on 10/26/79.

Technician: Ram Narasagoudar

With the application of silver solution there was more yellow coloration than that of upper left quadrant (protocol 6). Although the pre-reduction was spotty, the teeth were darker than those of upper left quadrant (protocol 6) after second application. Looked fairly metallic after 10 X.

Third tooth from the back was brush plated with 50 gpl AgF + 300 gpl KSCN (5.6 pH) at ∿20 mA and ∿1-1.5 V for 5 minutes.

Second tooth from the back was amalgamated with Spheraloy.

Quadrant: upper left

Protocol 6: 100 gpl $AgNO_3$ + HNO_3 (2.2 pH) - sat. $FeSO_4$ + H_2SO_4 + 1.0 gpl thiourea (2.1 pH), 10X

The reducing solution was prepared from a one day old stock solution of sat. $FeSO_4$ + H_2SO_4 (2.1 pH). However, the thiourea addition was made on 10/26/79. Calgiswabs had contaminated this solution.

Technician: Lucy Anderson

Less yellow coloration than that of upper right quadrant (protocol 4). Pre-reduction was spotty. Looked fairly metallic after 10 times.

Third tooth from the back was brush plated with 50 gpl AgF + 300 gpl KSCN (5.6 pH) at ∿20 mA and ∿1-1.5 V for 5 minutes. This tooth appeared more shiny than that in upper right quadrant (protocol 4).

Second tooth from the back was amalgamated with Spheraloy.

Quadrant: lower right

Protocol 1: 100 gpl AgF + NH_4OH (7.8 pH) - 10 ml/l N_2H_4, 10X

The hydrazine reducing solution was one day old.

Technician: Fred Chen

Less yellow coloration than lower left quadrant (protocol 5) on silver solution application. Even though the pre-reduction was spotty, it was more dark than the lower left quadrant and looked more metallic after third application.

Quadrant: lower left

Protocol 5: 100 gpl AgF + HNO_3 (5.5 pH) - sat. $FeSO_4$ + H_2SO_4 + 0.3 gpl thiourea (2.1 pH), 10X

The reducing solution was prepared from a one day old stock solution of sat. $FeSO_4$ + H_2SO_4 (2.1 pH). However, the thiourea addition was made on 10/26/79. Calgiswabs had contaminated this solution.

Technician: Thomas O'Keefe

More yellow coloration than lower right quadrant (protocol 1) with silver solution application. However, it was less than upper right quadrant (protocol 4). Pre-reduction was spotty.

Conclusions

The in vivo monkey and rat metal plating seemed to be satisfactory. The basic objective was to compare the effectiveness of four different plating systems to wear resistance and caries prevention. This was the first time that brush plating had been attempted in vivo. The first attempts (10/25/79) were probably acceptable, but those plated on 10/26/79 were much better and more nearly approached in appearance the in vitro brush plated teeth. The new systems which employ thiourea additions are expected to perform better than the straight $FeSO_4$ reducing solutions. The $AgNO_3$ solution pH used in these tests may not be optimum, and this will be checked further during the next quarter. More work will also be initiated on finding other additives which may enhance the properties of the plated metal deposits.

III. STANDARD OPERATING PROCEDURE

1. Ivory

The ivory was purchased from DELS Ivory Company, 34 County Road, E. Freetown, MA 02717, and stored in glycerin immediately. In preparing samples, the ivory was first sliced perpendicularly to the longitudinal axis into disks with a thickness of about 1 cm. Then the disk was cut perpendicularly to radial direction into pieces with dimensions of about 1 x 1.5 x 0.2 cm. In this way of cutting, the silver plating solution can be applied to the surface which is perpendicular to the ivory tubules and most similar to the orientation of human teeth. A Felker Di-Met Model No. 80-BQ cutting machine produced by Felker Manufacturing Company with Felker diamond blade which has a nominal size 10 x .032 x 1 in. and 1550 operation R.P.M. were used first. Then the cutting tool was changed for a 10-1010 Cut-Off Machine and carbide blade both made by Buehler Ltd. The blade is always lubricated with water during cutting. The ivory must be stored in glycerin to prevent cracking and storing too long in water may cause a surface bacterial growth. Before plating the ivory pieces are treated in the following sequence: ivory from glycerin, wash, $NaHCO_3$ scrub, wash, polish on diamond and then 600 grid sandpaper wheels, demineralized water wash and dry, 42.5% H_3PO_4 etch 1 min, wash (demineralized water) and dry. Demineralized water is always used during treating of ivory because any chloride ion from tap water may form a AgCl precipitate while plating with silver solution.

2. Teeth

Source: Roll Dental Clinic, Fort Leonard Wood, Missouri

Name of contact person

Phone number: 314-368-1171

The teeth are divided into three groups:

- I Good teeth
- II Bad teeth, children's teeth
- III Filled teeth, amalgam and polymer

and stored in glycerin to avoid damage and bacterial growth.

Preparation:

Wash with tap water and brush with saturated $NaHCO_3$ using a toothbrush, wash, rinse with demineralized water at least three times and keep the teeth in demineralized water until use; do not keep the teeth in water for more than 24 hours.

Etching:

Blot dry teeth. Etching agent: 42.5 wt% H_3PO_4, from concentrated 85.5% H_3PO_4 (Fisher Scientific Co., NJ). The etching agent is applied to the tooth or piece of ivory with a cotton swab (Q-tip) for 1 min. During the etching the swab is moved around on the sample. After etching, the tooth is washed thoroughly with demineralized water.

Cold Mounting:

The tooth is first ground and polished on the diamond wheel to yield a flat surface. Astro-met Cold Mount Mold Release, Met-a-test Cold Mount Powder, and Quickmount Liquid Ingredient were ordered from Precision Scientific Company. The release agent was smeared on a glass plate and the inside wall of a section of copper tube which had a diameter of 2.6 cm. Then the tooth and the copper ring were seated on the glass plate in such a way that the tooth is surrounded by the ring but not in the center of the ring. This orientation would give enough room on the resin so that it could be clamped for the pull test. Two parts of cold mount powder to one part of liquid by volume are used for the mix. The powder is poured into the liquid followed by stirring for at least 45 sec. Then the mixed resin is slowly poured over the tooth until the tooth is nearly covered. Usually 30 ml powder and 15 ml liquid would be enough for 6 teeth. Also, the amount of powder needed is a little bit more than recommended by the factory. After the resin has set for at least 30 min it can be polished on the diamond wheel. The crown of the tooth, which was already inlaid in the resin, was polished first to expose dentin, and then the root of the tooth was polished to make the mount about 0.8 cm in height. Finally the dentin side was polished on the 600 grid sandpaper wheel. During polishing, the resin with the tooth was moved slowly in the opposite direction to the rotation of the wheel.

3. Chemicals

Compound		Manufacturer
AgF	(preferred)	PCR Inc., P.O. Box 1466, Gainesville, Florida 32602 Ventron, Alfa Division, 152 Andover St., Danvers, MA 01923
$AgNO_3$ 99.99%		Research Organic/Inorganic Chemical Corp., 11686 Sheldon St., Sun Valley, CA 91352
$FeSO_4 \cdot 7H_2O$		Fisher Scientific Co., Fair Lawn, NJ 07410
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$		Fisher Scientific Co., Fair Lawn, NJ 07410
Thiourea NH_2CSNH_2		Fisher Scientific Co., Fair Lawn, NJ 07410
Urea NH_2CONH_2		Fisher Scientific Co., Fair Lawn, NJ 07410
Phosporic acid H_3PO_4		Fisher Scientific Co., Fair Lawn, NJ 07410
Ammonium Hydroxide NH_4OH		Fisher Scientific Co., Fair Lawn, NJ 07410
Hydrochloric acid HCl		Fisher Scientific Co., Fair Lawn, NJ 07410
Sulfuric acid H_2SO_4		Fisher Scientific Co., Fair Lawn, NJ 07410
Nitric acid HNO_3		Fisher Scientific Co., Fair Lawn, NJ 07410

Compound (continued)	Manufacturer (continued)
Sodium Hydroxide $NaOH$	Fisher Scientific Co., Fair Lawn, NJ 07410
Ag Standard (AAS measurements) 1,000 ppm	Fisher Scientific Co., Fair Lawn, NJ 07410
L-Ascorbic acid C_6H_8O	Aldrich Chemical Co., Inc., Milwaukee, WI
Hydrazin N_2H_4	Eastman Kodak Co., Rochester, NY 14650
Toothpaste	Crest Mint Flavor with Fluoride

4. Solutions

AgF - Solutions have to stand for at least 24 hours for complete dissolution and stabilization of pH. Natural pH 6-8 (using 2 M KF bridge and cathodes #1, calomel). Adjust pH by addition of $NaOH$, NH_4OH, or HNO_3.

Ex. 100 g/l AgF - 25 ml solution

$$\frac{100\text{ g} \times 25\text{ ml}}{1000\text{ ml}} = 2.5\text{ g in 25 ml demineralized } H_2O$$

$AgNO_3$ - Solutions have a natural pH around 4. For pH measurements use 1 M KNO_3 bridge and cathode #1. Adjust pH with HNO_3 or $NaOH$.

N_2H_4 - Solution is prepared from concentrated N_2H_4 to 10 ml/l using demineralized H_2O.

$FeSO_4$ - Change pH of demineralized H_2O to 1.8-2.0 with H_2SO_4, measure pH with combination pH electrode. Add $FeSO_4$ to the water and stir with magnetic stirrer (low to medium speed setting) for 1 hour. Use water bath to keep solution temperature stable. The solution has to be saturated. Check pH and add H_2SO_4 if needed. The saturated $FeSO_4$ solution has to be prepared the same day because of oxidation of ferrous to ferric with time. If 1 g/l thiourea is desired in, for instance, 30 ml solution, mix 27 ml sat. $FeSO_4$ with 3 ml of a 10 g/l thiourea solution.

HNO_3 - for dissolving silver for AA analyses (used for rate studies). 50% of bottle concentrated HNO_3 - 1 part HNO_3 + 1 part demin. H_2O.

H_3PO_4 - for etching. 50% of bottle concentrated H_3PO_4 gives 42.5 wt% H_3PO_4.

5. pH Adjustment

Calibrate pH meter using standard pH solutions in the ambient pH range. The calomel electrode has to be cleaned before it is immersed in a different bridge solution, KNO_3 or KF. For this purpose there is a hole, covered by a rubber ring, and a pressure bottle containing 4 M KCl solution is pushed and pressed until one drop of electrode solution has come out from the tip of the electrode.

If a bridge is used, the tip of the separatory funnel containing the bridge solution has to be immersed in the solution to be measured together with a glass electrode. To avoid damage to the electrode, keep the tip of the separatory funnel below the top of the glass electrode. After every pH measurement, drain some of the bridge solution and throw it away, then rinse the electrode and the tip of the separatory funnel with demineralized water.

If low or high pH is desired, a stronger acid or base can be used for pH adjustment to avoid changes in concentration; otherwise, use a more diluted acid or base.

6. Plating

After etching and thorough rinsing, the tooth or ivory is ready for plating.

No Prereduction:

Apply Ag^+ solution with a cotton swab (a brush can also be used as a substitute for the swab) for 10-15 sec. and then reducing solution ($FeSO_4$ or N_2H_4) for 30 sec. and reapply the Ag^+ solution for 20 sec. Rinse the specimen with demineralized water. Repeat this procedure 10 times, or for the desired number of repetitions.

With Prereduction:

Apply Ag^+ solution with a cotton swab for 1 min. Rinse with demineralized water. Apply reducing solution for 1 min. and rinse. Then repeat 9 times, if not otherwise mentioned, the procedure for no prereduction as described above.

Photoreduction:

No prereduction - apply 4 drops of Ag^+ solution on the specimen and photoreduce 1/2 inch from light source for 1 min, intensity set on medium.

With prereduction - apply Ag^+ solution for 1 min., rinse and photoreduce for 1 min.

After the first reduction step, there are 9 repetitions:

$$9X \left\{ \begin{array}{l} \text{Ag}^+ \text{ solution 10-15 sec} \\ \text{Reducing solution } \sim 30 \text{ sec} \\ \text{Ag}^+ \text{ solution 20-25 sec (same swab as above)} \\ \text{Rinse with demineralized water} \end{array} \right.$$

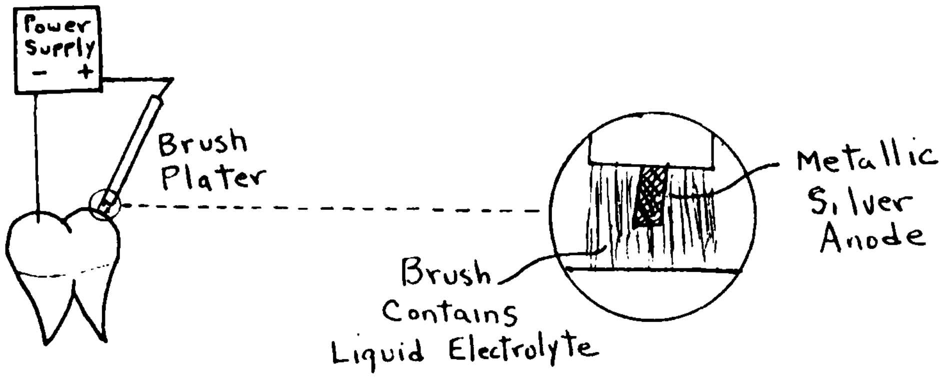
During plating visual observations should be made. Interesting points are:

- formation of Ag_3PO_4, yellow deposit at first Ag^+ application
- darkness after reducing agent is applied
- does the specimen turn metallic and after how many applications
- is the deposit homogeneous
- is the deposit metallic or chalky

Resistance can be measured after 5 and 10X if not otherwise mentioned. Low resistance means a continuous silver deposit, and a 1 ohm resistance or less after 10 repetitions is desirable.

7. Brush Plating

Brush plating is possible only after electroless deposition of a continuous silver film. The experimental arrangement is shown below.



A Sorensen Q Nobatron QRB 40-75 DC power supply with limits of 800 mA and 50 V was used. A 6100 solid state electrometer produced by Keithley Instruments was used as the voltmeter and a Western Instruments, Daystrom Inc., Model 931 as the ammeter (0.01-150 mA reading range). An alligator clip is attached to the ivory and is made the cathode. The brush, which was bought from J.N.T. Mfg. Co. and had silver wire in the center, was used as anode. Continuous brush movement during the plating process is desirable but the wire anode should not touch the ivory. The silver anode area seems important, if a high cathode current density (50 mA/cm^2) and pleasing plated surface are desired. Blackening on the plated surface may be caused by too high a current density or too low a silver concentration in the electrolyte or insufficient electrolyte in the brush.

Several kinds of brush plating solutions have been used. Mostly used is the 50 gpl AgF + 300 gpl KSCN solution (pH 7), which was made up by mixing 5 ml 100 gpl AgF (pH 5 previously adjusted with HNO_3) and 5 ml 600 gpl KSCN (natural pH about 6). NaSCN can be used to substitute for KSCN and behave similarly to it. The maximum AgF concentration in 300 gpl $Na_2S_2O_3$ was a little bit more than 30 gpl. More Ag^+ in the solution would cause precipitation. Commercial SILV-R-COTE solution and pyrophosphate solution [25 gpl $AgNO_3$ + 30 gpl $Na_4P_2O_7 \cdot 10\,H_2O$ + 50 gpl $(NH_4)_2SO_4$ + 50 gpl KNO_2 + 60 gpl 25% NH_4OH (pH 9.4)] did not give better results than KSCN solution did. 45-55 mA/cm^2 is the current density range usually applied, and to obtain such a high current density the modified anode brush must be used. Voltages applied to obtain this current density varied from 0.4 volt to 1.0 volt, depending on the solution used. A low voltage was needed for KSCN solution and a high voltage for $Na_2S_2O_3$ solution and medium for SILV-R-COTE and pyrophosphate solution.

8. Testing

A. Resistance

Resistance is measured using a Keithley 177 Microvolt DMM instrument. Try to keep the electrodes at a constant distance from each other. Make sure the sample surface is dry. As low resistance as possible is desired, because it indicates that the silver layer is continuous.

B. Wear Resistance

A 50 wt% toothpaste solution is made out from Crest and demineralized water. The specimen is put in a sample holder and attached with double-stick tape to a scale, Hanson Dietetic Scale Model 1440. The brush (#11 Abbott Robinson Bristle Brushes) is attached to a variable constant speed motor unit (Tekmar Co., Cincinnati, OH, Model RM18); 200 rpm is used (gear II and 200).

The scale is zeroed with the specimen and then the scale and the specimen is moved upwards against the brush until the scale reads the desired value of applied force for testing (10 or 20 g). Check from two directions perpendicular to each other that the brush touches the specimen on a relatively flat and representative spot. When the alignment is ready, the rotator and a stop watch can be turned on. Check scale reading and adjust if needed. Add toothpaste solution, by eyedropper, to the brush as it becomes depleted. After the brushing is finished, rinse the specimen and brush with demineralized water and blot dry the brush using a paper towel. The wear spots are examined with a microscope and numbers assigned to them indicating the degree of wear (0-10)--ten (10) showing the least wear; completely shiny, metallic silver and (0) showing the most wear; ivory or enamel showing through in nearly all areas of the spot.

C. Procedures for SEM Study

The procedures vary somewhat depending on what may be done to the sample after SEM study.

For instance, if no further treatments are to be performed on the sample, it is then attached to a plug with either silver print or copper print. This procedure applies to ivory pieces and the use of copper print if x-ray analysis is to be performed in addition to pictures of the surface structure (3000X). If the sample is a tooth, it is wrapped in aluminum foil and electrical connections insured with silver print or copper print. The general information obtained from these observations is an idea of the relative amounts of metal coverage and the grain size of the deposit.

If further treatments are desired, such as acid dissolution for a rate study experiment, the amount of copper print is kept to a minimum and carefully removed with acetone prior to additional treatment. The same is also true if a shear or wear test is to be run later. If, however, all the tests are run first, they are generally done in such a manner as to leave enough undisturbed surface for observation. Again the general information obtained is the morphology and relative ideas of coverage. The coverage is determined by x-ray analysis and identification of areas of the substrate showing through (Ca and P). The depth of penetration of the shear test is often determined in the same manner. And in a few cases the wear spots are examined in a similar manner.

D. Rate Studies

The tooth or ivory is covered with electroplater's tape with the exception of a circular area 1/8 or 1/4 inch in diameter. The tape has to be tight to prevent any penetration of solution. The desired plating is then made. The free surface silver is dissolved with 50% of bottle concentration HNO_3, one drop at a time and then it is rinsed with demineralized water. The sample rests in a funnel during dissolution and drains directly into a 100 ml volumetric flask. This collecting flask contains 1.5 ml 50% HNO_3. After all the silver is dissolved the bottles are filled to the mark with 2 ml 50% HNO_3 and demineralized water. The dissolved area is measured, and the solutions are measured by atomic absorption spectrometer (AAS). For the AAS measurements standard Ag solutions are prepared. 1 ml 50% HNO_3 is added with a given amount of 1.000 ppm silver standard in a 50 ml bottle, which then is filled to the mark

12 ppm standard - 600 μl 1.000 ppm silver standard
8 ppm standard - 400 μl 1.000 ppm silver standard
4 ppm standard - 200 μl 1.000 ppm silver standard
2 ppm standard - 100 μl 1.000 ppm silver standard

The range for the rate studies varies from 0.2 ppm to 10 ppm.

E. Shear Stress Tests

The surface to be amalgamated is cleaned with acetone and blown dry with N_2. A piece of masking tape, which had been punched with a 1/8" puncher, is put on the surface making an area of .013 sq in for amalgamation. A cylindrical section of teflon tube, 1/4" in diameter and 0.3 cm high, is used as a mold for amalgamation. The mold is stuck to a section of masking tape, containing a 1/4" circular hole, in such a way that the ring just matches the hole on the tape. Then the mold is put on the test piece and attached with the masking tape which was already on the mold. The 1/8" diameter area should be within the confines of the mold. A pellet of fine cut non-zinc alloy was mixed with a drop of mercury, obtained from an E universal mercury dispenser, on a Caulk Vari-mix II triturator for 10 seconds at medium-2 speed. Then the amalgam is immediately condensed into the teflon mold on the sample with Densco Condensaire plugger which was driven by N_2 at 30 psi. The samples are set and allowed to harden in a water bath for 24 hours kept at 37°C. The shear test is accomplished by placing a looped wire around the teflon mold and applying a force using a Dillon Universal Test Machine. The number of pounds required to failure divided by 0.013 inch square gives the shear stress. The test piece remains fixed in the lower jaws during shearing, and the wire moves upward, applying the shearing stress to the vertically oriented test surface.

F. Procedures for X-ray Diffraction Analysis

Generally, only ivory samples are used due to ease of mounting. The samples are mounted in a clear plastic sheet ∿5 mm thick with a large hole ∿ 2 cm in diameter with scotch tape in such a manner that the surface of the ivory is just flush with the surface of the plastic. The angles start

$\sim$12°-80°. The instrument settings (Siemens) are as follows. The Ge as per instructions. The interpretation of the results is aided by comparison with previous spectra. The general purpose of this procedure is to determine the amount of and type of species present, such as the relative amounts of Ag, $AgPO_4$, Ca, P, $CaPO_4$, or other compounds depending on the materials used in the first steps and prereduction.

IV. ADDITIVE STUDY

Ferrous sulfate reducing solution gives a loose and powdery Ag deposit. The addition of a small amount of thiourea improves the properties of the silver layer. Thiourea has a high complex stability constant ($\beta = 9.4$) with silver ions. It is believed that this organic compound forms a complex with Ag^+ ions, thus decreasing the amount of easily reduced Ag^+ in the solution. More Ag adheres to the sample surface, indicating that nucleation takes place there. The grain size is decreased, resulting in a denser deposit. There are many other non-toxic organic compounds with a high β-value for Ag^+. More than thirty compounds were tried as additives in the saturated ferrous sulfate solution. The additive concentration was 1 gpl, which was chosen after evaluating screening tests where the range 0.1 to 10.0 gpl was tried. The concentration of the $AgNO_3$ solution was 200 gpl and the pH ranged from 2.7 to 4.0. The deposits with additives were evaluated for wear resistance and conductivity, as well as from the physical appearance of the silver deposits.

Some of the most promising additives are listed in Table 1. Usually the organic compounds containing sulfur give a more metallic looking silver deposit. The most promising additive was cysteine, an amino acid, that formed a homogeneous and dense deposit; see Figure 1a. The silver layer became metallic after only a few repetitions and from the low electrical resistance at 5X; see Table 2. One can see that the deposit is continuous. The build-up of silver between 5X and 10X is slow. The wear resistance is almost the same as for thiourea, but the pH and concentration of the solutions have not been optimized for cysteine.

Another promising additive is methionine; Figure 1b. This amino acid gives a poor initial reduction (see the high electrical resistance at 5X in Table 2), but the build-up of silver between 5X and 10X is better than for cysteine. The deposit is similar to thiourea (Figure 1c) in physical appearance, but it does not have as much metallic luster as when cysteine is used. The limitations of cysteine and methionine as additives in the ferrous sulfate solution should be overcome as soon as the plating conditions are optimized. Without optimization the additives give a denser deposit than when no additive is used; see Figure 1d.

TABLE 1

Additive	Chemical Composition	Stability Constant	
Cysteine	$C_3H_7O_2NS$	$K_1(Cu^{2+})$	19.2
Methionine	$C_5H_{11}O_2NS$	$\beta_2(Ag^+)$	9.62
Cystine	$C_6H_{12}O_4N_2S_2$		
Proline	$C_5H_9O_2N$	$\beta_2(Ag^+)$	16.8
Glutamic acid	$C_5H_9O_4N$	$\beta_2(Cu^{2+})$	14.8
Thiourea	CH_4N_2S	$\beta_2(Ag^+)$	9.4

$\beta_2 = K_1 + K_2$

$K_1 \quad Ag^+ + L \rightleftharpoons Ag^+L$

$K_2 \quad Ag^+L + L \rightleftharpoons Ag^+L_2$

L = ligand

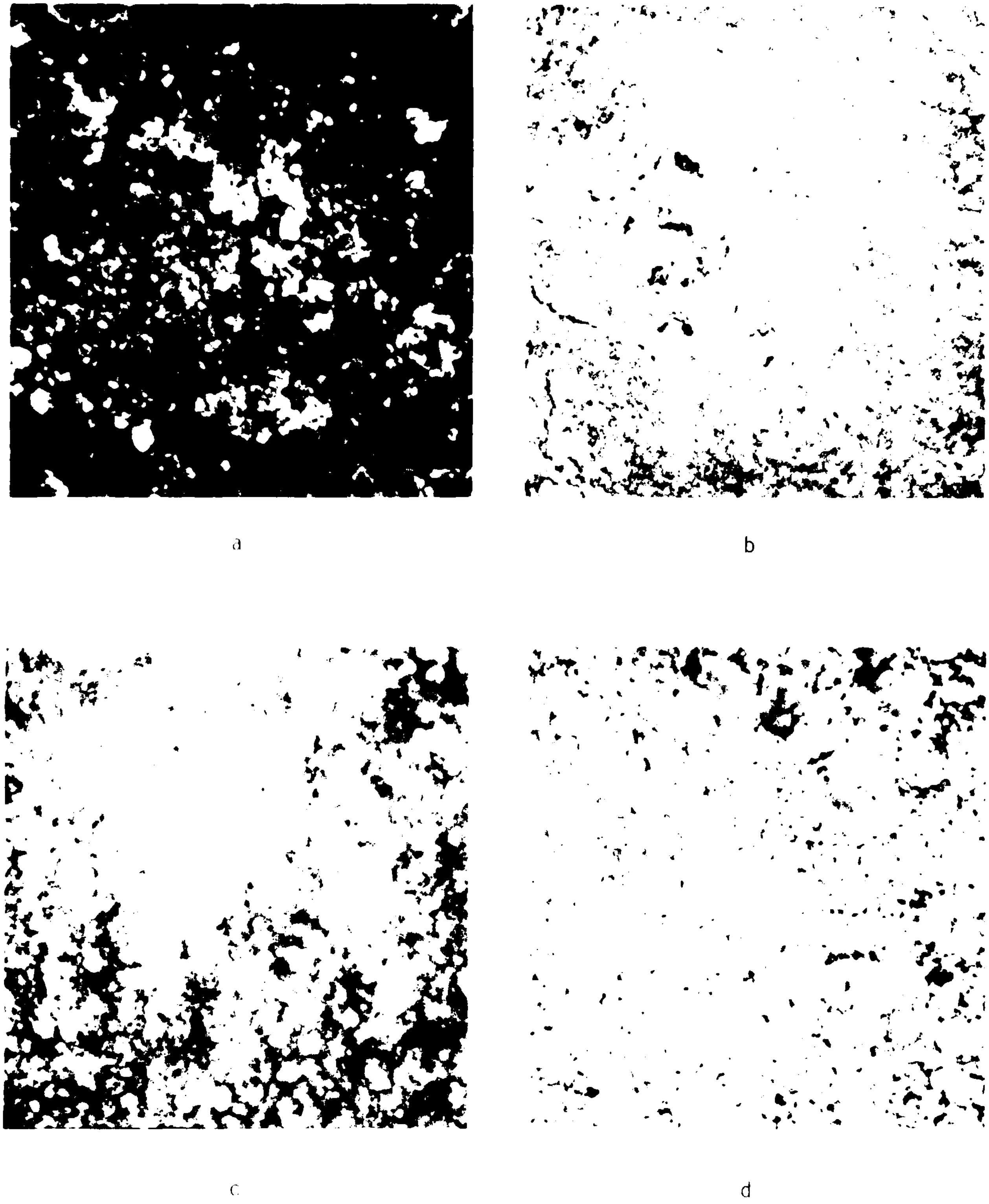
TABLE 2

Additive	Electrical Resistance (Ω)* 5X	10X	Wear Resistance* 2 min/10 g
Cysteine	3.1	0.88	5.5 ± 3.5
Methionine	100×10^3	1.02	4.0 ± 3.4
Thiourea	12	0.78	5.3 ± 3.9

Plating solutions: 200 gpl $AgNO_3$, saturated $FeSO_4 \cdot 7H_2O$ + 1 gpl additive. Tests were made on ivory.

*Average electrical resistance and wear resistance from 10-12 samples.

Concentrations and pH's are not optimized for cysteine and methionine.



a

b

c

d

Figure 1. Micrographs of ivory treated as follows: 1 min. 42.5 H_3PO_4, 1 min. 200 gpl $AgNO_3$, 1 min. saturated $FeSO_4$ + 1 gpl additive. 9 x $AgNO_3$ - $FeSO_4$ + additive - $AgNO_3$. The additives were: a. cysteine, b. methionine, c. thiourea, and d. no additive. Magnification 3000x.

V. PRETREATMENT

Silver phosphate is formed when a silver solution reacts with hydroxyapatite. The Ag_3PO_4 is not completely reduced by $FeSO_4$, and a powdery layer remains between the hydroxyapatite and the silver layer. The intermediate layer of high Ag and P contents seems discontinuous and weak with regard to adherence of amalgam, which is not desirable. It is possible to avoid formation of Ag_3PO_4 by treating the etched substrate (ivory or enamel) with SnF_2 prior to applying the Ag solution. Tin fluoride reacts with organic material to form a tenacious layer (ref. 1), which prevents diffusion. This chemical has also been used in topical fluoride solutions applied to prevent caries. The use of SnF_2, and similar chemical compounds, in the plating process appears to offer some very attractive improvements to the original process, and its use will be investigated to a greater extent in the future.

A. Materials and Methods

Tin fluoride solutions are prepared by dissolving SnF_2 in demineralized water at concentrations of 1, 5, 5.7, and 10%. The pH ranges from 2.7 to 4.0; the natural pH, depending on concentration, varies from 2.7 to 3.2, the lower the concentration the higher the pH. Tin fluoride solutions are unstable and need to be prepared the same day as they are used.

The substrate was first etched with 42.5% H_3PO_4 for one minute and then the SnF_2 solution was applied with a cotton swab for three minutes. Silver nitrate was applied to the substrate for one minute and then the $FeSO_4$ solution for one minute, followed by 9 repetitions of silver nitrate-ferrous sulfate-silver nitrate sequence. The sample was thoroughly rinsed between the applications.

A $PdCl_2$-$SnCl_2$ solution was also tried as a pretreatment. This solution reduced the Ag^+, but a white precipitate was formed, which was believed to be AgCl. More testing is needed to properly evaluate this system.

B. Results of SnF_2 Pretreatment

The properties of the SnF_2 pretreated silver deposits were compared to non-pretreated deposits. The results indicated that the amalgam adherence was significantly improved and an increase in wear resistance was observed; see Table 3. SEM studies showed that the porous Ag_3PO_4 layer was eliminated. The different layers recognized were ivory with traces of tin and silver and an intermediate layer with silver, tin, and ivory, and at the surface pure silver. Very little or no Ag or Sn was found in the x-ray diffraction pattern after the etched ivory samples had been treated with SnF_2 and $AgNO_3$, maybe because of a too thick amorphous layer. When SnF_2 solution was mixed with $AgNO_3$ solution a black precipitate was formed. The powder pattern was made on a Debye-Scherrer x-ray camera, and a typical pattern for reduced silver was obtained. Pure SnF_2 solution did not perform satisfactorily as a reducing agent by itself, because the silver deposit had a very low conductivity and contained tin.

The results described above seem very promising. Further investigations are needed in order to optimize concentration, pH, and residence time.

TABLE 3

Pretreatment	No. of Samples	Shear Stress (psi)	No. of Samples	Wear Resistance 2 min/10 g
3 min SnF_2	80	714	11	6
no	45	456	9	4

Ivory samples were etched 1 min. with 42.5% H_3PO_4

-- 1%-10% SnF_2 solution

-- 200 gpl $AgNO_3$ pH 2.8

-- saturated $FeSO_4$ with or without 1 gpl thiourea

REFERENCES

1. P. Gron, "Chemistry of Topical Fluorides", Caries Res. 11 (Suppl. 1): 172-204 (1977).

SECTION A

DEPOSITION RATE OF METALLIC Ag ON IVORY AND ENAMEL

THOMAS J. O'KEEFE
Graduate Center for Materials Research
University of Missouri-Rolla
Rolla, MO 65401

RAMAGOUDA A. NARASAGOUDAR
30 Gould Center
Gould Inc.
Rolling Meadows, IL 60008

LUCILLE ANNE ANDERSON
44 Markham Road
Princeton, NJ 08540

This investigation was supported in part by DADA Contract 17-73C-3087 from the U. S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD 21701.

The influence of various process parameters on the chemical deposition of Ag on ivory and enamel was investigated. Both $AgNO_3$ and AgF were used with various chemical reducing agents at temperatures from 7°C to 37°C. Evaluation of the amount of adherent silver as a function of these variables was made.

I. INTRODUCTION

The desirability of having a material which can be bonded to tooth structure to function as an adhesive intermediate or as a barrier to further reaction has long been recognized.[1,2] With this objective in mind, research studies have lead to the development of a technique[3] whereby metals such as silver can be chemically deposited on teeth.[4] The majority of the work has been in vitro, but animal experiments have also been conducted.[5] The results of the work to date indicate distinct possibilities for the use of such metal films in the field of dentistry. Of course, substantial development work and testing are still required before the use of such metal films becomes a reality, but the basic technology involved in using the process has been verified. The bulk of the research has been done in conjunction with the U.S. Army Medical Research and Development Command and some of the facts that have been established are (1) this system of metallizing teeth is feasible, (2) the metal coating is firmly adherent for a period in excess of 6 months, and (3) amalgam will interact with the metallized surface.

In evaluating the behavior of the deposited metal films there are a number of factors which appear to be important. The amount of metal or rate of adherent metal deposited, the morphology and grain size of the metal film, and the chemical system used for deposition are examples of parameters which have been used for preliminary screening. Initial research was conducted using hydrazine, which performed satisfactorily as the reductant, but it was felt that a less harsh reagent would be desirable for clinical use. This study was instigated as part of the program to find suitable alternatives to hydrazine. The rate of deposition is critical to the total time required for placement of an acceptable metal layer. The durability of the metal film is not only a function of its thickness, thus comparisons among various chemical systems can't be made on the basis of the amount of silver alone. When the deposit is very loose, nodular, and porous, the wear resistance and adherence of amalgam are lower, even if the silver layer is relatively thick. The objective of this research was to determine the amount of adherent silver remaining on ivory or enamel after applying 10 repetitions of the plating solutions using different reducing agents, and to evaluate the morphology of the resultant deposit.

II. MATERIALS AND METHODS

Ivory was used in most of the tests (since it is similar in some respects to the human tooth material) because a large number of flat samples could be obtained from the same piece, thus minimizing substrate effects. Previous tests have shown that screening experiments could be conducted using ivory since comparable results were obtained when tooth enamel (in vitro) was used. However, extracted human teeth were also used for silver deposition on enamel in some tests. The ivory samples (∿1.5 cm^2 in area and ∿3 mm thick) were cut in such a way that the surface to be plated was perpendicular to the radial direction of the tusk. The cut ivory samples and the extracted teeth were stored in glycerin until ready for plating.

All the solutions were prepared from reagent grade materials. Demineralized water was used for making the solutions and for washing the samples. The source of silver was either 1 M AgF (pH ∿6.7) or 1 M $AgNO_3$ (pH ∿4), and the reducing solutions were 10 ml/l hydrazine (pH ∿9), 150 g/l ascorbic acid (pH $\sim$2), or saturated ferrous sulfate with or without 0.20 g/l proprietary organic (pH $\sim$2, adjusted with dilute H_2SO_4). The iron solutions were prepared by saturating water or a solution containing 0.25 g/l proprietary organic (as the case may be) with $FeSO_4 \cdot 7H_2O$ and then adjusting the pH of the supernatant solution. All the reducing agents were prepared fresh and were not used if more than 8 hours old.

The samples were prepared for plating by washing with tap water, scrubbing the surface to be plated with a $NaHCO_3$ soaked denture brush, washing with tap water, (wet polishing only ivory on 70 micron diamond disc and 600 grit emery paper with tap water), etching with 42.5 wt % H_3PO_4 for 1 minute, washing with water and blotting dry with paper. The entire sample surface, except the area to be plated, was masked by using electroplater's tape which contained a hole of 1/8", 3/16", or 1/4" punched diameter. Cotton swabs soaked in the respective solutions were used for applying the plating solutions. One application or repetition consisted of applying the silver solution (swab 1) for $\sim$5 seconds, then applying the reducing solution (swab 2) for $\sim$5 seconds, waiting for $\sim$30 seconds without disturbing the surface, reapplying silver solution from swab 1 for $\sim$5 seconds, and washing the surface with water. This procedure was repeated to give the desired number of repetitions, which was ten for these experiments.

Representative samples were used for SEM morphological studies. After removing the tape these and the rest of the deposits were dissolved in only a few drops of 50 vol % HNO_3 for atomic absorption analysis. An additional amount of HNO_3 was added to the diluted solutions so that they contained 1 vol % HNO_3.

For temperatures other than 25°C a water bath was employed where all the containers of solution, including wash water, were immersed in the bath. The teeth were also kept in water at the test temperature. A deep tray was used without any water in it to place samples during plating.

III. RESULTS

1. Rates of Deposition

The average rates and standard deviations of adherent silver deposited for a total of 10 repetitions are given in Table I. The parameters investigated were (a) type of silver salt, (b) reducing agents, (c) addition agents, and (d) temperature. The bulk of the testing was performed on ivory, but enamel was also used at ambient temperatures for comparison. The number of samples varied from 2 to 5 for any given test condition.

With $AgNO_3$, the average amount (rate) of adherent silver was higher than that obtained from AgF in all the tests on an ivory substrate. A similar trend was also observed at 25°C on human tooth enamel, except with the ascorbic acid reducing agent, where the rate decreased considerably. With the addition of 1 M $KF \cdot 2H_2O$ to 1 M $AgNO_3$ the rates of deposition on ivory decreased and approached those obtained from 1 M AgF.

The addition of the proprietary additive to the sat. $FeSO_4$ increased the rate of deposition on both ivory and enamel. In general, on ivory, the rates obtained with ascorbic acid or hydrazine were higher than those for $FeSO_4$. Also, the rates obtained on enamel were usually lower than those on ivory. When AgF was used, the rates of deposition on ivory increased with increasing temperature. A plot of log (adherent silver deposited) vs 1/T is shown in Figure 1 when AgF solutions were used. There was no systematic trend in reaction rates in the case of $AgNO_3$ solutions, either with or without KF additions.

TABLE I

Average Rate of Silver Deposited (in mg/cm^2 on a 1/8" Circle Area) on Ivory and Human Tooth Enamel for Various Systems as a Function of Temperature After 10 Repetitions[a]

Silver Solution	Reducing Solution	7°C	16°C	25°C	25°C	37°C
		Ivory	Ivory	Ivory	Tooth Enamel	Ivory
1 M AgF (6.7 pH)	Sat. $FeSO_4$ (2 pH)	1.61 (0.22)	2.02 (0.11)	2.06 (0.39)	1.38 (0.08)	2.52 (0.06)
	Sat. $FeSO_4$ + 0.2 g/l proprietary additive (2 pH)	2.22 (0.22)	2.81 (0.38)	2.76 (0.60)	1.60 (0.15)	2.99 (0.58)
	10 ml/l hydrazine	2.23 (0.06)	3.24 (0.43)	3.55 (0.22)	1.25 (0.21)	4.14 (0.74)
	150 g/l ascorbic acid	3.10 (0.34)	3.99 (0.35)	4.52 (0.39)	2.42 (0.54)	5.01 (0.25)
1 M $AgNO_3$ (4 pH)	Sat. $FeSO_4$ (2 pH)	2.43 (0.62)		3.27 (0.69)	3.25 (1.20)	2.89 (0.34)
	Sat. $FeSO_4$ + 0.2 g/l proprietary additive (2 pH)	3.02 (0.55)		5.69 (0.80)	5.87 (1.22)	4.20 (0.54)
	10 ml/l hydrazine	2.59 (0.20)		4.09 (0.40)	1.76 (0.57)	5.53 (0.08)
	150 g/l ascorbic acid	5.96 (0.50)		5.81 (0.35)	0.39 (0.11)	5.84 (0.33)

TABLE I (Continued)

Silver Solution	Reducing Solution	7°C Ivory	16°C Ivory	25°C Ivory	25°C Tooth Enamel	37°C Ivory
1 M $AgNO_3$ + 1 M $KF \cdot 2H_2O$ (6.4 pH)	Sat. $FeSO_4$ (2 pH)	1.75 (0.31)		1.63 (0.22)		1.68 (0.50)
	Sat. $FeSO_4$ + 0.2 g/l proprietary additive (2 pH)	2.98 (0.48)		2.74 (0.47)		2.74 (0.11)
	10 ml/l hydrazine	2.14 (0.04)		3.89 (0.91)		3.77 (0.77)
	150 g/l ascorbic acid	2.92 (0.06)		4.01 (0.23)		4.38 (0.12)

---

a. The standard deviation is given in the parentheses.

2. Morphologies

The morphologies of the silver deposits on both ivory and enamel substrates are shown in Figures 2-9. Figure 2 gives a macroscopic view of three typical deposits, each with a diameter of 1/8 inch. The top deposit, obtained with hydrazine, is shiny and metallic in appearance. The one in the center, obtained from $FeSO_4$, is chalky but a dark grey matte finish is produced when the additive is present in the $FeSO_4$ solution, as shown by the bottom deposit. The effects of reducing agents and the additive on the morphology of the Ag deposit on enamel are shown in Figures 3, 4, and 5. The hydrazine reduced deposit is smooth, dense, and continuous which is highly desirable. A similar deposit is obtained when AgF is used instead of $AgNO_3$. The use of $FeSO_4$ as the reductant with AgF or $AgNO_3$ gives a deposit which is granular and discontinuous, as shown in Figure 4. However, with the use of 0.2 gpl proprietary additive in the $FeSO_4$, the grain size of the deposit made from AgF solutions is reduced and becomes more dense and continuous (see Figure 5), approaching that of the hydrazine deposit. A similar reduction in grain size and increase in density was not obtained with the $AgNO_3$ source and an additive concentration of 0.2 gpl. However, there are indications that a higher concentration of additive would assist in reducing the crystallite size. Ascorbic acid gives a deposit which has a relatively large grain size and an open structure similar to that shown in Figure 4.

The anion effect on the morphology of the deposits on the ivory substrate is shown in Figures 6, 7, and 8, using $FeSO_4$ + additive as the reductant. The deposit obtained with AgF has a small grain size with areas that are fairly dense and continuous (Figure 6). However, with $AgNO_3$ solutions the grain size is relatively large and the structure appears to be less dense (Figure 7). With the addition of KF to $AgNO_3$ the structure of the deposit appears to revert back to that produced by AgF (Figure 8). The degree to which this change occurs might depend on the relative concentration of KF.

3. Technique of Application

The technique of application has a significant influence on both the morphology and rate of deposition, particularly when $FeSO_4$ is the reducing agent. The two parameters studied with regard to the technique were relative application pressure (light versus heavy) and method of application (continuous contact with the swab versus no contact with the swab, during reduction). If the swabs are moved continuously and with heavy pressure over the surface during deposition, the film appears to rub off and become spotty, exposing the underlying substrate.

The dispersive x-ray analyses showed the white areas to be silver and the dark areas to be Ca, P, and traces of Ag. Some pores or canals can be seen exposed on the surface. The porous, large grained structure obtained when the swab is not contacted with the surface during plating is modified into a fine grained, dense, and discontinuous structure with increased rubbing pressure and agitation by the swab. This tendency to spall and produce a spotty deposit decreases with the use of the additive in $FeSO_4$. When a constant application pressure is used, the level of solution agitation might also be expected to alter the morphology and rate to some degree.

IV. DISCUSSION

If chemically deposited metals are to find application in dentistry it is imperative that certain criteria be met. The properties of the metal film should approach those of the bulk silver and the chemical system must be stable and non-toxic and capable of producing consistent, reproducible, and serviceable deposits. There are certain parameters that are known to be important in characterizing and evaluating metals[6] produced by deposition processes, because it has often been shown that these are good indicators of the results that will be obtained during use. All testing to date, both in vitro and in vivo, reveals that those properties of most interest are strongly structure sensitive.[7] Any factor which can alter structure will play a role in determining the final nature of the metal film. Thus a basic understanding of such features as grain size, continuity, density, conductivity, and thickness of the metal, and the factors which influence them, is very desirable.

The ionic nature of the solutions from which deposition occurs strongly affects the metal structure, with the level of complex ion formation being one of the dominating factors. The Ag^+ ions are in equilibrium with $AgF_{(aq)}$ or $AgNO_{3(aq)}$ in their respective solutions with the stability constants[8] for the respective reactions being

$$Ag^+_{(aq)} + F^-_{(aq)} = AgF_{(aq)}$$

$$K_{298} = \frac{a_{AgF}}{a_{Ag^+} \cdot a_{F^-}} = 2.5$$

and

$$Ag^+_{(aq)} + NO_{3(aq)}^- = AgNO_{3(aq)}$$

$$K_{298} = \frac{a_{AgNO_3}}{a_{Ag^+} \cdot a_{NO_3^-}} = 0.63$$

These values indicate that in AgF solutions the complexed form of silver, viz. $AgF_{(aq)}$, is predominant whereas Ag^+ is predominant in $AgNO_3$ solutions. Also from potential-pH diagrams for Ag-F-H_2O and Ag-H_2O systems it was clear that $AgF_{(aq)}$ and $Ag^+_{(aq)}$ were the stable species respectively in the region of interest at unit activity. Some potential measurements made on the solutions tended to verify that the a_{Ag^+} in 1 M AgF solutions was about half of that in 1 M $AgNO_3$. From Figures 6 and 7 it can be seen that a smaller grain size deposit is obtained with AgF than with $AgNO_3$. However, the $AgNO_3$ solution can be altered to produce a smaller grain size with the addition of KF as shown in Figure 8. It appears that complexing the silver ion produces a reduction in grain size.

In the case of hydrazine as a reducing agent it has been reported[9] that N_2 gas is liberated as follows:

$$N_2H_5^+ = N_2 + 5H^+ + 4e$$

The N_2 evolution helps in stirring the solutions, consequently reducing the diffusion boundary layer, δ. Another important side reaction with N_2H_4 is[9]

$$3N_2H_4 = N_2 + 4NH_3 \qquad \Delta G° = -117.0 \text{ kcal}$$

The ammonia produced in this manner can readily complex with Ag^+ by

$$Ag^+_{(aq)} + NH_{3(aq)} = AgNH^+_{3(aq)}$$

$$K_{298} = \frac{a_{AgNH_3^+}}{a_{Ag^+} \cdot a_{NH_3}} = 10^{3.31} = 2.04 \times 10^3$$

and

$$Ag^+ + 2NH_3 = Ag(NH_3)^+_{2(aq)}$$

$$K_{298} = \frac{a_{Ag(NH_3)_2^+}}{a_{Ag^+} \cdot a^2_{NH_3}} = 10^{7.22} = 1.66 \times 10^7$$

Thus the formation of a strong ammonia complex and the agitation by N_2 probably leads to a very fine grain size deposit which is a characteristic of hydrazine deposits, as shown in Figure 3.

The 10 ml/l N_2H_4 had a pH of about 9.0. Higher concentration of N_2H_4, having a pH of more than 9, was not used since it would be too severe for the oral environment and the risk of toxicity would increase. The $FeSO_4$ solutions at pH 2 were quite stable with respect to self oxidation. However, as the pH increased they were less stable with a visual indication of change in color from green to yellowish brown. Also, as the pH increases, the possibility of iron hydroxide precipitation increases.

Although Ag_2SO_4 is sparingly soluble in water it does not seem to precipitate when Ag and Fe solutions are mixed, probably because of the following reasons:

(1) The solubility of Ag_2SO_4 increases with decreasing pH;

(2) the concentration of ionic Ag is low due to reduction by Fe^{+2}; and

(3) Ag^+ can be complexed[9] according to

$$Ag^+_{(aq)} + SO_4^={}_{(aq)} = AgSO_4^-{}_{(aq)}$$

$$K = \frac{a_{AgSO_4^=}}{a_{Ag^+} \cdot a_{SO_4^=}} = 20.0$$

The present study has dealt with only the adherent metal on the substrate. Most of the adherent silver is probably deposited by electroless reduction and this amounts to about 0.3 to 2% of the total available silver from the solution. There does seem to be a definite catalytic effect of the silver in influencing the deposition process. It must be recognized that the rate for total silver reduced will be orders of magnitude higher than the values reported. There is always a substantial amount of silver visually present on the applicator swabs, but this is not involved in the tooth plating to any extent.

When addition agents are used higher rates and smaller grain sizes result. Probably the additive adsorbs on the surface and increases the polarization for deposition. The mechanism involved is probably similar to that for normal electrodeposition reactions where a suitable additive will cause an increase in nucleation and a decrease in grain growth.

The ivory has a higher organic content than enamel and it is also more permeable to the solutions. The former may account for the difference in deposit morphologies noted, while the latter may partially explain the higher observed rates. If solution can penetrate into the substrate more easily, then additional sites might be produced for silver reduction below the actual surface. This condition might also increase the catalytic activity of the surface, by providing more metal nuclei to serve as centers for cation adsorption and reduction.

Since the time of reaction was identical in all the tests, the amounts of adherent silver deposited can be compared directly for the various parameters under investigation. The total amount of silver reduced during the experiment would greatly exceed the quantity that remained in the deposited film however. It was estimated that less than two percent of the available silver is present as the surface coating. Therefore, the plot of log (adherent silver) vs 1/T is not truly an Arrhenius type plot in that it does not signify the actual rate of silver reduced. The apparent activation energies calculated between 16 and 37°C from this plot are less than 2 kcal/mole which suggests that the plating process might be diffusion controlled. The qualifications mentioned previously would certainly limit the level of confidence that could be placed in alluding to such a mechanism.

The rates obtained at 7°C do not fall on the same straight line as the 16, 25, and 37°C values. At 16°C there appears to be a change in slope. This might indicate a different mechanism for the silver reduction step or could also be caused by changes in the solution chemistry at the lower temperatures.

An evaluation of the rate studies and the morphologies of the silver produced were helpful in indicating the parameters of importance for the plating of teeth. The reducing agent concentrations used were assumed to be nearly optimum, except for the hydrazine. It is possible that increased rates may be obtained by increasing the hydrazine concentration. However, reasonable rates were obtained at the levels used, and increasing the concentration caused a higher pH and increased the toxicity of the system. Additional tests are needed to establish the effect of solution pH on the rate and morphology of the silver film. Rough screening evaluations were made prior to selecting the conditions for this study, but the values may not be optimum. The organic additive appeared to yield a denser, more homogeneous deposit and more research in this area seems merited.

The overall process for chemically plating teeth is relatively simple, but the mechanism of deposition appears to be rather complex. The system is very sensitive to the solution chemistry and deposition parameters employed and in many respects the behavior is similar to that observed in normal electroplating practice. There is much to be learned about the basics involved in the process, but the system seems to offer some interesting possibilities as an intermediate substrate material on teeth.

CONCLUSIONS

The amount of adherent silver that is chemically deposited on ivory or enamel is affected by the reducing agent employed in the process. $AgNO_3$ salts yield thicker deposits than AgF when their natural pH's (4 and 6.7 respectively) are used, but the addition of fluoride ion to the $AgNO_3$ solution reduces the Ag film thickness, indicating an influence of anion complexing. The Ag deposit morphology is also affected by the reducing agent used, with hydrazine giving the most metallic appearing surface. $FeSO_4$ gives satisfactory deposits, but the use of organic additives enhances their appearance. In general, the metal deposition process has been shown to be sensitive to the chemical parameters used in producing the Ag film.

FIGURE CAPTIONS

Figure 1. Effect of temperature on the quantity of adherent silver deposited after 10 repetitions of the plating sequence.

o-o 150 gpl ascorbic acid

□-□ 10 ml/l N_2H_4

Δ-Δ sat. $FeSO_4$ + 0.2 gpl organic additive

●-● sat. $FeSO_4$ + H_2SO_4

Figure 2. Typical silver deposits obtained on enamel from 1 M $AgNO_3$ with the following reducing agents (10 repetitions).

Top - 10 ml/l N_2H_4

Center - sat. $FeSO_4$ + H_2SO_4 (2 pH)

Bottom - sat. $FeSO_4$ + H_2SO_4 + 0.20 gpl organic additive

Figure 3. SEM micrograph of a typical silver deposit obtained on enamel with 1 M $AgNO_3$ - 10 ml/l N_2H_4 (10 repetitions). 3000X.

Figure 4. SEM micrograph of a silver deposit on enamel produced by 1 M AgF - sat. $FeSO_4$ + H_2SO_4 (2 pH) (10 repetitions). 3000X.

Figure 5. Effect of 0.20 gpl organic additive on the morphology of silver deposit on enamel produced by 1 M AgF - sat. $FeSO_4$ + H_2SO_4 (10 repetitions). 3000X.

Figure 6. SEM micrograph showing a silver deposit on ivory obtained from 1 M AgF - sat. $FeSO_4$ + H_2SO_4 + 0.20 gpl organic additive (2 pH) (10 repetitions). 3000X.

Figure 7. SEM micrograph of a silver deposit on ivory obtained from 1 M $AgNO_3$ - sat. $FeSO_4$ + H_2SO_4 + 0.20 organic additive (2 pH) (10 repetitions). 3000X.

Figure 8. SEM micrograph showing the silver deposit obtained on ivory from 1 M $AgNO_3$ + 1 M $KF \cdot 2H_2O$ - sat. $FeSO_4$ + H_2SO_4 + 0.20 gpl organic additive (2 pH) (10 repetitions). 3000X.

Figure 9. SEM micrograph of a silver deposit obtained on ivory with heavy pressure and continuous swab movement from the system 1 M $AgNO_3$ - sat. $FeSO_4$ + H_2SO_4 (10 repetitions). 3000X.

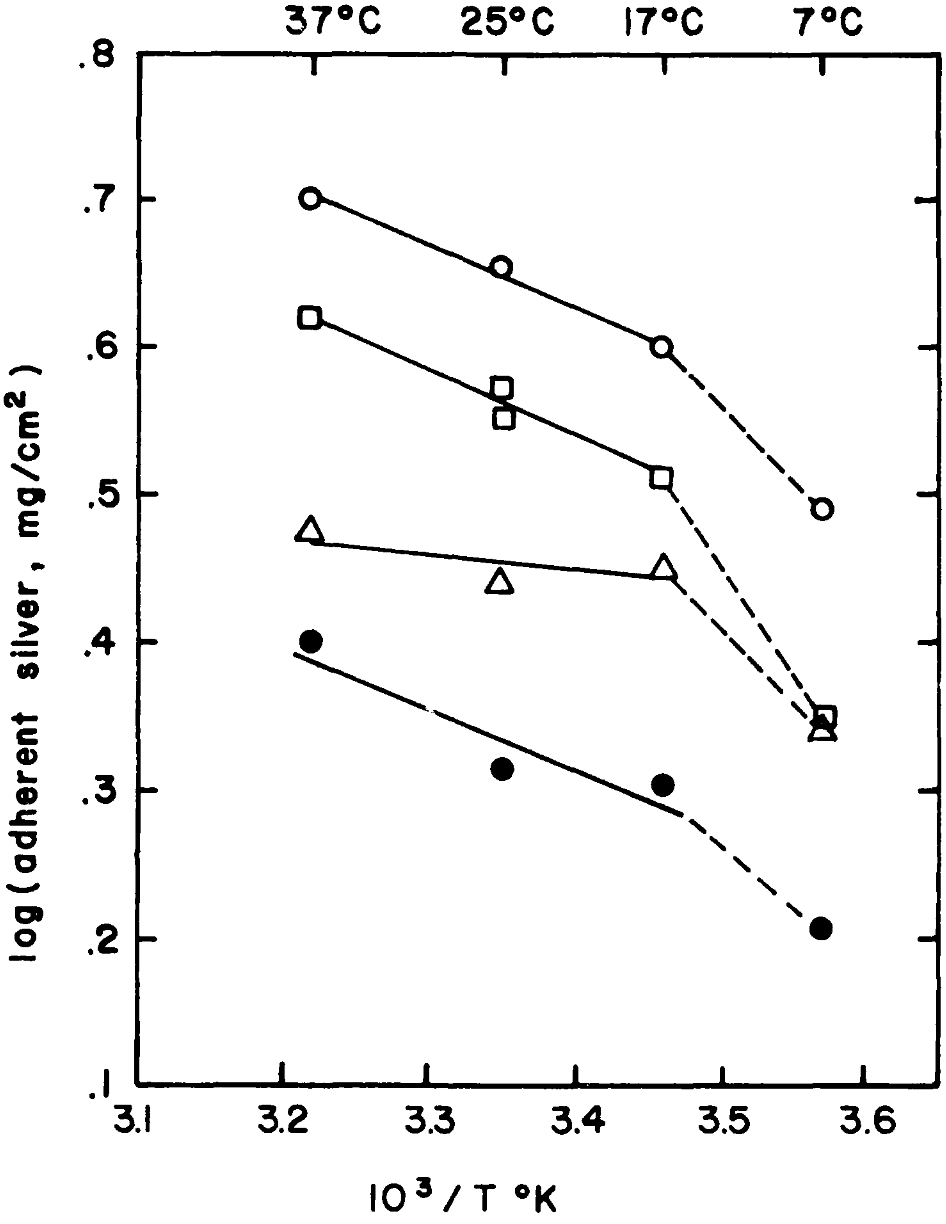


Figure 1. Effect of temperature on the quantity of adherent silver deposited after 10 repetitions of the plating sequence.

o-o	150 gpl ascorbic acid
□-□	10 ml/l N_2H_4
Δ-Δ	sat. $FeSO_4$ + 0.2 gpl organic additive
●-●	sat. $FeSO_4$ + H_2SO_4

Figure 2. Typical silver deposits obtained on enamel from 1 M $AgNO_3$ with the following reducing agents (10 repetitions).

Top - 10 ml/l N_2H_4

Center - sat. $FeSO_4$ + H_2SO_4 (2 pH)

Bottom - sat. $FeSO_4$ + H_2SO_4 + 0.20 gpl organic additive

Figure 3. SEM micrograph of a typical silver deposit obtained on enamel with 1 M $AgNO_3$ - 10 ml/1 N_2H_4 (10 repetitions). 3000X.

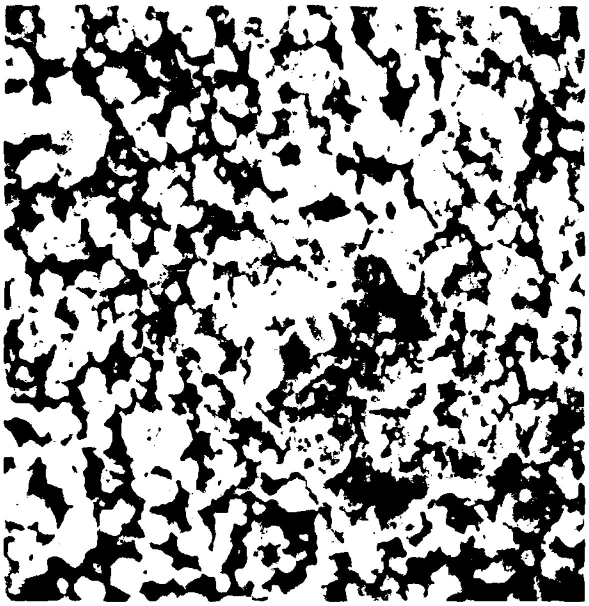


Figure 4. SEM micrograph of a silver deposit on enamel produced by 1 M AgF - sat. $FeSO_4$ + H_2SO_4 (2 pH) (10 repetions). 3000X.

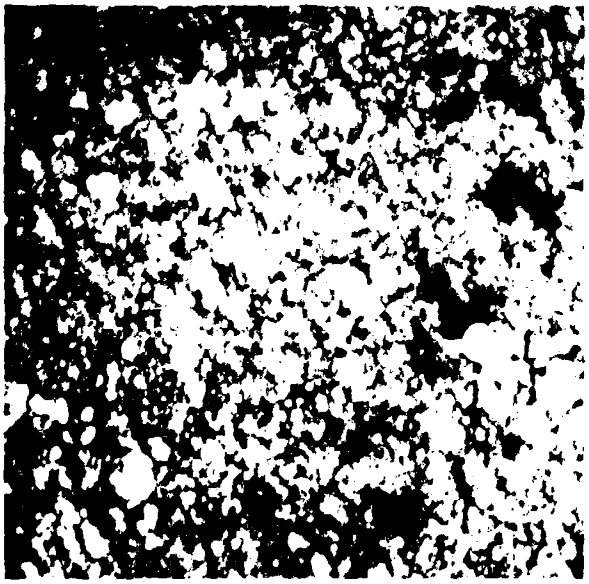


Figure 5. Effect of 0.20 gpl organic additive on the morphology of silver deposit on enamel produced by 1 M AgF - sat. $FeSO_4$ + H_2SO_4 (10 repetitions). 3000X.

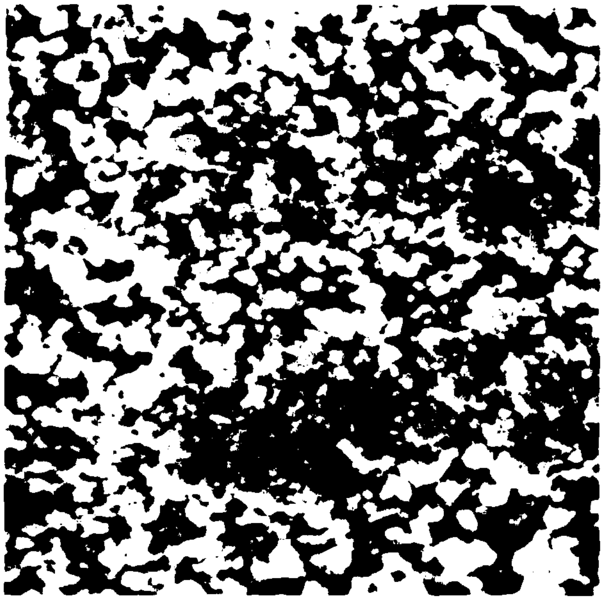


Figure 6. SEM micrograph showing a silver deposit on ivory obtained from 1 M AgF - sat. $FeSO_4$ + H_2SO_4 + 0.20 gpl organic additive (2 pH) (10 repetitions). 3000X.

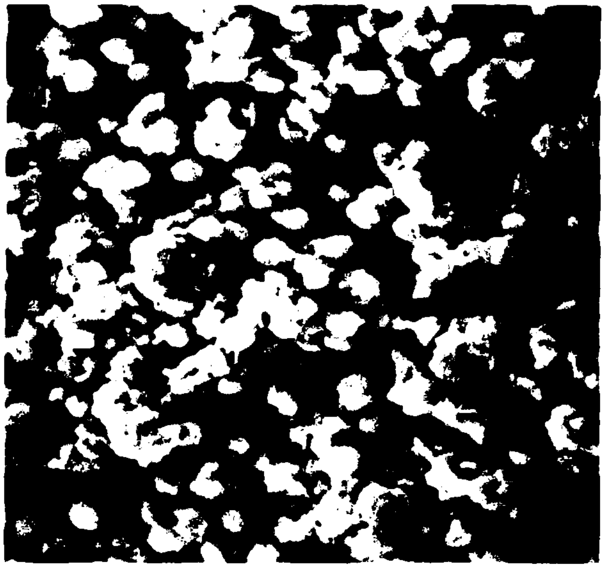


Figure 7. SEM micrograph of a silver deposit on ivory obtained from 1 M $AgNO_3$ - sat. $FeSO_4$ + H_2SO_4 + 0.20 organic additive (2 pH) (10 repetitions). 3000X.

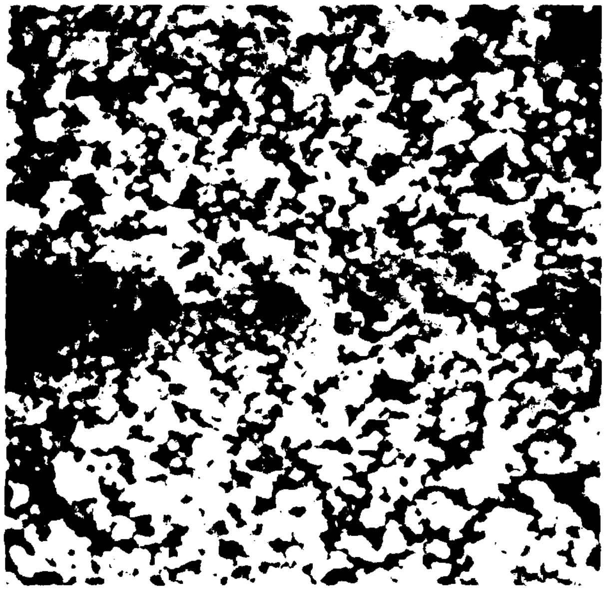


Figure 8. SEM micrograph showing the silver deposit obtained on ivory from 1 M $AgNO_3$ + 1 M $KF \cdot 2H_2O$ - sat. $FeSO_4$ + H_2SO_4 + 0.20 gpl organic additive (2 pH) (10 repetitions). 3000X.

ACKNOWLEDGEMENT

This research was partially supported by Grant No. DADA-17-73C-3087, Department of the Army, U.S. Army Medical Research and Development Command.

REFERENCES

1. Anbar, M., and Farley, E. P., Potential Use of Organic Polyphosphonates as Adhesives in the Restoration of Teeth, J. Dent. Res., 53(4): 879-888, 1974.
2. Buonocore, M. G., Caries Prevention in Pits and Fissures Sealed with an Adhesive Resin Polymerized by Ultra Violet Light: A Two Year Study of a Single Adhesive Application, J. Am. Dent. Assoc., 82: 1090, 1971.
3. O'Keefe, T. J., and Christie, R. D., Electroless and Chemical Metal Deposition on Human Tooth Enamel, J. Dent. Res., 56(6): 595-602, 1977.
4. O'Keefe, T. J., Electroless Plating Method for Treating Teeth, U.S. Patent 3,995,371, December 7, 1976.
5. Cutright, D. E., Woody, R. D., O'Keefe, T. J., and Hoffman, J. I., The Use of Electroless Metal Coatings as Preventive Materials--A Preliminary Primate Study, J. Prev. Dent., 4: 37-42, 1977.
6. Raub, E., and Muller, K., "Fundamentals of Metal Deposition", Elsevier, pp. 65-74, 166-172, 229-246, 1967.
7. Guy, A. G., "Elements of Physical Metallurgy", Addison-Wesley Publishing Co., p. 43, 1960.
8. Smith, R. M., and Martell, A. E., Editors, "Critical Stability Constants", Plenum Press, New York, 1976.

9. Burkin, A. R., "The Chemistry of Hydrometallurgical Processes", D. Van Nostrand Inc., Princeton, New Jersey, pp. 124-125, 1966.

SECTION B

APPLICATION OF BRUSH PLATING TO DENTAL MATERIALS

By

SZU-CHAIN FRED CHEN, 1952-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN CHEMISTRY

1980

Approved by

William J James (Advisor)

PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by the Journal of Dental Research. Pages 1-21 will be presented for publication in that journal. Appendix has been added for purposes normal to thesis writing.

ABSTRACT

The feasibility of depositing a Ag film onto ivory and teeth previously chemically coated with Ag using a brush plating technique has been studied. The two most desirable properties, wear and amalgam shear resistance of the electroless Ag deposits were considerably improved. Current density and plating time turned out to be the two most important operating parameters among others, such as electrolyte concentration, pH, anode/cathode area, etc. SEM studies on morphology and energy dispersive x-ray studies on fractured surfaces indicated that layers formed in the electroless Ag film and this layering was believed to be critical to the amalgam shear resistance.

ACKNOWLEDGEMENTS

I would like to express my appreciation to Dr. William J. James, my advisor, for his keen insight and guidance in this research. I would also especially like to thank Dr. Thomas J. O'Keefe for his many valuable suggestions throughout the course of this research and his help in preparing the manuscript. I would like to acknowledge Dr. Ramagouda Narasagoudar who gave me helpful advice and technical assistance. The technical assistance provided by John Thompson who did all the SEM analysis in this research is also greatly appreciated.

I wish to acknowledge the financial assistance provided by the U. S. Army Medical Research and Development Command, Fort Detrick, Frederick, MD.

Finally, a great deal of thanks is owed to Mrs. Nina Haas for her efforts in typing this manuscript.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Figures Page

LIST OF ILLUSTRATIONS

Appendix

LIST OF TABLES

Tables Page

LIST OF TABLES

Appendix

Tables Page

INTRODUCTION

In an attempt to improve the adherence of various applied coatings used in dentistry, a process was developed to chemically plate silver onto tooth enamel.[1] The metallic film has a number of potential applications, such as a pit and fissure sealant or as an adhesive intermediate for use in conjunction with other materials. The process involves the deposition of silver from one of its aqueous salt solutions, using a suitable reducing agent, such as hydrazine or ferrous sulfate. Such films have exhibited good wear resistance and the ability to enhance amalgam adherence, two desirable properties of metal films used in these applications. However, due to the nature of the process, the thickness and metallurgical properties of the silver obtained are often limited because the rate of deposition is relatively low.

One possible means of circumventing the metal thickness limitation was by brush plating,[2] after the initial silver film had been deposited. Brush plating is a process, whereby localized electrodeposition is possible without totally immersing the workpiece in a plating solution. A hand held cylinder, containing a centrally located silver wire which is surrounded by a fibrous, absorbent, brush-like material, serves as the anode. Electrolyte held in the fibrous material completes the electrical circuit between the anode and the silver layer, which is the cathode. Energy for plating is supplied by a D.C. rectifier.

One of the major objectives of this study was to determine the feasibility of brush electroplating a metal film onto ivory or teeth, previously coated with silver, and to evaluate the observed properties, such as wear resistance and amalgam adherence. The influences of various plating process parameters, such as current density, solution concentration, electrolyte pH, deposition time, etc., on these properties were also studied.

MATERIALS AND METHODS

All ivory samples were prepared so as to provide a consistent orientation for plating. The ivory was cut perpendicularly to its longitudinal axis into disks 1 cm in thickness, using a diamond saw, and water as a lubricant. Then, the disk was cut perpendicularly to its radial direction into pieces of approximately 0.2 cm in width and 2 cm in length. The silver solution was applied on the 1 x 2 cm face because this provides a perpendicular orientation for the tubules.

The ivory pieces were polished on a diamond wheel and 600 grit emery paper, and then electrolessly plated using 100 gpl AgF (about pH 5.3), saturated $FeSO_4$ solution plus an organic additive (about pH 2). The AgF solution was aged for at least one day, while the $FeSO_4$ solution was freshly prepared for use. The procedure for electroless plating has been described previously.[3]

After the samples were electrolessly plated and the electrical resistances were sufficiently low, brush plating commenced. Direct current was provided by a Sorenson power supply. A Keithley electrometer and an ampere meter were used for measuring the voltage and current, respectively.

Figure 1 shows the schematic of the brush anode and the arrangement of the apparatus used for brush plating. The ivory or tooth was made the cathode, with about 0.5 cm^2 of its area covered by the anode brush. The electrolyte, a mixture of AgF and KSCN solution, was introduced by an eye-dropper into the brush and onto the surface to be plated. To initiate the plating procedure, a low current was used which was then immediately adjusted to the desired value. During the plating process, contact to the sample surface was made by repetitive back and forth strokes of the brush, taking care that the silver wire not touch the cathode. After plating, the ivory or tooth was immediately and thoroughly washed and dried. Various cathode current densities, AgF concentrations, electrolyte pH, complexing agents, and additives were used and their effects on the properties of the silver deposits were evaluated.

Wear tests were conducted, using an Abbott-Robinson No. 11 soft bristle brush attached to a variable speed electric motor (208 rpm, surface speed 20 cm/sec). The ivory or tooth sample was fastened onto a Petri dish using double-faced Scotch tape. The dish in turn was fixed similarly to the top of a spring loaded scale (1 gram intervals) which was placed on a laboratory jack. The sample, as well as the scale, was raised until it touched the brush and the desired weight was placed on the brush. A 50 wt% slurry of Crest toothpaste was poured onto the sample and motor turned on for a predetermined time interval. Then the sample was removed, washed, dried, and examined under an optical microscope for qualitative evaluation. A relative wear number of 0-10 was assigned, 0 corresponding to a substantial exposure of the substrate and 10 corresponding to that of a silver deposit with no visible sign of damage. The wear numbers were only arbitrary in that they varied with test conditions (applied force, brushing time, stiffness of brushes, etc.), but were useful for comparisons of different plating parameters.

Shear tests were performed to evaluate the adherence of silver deposits to ivory or teeth, and that of amalgam to silver deposits simultaneously. For shear testing, the tooth was cold mounted in plastic to allow easier clamping to the testing machine. The area to be amalgamated was restricted by placing a piece of punched masking tape on the surface of the ivory or tooth. A Teflon tube of about 0.2 cm in length with a cross sectional area slightly larger than that to be amalgamated was fastened over the restricted area of the surface by using masking tape. The amalgam was made by triturating a pellet of Fine Cut Alloy* with mercury for 7 seconds using a Caulk Vari-Mix II Triturator, and then condensed into the Teflon mold. After 24 hours, the shear stress was determined using a manually operated Universal Testing Machine.

---

*The L. D. Caulk Co., Milford, Delaware 19963.

RESULTS

Homogeneous metallic deposits, possessing low resistance (from 0.001 to 0.50Ω), were obtained in three minutes by using the brush electroplating technique. In general, brush electroplating greatly improved the wear resistance and slightly improved the amalgam resistance over values obtained when only electroless plating was employed.

The addition of complexing agents to AgF electrolytes reduced the polarization potential by 1 to 5 volts, gave more homogeneous deposits and improved wear and amalgam shear resistances. For the experimental conditions chosen, KSCN[4] solution was the most effective depolarizer, and accordingly, 300 gpl KSCN was used in conjunction with AgF as the standard brush plating solution. Lower KSCN concentrations resulted in a lower solubility of AgF, a higher polarization potential and powdery deposits. Thiosulfate salts[5] and a commercial silver brush plating electrolyte were also evaluated. In general, thiocyanate salts gave a yellowish deposit with a metallic luster. The deposits made with thiosulfate salts were more nodular and less metallic in appearance, and showed an intermediate nodular growth and gray color with the commercial electrolyte. In terms of wear and amalgam shear resistance, there was no profound difference between different complexing agents used. Several additives, such as thiourea,[6] ammonium thiosulfate[7] and potassium iodide,[4] were tested in a concentration range less than 0.5 gpl, but no significant effects on the resultant properties were found.

Preliminary screening tests,[8] statistically designed, were conducted and showed that the current density and plating time had significant effects on amalgam shear strength and wear resistance. The tests indicated that increasing the current density from 20 to 60 mA/cm^2, averaged over all levels of other variables, raised the amalgam shear stress by about 250 psi* and the wear number by 5 to 6. Increasing the plating time from 2 to 6 minutes reduced the amalgam shear stress by 200 psi but raised the wear number by 4. Increasing the AgF concentration from 20 to 50 gpl and the electrolyte pH from 3 to 7 had small negative effects on amalgam shear resistance and small positive effects on wear resistance.

Based on the screening tests, more detailed experiments were carried out and the results are shown in Tables 1 and 2. Each wear number in the Table is the average of 2 measurements, and each shear stress value is the average of 5 measurements. The results in Table 1 show that high current densities can improve the wear number by a factor of ~4, compared with low current densities. For samples which were only electrolessly plated, a wear number of 2 to 3 was obtained. Morphology studies revealed that a higher AgF concentration in the electrolyte reduced the nodular nature of the deposits, but it did not have a noticeable effect on wear resistance as long as no extensive concentration polarization existed at higher current densities. When the Ag anode area was insufficient, a black spongy and coarse deposit with very poor wear resistance formed, particularly at low AgF concentrations. Increasing the plating time from 3 to 6 minutes increased the wear number by about 3. Experiments conducted using various

---

*To convert pounds per square inch, psi, to kilopascals, kPa, or kilonewtons per square meter, kN/m^2, multiply by 6.8948.

time and current density combinations (e.g., 18 minutes at 10 mA/cm^2 or 3 minutes at 60 mA/cm^2), and at a constant number of coulombs, gave similar wear resistances.

The overall amalgam shear resistances of the Ag deposits were improved by 600 to 700 psi, compared with samples only electrolessly plated. Also, the variability range of amalgam shear strength was reduced. Results in Table 2 indicate that an intermediate AgF concentration and a relatively high current density are desirable for improving the amalgam shear resistance. The amalgam shear resistance appeared to be insensitive to the AgF concentration and the current density, except for relatively high values of 30 and 40 gpl AgF at 60 mA/cm^2. The amount of lateral diffusion of Hg from the amalgam on the plated surface was considerably more pronounced on brush plated surfaces than on those electrolessly plated. Amalgam trituration conditions also appeared to influence the adhesion of amalgam to the Ag deposits. Measurements on 17 random samples showed the amalgam shear stress to be about tripled when trituration was decreased from 10 to 7 seconds.

Increasing the plating time to 6 minutes slightly improved the amalgam shear resistance for low current density films, but decreased the amalgam shear resistance for those produced using high current densities. Further increases in plating time were also detrimental to the amalgam shear resistance of low current density deposits. For a constant number of coulombs (5.4), the amalgam shear resistance was about 1400 ± 150 psi for current densities of 10 and 20 mA/cm^2, and increased to about 2300 ± 700 psi for 40 and 60 mA/cm^2. This again indicates a higher current density is more desirable for amalgam shear resistance, although the deviations at high current densities are greater than those at low current densities.

A typical deposit morphology for the electroplated Ag is shown in Fig. 2. In general, smooth deposits were obtained for low pH solutions, with a noticeable increase in nodule formation as the pH increased. There was no influence on wear and amalgam shear resistance for deposits made from lower pH solutions. However, the wear resistance decreased and the amalgam shear resistance slightly increased as the pH level was raised above 7.

The anode area played a very important role on the surface structure, nodule formation and appearance of the Ag deposits. A higher anode/cathode area (2.5 versus 0.8) gave rise to less nodular growth, higher reflectivity, better amalgam shear resistance, and a depolarizing effect of as much as 0.4 volts during plating. However, only the apparent anode area was calculated. The effective anode area is only approximately proportional to the apparent anode area because the current distribution varies with both the position of the wire and the location around its diameter.

X-ray diffraction patterns showed the deposits to have a random orientation similar to that of bulk silver, with some tendency toward a (111) preferred orientation at low current densities and brief plating times. The orientations of the Ag were similar whether deposited by electroless or brush plating techniques, particularly when the brush plating current density (10 mA/cm^2) gave an equivalent deposition rate to the electroless plating. The thickness of the Ag film after 3 minutes of electroplating was ~12μ, about 3 times greater than that of standard electroless deposits obtained in 10 minutes. Thus, in a unit time, high current density brush electroplating can produce a deposit 10 times thicker than that obtained with the electroless plating technique.

A number of cross sections of fractured surfaces was examined by SEM and energy dispersive x-ray techniques. Figure 3 shows an example of these fractured surfaces. Traces of Ag or Ag^+ were found to penetrate as deeply as 20-25μ into the hydroxyapatite. An amorphous layer[9] (B), possibly organic in nature and with a considerably lower P/Ca content than that of hydroxyapatite, formed by etching with 50 vol% H_3PO_4. After the Ag^+ solution was applied to the surface in the standard electroless plating process, a distinctive layer (C) often formed beneath the amorphous layer. The elemental analysis of the underlying film showed it to be highly concentrated in Ag and P and very low in Ca. The formation of Ag_3PO_4 at this stage was verified by x-ray diffraction and by a change in color from white to yellow on the surface of the ivory. After two repetitions, a layer (A) essentially Ag built up over the amorphous layer. When the electroless process was completed (10 repetitions of reduction), layer C was unchanged whereas the original amorphous layer contained a low Ag content with a small amount of P and Ca. The composition and thickness of the various layers appeared to be dependent on the experimental processing parameters. By using the brush electroplating technique, more Ag was deposited with no apparent demarcation between electroless and electroplated Ag.

After amalgam shear testing, a combination of the different layers described above or of hydroxyapatite was present on the tested surface, with the relative amount of each determining the final amalgam shear strength. Seldom did failure occur between the electroless and electroplated Ag.

DISCUSSION

The results of tests on individual process parameters are in good agreement with those from the statistical design. Certain properties, particularly wear resistance, of the electroless Ag deposits can be improved by the brush plating technique as shown in Table 1.

The thickness or amount of deposited Ag seems to be important to wear resistance. The actual film thickness is about 60% greater than that predicted by Faraday law calculations, indicating that the Ag deposits may be porous. However, the influence of porosity on the wear resistance is not clear at this time. More contiguous, denser deposits would be expected to exhibit better properties.

The brush plating seems to improve the amalgam shear resistance and reduce the variability of it by providing a thicker Ag deposit, reducing the degree of Hg penetration and preventing contact with the Ag_3PO_4 layer. However, in terms of adhesion to the substrate, the original electroless Ag layer is more important than the electroplated layer deposited over it. The layering of the Ag deposits formed in the electroless process appears critical to the amalgam shear strength. More studies on the mechanism of the formation of these layers and their influences are needed, if the amalgam shear resistance is to be improved. Some other factors as described below also influence the amalgam shear resistance. Amalgam conditions (trituration parameters, composition, dryness, curing time, etc.) are critical because of the subsequent reaction with the thin Ag layer. The penetration and depth of the zone of interaction can cause different failure to occur at different depths through the deposit.

Variations in observed strength result from the inherent resistance to shear of the various layers. Changes of orientation in different locations on the ivory samples are almost uncontrollable and this also influences the adhesion of Ag deposits.

The morphology of the Ag deposits is related to the operating parameters, with many of the observed features being explainable in terms of changes in the polarization behavior induced by the parameters. Any factors leading to a depletion of Ag^+ ions in the vicinity of cathode or in the double layer causes concentration polarization and an expected decrease in the particle size and increased tendency toward powdery deposits. In general, the trends observed in the structural modification with changes in the operating parameters are similar to those expected for any electrochemical plating process.[10]

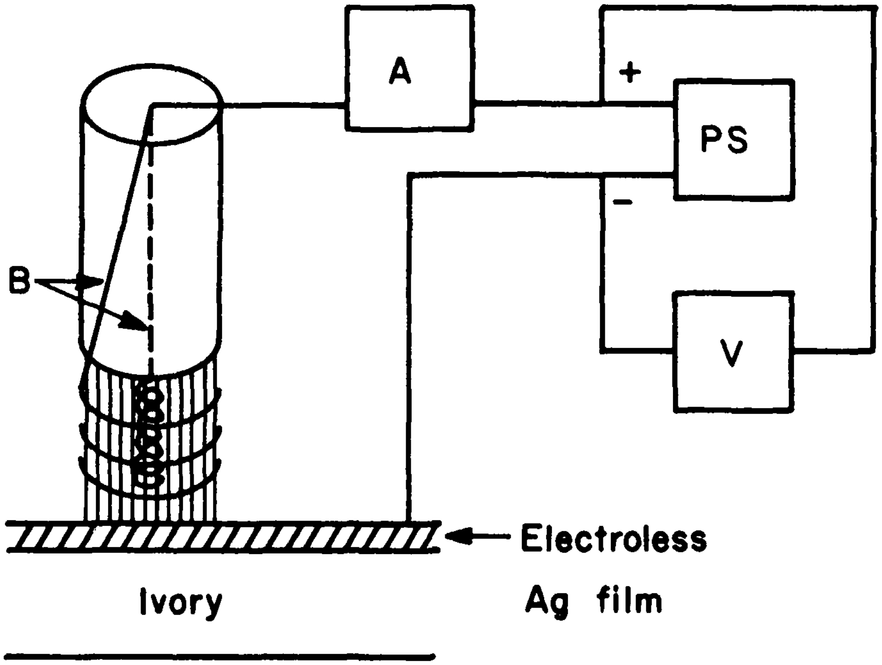
CONCLUSIONS

The brush electroplating technique improves the wear resistance of the Ag deposit. When compared to electroless plating, the brush electroplating technique results in Ag deposits which show a pronounced increase in wear resistance and an improvement in amalgam shear resistance together with a lesser degree of scatter in the data. Operating parameters, such as complexation, current density, time, time-current density relationship, AgF (electrolyte) concentration, anode/cathode area, pH, all influence the properties of the Ag deposits. Chemical layering within the deposits influences the shear stress values. Accordingly, studies of the mechanism of the formation of these layers are important if the amalgam shear resistance of the Ag deposits is to be improved.

Figure 1. Schematic of the Brush Anode and the Arrangement of the Apparatus.

Figure 2. Scanning Electron Micrograph Showing a Typical Morphology of Electroplated Ag Deposits. Plating Conditions: 50 gpl AgF + 300 gpl KSCN (pH 7.2), 55 mA/cm^2, 0.9V, 6 minutes. (X3000).

Figure 3. Scanning Electron Micrograph Showing the Presence of Layers During the Electroless Plating Process. Plating Conditions: 100 gpl AgF (pH 5.3) with Saturated $FeSO_4$ + 0.5 gpl Thiourea (pH 2), 2 Repetitions of Reduction. A = silver layer, B = amorphous layer, C = Ag_3PO_4 layer. (X3000).



A: Ampere meter
B: Silver wire in the center and wrapped around a fiber brush
PS: Power supply
V: Potential meter
+: Anode
−: Cathode

Figure 1

Figure 2

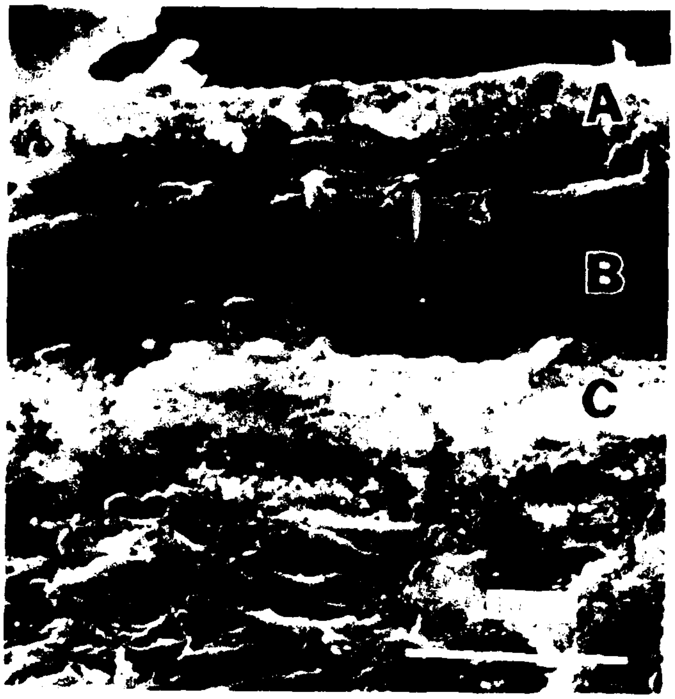


Figure 3

TABLE I

EFFECT OF C.D. AND AgF CONCENTRATION ON WEAR OF BRUSH PLATED IVORY

C.D. (mA/cm^2)	WEAR			NUMBER
	AgF concentration (gpl)			
	15	30	40	50
10	2.0 ± 2.8	2.0 ± 2.8	3.0 ± 1.4	2.5 ± 2.1
20	4.5 ± 0.7	4.0 ± 0.0	5.5 ± 2.1	4.0 ± 0.0
40	8.5 ± 0.7	6.5 ± 0.7	5.0 ± 0.0	7.5 ± 0.7
60	9.5 ± 0.7	9.0 ± 0.0	8.5 ± 0.7	8.5 ± 2.1

*20g force for 6 min; samples plated 3 min.

TABLE II

EFFECT OF C.D. AND AgF CONCENTRATION ON AMALGAM ADHERENCE FOR BRUSH PLATED IVORY

C.D. (mA/cm^2)	Shear Stress (P.S.I.) AgF concentration (gpl) 15	30	40	50
10	1709 ± 388	1623 ± 337	1629 ± 307	1112 ± 386
20	1691 ± 461	1640 ± 267	1644 ± 423	1477 ± 181
40	1498 ± 379	1688 ± 267	1080 ± 484	1618 ± 433
60	1531 ± 393	2285 ± 585	2109 ± 395	1555 ± 360

REFERENCES

1. O'Keefe, T. J. and Christie, R. D.: Electroless and Chemical Metal Deposition on Human Tooth Enamel, J. Dent. Res. 56: 595-602, 1977.
2. Groshart, E.: Brush Plating Techniques, Metal Finishing, 65: 75-78, 1967.
3. O'Keefe, T. J.: Feasibility Study on a Process for Electroless Metal Deposition In Pits and Fissures of Teeth for Use in Preventive Dentistry, Annual Report of U. S. Army Medical Research and Development Command: 1979, p. 2 and p. 5.
4. Suzuki, Y., Ura, M., Asai, O and Minakawa, T. (Hitachi, Ltd.): Post-treatment of Silver-plated Products, Jpn. Kokai Tokkyo Koho 79 40, 241 (Cl. C25D3/46), 29 Mar, 1979.
5. Granier, L. J.: Polyspecific Self-silvering of Metals, Fr. 2,063,340 (Cl. C 230), 13 Aug 1971.
6. Wernick, S. and Evans, U. R.: Electrolytic Polishing and Bright Plating of Metals, 1st ed., London, Great Britain: Alvin Redman Ltd., 1948, p. 93.
7. Guidebook and Directory of Metal Finishing, 46th ed., Hackensack: Metals and Plastics Publications, Inc., 1978, p. 315.
8. Chen, S. F.: Application of Brush Plating to Dental Materials, M.S. Thesis of University of Missouri at Rolla, 1980.
9. Gustafson, G. and Sundström, B.: Enamel: Morphological Considerations, J. Dent. Res., 54: B114-B120, 1975.
10. Glasstone, S.: The Fundamentals of Electrochemistry and Electrodeposition, American Electroplaters' Society, 1943, pp. 66-80.

VITA

Szu-Chain Fred Chen was born on October 8, 1952 in Taipei, Taiwan, Republic of China. He received his primary and secondary education in Taipei. After receiving a Bachelor of Science degree in Chemistry from the Soochow University in Taipei in June 1975, he served as a second lieutenant in the Chinese Air Force for two years.

He has been enrolled in the Graduate School of the University of Missouri-Rolla since August 1977 and has been a research assistant in the Graduate Center for Materials Research since January 1978.

APPENDIX

STATISTICAL DESIGN FOR SCREENING VARIABLES OF BRUSH PLATING ON IVORY

Table I. Matrix for Eight Run Design[1]

	Random	Variables*						
Run No.	Ordering	X_1	X_2	X_3	X_4	X_5	X_6	X_7
1	3	+	+	+	-	+	-	-
2	8	+	+	-	+	-	-	+
3	1	+	-	+	-	-	+	+
4	7	-	+	-	-	+	+	+
5	2	+	-	-	+	+	+	-
6	5	-	-	+	+	+	-	+
7	6	-	+	+	+	-	+	-
8	4	-	-	-	-	-	-	-

*The "+" denotes the upper limit and the "-" the lower limit.

Table II. Variables and the Limits

Variables	Lower Limit (-)	Upper Limit (+)	Center Points
X_1, AgF concentration (g/ℓ)	20	50	35
X_2, plating time (min)	2	6	4
X_3, current density (mA/cm^2)	20	60	40
X_4, electrolyte PH	3	7	5
X_5, dummy			
X_6, dummy			
X_7, dummy			

Table III. Complete Design with Center Points Run-Order Randomization

Run No. After Random Ordering and Including Center Points	X_1 AgF conc. (g/ℓ)	X_2 Plating Time (min)	X_3 Current Density (mA/cm^2)	X_4 Electrolyte pH	X_5 Dummy	X_6 Dummy	X_7 Dummy	Original Run No.
I	35	4	40	5				Cp*
II	+ 50	− 2	+ 60	− 3	−	+	+	3
III	+ 50	− 2	− 20	+ 7	+	+	−	5
IV	+ 50	+ 6	+ 60	− 3	+	−	−	1
V	− 20	− 2	− 20	− 3	−	−	−	8
VI	35	4	40	5				Cp
VII	− 20	− 2	+ 60	+ 7	+	−	+	6
VIII	− 20	+ 6	+ 60	+ 7	−	+	−	7
IX	− 20	+ 6	− 20	− 3	+	+	+	4
X	+ 50	+ 6	− 20	+ 7	−	−	+	2
XI	35	4	40	5				Cp

---

*Center points.

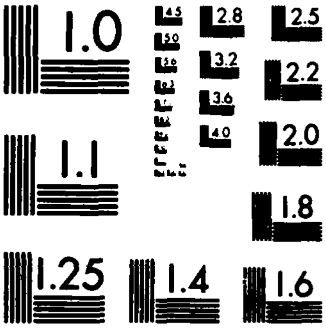
Table IV. Measured Responses

Run No. After Random Ordering and Including Center Points	Y_1 conductance (Ω^{-1})	Y_2 shear stress (p.s.i.)	Y_3 wear no.
I	167	954	8
II	48	1436	6
III	14	866	0
IV	1000	867	10
V	18	885	0
VI	59	966	6
VII	83	1304	6
VIII	143	977	10
IX	40	1056	1
X	19	746	8
XI	333	800	7

ESTIMATION OF SIGNIFICANCE

AD-A134 475 FEASIBILITY STUDY ON A PROCESS FOR ELECTROLESS METAL DEPOSITION IN PITS A..(U) MISSOURI UNIV-ROLLA T J O'KEEFE AUG 80 DADA17-73-C-3087 2/2

UNCLASSIFIED F/G 6/5 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

Main Effect

Estimation of main effect of x_i,

$$E_{x_i} = \frac{\Sigma(\text{responses at high } x_i) - \Sigma(\text{responses at low } x_i)}{\text{half the number of runs}}$$

Assessment of the Main Effects

Method A (using the center points)[2]

Estimation of confidence interval = main effect estimate $\pm\, ts/\sqrt{N/4}$

where t = 2.920 for 90% confidence from student's t-statistic[3] with

2 degrees of freedom (from 3 center points)

N = number of runs in the design (excluding center points)

s = response error estimate from the center points

$= \sqrt{\Sigma(y_i-\bar{y})^2/(r-1)}$

r = number of center points and

(r-1) = degrees of freedom

If the confidence interval includes zero, the variable does not have significant effect on the measured response at the stated confidence level (90% in this case). However, if it does not include zero, the effect is significant at the stated confidence level.

Method B (using the dummy variables)[1]

Confidence level = $100(1-2\alpha)$

where α is obtained from student's t-statistic graph of α versus t (Figure 1 or similar plots) for n degrees of freedom (n = number of dummy variables), and

$$t = \left|\frac{\text{Main Effect Estimate}}{\text{Standard Error of an Effect } (\text{S.E.}_{\text{eff}})}\right|$$

and

$$\text{Standard Error of an Effect } (\text{S.E.}_{\text{eff}}) = \sqrt{\frac{\Sigma E^2_{\text{dummy}}}{n}}$$

Table V. Main Effect Estimate and Significance Tests for Conductance (Y_1)

Variables	Main Effect Estimate, $E_{xi} = \frac{\Sigma_+ - \Sigma_-}{4}$	Method A (90% C.I.) $E_{xi} \pm ts/\sqrt{N}/4$	Method B		
			$t = \frac{E_{xi}}{S.E._{eff}}$	α^*	C.I. = $100(1-2\alpha)$
X_1	$\frac{1000+19+48+18-40-14-83-143}{4} = 201$	-84 to 486	0.79	0.245	51%
X_2	$\frac{48+83+143+18-1000-19-40-14}{4} = -195$	-480 to 90	0.77	0.25	50%
X_3	$\frac{1000+48+14+83-19-40-143-18}{4} = 231$	-54 to 516	0.91	0.215	57%
X_4	$\frac{19+14+83+18-1000-48-40-143}{4} = -274$	-559 to 11	1.08	0.18	64%
X_5	$\frac{19+48+14+143-1000-40-83-18}{4} = -229$	-514 to 56	0.91	0.215	57%
X_6	$\frac{1000+19+83+143-48-40-14-18}{4} = 281$	-4 to 566	1.11	0.175	65%
X_7	$\frac{1000+14+143+18-19-48-40-83}{4} = 246$	-39 to 531	0.97	0.20	60%

Table V (Continued)

Method A:

$r = 3,\ t = 2.920,\ N = 8$

$$S = \sqrt{\Sigma(Y_i-\bar{Y})^2/(r-1)} = \sqrt{\frac{(167-186)^2+(59-186)^2+(333-186)^2}{2}} = 138$$

For 90% C.I. $ts/\sqrt{N/4} = (2.920)(138)/\sqrt{8/4} = 285$

For X_1, $201 - 285 = -84,\ 201 + 285 = 486$

Method B:

$$S.E._{\text{eff}} = \sqrt{\frac{(-229)^2+(281)^2+(246)^2}{3}} = 253$$

$$t = \frac{E_{xi}}{S.E._{\text{eff}}} = \frac{E_{xi}}{253}$$

$$t\ (\text{for } X_1) = \frac{201}{253} = 0.79$$

[*] See Fig. 1.

Table VI. Main Effect Estimate and Significance Tests for Shear Stress (Y_2)

Variables	Main Effect Estimate, $E_{xi} = \frac{\Sigma_+ - \Sigma_-}{4}$	Method A (90% C.I.)	Method B		
		$E_{xi} \pm ts/\sqrt{N}/4$	$t = \frac{E_{xi}}{S.E._{eff}}$	α*	C.I. = 100(1-2α)
X_1	$\frac{1436+866+867+746-885-1304-977-1056}{4} = -77$	-269 to 115	0.49	0.33	34%
X_2	$\frac{867+977+1056+746-1436-866-885-1304}{4} = -211$	-403 to -19	1.34	0.14	72%
X_3	$\frac{1436+867+1304+977-866-885-1056-746}{4} = 258$	66 to 450	1.64	0.10	80%
X_4	$\frac{866+1304+977+746-1436-867-885-1056}{4} = -88$	-280 to 104	0.56	0.28	44%
X_5	$\frac{866+867+1304+1056-1436-885-977-746}{4} = 12$	-180 to 204	0.08	>0.40	<20%
X_6	$\frac{1436+866+977+1056-867-885-1304-746}{4} = 133$	-59 to 325	0.85	0.23	54%
X_7	$\frac{1436+1304+1056+746-866-867-885-977}{4} = 237$	45 to 429	1.51	0.115	77%

Table VI (Continued)

Method A:

$r = 3,\ t = 2.92,\ N = 8$

$S = \sqrt{\Sigma(Y_i-\bar{Y})^2/(r-1)} = \sqrt{(954-907)^2+(966-907)^2+(800-907)^2/2} = 93$

For 90% C.I. $ts/\sqrt{N/4} = (2.920)(93)/\sqrt{8/4} = 192$

For X , $-77-192 = -269,\ -77+192 = 115$

Method B:

$S.E._{eff} = \sqrt{\dfrac{(12)^2+(133)^2+(237)^2}{3}} = 157$

$t = \dfrac{E_{xi}}{S.E._{eff}} = \dfrac{E_{xi}}{157}$

$t(\text{for } X_1) = \dfrac{77}{157} = 0.49$

*See Fig. 1.

Table VII. Main Effect Estimate and Significance Tests for Wear Resistance (Y_3)

Variables	Main Effect Estimate, $E_{xi} = \frac{\Sigma_+ - \Sigma_-}{4}$	Method A (95% C.I.) $E_{xi} \pm ts/\sqrt{N/4}$	Method B		
			$t = \frac{E_{xi}}{S.E._{eff}}$	α*	C.I. = $100(1-2\alpha)$
X_1	$\frac{6+0+10+8-0-6-10-1}{4} = 1.8$	-1.2 to 4.8	1.2	0.16	68%
X_2	$\frac{10+10+1+8-6-0-0-6}{4} = 4.3$	1.3 to 7.3	2.9	0.03	94%
X_3	$\frac{6+10+6+10-0-0-1-8}{4} = 5.8$	2.8 to 8.8	3.9	0.015	97%
X_4	$\frac{0+6+10+8-6-10-0-1}{4} = 1.8$	-1.2 to 4.8	1.2	0.16	68%
X_5	$\frac{0+10+6+1-6-0-10-8}{4} = -1.8$	-4.8 to 1.2	1.2	0.16	68%
X_6	$\frac{6+0+10+1-10-0-6-8}{4} = -1.8$	-4.8 to 1.2	1.2	0.16	68%
X_7	$\frac{6+6+1+8-0-10-0-10}{4} = 0.3$	-2.7 to 3.3	0.2	>0.40	<20%

Table VII (Continued)

Method A:

$r = 3,\ t = 2.920$

$$S = \sqrt{\Sigma(Y_i-\bar{Y})^2/(r-1)} = \sqrt{\frac{(8-7)^2+(6-7)^2+(7-7)^2}{2}} = 1$$

For 95% C.I. $ts/\sqrt{N/4} = 4.303 \times 1/\sqrt{8/4} = 3.0$

For X_1, $1.8-3.0 = -1.2$, $1.8+3.0 = 4.8$

Method B:

$$S.E._{eff} = \sqrt{\frac{(-1.8)^2+(-1.8)^2+(0.3)^2}{3}} = 1.5$$

$$t = \frac{E_{xi}}{S.E._{eff}} = \frac{E_{xi}}{1.5}$$

$$t(\text{for } X_1) = \frac{1.8}{1.5} = 1.2$$

*See Fig. 1.

Figure 1. Plot of α versus t for Three Degrees of Freedom.

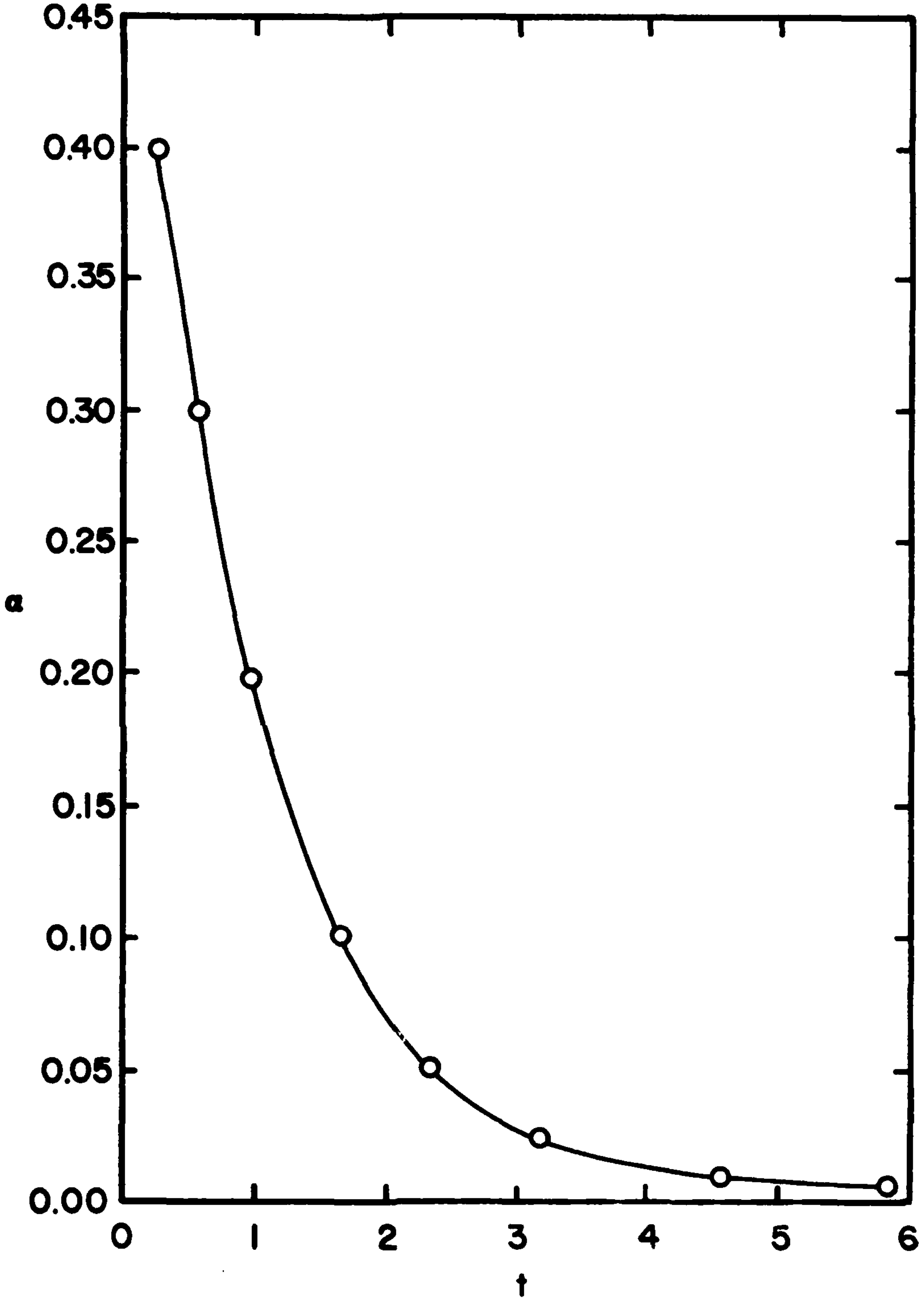


Figure 1

REFERENCES

1. Stowe, R. A. and Mayer, R. P.: Efficient Screening of Process, Industrial and Engineering Chemistry 58: 36-40, 1966.

2. Murphy, T.D., Jr.: Design and Analysis of Industrial Experiments, Chemical Engineering, 84: 168-182, 1977.

3. Perry, R. H. and Chilton, C. H.: Chemical Engineers' Handbook, 5th ed. New York: McGraw-Hill Book Co., 1973, p. 1-40.

DISTRIBUTION LIST

4 copies

HQDA (SGRD-SI)
Fort Detrick
Frederick, MD 21701

12 copies

Defense Technical Information Center (DTIC)
ATTN: DTIC-DDA
Cameron Station
Alexandria, VA 22314

1 copy

Dean
School of Medicine
Uniformed Services University of the
Health Sciences
4301 Jones Bridge Road
Bethesda, MD 20014

1 copy

Superintendent
Academy of Health Sciences, US Army
ATTN: AHS-COM
Fort Sam Houston, TX 78234

FILM

11