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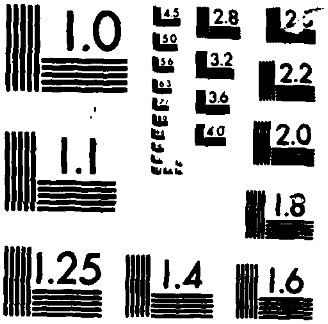

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STUDY OF A PROCESS FOR THE DEPOSITION OF A METAL ADHESIVE INTERMEDIATE FOR USE IN REMOVABLE PROSTHETIC APPLIANCES

FINAL REPORT

by

Thomas J. O'Keefe

April 1984

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FOREWORD

In conducting the research described in this report, the investigator(s) adhered to the "Guide for the Care and Use of Laboratory Animals," prepared by the Committee on Care and Use of Laboratory Animals of the Institute of Laboratory Animals Resources, National Research Council (DHEW Publication No. (NIH) 78-23, Revised 1978).

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INTRODUCTION

Over the period from May 1973 to February 1983 research was conducted to develop a technique for chemically depositing metallic silver on teeth. Initially, the primary emphasis was to use the metal layer as a pit and fissure sealant. In time the emphasis was shifted to include the possible use of the film as an adhesive intermediate. The idea was to first obtain a stable, adherent metallic silver layer onto tooth structure. Once the silver was in place it was assumed that amalgam filling material could then be chemically bonded to the metal layer, providing a stronger attachment which would be less susceptible to micro-cracks and micro-leakage.

Some feasibility studies had been conducted prior to February 1983 on the process and it was shown to be feasible. Using this as a starting point, a research program was initiated to determine the effects of various process parameters on the resulting film and its properties. The properties thought to be most important were resistance to wear, adherence and ability to react properly with amalgams. Throughout the study various evaluative techniques were employed and included physical and chemical analyses of the surfaces, hardness and wear tests, electrochemical tests such as deposition rates and potential measurements and electrical conductivity.

The actual chemical process remained basically similar throughout the research but the chemical, physical and electrochemical specifics were varied as required to enhance or improve the coating properties.

The basic technique involved pre-treating or etching the tooth structure, followed by a series of repetitions of steps which included applying an ionic silver solution to the tooth and then reducing the ions with a suitable chemical reagent. The thickness of the silver layer increased with the number of repetitions and parameters used in the process.

The following report will deal chronologically with the principal highlights, results and conclusions obtained from the studies.

SUMMARY

I. Report Period Ending July 1974

The major objectives of the work were indicated to be:

1. To investigate some of the main parameters influencing the electroless deposition of metal onto teeth. This involved altering the process variables such as chemical systems, concentrations, times of application, surface preparation and etching, etc., and evaluating the results.
2. To find metal systems, other than Cu and Ni, preferably noble metals, which could be plated. Initially, only Ni and Cu had been deposited. Preliminarily, Ag was chosen as the metal which would receive the major emphasis.
3. To use information gained through studies such as those outlined in (1) above to find methods which would yield a satisfactory deposit by means of an applicator system. Initially, only complete immersion of the tooth in the solutions gave a suitable metal coating, and obviously beaker flooding or dam-type processes would be undesirable.
4. To reduce the time required for metal deposition to some feasible value, preferably less than 15 minutes. This, of course, was to be conducted in conjunction with (3) above.
5. To characterize the tooth surfaces and deposits by means of scanning electron microscopy (SEM), X-ray analysis and Auger analysis. There were numerous secondary objectives as well, and many of them became more obvious as the research progressed.

Cont'd

The highlights and conclusions were:

1. A process has been perfected which allows extracted teeth to be electrolessly plated using cotton swab applicators to apply the solutions;
2. Both copper and silver coatings have been successfully applied by the swab applicator technique;
3. Metal adherence to the tooth seems to be good, and rough estimates of the bond strength are 1000 psi. This value is in line with strengths obtained for commercial electroless plating on plastics. The coatings will resist abrasion using standard dental hand tools (such as picks) but can be removed with rotary tools (such as abrasion or polishing wheels).
4. Thicknesses of the order 0.0003 inches have been obtained for the standard plating process now being used. The time required to produce this thickness was approximately 8 minutes. The amount of metal deposited is directly proportional to the time of plating. Thus, thicker deposits may probably be obtained, but the time required would be increased.

II. Report Period Ending July 1975

A gold film was successfully deposited onto tooth enamel using hydrozinc. In general, this was viewed as an advance, however, employing hydrozinc was thought to be objectionable for either gold or silver and a substitute was felt to be desirable.

One major advance during this period was the first in vivo research on monkeys at Walter Reed Army Hospital and was reported as follows.

During November 1974, the first attempts to apply the metal deposits in vivo were attempted at the U.S. Army Institute of Dental Research (USAIDR) Laboratories, Walter Reed Army Hospital, Washington, DC. A total of six monkeys had certain previously selected teeth plated by either Ag or Au. An amalgam filling material was also applied to a few of the plated teeth. The plating process seemed to be relatively easy to apply, and, in general, the overall behavior and results were similar to those obtained during in vitro studies. It was also agreed that there was no apparent tissue damage. Both AgF and $AgNO_3$ solutions were used, and the fluoride seemed to be less reactive to the tissue than the nitrate in areas where solution got on the tissue. When this occurred, there was a darkening that resulted.

The animals were kept on a regular diet and checked periodically by USAIDR personnel. Details of the protocol were also kept for the record. A more complete report of the tests, with a more detailed analysis of results will probably be completed and published by USAIDR in the near future. We also hope to be able to perform SEM studies on some of the teeth to determine the character of the deposits that remain.

One problem that did arise was the appearance of the black layer that remained after the metal deposit was worn away. This is less of a difficulty in the pit and fissure areas, but could present an aesthetic problem. As mentioned previously, this is probably a very finely divided Ag deposit, and may be necessary to provide adequate bonding. Work is now being conducted in this area to determine the exact nature of this dark layer and to see if some modificiations to the process might alleviate or eliminate it.

In addition, improved characterization of the metal-tooth interface by means of Electron Spectroscopy for Chemical Analysis (ESCA) was accomplished. The chemical nature of the surfaces became more clearly established and it was proven that metallic silver was present after the first repetition as shown in Table 1.

III. Report Period Ending July 1976

Experimentally, the research emphasized testing of the adherence of the films in shear, evaluation of the thickness of the silver and characterizing the nature of the surfaces using ESCA, X-ray diffraction and SEM techniques.

A manuscript was also submitted for publication to the Journal of Dental Research.

The deposit thickness as a function of number of repetitions was determined and is shown in Figure 1. Silver fluoride (120 g/l) and hydrozinc (10 ml/l) was used to make the deposits.

IV. Report Period Ending April 1977

Research included evaluation of the film conductivity, continued characterization (ESCA, SEM, tensile testing and transmission electron microscopy) and kinetic studies on the rate of formation of the film were initiated. Papers entitled "Electroless and Chemical Metal Deposition on Human Tooth Enamel" and "Caries Prevention by Electroless Deposition of Metals-A Preliminary Primate Study" were published in the Journal of Dental Research in June 1977 and Journal of Preventive Dentistry in Jan/Feb 1977, respectively.

The major objective at this stage became finding a suitable alternative to hydrozinc as the chemical reducing agent as toxicity was felt to be a concern. Also, the solution pH was too harsh and a more neutral solution was needed.

TABLE 1

ESCA analysis of tooth surfaces at different stages during electroless deposition (carbon counts excluded).

	P^{+5}	Sn^{+2}	Ag^{+}	Ag^{0}	Ca^{+2}	F^{-}	Ca/P
Standard tooth	17.35	0	0	0	82	0	4.7
Etch 1 min in 50% H_3PO_4	19.1	0	0	0	76	4.5	4.0
Etch (as above) + 3 hr soak in 10% SnF_2	4.2	74.0	0	0	12	9.3	2.9
Etch (as above) + 3 hr soak in 100 gpl AgF	3.9	0	70	0	16.8	8.5	4.2
Etch (as above) + 3 hr soak in 100 gpl AgF + reduction by Hydrazine	4.3	0	19.9	65	5.9	4.8	1.4

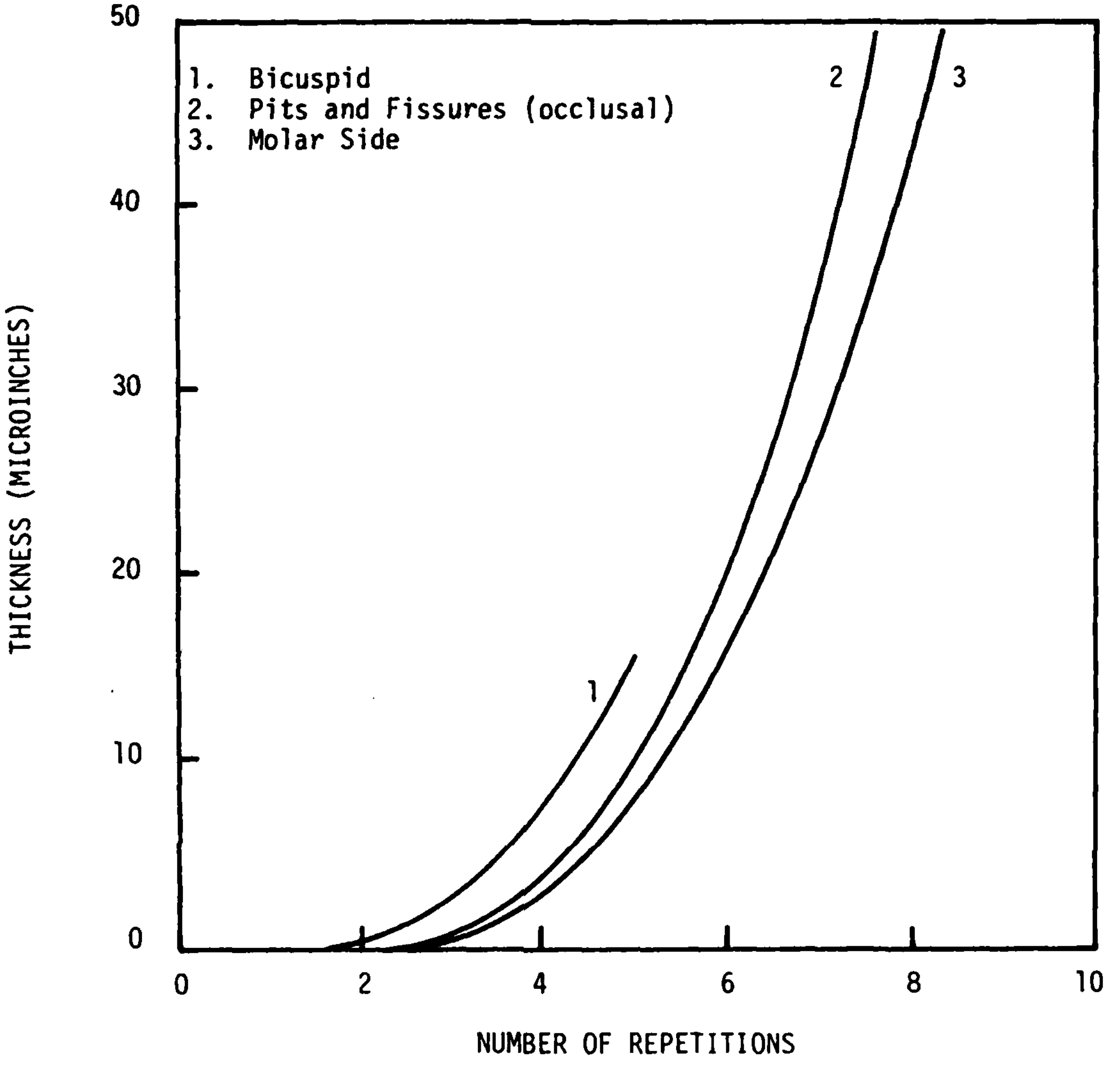

1. Bicuspid
2. Pits and Fissures (occlusal)
3. Molar Side
THICKNESS (MICROINCHES)
NUMBER OF REPETITIONS
0
10
20
30
40
50
0
2
4
6
8
10
1
2
3

Figure 1

After feasibility screening, ferrous sulfate was chosen as the potential reducing agent. Comparisons of the amount of silver deposited using ferrous sulfate and hydrozinc are shown in Figures 2, 3, 4 and 5. In general, the deposits made using ferrous sulfate were reasonable, but were not felt to be of equal quality to those made using hydrozinc.

Another in vivo test was made at Walter Reed Army Hospital using monkeys and rats and the protocol summary is given in Table 2.

The consensus at this stage was that (1) this system of metallizing teeth is feasible, (2) the metal coating is firmly adherent for a period in excess of 6 months, (3) the color is objectionable if the entire crown is coated but appears identical to amalgam if selectively applied to the pits and fissures, (4) amalgam will interact with the metallized surface, (5) preliminary studies indicate antibacterial and antiplaque potential, and (6) many of the problems inherent in conventional pit and fissure sealants are obviated.

V. Report Period Ending August 1978

The search for improved reducing agents became the central theme of the research. It was decided that one avenue of approach would be to chemically alter the reducing solutions by the use of addition agents or to pre-treat the tooth surface initially to enhance the reaction and improve the resulting metal structure.

Alternate reducing agents were tested and the results are given in Tables 3 and 4. Electrical resistance was used as an initial indicator of metal continuity and quantity.

Conclusions from these data were that the etching step was critical to the process and that sugars (such as glucose) and stannous ion might be possible reducing agents.

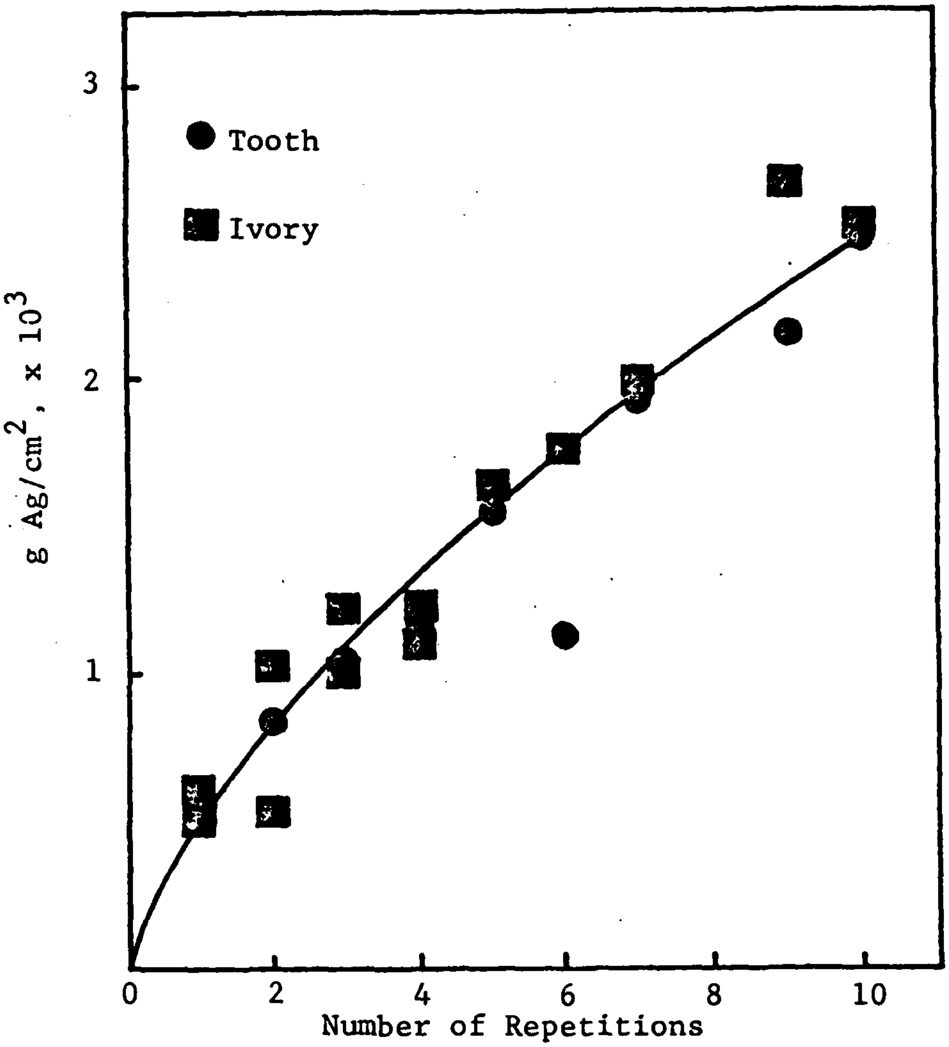


Figure 2. Grams of silver deposited per square centimeter of substrate as a function of the number of repetitions of a sequence for the sequence AgF 100gpl, pH6.5 - $FeSO_4$ saturated solution, pH 3.5. The substrate had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

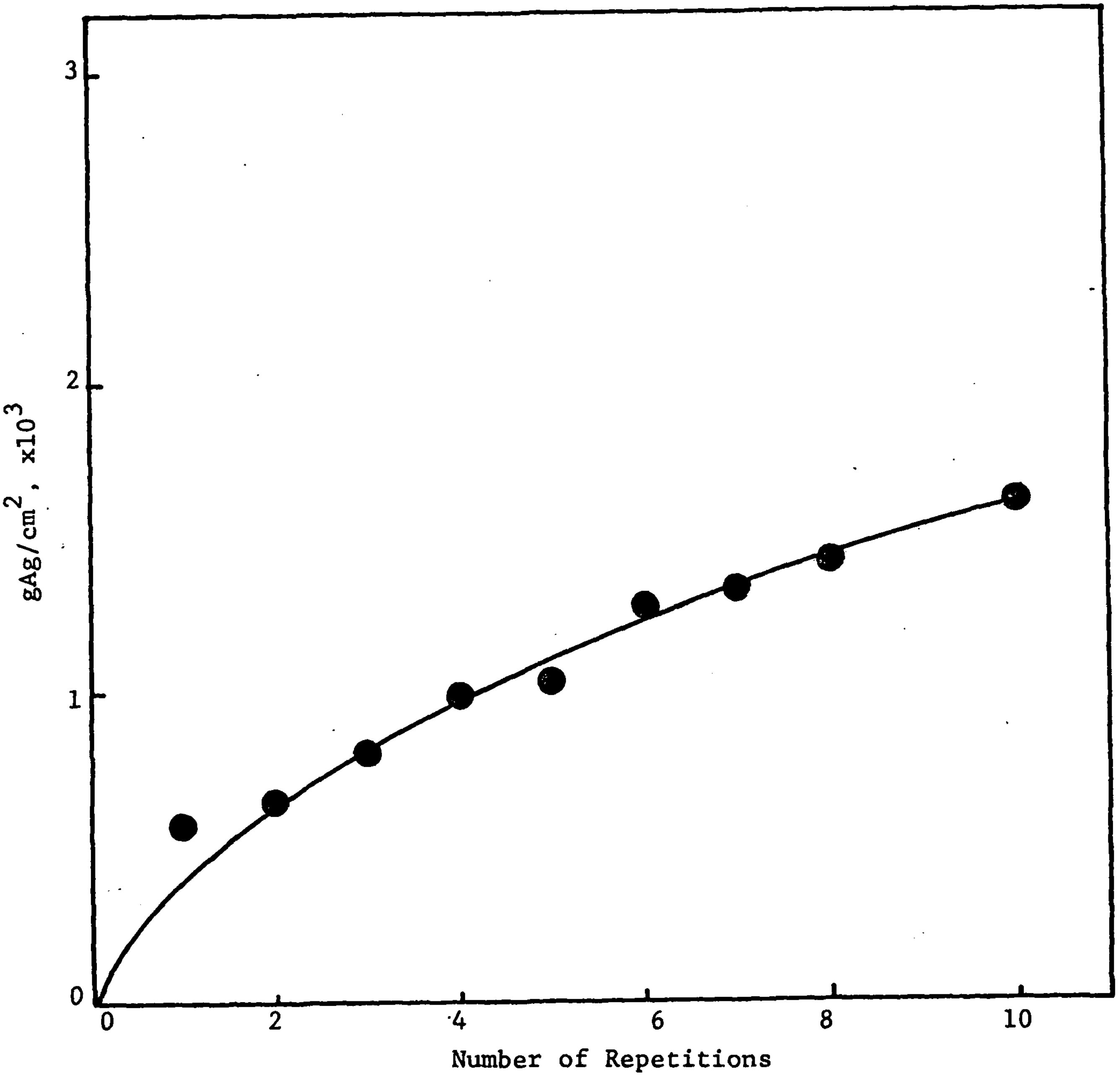


Figure 3. Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [$AgNO_3$ 120gpl, pH4.0 - $FeSO_4$ 200gpl, pH3.5] The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

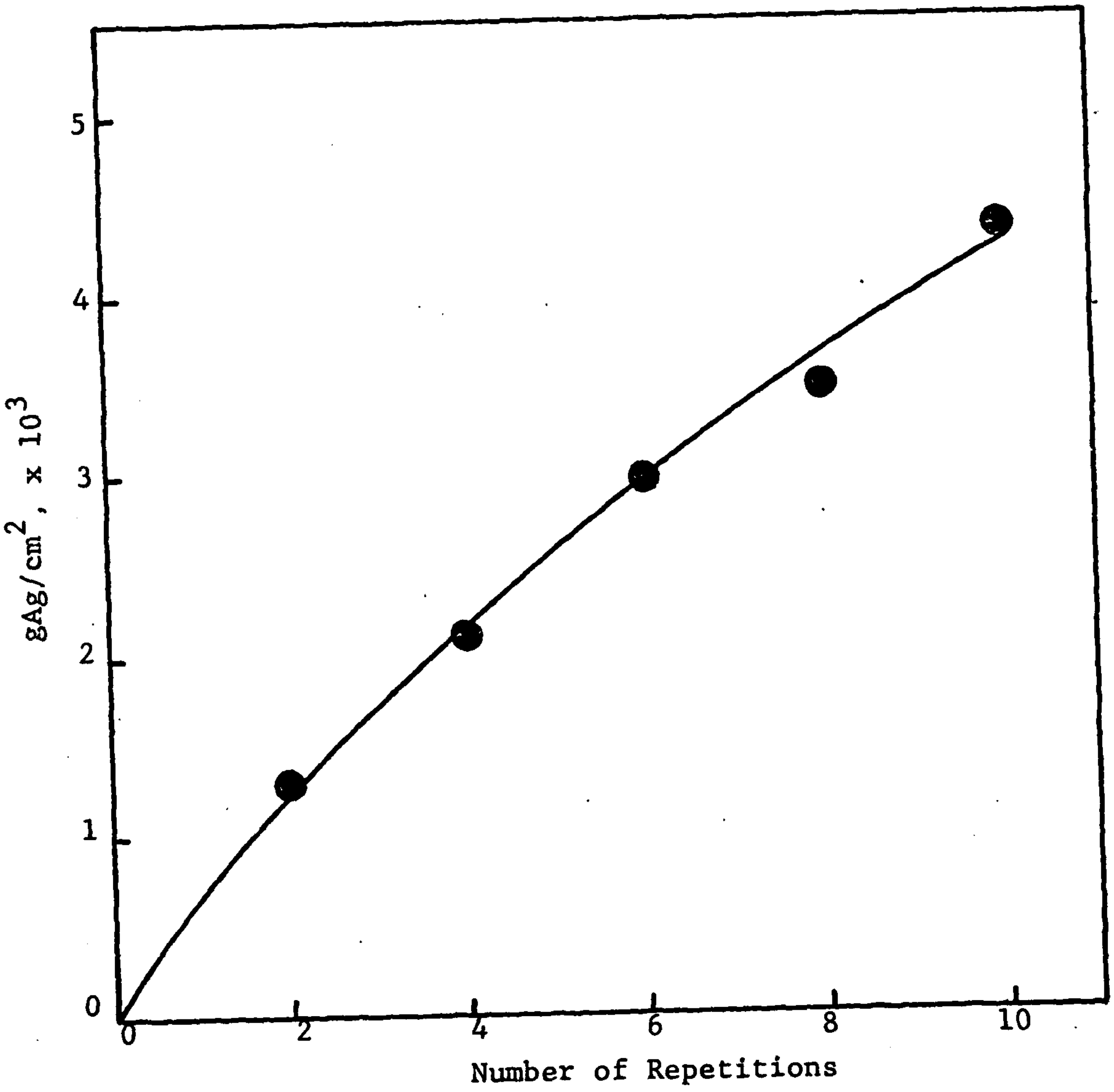


Figure 4. Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [AgF 80gpl, pH 8.75 with NH_4OH - N_2H_4 10 ml/l, pH 9.0]. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

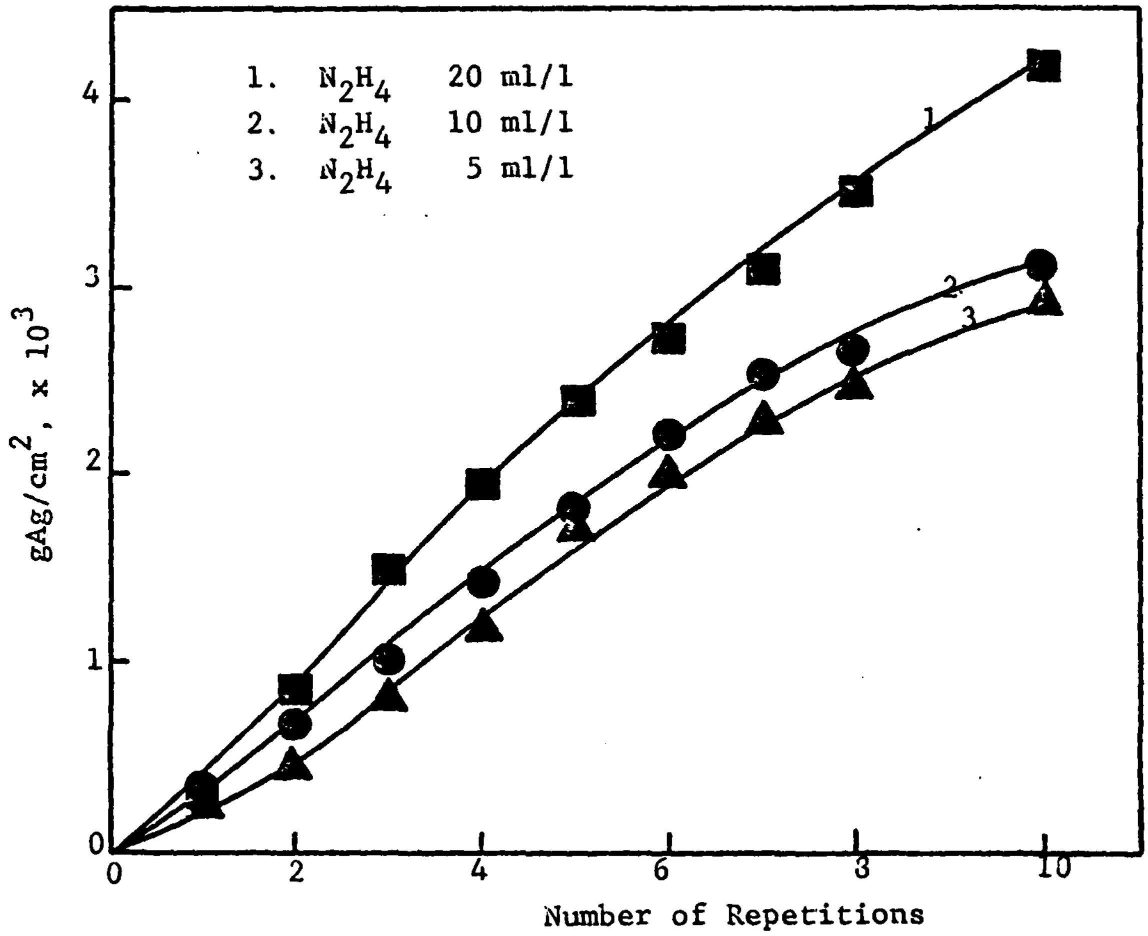


Figure 5. Grams of silver deposited per square centimeter of ivory as a function of the number of repetitions of a sequence for the sequence [$AgNO_3$ 120gpl, pH 8.75 with NH_4OH - N_2H_4, pH 9.0]. The ivory had received a 1.0 minute, 42.5% H_3PO_4 etch, and was then rinsed prior to plating.

TABLE 2

Summary of protocol on plating of animals at Walter Reed Army Hospital.

A. Monkeys

M-397

Quadrants plated - upper right, lower left.
Etch - 1.0 minute 42.5% H_3PO_4, rinse.
Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution
+ .1 gpl, SnF_2, pH 6] 10X.

Incline planes etched well, but not bottom of fissures. Large amount of yellow phosphate formed before first Fe^{++} reduction. 10 Ω/cm after 5 applications. On incline planes, white appearance with start of 8th application. .7 Ω/cm to 30 Ω/cm between 2 incline planes after 10 repetitions. Less than 1 Ω/cm over rest of teeth after 10 repetitions. First molars then covered with amalgam. Applied by R. Christie.

P-483

Quadrants plated - upper right, lower left.
Etch - 1.0 minute 42.5% H_3PO_4, rinse.
Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH 6] 10X.

Incline planes etched well, but not bottom of fissures. Yellow phosphate again formed before 1st Fe^{++} reduction. 15-150 Ω/cm after 5 repetitions. White color after 10th application. 0.5-7.0 Ω/cm. 2nd molars covered with amalgam. Applied by R. Christie.

P-512

Quadrants plated - upper right, lower left.
Etch - 1.0 minute 42.5% H_3PO_4, rinse.
Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH 6] 10X.

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

H-395

Quadrants plated - upper right, lower left.
Etch - 1.0 minute 42.5% H_3PO_4, rinse.
Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH 6] 10X.

Incline planes etched well, but not bottom of fissures. Yellow phosphate again formed before 1st Fe^{++} reduction. Upper right 1.5-200 Ω/cm after 10 repetitions. Lower left 7-150 Ω/cm after 10 repetitions. 2nd molars received amalgam. Applied by Lt. Col. R. Woody.

TABLE 2 (cont'd)

H-336

Quadrants plated - upper right, lower left.
Etch - 1.0 minute 42.5% H_3PO_4, rinse.
Deposition - [AgF 100 gpl - N_2H_4 10 ml/l] 10X.

Etch good. Upper right - medium yellow phosphate, rate of reduction high. 4-7 Ω/cm after 3rd repetition. 0.2-0.5 Ω/cm after 10th repetition. Electroplated 1st & 2nd bicuspids, 1st molar. 0 Ω/cm after electroplate. Lower left - loose, medium yellow phosphate. 0-0.1 Ω/cm after 10 repetitions. Applied by R. Christie.

B. Rats

All plated with following sequence.
Etch - 1.0 minute 42.5% H_3PO_4, rinse.
Deposition - [AgF 100 gpl - $FeSO_4$ saturated solution, pH 6] 10X.

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

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

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

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

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

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

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

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

TABLE 3

Average resistance values of the Ag plated tooth enamel as a function of the reducing agent and the pH of the AgF solution. The sequence of operation was: glycerin storage, water wash, $NaHCO_3$ scrub, water wash, saline solution, WB, 42.5% H_3PO_4 etch for 60 sec, WB, AgF + reducing agent (10X). The residence time between successive applications was the usual 30 sec unless otherwise noted.

Reducing Agent	100 gpl AgF solution		
	pH = 0.5 with HNO_3 Ω	pH = 7.4 Ω	pH = 8.3 with NH_4OH Ω
Saturated SnF_2 (pH = 2.6)	4.0×10^{3a}	5.3×10^{3a}	1.5×10^{5a}
Saturated $SnSO_4$ (pH = 1.6)	5.9×10^{4a}	9.9×10^{2a}	7.4×10^{6a}
Saturated FeF_2 (pH = 4.2)	7.4×10^{7a}	7.9×10^{7a}	4.0×10^{7a}
400 gpl Dextrose (pH = 4.7)	∞^{b}	∞^{b}	∞^{b}
Saturated Dextrose (pH = 4.7)	$> 10^{7a,b}$	--	--
Saturated CoF_2 (pH = 5.5)	1.9×10^{7c}	1.2×10^{8c}	∞^{c}
280 gpl $CoSO_4 \cdot 7\ H_2O$ (pH = 3.2)	1.3×10^{6a}	7.5×10^{3a}	∞^{a}
Saturated hydroquinone (pH = 3.8)	5.0×10^{7c}	24^{c}	0.4^{c}
10% H_2O_2 (pH = 3.9)	--	∞^{d}	$> 10^{7d}$
Saturated $Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$	--	5.5	--

[a] 5 minute intervals between applications

[b] 5 applications

[c] formaldehyde storage

[d] saline storage

TABLE 4

Average resistance values of the Ag plated tooth enamel as a function of the reducing agent and the pH of the $AgNO_3$ solution. The sequence of operation was: glycerin storage, water wash, $NaHCO_3$ scrub, water wash, saline solution, WB, 42.5% H_3PO_4 etch for 60 sec, WB, $AgNO_3$ ↼ reducing agent (10X). The residence time between successive applications was the usual 30 sec unless otherwise noted.

	100 gpl $AgNO_3$		
Reducing Agent	pH = 0.5 with HNO_3 Ω	pH = 6.2 Ω	pH = 8.3 with NH_4OH Ω
Saturated SnF_2 (pH = 2.6)	$2.9 \times 10^{7a}, \infty^{a}$	3.7×10^{7a}	∞^{b}
Saturated $SnSO_4$ (pH = 1.6)	1.9×10^{7b}	1.9×10^{7b}	1.8×10^{7b}
Saturated FeF_2 (pH = 4.2)	3.0×10^{7a}	∞^{a}	3.2×10^{7b}
400 gpl $FeCl_2 \cdot 4\ H_2O$ (pH = 0.9)	$\infty^{a}, 8.9 \times 10^{7a}$	8.6×10^{7a}	↼↼
400 gpl $FeSO_4 \cdot 7\ H_2O$ (pH = 3.3)	∞^{a}	48^{a}	↼↼
400 gpl $FeSO_4 \cdot 7\ H_2O$ (pH = 5.5 with NH_4OH)	↼↼	$1.3 \times 10^{2b,c}$	↼↼
Saturated CoF_2 (pH = 5.5)	1.5×10^{7c}	8.8×10^{7c}	1.1×10^{8c}
280 gpl $CoSO_4 \cdot 7\ H_2O$ (pH = 3.2)	$1.7 \times 10^{7b,c}$	$\infty, 1.2 \times 10^{8b,c}$	$4.4 \times 10^{7b,c}$
400 gpl Dextrose (pH = 4.7)	∞^{a}	∞^{a}	∞^{a}
400 gpl Glucose (pH = 4.8)	∞^{a}	∞^{a}	$1.5 \times 10^{7a,b}$
Saturated hydroquinone (pH = 3.8)	1.0×10^{5c}	1.4×10^{5c}	0.5^{c}
10% H_2O_2 (pH = 3.9)	8.9×10^{7d}	7.3×10^{7d}	9.8×10^{7d}

[a] 5 applications

[b] 5 minute intervals between applications

[c] formaldehyde storage

[d] saline storage

VI. Report Period Ending August 1979

Advances during this period included the use of ascorbic acid as a reducing agent, substantial improvement in the silver metal coating made using ferrous ion by using low concentrations of an organic additive (thiourea) and the use of electrolytic brush plating on top of the electroless coating to improve the properties and development of a wear test for the films. In addition, another in vivo test was planned.

The effect of thiourea in increasing the rate of deposition of silver is shown in Table 5.

Shear tests using amalgam were also made and some of the values are given in Table 6.

A statistical screening test was also made and the variables and limits used are given in Table 7. The results of the test are summarized in Table 8.

Some of the conclusions that could be made through this stage of the research were:

1. The conductance of the deposit is improved by lowering the pH of the $FeSO_4$ solution or adding thiourea to the reductant. The optimum values of various parameters appear to be 5.3 pH 100 gpl AgF, 2 pH saturated $FeSO_4$ with 0.5 gpl thiourea for both ivory and enamel substrates.
2. The rate of deposition increases with increasing AgF pH (5.3 better than 1.5) or concentration (100 gpl better than 50 gpl), or using thiourea in the reductant (0.5 is the optimum for a range of 0.0 to 1.0 thiourea).
3. Morphologically, the grain size of the deposit decreases with the use of thiourea and the optimum concentration appears to be 0.5 gpl when 100 gpl AgF and saturated $FeSO_4$ pH are 3.3 and 2.0, respectively, for

TABLE 5

Effect of thiourea and AgF pH on the rate of Ag deposition on ivory. Plating Conditions: 100 gpl AgF (pH varying) < sat. $FeSO_4$ + H_2SO_4 + 0 or 0.25 gpl thiourea (2 pH), 10X, 1/4" dia. circle plated.

AgF pH	Thiourea (gpl)	Resistance (Ω)	Rate (mg of Ag/cm^2)	% Increase with Thiourea
6.85	0.25	0.17	2.63	10.5
6.85	0.0	0.54	2.38	<<
5.1	0.25	0.37	3.59	103
5.1	0.0	10.36	1.77	<<
1.8	0.25	0.48	3.75	119
1.8	0.0	≈24	1.71	<<

TABLE 6

Shear test results on ivory substrate[a] (42.5% H_3PO_4 etch, WB, Ag→Fe sequence, 10X, WB).
Amalgam condensed by hand.

Method of Application	Shear Stress (psi)				
	Oraloy	Optaloy			Caulk Spherical
		"OP"	"C"	"B"	"OP"
I. 100 gpl AgF + HNO_3 (≈3.8 pH) → sat. $FeSO_4$ + H_2SO_4 (2 pH) System					
Standard[b]	672 ± 406 (4, 0→1025)	872	895	376	337
Standard Reverse[c]		657	265	294	
Prereduction[d] + Standard[b]	732 ± 427 (3, 0→1167)				
Standard[b] (using 0.5 gpl thiourea in reducing solution)	1284 ± 889 (6, 0→2887)				
Prereduction[d] + Standard[b] (using 0.5 gpl thiourea in reducing solution in both steps)	1396 ± 742 (3, 0→1920)				
II. 100 gpl AgF + NH_4OH (7.3 pH) → 10 ml/1 N_2H_4 System					
Standard[a]	1397 ± 249 (7, 0→1700)	728 ± 239 (3, 0→1000)	602 ± 492 (4, 0→1333)	278	
Standard Reverse[b]			964		

[a] Shear stress values of 0 psi are not considered in the calculation of average or the standard deviation.
Number of samples with non-zero stress and the spread of values are given in parentheses.

[b] Standard procedure of plating: Ag^+ solution → reducing solution.

[c] Standard reverse: reducing solution → Ag^+ solution.

[d] Prereduction: Ag^+ solution → water wash → reducing solution.

TABLE 7

Variables and the limits.

Variables	Lower Limit (-)	Upper Limit (+)	Center Points
X_1, AgF Concentration (g/l)	50	100	75
X_2, pH of AgF	1.5, 1.85[a]	5.3, 5.1[a]	4.2
X_3, pH of Saturated $FeSO_4$	2.0	3.5, 3.35[a]	2.7
X_4, Thiourea Concentration (g/l)	0.0	0.5	0.25
X_5, Residence Time (sec)	30	90	60
X_6, Application Technique	no rub	rub	medium rub
X_7, Dummy			

[a] The pH limits changed after aging the solutions (even though they were the same after initial adjusting).

TABLE 8

Summary of statistical screening of variables for electroless Ag deposition on ivory ($AgF-FeSO_4$ system, refer to the fourth quarterly report for 1978-79).

Responses →	Conductance		Rate		Wear Resistance		Shear Stress	
Variables	Main Effect Estimate Ω^{-1}	Confidence Level (%)	Main Effect Estimate (mg/cm^2)	Confidence Level (%)	Main Effect Estimate	Confidence Level (%)	Main Effect Estimate (psi)	Confidence Level (%)
X_1, AgF Concentration (gpl)	1.58	48	0.83	>99	0	<20	381	90
X_2, AgF pH	1.31	42	0.54	>99	1.0	36	447	92
X_3, Saturated $FeSO_4$ pH	-3.81	74	-0.33	>99	0	<20	-541	94
X_4, Thiourea Concentration (gpl)	4.66	78	1.00	>99	4.5	68	303	88
X_5, Residence Time (sec)	1.12	36	-0.29	>99	0	<20	183	80
X_6, Application Technique	6.93	84	0.63	>99	-2.5	50	105	70
X_7, Dummy	-1.67	50	-0.0025	50	2.5	50	55	50

both ivory and enamel substrates. However, at AgF pH's higher than 3.3, the thiourea might have less of an effect in reducing the grain size although other properties such as wear resistance might improve as noted below.

4. The wear resistance improves with the use of thiourea and with increasing pH of AgF. The optimum conditions for enamel substrates appear to be 5.4 pH 100 gpl AgF and 2 pH saturated $FeSO_4$ with 0.3 gpl thiourea.
5. The shear strength of the amalgamated deposit increases with the use of thiourea. The shear strength of the amalgamated silver deposits obtained from $FeSO_4$ approached that of N_2H_4 reduced deposits when 0.5 gpl thiourea was used in 2 pH saturated $FeSO_4$ solution with 3.8 pH 100 gpl AgF for ivory substrate.

VII. Report Period Ending August 1980

Laboratory work was conducted to define an optimum delivery system for use in a third in vivo test at Walter Reed Army Hospital. The latter was to test the film in reducing decay in caries susceptible rats.

Topical pre-treatment with various solutions was also examined and it seemed that the application of SnF_2 for a few minutes prior to plating was very beneficial as shown in Table 9.

At this stage a "Standard Operating Procedure" was written in order to establish all the operating procedures, methods and materials employed in the process and was reported as follows.

TABLE 9

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

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 RPM 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 an 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 are 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, FL 32602 Ventron, Alfa Division, 152 Andover Street, Danvers, MA 01923
$AgNO_3$ (99.99%)	Research Organic/Inorganic Chemical Corp., 11686 Sheldon Street, Sun Valley, CA 91352
$FeSO_4 \cdot 7\ H_2O$	Fisher Scientific Co., Fair Lawn, NJ 07410
$Fe(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$	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

Compound (continued)	Manufacturer (continued)
Nitric Acid HNO_3	Fisher Scientific Co., Fair Lawn, NJ 07410
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 cathode #1, calomel). Adjust pH by addition of NaOH, NH_4OH, or HNO_3.

Ex. 100 g/l AgF - 25 ml solution

100 g x 25 ml/1000 ml = 2.5 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 saturated $FeSO_4$ with 3 ml of a 10 g/l thiourea solution.

$\underline{HNO_3}$ - For dissolving silver for AA analyses (used for rate studies). 50% of bottle concentrated HNO_3 = 1 part HNO_3 + 1 part demineralized H_2O.

$\underline{H_3PO_4}$ - 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$_2$H$_4$) 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:

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

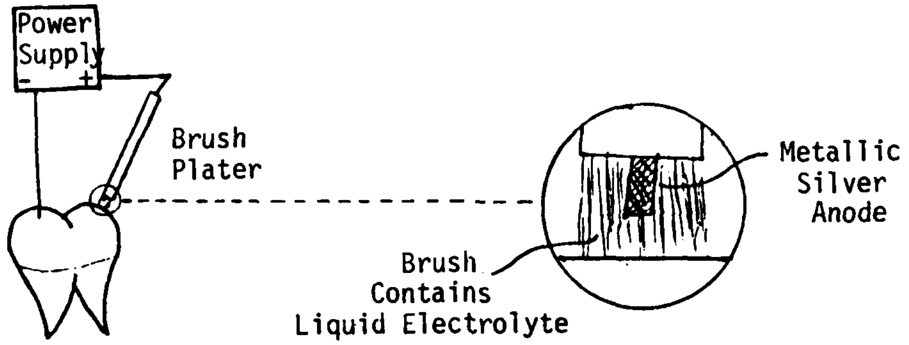
During plating visual observations should be made. Interesting points are:

- formation of Ag$_3$PO$_4$, 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 mentioend. 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 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 of 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 zero (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 0.013 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 sec 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 in 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 ≈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 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.

VIII. Report Period Ending August 1981

Emphasis during this year had been on refining and optimizing the existing silver delivery system and initiating efforts to evaluate the use of the layer with amalgam fillings.

Citric acid was also found to be a possible substitute for the harsher phosphoric, and SnF_2 appeared to improve the adherence of amalgam when it was placed on the tooth after etching.

Cysteine also seemed to function well as an additive in place of thiourea. A summary of the influence of these various conditions on the shear stress and wear resistance is given in Table 10.

A manuscript entitled "Deposition Rate of Metallic Ag on Ivory and Enamel" was submitted for publication to the Journal of Dental Research (actual publication was February 1982).

IX. Report Period Ending February 1983

The final effort was concerned with optimizing the adhesion of the metal film and minimizing the number of very low shear stress values. This amounted to reducing the scatter in the shear stress values. In this respect, one of the factors which seemed to be of great importance was the degree of initial dryness of the tooth surface. Another factor, but one which was in some respects was out of our control, was the trituration behavior of the amalgam. Lack of homogeneity, in terms of the mercury content, presented some problems since it seemed that small differences could effect the adherence. Some tests using commercially available amalgams were conducted and the results given in Table 11.

TABLE 10

The samples were treated in the following manner: 1 min 42.5% H_3PO_4 or 1 min 50% citric acid, 3 min 50 gpl SnF_2 or no. 1 min 200 gpl $AgNO_3$ pH 2.85, 1 min $FeSO_4$ + 1 gpl thiourea or 1 gpl cysteine. 9 repetitions of $AgNO_3$ < $FeSO_4$ + additive < $AgNO_3$. Numbers in parentheses are the amounts of tests.

	Shear Stress (psi) Dentin	Wear Resistance Ivory	Wear Resistance Enamel*
H_3PO_4 etch	728 ± 421 (13)	5.58 ± 2.57 (12)	5.08 ± 2.39 (12)
Citric acid etch	1080 ± 467 (15)	7.00 ± 3.28 (12)	0 ± 0 (12)
SnF_2 pretreatment	1003 ± 380 (12)	8.42 ± 0.90 (12)	6.00 ± 1.26 (6)
No pretreatment	852 ± 536 (16)	4.17 ± 2.79 (12)	4.17 ± 2.99 (6)
Thiourea additive	789 ± 351 (11)	6.67 ± 2.74 (12)	5.83 ± 2.86 (6)
Cysteine additive	1105 ± 601 (11)	5.92 ± 3.26 (12)	4.33 ± 1.75 (6)
SnF_2 < Thiourea†	951 ± 312 (6)	8.00 ± 1.10 (6)	7.00 ± 0 (3)
SnF_2 < Cysteine	1055 ± 463 (6)	8.83 ± 0.41 (6)	5.00 ± 1.00 (3)

*The enamel samples etched with citric acid are excluded from the average numbers in all cases except the comparison between H_3PO_4 and citric acid.

†The samples were preheated with SnF_2 and the $FeSO_4$ solution contained either thiourea or cysteine.

Note: Samples were aged in H_2O at 37°C for 24 hours.

TABLE 11

Comparison of shear stress values of different amalgams on silver foil.

Alloy Pellet	Amount of Hg (%)	Trituration Time (sec)	Shear Stress (psi)
Fine Cut Caulk	51	7	1049 ± 392 (3)*
Fine Cut Caulk Non-zinc	51	10	1218 ± 481 (3)
Aristaloy	52	8	1435 ± 544 (4)
Aristaloy	55	8	1344 ± 276 (4)
Aristaloy	57	8	1560 ± 559 (4)

*Numbers in parentheses indicate number of tests.

Mordants were evaluated as well, but with mixed results, and Fe^{+3}, Zr^{+4} and Ti^{+3} did not perform as well as the one that had been used previously, Sn^{+2}.

The final modifications used to improve the process are listed in Tables 12 and 13, and similar tests on dentin are given in Table 14.

X. Summary and Conclusions

The general feeling of those involved in the process (including Dr. J. O'Connell formerly of American Hospital, whose group conducted considerable research on the process) is that a chemically viable procedure has been developed to coat teeth with silver. The metal film properties have been continually improved over the years. Additional advances are probably possible as needed to address any shortcomings that become evident during use.

As a final summary, a description of the electroless plating procedure that gave the best, most reproducible results is given. The procedure consists of four important stages: etching, pre-treatment, pre-reduction and the repetitions (metal ion-reducing agent) for plating.

A. Standard Procedure for Electroless Plating

Substrate: exposed dentin or polished ivory

1. Etching
   a. Rinse with demineralized water.
   b. Blot dry (in some instances different drying conditions are used).
   c. 1 min 50% citric acid in water, natural pH, move Q-tip during etching (dentin); 1 min 42.5% H_3PO_4 (ivory).
   d. Rinse with demineralized water.
   e. Blot dry or nitrogen-acetone when stated.

TABLE 12

Drying samples at different stages of electroless plating using nitrogen and acetone.

Silver plating: Plating procedure "A", with 200 gpl $AgNO_3$ pH 2.85
Substrate: Ivory
Amalgam: Spheraloy, 2 pellets, 44% Hg, 5 sec trituration time, M<2 setting

Drying	Number of Tests	Shear Stress (psi) Individual Values	Shear Stress (psi) Mean & St. Dev.
before 1 min 42.5% H_3PO_4	3	1708, 1262, 838	1269 ± 435
before 3 min 50 gpl SnF_2	3	2454, 1908, 1792	2051 ± 354
before 1 min 200 gpl $AgNO_3$ pH 2.85	3	1469, 1292, 1169	1310 ± 151
before 1 min sat $FeSO_4$ + 1 gpl Cysteine	3	1885, 1085, 2038	1669 ± 488
before first $Ag^{+} < Fe^{+2} < Ag^{+}$	3	2015, 1062, 1723	1600 ± 488
before all $AgNO_3$ applications	3	2631, 2269, 1915	2272 ± 358
before every step	3	2485, 1085, 2038	1869 ± 715
control*	3	1154, 754, 1177	1028 ± 238

*Blot dried before every step.

Note: Every sample was burnished before amalgamation.

TABLE 13

Ivory: Modifications on standard procedures and effect on shear stress.

Modifications	Exp. No.	Drying with $N_2 \leftarrow \text{Acetone} \leftarrow N_2$ (before)	Drying with $N_2 \leftarrow \text{Acetone} \leftarrow N_2$ (during)	Shear Stress (psi)	No. of Tests
Without SnF_2; no cysteine	1	Prereduction		431 ± 122	4
Without SnF_2; cysteine	2	Prereduction		850 ± 268	4
AgF all steps; 1 min AgF before SnF_2 (pretreatment)	3	a) AgF b) Pretreatment c) Three first repetitions	Prereduction	135 ± 81	4
AgF all steps; 1 min AgF before SnF_2 (pretreatment); prereduction twice	4	a) AgF b) Pretreatment c) Prereduction d) Three first repetitions		1419 ± 612	5
AgF (prereduction); $AgNO_3$ (repetitions)	5	a) Pretreatment b) Three first repetitions		1272 ± 461	3
AgF before SnF_2 (pretreatment); AgF (prereduction), $AgNO_3$ (repetitions)	6	a) AgF b) Pretreatment c) Three first repetitions	Prereduction	541 ± 340	3
AgF in all steps; standard procedure with modified drying conditions	7	a) Pretreatment b) Three first repetitions		2252 ± 319	4

TABLE 14

Dentin: Modifications on standard procedure and effects on shear stress.

Modifications	Shear Stress (psi)	Maximum and Minimum Values	Number of Tests
$AgNO_3$ all steps; SnF_2 kept wet for prereduction	1100 ± 647	2038; 477	6
AgF (prereduction); $AgNO_3$ (repetitions)	910 ± 104	1015; 808	3
AgF before SnF_2 (pretreatment; $AgNO_3$ (repetitions)	461 ± 133	538; 308	3
AgF all steps; 1 min AgF before SnF_2 (pretreatment); 1 min AgF after SnF_2 (pretreatment)	1289 ± 409	1615; 692	4
AgF all steps; 1 min AgF before SnF_2 (pretreatment); SnF_2 left wet for prereduction; 2 more SnF_2 (pretreatment) followed by 1 min AgF with SnF_2 left wet	1092 ± 186	1315; 862	4
$AgNO_3$ all steps; standard procedure with modified drying conditions*	1461 ± 300	1892; 977	19

Note:
1) Samples were always nitrogen-acetone dried for AgF before pretreatment.
2) Drying steps: before pretreatment, prereduction, and three first repetitions.
3) All samples dried with nitrogen-acetone but *.
4) *Dried with nitrogen-acetone-ether.

2. Pre-treatment

    a. 3 min 50 gpl SnF_2 in water (fresh solution), natural pH, move Q-tip during application.

    b. Rinse with demineralized water.

    c. Blot dry (or left wet without rinsing in some experiments).

3. Pre-reduction

    a. 1 min 200 gpl $AgNO_3$ pH 2.85 (let silver solution age 2 days before use, adjust pH with HNO_3), move Q-tip during application.

    b. Rinse with demineralized water.

    c. Blot dry.

    d. Saturated $FeSO_4$ in water, pH adjusted to ≈ 1.8 with H_2SO_4 before $FeSO_4 \cdot 7\ H_2O$ addition. Saturation by constant stirring $\geq$ 45 min (fresh solution < 8 hrs old). Add <u>cysteine</u> to concentration <u>1 gpl</u>. Apply solution <u>1 min</u>, move Q-tip during application.

    e. Rinse with demineralized water.

    f. Blot dry or nitrogen-acetone when stated.

4. Repetitions (9 repetitions)

    a. 10 sec Ag^+ solution, move Q-tip, set it aside.

    b. 30 sec $FeSO_4$-cysteine solution, move Q-tip.

    c. 20 sec Ag^+ solution, move Q-tip, same as above.

    d. Rinse with demineralized water.

    e. Blot dry or nitrogen-acetone in the first three repetitions.

B. Drying Conditions

Normally, during plating the samples are blotted dry after rinsing them with demineralized H_2O between reagent applications.

When using nitrogen-acetone for drying, the drying procedure consists of blowing with nitrogen, then applying acetone with a swab and blowing with nitrogen once more.

C. Burnishing

The burnishing is accomplished using the tip of the Dense Condensaire plugger, moving it uniformly over the plated surface with a light touch.

D. Condensation

The standard method for condensation is to divide the triturated piece of amalgam into three equal size portions and condense one at a time on the sample. Suitable modifications and established conditions are explained in Table 5 in this report.

E. Preparation of Samples for Plating

1. All teeth were kept in glycerin after extraction.
2. All teeth were scrubbed using $NaHCO_3$ slurry and rinsed with demineralized H_2O, at least five rinses.
3. Crowns were polished with diamond wheel.
4. Teeth were mounted in fast setting resin.
5. Roots were polished with diamond wheel.
6. Surface of exposed dentin was polished with 600 grit emery paper.
7. All samples were kept in demineralized H_2O.
8. A group of teeth was blotted dry before plating (group A); other group was dried using 1 min N_2; 1 min Acetone with swab; 1 min N_2 (group B).

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