Galvanic Degradation of Amalgam Restorations

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Amalgam restorations in contact with saliva and tissue fluid act as concentration cells. The galvanic current is associated with selective attack of the γ_2 phase and loss of mechanical properties. Tin is deposited in the underlying dentin. Cavity liners do not stop the degradation.

Schoonover and Souder[1] suggested that dissimilar fluids in contact with the several surfaces of a metallic restoration could act as a galvanic "concentration cell." Schriever and Diamond[2] measured electrode potentials and resistances of tissues and oral fluids. Their circuit analysis showed that the current through a restoration is a function of the amalgam-saliva and amalgam-tissue fluid potentials and resistances. It is independent of the presence or disposition of other restorations. Their clinical survey showed typical contact resistances of about 1 megohm and potentials of about 80 mv. They could not correlate high potentials with pathologic conditions but suggested that "the electric current hastens the solution of the fillings and assists in transporting the ions to and through the tissues." Phillips, Phillips, and Schnell[3] offered little hope that dental cements and liners would add significantly to the resistance of the circuit. Massler and Barber[4] observed blackening of dentin in extracted teeth adjacent to amalgam but found no indication that properties were impaired. Schoonover and Souder[1] noted that restorations in extracted teeth were sometimes corroded so severely that "the amalgam had apparently lost much of its strength and could be crumbled between the fingers." Jorgensen[5] suggested that the corrosion reaction in the vicinity of the margins is associated with release and reabsorption of mercury. Mateer and Reitz[6] reported the conversion of Sn_7Hg (γ_2) to $Sn0_2$ and Sn_2S_3 near the cavity walls; the depositing in situ anchored and sealed the restoration.

The present study deals with electronic instrumentation to measure galvanic potentials in a clinical situation and, with the use of extracted teeth, to relate corrosion of amalgams to mechanisms, structural changes, and loss of strength.

The clinical measurements trace the amalgam-tissue fluid potentials of a normal mouth when replacing an old amalgam restoration. In laboratory studies of metallographic sections of extracted teeth, the microprobe was used to identify elements associated with the black dentin discoloration. Statistical analysis was made to correlate the discoloration with the presence of cavity liners. The effect of corrosion on strength was assessed by microhardness tests on partially corroded restorations.

Materials and Methods

The potential of the amalgam-tissue fluid interface was measured by a solid state potentiometer* with an input impedance of about 0.04 megohms. It was expected that this relatively low impedance would "load" the circuit, but the values were stable and reproducible. Tests with a 15 megohm vacuum tube voltmeter showed that "loading" could be eliminated, but that the precautions in zero adjustment, grounding, and isolating of leads made it unsuitable for use in the clinic.

Polymer-insulated copper wire was used for electrodes. One, wet with saliva, was gripped in the patient's hand. The other was touched to the patient's tongue, and the instrument was zeroed. This electrode then was placed firmly on the exposed surface of

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* Hewlett-Packard Model 2B2A X-Y recorder, Pasadena, Calif.

TABLE
STATISTICAL CORRELATION: PRESENCE OF CAVITY LINERS VS DISCOLORATION IN EXTRACTED TEETH CONTAINING AMALGAM RESTORATIONS

	Clear	Discolored	Totals
Liner	66 (11%)	146 (25%)	212 (36%)
No liner	111 (19%)	265 (45%)	376 (64%)
Totals	177 (30%)	411 (70%)	588 (100%)

each restoration. Instrument deflection was assumed to be proportional to the magnitude of the potential of the amalgam-tissue fluid interface.

An X-ray microprobe* survey was made on extracted teeth that had been polished metallographically in a direction away from the tooth structure so that amalgam constituents would not be mechanically smeared onto the hard tissue. A rectangular area, a portion of amalgam and adjacent discolored dentin, was first displayed on oscilloscope by secondary current modulation. This was followed by X-ray fluorescent images; mercury, first order 1.242 A LiF; silver, first order 4.154 A PET; and tin, first order 3.609 A LiF.

For statistical analysis of the interrelation of cavity liners and discoloration, 870 metallographically sectioned extracted teeth that contained amalgam restorations were examined. Of these, 282 (32%) were eliminated because of uncertainty as to whether a liner had initially been present, or whether the discoloration was clearly associated with an adjacent amalgam. The remaining speciment were examined under a binocular microscope and tallied into four categories based on whether they were discolored, and whether they had liners (Table).

Some of the metallographically sectioned teeth showed only superficial conversion of γ_2 to corrosion products. In the majority of instances, corrosion had occurred throughout the body of the amalgam. In six instances, an intermediate condition was observed, ie, the outer portions were attacked and converted but the central portions retained what appeared to be the original "as set" microstructure. Microhardness traverses were made across these restorations using a Knoop diamond indenter with a 200 gm load. The microstructure associated with each impression was recorded and indication of embrittlement was sought by comparison of hardness numbers and by examination of the deformed regions associated with each impression.

* MAC-5S3, Materials Analysis Corp., Palo Alto, Calif.

Results and Discussion

The lower curve of Figure 1 indicates the variation of potential at the amalgam-cavity interface for a patient in which the amalgam in tooth no. 3m was 1 month old; amalgam in no. 31 was 6 years old and others were considerably older. The second curve shows the effect of placing a new mesio-occlusal distal (MOD) amalgam restoration, no. 30, which replaced a DO and an MO amalgam restoration. Its potential has locally upset the galvanic status quo. These sharp deviations from the mean tend to level out over a period of months, as shown by the two upper curves. These curves were displaced on the vertical scale for clarity and the only significance that should be ascribed to these arbitrary units is whether the deviation from the mean is highly positive or negative. The electrode potential of the newly placed amalgam was about 450 mv, compared with about 35 mv for those that were aged. In these measurements the amalgam cavity interface was negative, with current through hard tissue fluids through the saliva path to the exposed amalgam surface, which was positive. From rough measurements of body resistance it may be deduced that this current is of the order of a few microamperes. For a 1 gm restoration containing 10% γ_2 (Sn-Hg), rough calculations of the Faraday equivalent for tetravalent tin indicate that such a current would cause complete conversion in about six years. Measurements show that the resistance of the saliva path is decreased by food residues (sugars and partially soluble fibers). A high resistance condition is restored by brushing and rinsing, but it is not likely that these differences significantly affect the galvanic current and, accordingly, the rate of corrosion of the amalgam.

The microprobe patterns of Figure 2 in-

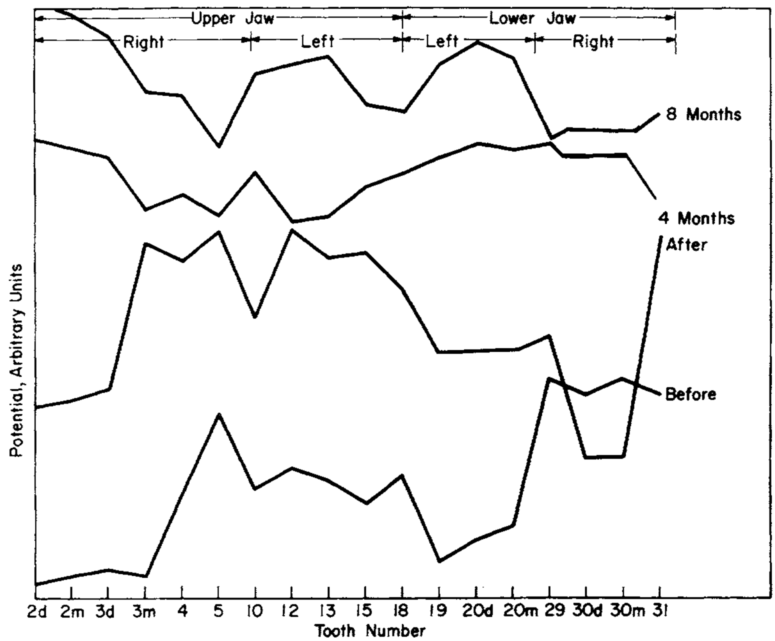

FIG 1.—Potential of amalgam-tissue fluid interface for restorations in a normal mouth. "Before" refers to initial condition in which amalgam in tooth no. 3m was 1 month old; amalgam of no. 31 was 6 years old and others were considerably older. "After" curve refers to condition after DO and MO restorations of tooth no. 30 were replaced with MOD restoration. Potentials four and eight months after this replacement are labeled. Maximum spread was about 450 mv, just after MOD restoration placement; spread diminished as restoration aged.

dicate that mercury and silver content of the blackened dentin is low; the tin content in the dentin adjacent to the amalgam is about as high as it is in the amalgam itself. This concentration decreases with distance (roughly corresponding to the optical blackening). The effect was observed on each of the five specimens examined. Unfortunately, the microprobe technique used here does not distinguish between tin in the elemental, ionized, or chemically combined forms. The simplest hypothesis therefore is suggested: the amalgam corrosion process releases tin ions which, dissolved in bone fluid, migrate as charge carriers through the dentin and are deposited in elemental form and appear as a black discoloration. Tin ions thus appear to be the charge carriers as they diffuse into the dentin. There they are deposited and give rise to the black discoloration. The charge then must be transferred to those atomic or molecular species that are associated with nerve currents throughout the body. These presumably complete the circuit through saliva to the exposed amalgam surfaces, which act as the second electrode of this complex concentration cell.

It should be possible to restrict this galvanic current and the associated corrosion by blocking the diffusion of tin ions. If conventional cavity liners accomplish this, it should be evidenced by absence of discoloration in dentin on metallographic sections of extracted teeth containing liners. The statistical data in the table do not support this hypothesis. One third of the teeth had liners. Of these, two thirds were discolored. This was statistically the same proportion as that of teeth with no liners. Therefore, it seems that the liners in specimens that were examined offered no detectable hindrance to the ion transport.

The six metallographic sections that

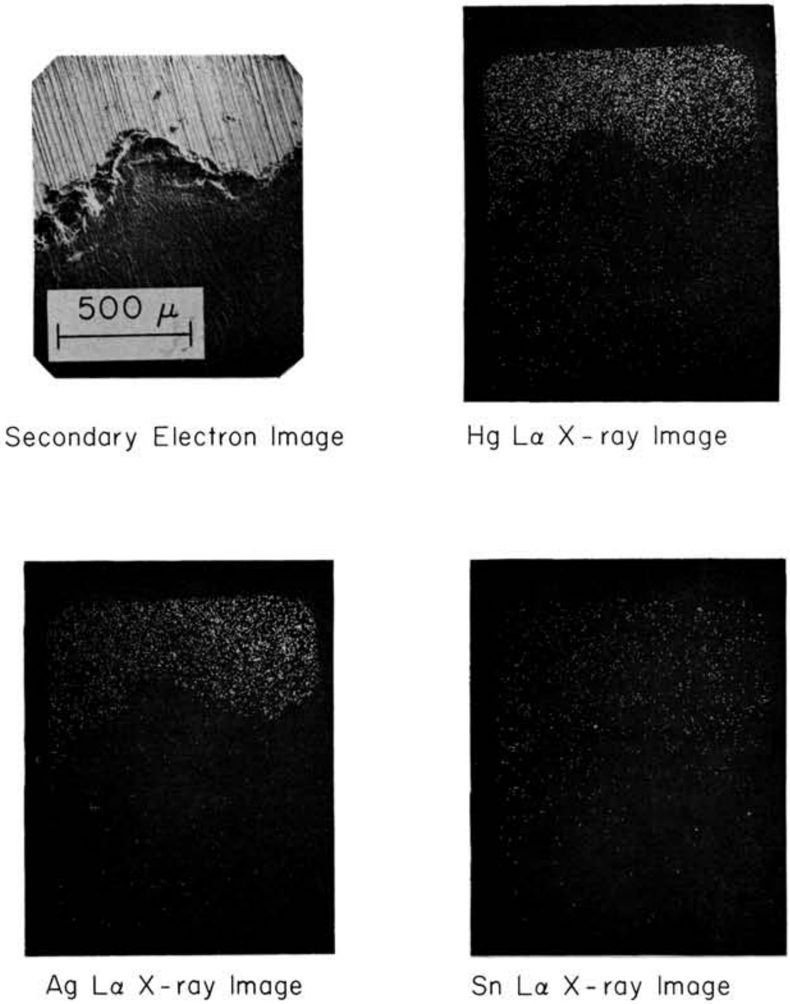

FIG 2.—Electron microprobe images of cavity-amalgam interface region in metallographic section of extracted tooth. Secondary electron image shows amalgam (white) separated by corrosion products from underlying dentin. Gray mottling of dentin near interface corresponds to region of optical discoloration. X-ray images indicate that tin has penetrated into dentin, but mercury and silver have not (orig mag $\times 50$, reproduced at 69%; $\mu = \mu m$).

showed incomplete conversion of Sn_7Hg γ_2 to corrosion product varied as to fineness of the microstructural constituents and amount of γ_2 in the unaffected regions. This presumably reflects differences in the original alloy, its particle size and initial mercury alloy ratio. The assumption was made that these factors would be constant throughout the original restoration and that mechanical properties, as indicated by microhardness measurements, would be uniform initially. Figure 3 shows that the Knoop hardness of the corroded portions of each restoration were generally lower than that of the unaffected region. The loss was severe in the heavily corroded regions of amalgams that had high initial hardness. Those with low initial hardness were less affected. Reduction in hardness is indicative of loss of strength. This idea is supported

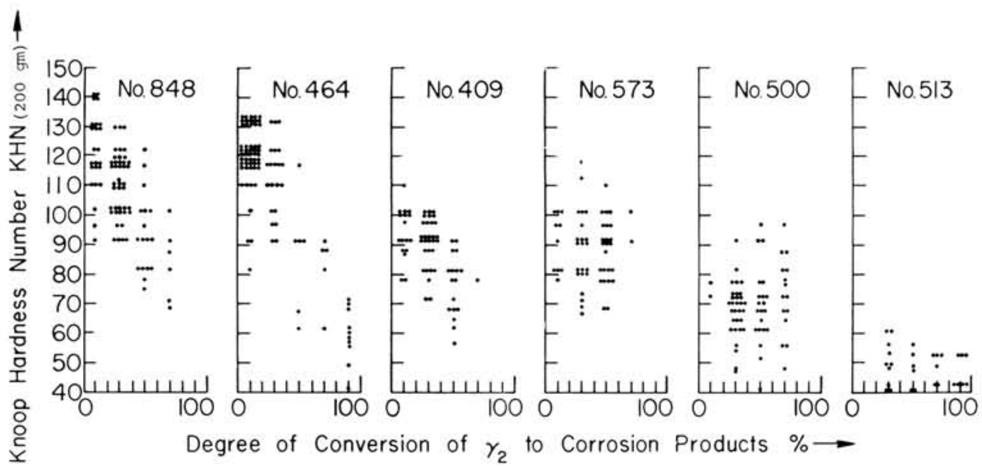

FIG 3.—Microhardness traverses on metallographic sections of amalgam restorations in extracted teeth. Of 870 random source teeth examined, these six showed gradual transition from severely corroded exterior portions of restoration to apparently unaffected structure in interior. Degree of conversion of γ_2 was estimated visually. Each dot represents one hardness determination. Amalgam of tooth no. 848 had high initial hardness but was severely weakened by corrosion. Amalgam of tooth no. 513 represents the opposite extreme. Its initial hardness was lower than that of the completely corroded regions of tooth no. 848. Corrosion caused no further reduction in hardness.

by visual observation (Figs 4-6), in which brittle fracture and fragmentation of structural constituents were observed in portions of amalgam that were deformed in making the indentation. This was most severe in the heavily corroded regions.

It is suggested that freshly placed amalgam restorations have adequate strength for prolonged service in the oral environment, but inadequate corrosion resistance. After a period of about a month during which beneficial sealing and anchoring takes place,[5,6] localized reaction in marginal regions with attendant mercuroscopic expan-

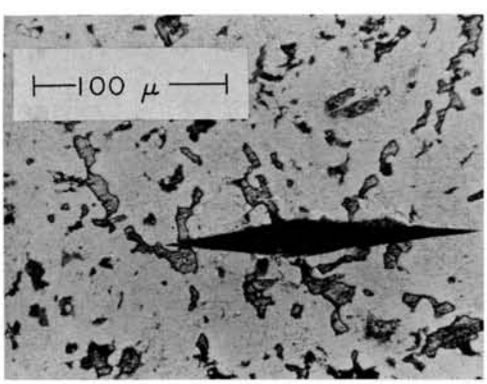

FIG 4.—Knoop diamond microhardness impression in uncorroded portion of amalgam restoration. Dark particles are Sn_7Hg γ_2 phase. Sharp outline of indentation indicates the γ-γ_1 matrix has sufficient ductility to plastically deform without fracture. $KHN_{(200\ gm)} = 110$. $\mu = \mu m$.

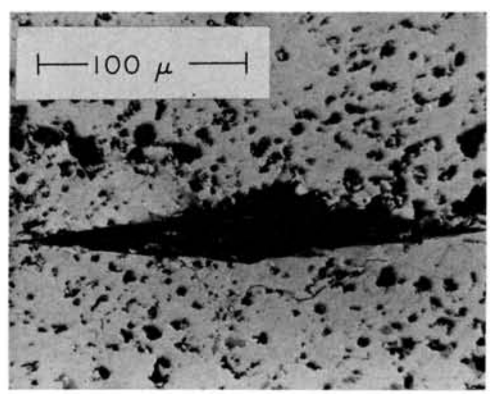

FIG 5.—Knoop microhardness impression in corroded portion of amalgam restoration shown in Figure 4. Dark particles are corrosion products from Sn_7Hg γ_2 phase, deposited in situ. Irregular outline of indentation and parallel crack at bottom indicates matrix has been embrittled. $KHN_{(200\ gm)} = 57$. $\mu = \mu m$.

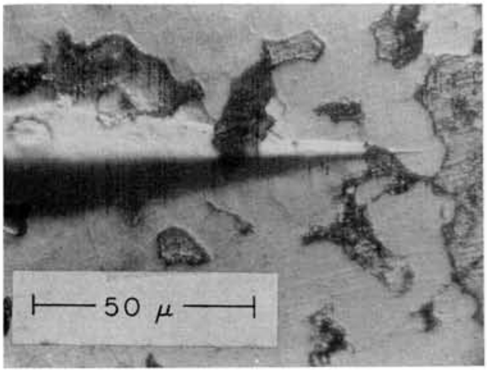

FIG 6.—Knoop microhardness impression in partially corroded portion of amalgam restoration of Figures 4 and 5. Most of the particles are Sn_7Hg γ_2, but one at top center has been partially converted to dark corrosion product. Sharp outline of indentation indicates matrix has not been embrittled severely. $KHN_{(200\ gm)} = 102$.

sion and fatigue flexing leads to margin guttering. Progressive electrochemical conversion, where rate is governed by galvanic conditions yet to be defined, embrittles the structure over a period of years. Loss of strength associated with microstructural degradation permits gross fracture under accidental conditions of high stress, which would have been withstood by the amalgam in its original condition.

Conclusions

Amalgam restorations are exposed to two electrolytes, saliva and tissue fluid of the dentin. Under these conditions, the amalgam-dentin interface becomes negative with decomposition of the γ_2 Sn-Hg phase and migration of tin into the dentin. This is associated with a galvanic current through the body-tissue-saliva circuit to the oral amalgam interface, which is positive. Common cavity liners apparently do not block this current flow. The corrosion process consumes the interconnected γ_2 phase and deposits tin-rich compounds. The corrosion interface progresses toward the center of the restoration over a period of years and reduces hardness and embrittles the matrix structure.

Prospects for increasing the service life of amalgam restorations lie in reducing the corrosion rate and the attendant structural degradation. This should be sought in metallurgical reduction, in the amount and degree of interconnection of the γ_2 particles, and in better liners to block the galvanic circuit.

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