A Polarographic Study on the Corrosion Tendency of Dental Amalgam

by

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Introductory

Dental amalgam is accepted as one of the most important materials in clinical dentistry, and it is variously affected according to the manipulating manners. A great majority of failures encountered in the amalgam filling is ascribed to an inadequate manipulation of this material [1, 2]. Thus success in the amalgam restoration is influenced, to a large extent, by its handling on the part of operator.

Among many kinds of tests done on amalgam, recent attention is paid to its tensile strength [3], but commonly employed tests are properties of crushing strength, flow and dimensional changes. On the other hand, as amalgam is used in oral cavity, its corrosion resistancy should be of prime importance and for this reason more attention must be paid into this direction.

The conventional method on investigating the corrosion of amalgam is to immerse it in a liquid to see what kind of corrosive behavior will take place over the range of a given length of time. The disadvantage of this method, however, lies in the inadequacy of testing to a minute degree and that it is timeconsuming. The latter fact should not be lost sight of, for the testing liquid tends to change its contents over the lapse of time, sometimes to the extent where it will not reflect clinical oral condition.

As an improvement on this conventional method, our Department of Dental Technology in Nihon University School of Dentistry has been engaged in the application of polarography, a traditional tool for the qualitative and quantitative analyses of metal alloys, for the corrosion testing of dental alloys. By this method, TSURUMAKI [4] proved that amalgam has an corrosion resistancy in human or artificial saliva which favorably compares with that of gold alloy. Since the structure of amalgam is not homogeneous in texture, it tends to corrode by reason of an electrolysis effect among the heterogenous alloy particles. The amalgam corrosion comes on the rough surface of the restoration and is directly connected with its mercury content, trituration, condensation, finishing and polishing procedures. The present paper is concerned with a polarographic investigation of the amalgam corrosion tendency in the following respects, 1) trituration and condensation methods, 2) finishing and polishing, 3) ratio of alloy and mercury, 4) mercury contents and 5) changes of temperature. It is to be recalled that polarography was first invented by Jaroslaw Heylowsky of Czechoslovakia in 1922 and it is primarily a means of qualitative and quantitative analysis in terms of voltage-current curves to be obtained in the electrolysis of reducible or oxygenate sub-

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stants. This apparatus was redesigned so as to work in the similar manner as the human oral cavity where minute corrosion of metals might be accurately observed. As in Fig. 2 below, test specimens are placed by pairs in a testing liuid and voltage-current curves under a given condition are thus be recorded.

By this means it was possible to obtain the type of curves given in Fig. 3, where

the horizontal axes represent an voltage and the vertical axes represent current, a larger volume of current corresponding to a proportionate degree of a material under consideration.

Fig. 1. Polarograph

Fig. 2. Retentive Apparatus of Test Specimens

Fig. 3. An Example of Corrosion Curves

Experiments

Exp. One : Influence of Trituration and Condensation Methods.

1-1. Material and Method.

Amalgam alloy used was one of usual commercial availability and its composition was : Ag 69 per cent, Sn 28 per cent, Cu 2 per cent, Zn 1 per cent, and its particle sizes were, larger than 100-mesh 13.0 per cent, 100-150 mesh 2.5 per cent, 150-200 mesh 14.0 per cent, 200-250 mesh

TABLE 1

	TRITURATION TIME (sec.)	CONDENSATION PRESSURE (Kg.)		CORROSION CURRENT (μ A.)		CRUSHING STRENGTH (Kg/cm ² .)
				2.2 V.	0.4 V.	
A	Mortar & pestle 60	Hand 0 2.5 mm.	2	2.4	6.0	2347
B	Mortar & pestle 60	Mechanical (A) 0 3.0 mm.	1	2.7	5.0	2142
C	Mechanical (A) 30	Hand 0 2.5 mm.	2	3.5	7.0	2579
D	Mechanical (A) 30	Mechanical (A) 0 3.0 mm.	1	2.0	4.0	2890
E	Mechanical (B) 30	Mechanical (B) 0 3.0 mm.	1	1.5	2.7	2904

Fig. 4

a. amalgamator (A), b. amalgamator (B), c. mortar and pestle

22.5 per cent and over 250-mesh 18.0 per cent.

2 g of this alloy and 3 g of mercury were then trituated in five different mixtures as is given on Table 1 and right after the trituration mercury was squeezed so that the resultant mixture mass had a ratio of 1:1 at the time of condensation. They were condensed by five methods into metal mold had dimensions of 30 mm long, 5.5 mm wide and 5.0 mm deep, and were exposed to air temperature of 37°C.

Of five different methods, an amalgamator (A) had a timing device attached with a rotating capsule and another amalgamator (B) had also a timing device but with a vibrating capsule and in addition the ordinary mortar and pestle were used. A mechanical condenser (A) was a type of rap, and other one (B) was a type of vibration. (Figs. 4 and 5)

A testing specimen thus prepared was removed from the metal mold after twenty-four hours, and was made to have 5.0 mm in width and 1.0 mm in thickness from the filling surface to be polished by sandpaper.

The entire testing specimen was coated with insulating material except for a filling

Fig. 5

a. Specimen, b. mold, c. condenser, d. mechanical condenser (A),
e. mechanical condenser (B)

surface and was immersed in water of 37°C for twenty-four hours. Then the specimen was split into two halves and were set at an interval of 20 mm (Fig. 6) in a solution of artificial saliva and voltage-current curves were measured after 60 seconds. It should be mentioned that in order to render the test to approach an actual oral cavity the artificial saliva with pH 6.8 was constantly maintained at the level of 37°C . Other pertinent conditions were that Span volt at the electrodes was 6 V for polarographic purposes, sensitivity was $1\ \mu\text{A}/\text{mm}$, and recording paper readings were $10\ \mu\text{A}/\text{cm}$ in length and $0.2\ \text{V}/\text{cm}$.

Fig. 6

Test specimens for crushing strength were prepared in the same conditions as were postulated for these of corrosion tendency and they were made into cylinder of 5 mm in diameter and 10 mm in height with measurements effected forty-eight hours later (Fig. 7).

Fig. 7

1-2. Results and Discussion.

Fig. 8 gives the corrosion curves of amalgams triturated and condensed under five different conditions. Out of A, B, C, D and E, the last method where a vibrating mechanical manipulative apparatus was used had the highest corrosive resistancy. A, B and C methods were found to have similar corrosive resistancy one another. Advantage of the mechanical means is also apparent in Table 1 where it has the highest crushing strength. This test was conducted under five different conditions by one operator and another test was performed where different skills were employed to inquire into their effects. Again, in the latter the same finding was obtained (Fig. 9).

As regards the trituration and condensation methods of amalgam, PHILLIPS [5], RYGE, DICKSON, SMITH et SCHOONOVER [6] have respectively reported that a mechanical methods are far better than a manual operation in respect of uniformity of the trituration and of strength of the amalgam, this being particularly true of the initial strength.

A matter of primary importance in condensation is that one must reduce the residual mercury as much as possible. Too much residual mercury will reduce the crushing strength, promote setting and thus encourage discoloration as well as corrosion of amalgam to be treated. For this reason, use of a mechanical means enable to increase the strength of amalgam matrix by enhancing the diffusion of mercury into the alloy particles and produced excellent restorations used even small amount of filling pressure, and adequate filling in the marginal region of amalgam will influence its corrosive resistancy to a large extent.

Fig. 8. Corrosion curves in terms of trituration and condensation methods

- A. Manual trituration with manual condensation.
- B. Manual trituration with mechanical condensation (A)
- C. Mechanical trituration (A) with manual condensation
- D. Mechanical trituration (A) with mechanical condensation (A)
- E. Mechanical trituration (B) with mechanical condensation (B)

Fig. 9. Corrosion curves in terms of operator skill

Symbols A, B, C and D indicate different operating skills

Exp. Two: Effects of Finishing and Polishing.

2-1. Method.

Finishing and polishing processes are much concerned with the corrosive resistance of amalgam and it is well-known that inadequacy in these stages will often bring about secondary caries, corrosion and discoloration of the amalgam restorations.

In this test specimens were finished and polished under six different conditions (Table 2) for comparison of their respective effects. Test specimens were the same as used in the previous test and the trituration and condensation methods were those of E in Fig. 8 above.

2-2 Results and Discussion.

Fig. 10 gives the corrosion curves measured on the test specimens finished and polished under six different conditions (A, B, C, D, E and F). Of them, D where soft Robinson brush was used had the highest corrosive resistancy the rest being in the order of felt wheel, tooth brush, sand-paper, non-polishing and finishing bur methods.

As is known from these findings, methods of finishing and polishing are largely related to resultant corrosive resistancy of the amalgam restorations. The marginal area of amalgam restorations are usually rough without finishing and polishing, even if operator employed proper condensation. The reason for ready discoloration and high corrosive tendency may be sought in the fact that the surface of amalgam is uneven where a combination of heterogeneous ions will be produced. Temperature in these processes is also important. When temperature at the time of polishing exceeds 65°C, mercury tends to become dissociated from the amalgam, which will mean weakened or defective spots in the mass of hardened amalgam [7].

Fig. 10. Corrosion curves in terms of polishing methods

A. No B. Finishing bur
C. Sandpaper D. Soft brush
E. Hard brush F. Felt wheel

TABLE 2
Effects of Finishing and Polishing Methods

	FINISH AND POLISH	CORROSION CURRENT (μ A.)	
		0.2 V	0.4 V
A	no	1.9	3.8
B	finishing bur	1.9	4.4
C	sandpaper 000	1.1	3.4
D	soft brush	0.5	1.9
E	hard brush	1.2	3.2
F	felt wheel	102	2.4

As indicated in Fig. 10, use of finishing bur in an apt illustration of this fact that a felt wheel generates more friction heat than a teeth brush. It is concerned, as this result, that in polishing of the amalgam restorations one should pay constant attention to rise of the temperature and that less uneven surface should be left.

Exp. Three: Influence of Alloy/Mercury Ratio.

3-1. Method.

As is given in Table 3, six different ratios alloy of and mercury were tried at the mixing process anywhere running from 1.0:2.0 to 1.0:1.0 but when they were filled, they were subjected to squeezing by means of a cloth so as to render the ratio equally half and half. Sandpaper was used for polishing purposes and otherwise the same processes were employed to as in Exp. 3.

3-2. Results and Discussion.

Fig. 11 gives the corrosion curves obtained on the effects of alloy/mercury ratio. Difference in this alloy/mercury ratio does not seem to have significant affect to the corrosion tendency of the amalgam. The same holds true of crushing strength (Table 3).

With reference to alloy/mercury ratio, WARE, DOCKING [8] and MIYAZU [9] among others have reported that in the case of pestle and mortar mixing what is prepared at a ratio of 1.0:1.2 has a fair crushing strength and the value reaches at a maximum when a ratio is 1.0:1.6. Further, in the case of mechanical mixing, PHILLIPS [10] has stated that when the amount of mercury to be added exceeds by 15 % of an adequate ratio, mercury content of restoration will increase by nearly 1.5 %, so that crushing strength will reduce by nearly 7 %. In the present test, only mechanical mixing was tried but no appreciable difference was detected on the part of different ratios in respect of their corrosion tendencies. This may be accounted for by the fact that excessive mercury was squeezed at the time of condensation, and efficiecy of the mechanical condenser. This finding is in keeping with that of SWEENEY [11] who has reported that when mercury is sufficiently squeezed out after trituration, it will cause no different effect in the physical property of the amalgam concerned.

Fig. 11. Corrosion curves in terms of alloy/mercury ratio

TABLE 3
Effects of Alloy and Mercury Ratios

	ALLOY : Hg	CORROSION CURRENT (μA)		CRUSHING STRENGTH (Kg/cm ²)
		0.2 V	0.4 V	
A	1.0:2.0	0.5	1.0	3245
B	1.0:1.8	0.5	1.0	2998
C	1.0:1.6	0.7	1.5	3114
D	1.0:1.4	0.7	1.3	3132
E	1.0:1.2	0.5	1.0	3009
F	1.0:1.0	0.5	1.0	3079

Exp. Four : Influence of Mercury Content.

4-1. Method.

Ratio of 1.0:1.6 of an alloy to mercury at the trituration was modified respectively to 1.0:1.4, 1.0:1.2, 1.0:1.0 and 1.0:0.8 at the condensing process by changing the amount of mercury to be squeezed. Effects of mercury

content were thus examined before and after the condensation so as to determine their corrosive behaviors. As the specimen containing larger amount of mercury was not easily made into a plate, it was tested in its cylindrical shape (Fig. 7). As shown in Fig. 12, a pair of test specimens were immersed in an acrylic vat so that they were exposed to the solution only on the surface and after 60 seconds following the pouring of artificial saliva of pH 6.8, one measured their voltage-current curves.

4-2. Results and Discussion.

Four different test results are given in Fig. 12 below where mercury content is respectively 60 %, 55 %, 50 % and 45 %. The first three of them showed more or less the same sort of corrosive tendency, whereas the last one (45 % mercury content) had somewhat better corrosion resistancy. As shown in Table 4, the more mercury is contained in the specimen, the less becomes the crushing strength.

As referred to elsewhere, residual mercury influences the amalgam restoration to the greatest degree and, in particular, its corrosion can be assigned to residual mercury in the surface region. The result of the experiment showed, when mercury exceeds by 50 %, it will tend to gather itself in the surface region on account of condensation, the mercury content in the surface region shall be increased compared with the other regions. According to NADEL [12], it is difficult to know exactly a relationship between corrosion and mercury content of the amalgam restoration clinically but concentration of mercury in the surface region means easy break of marginal area, coarse surface and, consequently, brings about the corrosion or discoloration. Therefore, it is quite necessary to take care that less excessive mercury will be gathered in the surface region, particularly in the initial stage of restoration.

Fig. 12. Corrosion testing apparatus

a. Electrode, b. Specimen, c. Acrylic vessel containing an artificial saliva

TABLE 4
Effects of Mercury Contents

	Hg (%)	CORROSION CURRENT (μA)		CRUSHING STRENGTH (Kg/cm ²)
		0.2 V	0.4 V	
A	58.3	6.6	11.1	1423
B	54.5	6.9	12.7	2028
C	50.0	6.6	11.0	2864
D	44.4	3.3	6.6	3281

Fig. 13. Corrosion curves in terms of mercury contents

Exp. Five: Influence of Temperature Changes.

5-1. Method.

This part of the tests were concerned with possible influence on the corrosion behavior of the amalgam owing to temperature changes in foods and drinks to be brought into the oral cavity. The instant maximum and minimum temperatures at the entry of these comestibles into the mouth were respectively assumed to be 80°C and 4°C,

the room temperature of $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$ being taken as a control. Test specimens were treated as in Table 5 and they were subjected to repeated heating and cooling processes.

5-2. Results and Discussion.

Fig. 14 gives the various corrosive curves obtained on these specimens, B, which was given temperature changes between R. T. to 4°C , showed less corrosive tendency than that of A was kept in R. T., C and D, were given high temperature changes, were less than A. This points out to the conclusion that the higher a given temperature, the more susceptible will be the restoration to corrosion. The crushing strengths are in the order of B, A, C and D.

From its composition of amalgam itself, it will become more corrosive with correspondingly reduced crushing strength in higher temperature. MIYAZU et al. [13], reported that 70°C is a maximum temperature. It will be able to be considered, on the other hand, this temperature-limit varies according to the length of time until temperature change affected after restoration was done. Temperature to which the restoration is exposed in the oral cavity is of only a short duration, and it will be also affected by the body temperature and that of saliva. These matters will need further investigation as they are directly associated with clinical dentistry.

TABLE 5
Effects of Temperature

	TEMPERATURE	CORROSION CURRENT ($\mu\text{A.}$)		CRUSHING STRENGTH (Kg/cm^2)
		0.2 V	0.4 V	
A	room temperature ($22 \pm 2^{\circ}\text{C.}$)	2.5	4.9	4036
B	4°C (1 min.) R. T (4 min.) 10 times.	2.0	3.8	4227
C	80°C (1 min.) R. T (4 min.) 10 times.	2.7	5.3	3988
D	4°C (1 min.) R. T (2 min.) 80°C (1 min.) R. T (2 min.) 10 times.	2.2	4.7	3211

Fig. 14. Corrosion curves in terms of temperature effects

- A. ($22^{\circ}\text{C} \pm 2^{\circ}\text{C}$) room temperature
 B. $4^{\circ}\text{C} \rightarrow \text{R. T.}$ (Fig. 10)
 C. $80^{\circ}\text{C} \rightarrow \text{R. T.}$ (Fig. 10)
 D. $4^{\circ}\text{C} \rightarrow \text{R. T.} \rightarrow 80^{\circ}\text{C} \rightarrow \text{R. T.}$ (Fig. 10)

Conclusions

Based on the various findings obtained as the results of tests described in the sections respectively, the following conclusions were obtained.

- 1) There exists a correlationship between the corrosive resistancy and crushing strength of dental amalgam.
- 2) Amalgam that is mechanically triturated and condensed has a higher corrosive resistancy than what is manually processed.
- 3) Difference in operator's skills seems to affect corrosive resistancy of amalgam

when either mechanical or hand condensation is employed. Amalgam, however, condensed by mechanical method, showed better corrosive resistancy than that of amalgam condensed by hand.

4) Polishing influences corrosion of the amalgam to a large extent. Particularly, coarse surface and excessive heating at the polishing manipulation cause corrosion to take place.

5) An alloy/mercury ratio of the amalgam at trituration will have no adverse effects when mechanical trituration is used and mercury is squeezed out as much as possible immediately prior to condensation.

6) When the amount of mercury in the amalgam restoration exceeds by 50 %, it will enhance its corrosion.

7) The higher is temperature, the more will be affected corrosion of amalgam but the temperature in the oral cavity in our daily life is never high enough to influence adversely.

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