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DIMENSIONAL CHANGES IN AMALGAM

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Dimensional Changes in Amalgam

Dimensional change during hardening

Importance. The change in dimension during hardening has long been considered a critical factor in evaluating dental amalgam as a filling material. G. V. Black rightly concluded that an amalgam with zero change would ideally be best, and that shrinkage and expansion should be kept to the lowest possible minimum.⁽¹⁾ This excellent advice is as good now as it was when he gave it seven or more decades ago. It has been the general impression among dentists and researchers that a slightly expanding alloy was much to be preferred over one with a slight shrinkage on hardening. In fact, most believe that no terminal shrinkage should be permitted. These concepts were introduced in the first specification for amalgam as proposed by Souder⁽²⁾ who believed that it was essential to have a linear expansion of 0.04 to 0.05% to compress the dentin (of course below its elastic limit) and to thus ensure sealing the cavity-restoration interface (especially the margin). No one knows the force or thrust

exerted by amalgam as it expands during hardening. Then, too, it was postulated that this slight expansion⁽²⁾ would compensate, at least in part, for the effect of the differential thermal expansion of the tooth (average value $8 \times 10^{-6}/^{\circ}\text{C}$)⁽³⁾ and of the amalgam (average value of $25 \times 10^{-6}/^{\circ}\text{C}$)⁽³⁾ so the first specification for alloy for dental amalgam (November 30, 1926) had the following requirement: "4. Setting changes.--Twenty-four hours after amalgamation the length shall have increased between one and ten microns per centimeter. If at any time during the test a contraction of more than four microns per centimeter is detected, the alloy shall be rejected."⁽⁴⁾ Identical wording was used in the first ADA specification.⁽⁵⁾ Subsequently this expansion value in the ADA specification was changed from +0.01 to +0.10% to +0.03 to +0.13% range⁽⁶⁾ so that "Certain alloys which are now on the border line in setting changes would be rejected as a result of harsh treatment in mixing and packing." Also, the former requirement which permitted

amalgams no more than 0.04% initial contraction was deleted as unnecessary with the new dimensional change range of +0.03 to +0.13%.⁽⁶⁾ All of the foregoing values were on unrestricted specimens at room temperature with a fiducial reading when the test specimen was 15 minutes old as timed from beginning the mix. It is known that a restricted specimen has less expansion than an unrestricted one.⁽⁷⁾ As an example, an unrestricted cylindrical specimen had an expansion of 0.12%, the same size specimen in a tube with both ends open +0.07%, and if one end of the tube was closed, about +0.03%.⁽⁷⁾ With the complex shape of cavities in practice, with varying degrees of roughness of cavity surfaces, and with the usual undercutting, one could obtain an infinite number of values for dimensional change during hardening because of variables that cannot be controlled clinically. Therefore, in specification testing it is desirable to use an unrestricted specimen. Even then values to within $\pm 15\%$ are considered good.

It is true that workers have shown that amalgam that shrank from 0.02 to 0.04% when measured on an unrestricted specimen did not present any clinical evidence of failure during the three years the 34 restorations were observed.⁽⁸⁾ Additional tests on 60 clinical restorations made with a high, tin-content, alloy which shrank about $0.31 \pm 0.03\%$ on an unrestricted specimen presented no clinical evidence of open margins or recurrent caries during three years (34 restorations) or for shorter periods (20 restorations).⁽⁹⁾ Other workers have shown by observation a marginal defect of 50 micrometers or more induces recurrent caries.⁽¹⁰⁾ Such a discrepancy is caused by a marginal excess of amalgam which breaks away or by marginal fracture caused by corrosion of the amalgam, or both.⁽¹⁰⁾ Certainly such large dimensional changes that would give a margin defect of 50 micrometers are not occurring in amalgam during hardening.

In 1957 the Federation Dentaire Internationale (FDI) adopted an international specification for alloy for dental

amalgam in which the linear setting change during hardening was restricted to 0 to +0.20% at 37°C on an unrestricted specimen with a fiducial reading when the specimen is 15 minutes old.⁽¹¹⁾ This was supposed to allow for the effects for mechanical amalgamation, testing at mouth temperature, and restriction of expansion in clinical restorations. The latest change, effective June 1, 1970⁽¹²⁾ is $0 \pm .20\%$ on an unrestricted specimen with a fiducial reading when the specimen is 5 minutes old and the amalgam is mixed and packed mechanically.

From the foregoing it can be seen that current laboratory practice in specification requirements is mostly theory derived on testing procedures that are perhaps too conventional to attempt to relate them to dimensional changes during hardening on clinical restorations. In fact, the actual clinical effects of the dimensional changes during hardening of the amalgam are unknown.

What one really would like to know are the actual dimensional changes during hardening in dental restorations, and the effect of such changes on the restoration-tooth interface. It is the authors' opinion that clinical findings will not reveal this because of the impossibility of setting up quantitative procedures in the mouth to measure dimensional change on restorations or the quantitative adaption of the set amalgam to the surfaces of the cavity. Some preliminary laboratory testing is being started at the National Bureau of Standards by the authors to quantitate adaption of amalgam to the cavity and to relate dimensional changes occurring on unrestricted laboratory specimens to such quantitative adaption measurements.

Effect of Composition. Black showed the critical effect of composition.⁽¹⁾ Gayler showed that the tin content of the powdered alloy was critical and set the limits of not less than 25 nor more than 26.8% tin.⁽¹³⁾ Less than 25% caused expansion, more than 26.8% caused shrinkage in the binary silver-tin system. Her measurements were made at 37°C on restricted specimens in

steel or composition "tooth" cavities. In 1965 an analysis of 83 alloys on the List of Certified Dental Materials as established by the American Dental Association showed tin contents ranging from only 25.3 to 27.0%.⁽¹²⁾ However, several years ago in the routine testing of alloys for amalgam certified by their respective manufacturers to the American Dental Association, one of the authors tested an alloy - Ag 62.2, Sn 32.7, Cu 4.9 and Zn 0.2% that complied with the flow and dimensional change requirements of the ADA specification which, because of the large tin content of about 33%, is at variance with the foregoing.^{(12) (14)}

A number of years ago an alloy was made in the USA with atomic proportions Ag_2SnCu (weight percentage approximately Ag 54, Sn 30, Cu 16, Zn none). This alloy had a linear setting expansion of from 0.02 to 0.03%.⁽¹⁴⁾ Here again the tin content was more than Gayler's maximum limit of 27.5%.

Heat treatment of the ingot changes the distribution of the silver-tin phases in the alloy and this may cause

differences in expansion during hardening but the authors are not familiar with such data in the literature. Annealing of freshly cut particles reduces the amount of dimensional changes during hardening of amalgams.⁽¹⁾ One must also realize that surface treatment of the alloy particles may alter the composition of the surface which is not reflected in the overall composition.

Effect of specimen preparation technic. Strader showed that the composition of a test specimen of dental amalgam varied in mercury content from one end to the other with an accompanying variation of dimensional change in different parts of the specimen.⁽¹⁵⁾ He quoted values of +0.19% for the bottom one third of the cylindrical mold to +0.06% for the top one third. Thus, the value one usually obtains is an average of the linear changes occurring in different sections of the specimen.

This presents another excellent reason for using the lowest amount of mercury that will give a packable mix with the removal of little or no excess mercury during condensation.

Of course, almost everyone who has tested dental amalgam is familiar with the wide variation of values for

dimensional changes during hardening that occurs with variations in the work done on the alloy-mercury mass during trituration and condensing and many other variables associated with the preparation of restorations. Gray was among the first to show this.⁽¹⁶⁾ For some reason G. V. Black believed that "Shrinkage and expansion of the amalgam used is not under the control of manipulation by the operator. This can be controlled only in the selection of alloy to be used."⁽¹⁾

Influence of the direction of condensation. Setting expansion is slightly greater (0.03 to 0.05%) parallel to the direction of pressure during condensation than at right angles to the direction of pressure when condensation by a piston is used. Evidently the orientation of the Ag_2Hg_3 (γ_1) and Sn_7Hg or Sn_8Hg (γ_2) phases are affected. No effect was noted when using hand condensation.⁽¹⁷⁾

Effect of length of specimen. As cylindrical specimen length (4 x 6, 4 x 4, 4 x 2 mm) decreased, the linear change increased.⁽¹⁸⁾

Effect of particle size. Gray^(16,19) was possibly the first to show that excessive expansion occurred with

coarse sized particles of alloy and with real fine particles there was shrinkage and that with the proper blend of sizes or surface area the "proper" expansion was obtained. Many other investigators have since confirmed this.

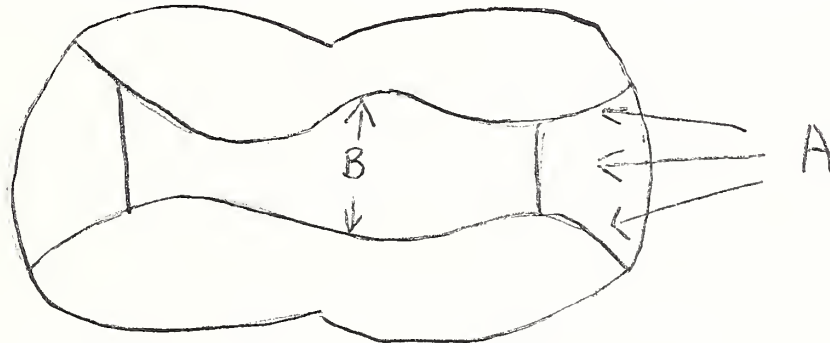
Effect of temperature at which test is conducted. Gray⁽¹⁶⁾ showed less expansion at 25°C than at 37.5°C while Mitchell et al⁽²⁰⁾ showed more.

Amount of dimensional change desired. As previously stated, zero dimensional change or as close as one can get to it is the most desirable--at least theoretically. There is a point at which expansion or shrinkage would be undesirable and that point would probably be where the magnitude of the dimensional change interferes with the adaption of the amalgam to the cavity surfaces.

As previously stated, the authors are beginning experiments with actual restorations in porcelain teeth in an attempt to determine the effects of various dimensional changes on hardening on the amount of space between the amalgam and cavity wall. Dimensional changes

will be determined on unrestricted specimens then the various amalgams with linear dimensional changes from +0.60 to -0.60% will be placed in the Class I, Class V and MOD cavity preparations in porcelain teeth. The quantitative adaption of the amalgam restorations to the cavity walls will be measured by air under pressure.

As regards such effects consider the following outline drawing of the occlusal view of an MOD restoration in a lower molar.



The approximal and gingival surfaces indicated by arrow A are most frequently involved in marginal leakage and recurrent caries. (10,21)

Would a contracting restricted restoration tend to tighten the apposition in A areas? Would an expanding amalgam tend to lessen the apposition? What happens at B with a contracting

or an expanding amalgam? To the best of the authors' knowledge it has never been determined whether these vulnerable areas are influenced by dimensional change values on an unrestricted expanding or shrinking amalgam.

Explanation of the dilation curve of amalgam during hardening. There has been much speculation on the

physical and chemical changes occurring during the hardening of amalgam and the shape of the resultant dilation curve. Winterhager, using quantitative x-ray diffraction methods on silver amalgams, with a varying silver content, showed a correlation between the amount of, and the time of, forming of γ_2 and γ_1 phases and the shape of the dilation curve. (22)

Dimensional changes caused by corrosion

Moisture and contamination. Schoonover and associates (23) showed that the mechanism of the large delayed expansion of moisture-contaminated amalgam made from alloys containing zinc was caused by the electrolytic dissociation of water by the zinc-containing amalgam into hydrogen and oxygen. As the hydrogen accumulates it builds up pressure

which caused the amalgam to flow out of the cavity or to elongate the unrestricted test specimen by several percent. Excessive corrosion as well as excessive expansion occurs. If mercury is released by the corrosion it will probably combine with the residual Ag_3Sn and matrix to form additional matrix with subsequent dimensional changes. In any event the delayed expansion of moisture-contaminated, zinc-containing amalgam is of sufficient magnitude to be manifested clinically by post-operative pain. (24,25)

How much delayed expansion occurs in amalgam restorations and the percentage of amalgam restorations that are so affected are not known. It is known that most of the alloys sold contain zinc. It is known that when one transfers a mouth mirror from room temperature and humidity conditions to mouth temperature and humidity that water condenses on the mirror until it rises above the dewpoint. In all probability this condensation of water occurs on amalgam increments as they are passed from the room to mouth environment unless the rubber dam is used. As very little rubber dam is used it may be that some of the extrusion of amalgam restorations from

the cavity is caused by such moisture contamination of zinc-containing amalgam. The authors are investigating this aspect under oral conditions.

Gamma 2 corrosion. The tin-mercury phase of amalgams (γ_2) is chiefly responsible for the corrosion of dental amalgam. (26,27) The free mercury released by the degradation of γ_2 recombines with the residual alloy Ag_3Sn particles (γ phase) to cause additional expansion. (20,26) The amount of this expansion is great and depends upon the amount of free mercury released, that is, the extent of the corrosion of the γ_2 phase. Jørgensen's data (26) show about 5% linear expansion per one percentage weight of released mercury. Obviously the way to rectify this situation is to eliminate the γ_2 phase without impairing the desirable properties of amalgam. It would appear that Johnson of the University of Virginia has accomplished this. (28)

Thermal effects

Differential thermal expansion of hard tooth tissue and amalgam. Recently the coefficient of thermal expansion

of human enamel was found to be $12 \times 10^{-6}/^{\circ}\text{C}$ (25-50°C) and for dentin $7.5 \times 10^{-6}/^{\circ}\text{C}$ (25-45°C)⁽²⁹⁾ and as previously stated for amalgam $25 \times 10^{-6}/^{\circ}\text{C}$.^(3,4) These differences in coefficients do cause different amounts of expansion and contraction when the amalgam restoration and the tooth is subjected to temperature fluctuations that occur in the mouth. This range is fairly wide for the anterior teeth, -9°C to 52°C⁽³⁰⁾ when measured on a relatively poor thermal conducting plastic filling material. In amalgam restorations temperatures as high as 80°C may be reached.⁽³¹⁾ So in the mouth the amalgam should expand and contract about twice as much as the tooth during changes in temperature. The amount is undoubtedly much greater as amalgam is a much better thermal conductor than the tooth so the amalgam will attain a much higher temperature and do it much more rapidly than will the tooth. Consequently there should be a very slight extrusion of the amalgam restoration from the cavity as amalgam is plastically deformed at temperatures occurring in the mouth when hot foodstuffs

are eaten. Limited laboratory tests confirmed this when amalgam fillings in glass molds were cycled between room temperature and 65°C in water. Some extrusion of the fillings occurred.⁽³²⁾ After a few cycles water was observed between the glass walls and the fillings. On cooling small water droplets would collect at the margin. γ-β transition in Ag-Hg system. Under mouth temperature conditions some of the Ag_2Hg_3 (γ_1) phase of dental amalgam changes over to the β silver-mercury phase with an accompanying volume shrinkage of 5% or an increase in porosity and with the liberation of free mercury.⁽³³⁾ This free mercury would combine with the unreacted alloy particles and the matrix which should result in some expansion.^(10,20)

Suggestions

The dimensional changes in amalgam during hardening are of a minor order compared to those occurring as a result of the moisture-contamination of zinc-containing amalgam and the expansion caused by reaction between the mercury, released by corrosion of the γ_2 phase, and the other phases.

Research, however, is needed to establish limits of the amount of expansion and contraction that can be tolerated without serious disarrangement of the amalgam-cavity surface interface.

Research is also needed to determine to what extent current zinc-containing amalgams are being contaminated by moisture during normal technical procedures in filling teeth and how much delayed expansion results. Such data are necessary in deciding if zinc or how much zinc should be permitted in alloys used for dental amalgam.

The development of amalgams without the γ_3 phase--the tin-mercury phase--is the only method that would eliminate the expansion caused by the reaction of the mercury, released on the corrosion of the tin-mercury phase, and the set amalgam.

The thermal expansion of amalgam cannot be meaningfully decreased so all patients with amalgam restorations should be advised to refrain from "bathing" the teeth in extremely hot and cold foodstuffs. This would also minimize the γ to β (Ag-Hg) transition in dental amalgam.

References

1. Black, G. V. Operative dentistry Vol. II. Technical procedure in filling teeth. Medico-Dental Publishing Co., Chicago, 1908.
2. Souder, Wilmer. Possibilities of a specification for dental amalgams. Bul. Chicago D. Soc. 5:4 July 24, 1925.
3. Souder, Wilmer. Physical properties of dental materials. JADA 12:509 May 1925.
4. Souder, Wilmer. Measurement and application of certain physical properties of dental amalgam. J. D. Res. 7:173 June 1927.
5. Taylor, N. O. Specification for Dental Amalgam Alloys, JADA, 17:112, 1930.
6. Paffenbarger, G. C. and Sweeney, W. T. Specifications and certifications for dental materials. (1934 revision of amalgam alloy specification.) JADA 21:658 April 1934.
7. Fischer, C-H., and Kleigmann, W. Das Dimensionsverhalten von Amalgamen in Kavitäten. Deut. Zahn-Mund-Kieferhk.

8. Phillips, R. W., Boyd, D. A., Healy, H. J. and Crawford, W. H. Clinical observations on amalgam with known physical properties. JADA 32:325 Mar. 1945.
9. McDonald, Ralph E. and Phillips, Ralph W. Clinical observations on a contracting amalgam alloy. J. D. Res. 29:482 Aug. 1950.
10. Jørgensen, K. D. and Wakumoto, S. Occlusal amalgam fillings: marginal defects and secondary caries. Sartryck Odont. Tidskrift 76:43, 1968.
11. Specification for alloy for dental amalgam. Inter. Dent. J. 9:241 Sept. 1959.
12. Guide to Dental Materials and Devices, 5th ed. (1970-1971). American Dental Association, Chicago, Ill. 60611.
13. Gayler, M. L. V. The setting of dental amalgams, Part III. Brit. Dent. J. 58:10 Feb. 15, 1935.
14. Souder, W. and Peters, C. G. Investigation of physical properties of dental materials. Dent. Cos. 62:305 March 1920.
15. Strader, K. H. Amalgam alloy: its heat treatment, flow, mercury content and distribution of dimensional change. JADA 38:602 May 1949.

16. Gray, A. W. Metallographic phenomena observed in amalgams. J. Nat. Dent. Assn. 6:513 June 1919.
17. Jørgensen, K. D. and Holst, K. Setting expansion of amalgam: influence of the direction of condensation. Acta Odonto. Scan. 22:201 June 1964.
18. Nagai, K, et al. Effect of specimen size on dimensional change of dental amalgam. Abstract 130, Program and Abstracts of Papers, 48th General Meeting, IADR, New York, 1970.
19. Gray, A. W. Contraction and expansion of amalgam with time. Physical Rev. 18:108 Aug. 1921.
20. Mitchell, J. A., Schoonover, I. C., Dickson, George and Vacher, H. C. Some factors affecting the dimensional stability of the silver-tin (copper-zinc) amalgams. J. Dent. Res. 34:273 April 1955.
21. Baumgartner, W. J., Bustard, R. E. and Fererabend, R. F. Marginal leakage of amalgam fillings. J. Pros. Dent. 13:346 March-April 1963.
22. Winterhager, H. Neuere Erkenntnisse der Vorgänge bei der Erhärtung von Dentalamalgamen. Deut. Zahnartz. Z. 23:1602 Dec. 1955.

23. Schoonover, I. C., Souder, W. and Beall, J. R.
Excessive expansion of dental amalgam. JADA 29:
1825 Oct. 1, 1962.
24. Skinner, E. W. and Phillips, R. W. The science of
dental materials. 6th ed. W. B. Saunders Co.,
London, p.348, 1967.
25. Anderson, J. N. Applied dental materials. 3rd ed.
Blackwell Scientific Publications, Oxford. p.311,
1967.
26. Jorgensen. K. D. The mechanism of marginal fracture
of amalgam fillings. Acta Odont. Scan. 23:347,
Aug. 1965.
27. Guthrow, C. E., Johnson, L. B. and Lawless, K. R.
Corrosion of dental amalgam and its component phases.
J. Dent. Res. 35:1372 Nov.-Dec. 1967.
28. Johnson, L. B. Elimination of the gamma-2 phase from
dental amalgams. Report presented at TMS-AIME meeting,
Cleveland, Ohio, Oct. 21, 1970. (The Metallurgical
Society of the American Institute of Mining and
Metallurgical Engineers, 345 East 47th Street, New
York, N. Y. 10017.)

29. Barton, J. A., Jr. and Dickson, G. Thermal and hygroscopic changes of tooth structure. Abstract 673, Program and Abstracts of Papers, 48th General Meeting, IADR, New York 1970.
30. Nelsen, R. J., Wolcott, R. B. and Paffenbarger, G. C. Fluid exchange at the margins of dental restorations. JADA 44:288 March 1952.
31. Takahashi, S. et al. Influence of heating and contamination upon mechanical properties of dental amalgams. Bul.Tokyo Dent.College 5:139 Dec.1964.
32. Unpublished report of dental research conducted at the National Bureau of Standards. 1962.
33. Johnson, L. B., Jr. X-ray diffraction evidence for the presence of β (Ag-Hg) in dental amalgam. J. Biomed.Material Res. 1:285, 1967.