

# NATIONAL BUREAU OF STANDARDS REPORT

**NBS PROJECT**

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REPORT ON DENTAL RESEARCH  
AT THE  
NATIONAL BUREAU OF STANDARDS

PROGRESS REPORT

January 1 to June 30, 1965

The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

## IMPORTANT NOTICE

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U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS



REPORT ON DENTAL RESEARCH  
AT THE NATIONAL BUREAU OF STANDARDS

1. Introduction

Research on dental materials, dental equipment and natural tooth structures was continued at the National Bureau of Standards during the half year ending June 30, 1965.

A list of reports issued, papers published and summaries of results obtained on work in progress are given below. Copies of the reports are appended.

2. Reports Issued

- NBS Report 8907 Pressure Exerted on Complete Dentures During Swallowing.  
NBS Report 8955 Crystal Growth of Bone Mineral.  
NBS Report 8958 The Structure and Properties of Dental Amalgam Alloys Prepared with Controlled Packing Pressures.  
NBS Report 8959 Hardening Shrinkage Forces in Direct Filling Materials.  
NBS Report 8964 The Steady-State Creep Behavior of Dental Amalgam.

3. Papers Published

- Blood-bone equilibrium in calcium homeostasis. J. MacGregor and W. E. Brown. Nature 205:359 Jan. 23, 1965.  
Clinical behavior of *o*-ethoxybenzoic acid-eugenol-zinc oxide cements. S. Civjan and G. M. Brauer. J. D. Res. 44:80 Jan.-Feb., 1965.  
Pressure-indicator-past patterns in duplicate dentures made by different processing technics for the same patient. J. B. Woelfel and G. C. Paffenbarger. JADA 70:343 Feb., 1965.  
Some physical characteristics of agar-impression materials. M. Ohashi, G. C. Paffenbarger and J. W. Stanford. J. Nihon Univ., School of Dentistry 7:11 Mar., 1965.  
The definition of alginate impression materials by a specification. M. Ohashi, G. C. Paffenbarger and J. W. Stanford. J. Nihon Univ., School of Dentistry 7:28 Mar., 1965.  
Clinical evaluation of complete dentures made of 11 different types of denture base materials. J. B. Woelfel, G. C. Paffenbarger, and W. T. Sweeney. JADA 70:1170 May, 1965.  
Phase rule considerations and the solubility of tooth enamel. W. E. Brown and B. Wallace. Annals of the Academy of Science May-June, 1965.  
Pyrolytic techniques. G. M. Brauer. J. Polymer Sci. Part C. Polymer Symposia No. 8, pp. 3-26 (1965).  
Resins and technics used in constructing dentures. G. C. Paffenbarger, W. T. Sweeney and J. B. Woelfel. Den. Clin. N. Am. pp 251 May, 1965.  
Dimensional changes of dental amalgam associated with strain release in the silver alloy particles. G. Dickson and R. M. Waterstrat. J. D. Res. 44:620 May-June, 1965.

4. Work in Progress

4.1 Natural Tooth Structure

(a) Structure of Calcified Tissues.

Solubility of calcium phosphates: Solubility studies on dicalcium phosphate dihydrate,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , in the system  $\text{Ca}(\text{OH})_2 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ , were carried out at 25.0°C and 37.5°C over the pH range 3.5 to 7.5. Evidence was obtained of complexing (or ion-pair formation) between calcium and phosphate; tentative instability constants for the ion pairs were calculated to



$$\text{be } \frac{(\text{Ca}^{++}) (\text{HPO}_4^{--})}{(\text{CaHPO}_4)} = 3.1 \times 10^{-3}$$

$$\text{and } \frac{(\text{H}^+) (\text{CaHPO}_4)}{(\text{CaH}_2\text{PO}_4^+)} = 4.1 \times 10^{-6}$$

respectively; the solubility product constant for  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  at  $37.5^\circ\text{C}$  was found to be  $(\text{Ca}^{++}) (\text{HPO}_4^{--}) = 2.1 \times 10^{-7}$ .

Structure of calcium phosphates: The crystallographic properties of the calcium potassium phosphate  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  were found to resemble closely those of glaserite,  $\text{NaK}_3(\text{SO}_4)_2$ . Since the structure of glaserite is known, the major structural features of  $\text{CaK}_3\text{H}(\text{PO}_4)_2$  can be deduced by analogy. Accordingly, cation-oxygen coordination in this compound has similarity to that found in the normal alkaline earth phosphates whose structures are known,  $\text{Sr}_3(\text{PO}_4)_2$  and  $\text{Ba}_3(\text{PO}_4)_2$ .

Preparation of materials: Continuation of the solubility and crystal structures and the reactivation and initiation of other programs have required the preparation and purification of a relatively large number of compounds which include  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ ,  $\text{CaCO}_3$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaHPO}_4$ ,  $\text{Ca}_9\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ , and  $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ . Preliminary work on the study of reactions of fluoride solutions with hydroxyapatite is largely complete.

Analytical procedure: Our method for analysis of calcium in the dilute solutions employed in our studies has not been entirely satisfactory. An atomic absorption apparatus is now being used and conditions of analysis suitable for our needs have been worked out.

Pore size distribution: A number of pore size distribution determinations have been made on natural calcium phosphates (e.g. bone) as well as laboratory preparations.

The affect of temperature of heating of anorganic bone between  $160^\circ$  and  $450^\circ\text{C}$  was studied as a function of the resultant changes in pore structure. The greatest pore area was found on the walls of pores between 20 Å and 40 Å diameter. Considerable compensation in total surface area was observed by a diminution in the area within these smaller pores accompanied by a simultaneous increase in the area of pores with diameters greater than about 120 Å.

The detailed shape of the pore area or pore volume profile consisting of peaks of varying intensities and shapes as a function of pore diameters appears to be characteristic of the substance, itself. For example, the pore volume profile of a sample of synthetic hydroxyapatite showed peaks at about 50 Å and 100 Å as did natural bone, despite the fact that the total surface areas of each of these samples differed by a factor of nearly 100. Even so, the relative heights and broadness of these peaks were not in agreement. This, however, might well have been caused by carbonates and/or other mineral species in the natural bone.

Octacalcium phosphate showed a pore volume profile which differed from that of hydroxyapatite. A sample of porous glass (used in molecular sieve applications) whose detailed pore structure had been well documented by independent investigators was determined as a check both on the equipment and the particular theory employed in this work. Thus, it appears possible that pore size distributions of known pure substances might be sufficiently characteristic to be used as an analytical tool for unknown mixtures of these substances.

#### (b) Organic Portion of Tooth Structure.

Chemical studies of dental calculus: Work on the gas chromatography of carbohydrate derivatives has proceeded toward the compilation of standard curves for each of the carbohydrates of interest in the organic portion of calculus. Excellent separation of N-acetyl galactosamine from N-acetyl glucosamine have now been achieved on a new non-polar liquid phase.

Preliminary work on the demineralization of calculus samples has been initiated and will proceed as samples are received. It is hoped that 100-200 samples can be processed in the next few months.



## 4.2 Metals

### (a) Amalgam

Additional studies were made of the relationships between condensation pressure and tensile strength, void content and mercury content of dental amalgam. A detailed report is appended.

Investigation of the viscoelastic behavior of dental amalgam was continued. A report on steady-state creep or viscous flow of amalgam is appended.

Stress-strain curves for dental amalgam were obtained using diffraction grating strain gages. The modulus values obtained, approximately  $7.5 \times 10^6$  psi, are considerably higher than the secant moduli reported in the literature. This difference results from the rapid loading (about 3 1/2 seconds) and consequent elimination or reduction of viscous and retarded elastic effects possible with the grating strain gages.

Studies of the thermal expansion of amalgam indicated that the coefficient of thermal expansion increases somewhat with increased mercury content. Data were also obtained on two irregularities in the thermal expansion curves, a large shrinkage on heating near 80°C followed by a larger expansion on cooling slightly above 50°C. The magnitude of these changes appears to be related to the mercury content of the amalgam.

### (b) Gallium alloys

Research program on gallium alloys has resulted in the development of an alloy which may be suitable for use as a dental restorative material. The alloy is prepared in much the same manner as dental amalgam, i.e., by triturating a metal powder with a liquid metal to form a plastic mass which will subsequently harden. The metal powder has a composition of 67% palladium and 33% gallium (Pd<sub>2</sub>Ga) and this powder is mixed with a liquid gallium solution containing about 10% tin. All mixing and handling operations have been satisfactorily performed using ordinary dental instruments and automatic trituration in a teflon capsule.

Recent laboratory tests in which the gallium-tin-palladium alloy was compared with ordinary dental amalgam produced the following results:

	<u>Dental Amalgam-</u>	<u>Gallium-Palladium Alloy</u>
Compressive strength at mouth temperature (37°C) specimens 7 days old	50,000	75,000
Early compressive strength specimens 1 hour old	10,000	23,000
Setting expansion (μ/cm) in 24 hrs.	0 to 20	0 to 8
Thermal expansion coefficient parts per million per °C (human teeth = approx. 10)	28	17
Hardness (Brinell)	70 to 90	150 to 200
Flow (%) using standard test from A.D.A. Spec. #1	1 to 3%	Less than 0.1%
Creep rate under a constant tensile load corresponding to 1/2 the ultimate tensile strength at room temperature (10 <sup>-8</sup> inches per inch per minute)	5,000	7





Values for compressive strength as high as 91,000 psi have been obtained and tensile strengths have ranged up to about 12,000 psi. The powdered alloy has an extremely fine particle size (1-20 $\mu$ ) which facilitates the attainment of a very smooth surface finish in the fully hardened mixture. The alloys's remarkable resistance to flow under an applied load together with its high one-hour strength, its retention of strength at elevated temperatures, its low setting expansion, high strength, thermal expansion coefficient close to that of human teeth, and its ability to wet the tooth structure offer a combination of properties which are unmatched in any contemporary filling material.

Early results from clinical tests in human patients have revealed no evidence of corrosion and no unusual effect on the pulp. Biological tests have so far indicated a rather severe tissue response in subdermal implants but similar tests on a commercial copper amalgam have also produced severe tissue reactions. An expanded program of clinical and biological testing is now being initiated which is expected to continue for several years or until sufficient information is obtained to insure that the use of this alloy as a dental restorative material would not constitute an undue hazard to the patient.

(c) Gold alloys.

An investigation of segregation in dental gold casting alloys has been initiated. The objectives are to establish a method of measuring segregation and to compare the degree of segregation with chemical composition, grain size, and solidification range. Preliminary results with the electron-probe indicate that segregation exists between copper and palladium, that is, where the copper concentration is high, the palladium concentration is low.

Jefferies' planimetric method was used to determine the grain size of alloys with and without nucleating agents (Grain Size in Dental Gold Alloy. J. P. Nielsen and J. J. Tuccillo. Presented at 43rd General Meeting IADR Toronto, July 1965) but having the same chemical composition. The alloy that did not contain a nucleating agent had approximately 6 grains per mm<sup>2</sup>, whereas the same alloy with a nucleating agent added had approximately 600 grains per mm<sup>2</sup>.

#### 4.3 Resins

(a) Silica-reinforced direct filling resins.

The incorporation of reinforcing fillers has been shown to improve most of the properties of direct, dental filling resins. One of the greatest improvements has been the reduction of the coefficient of thermal expansion by a factor of 4 or 5 to about 20 ppm/°C; this has been accomplished with the use of a gap-grading of irregular particles of vitreous silica or with gap-graded spherical particles of soda-lime glass. Theory predicts that gap-graded spherical particles of vitreous silica should result in a further lowering of the thermal expansivity of such composite materials toward the 10 ppm/°C of hard tooth tissues. The latter filler was produced by calcining cleaned, quartz sand, and then passing the resulting cristobalite through a plasma jet. This melted and spheroidized the particles, which were then quenched in a water bath.

Similar spheroidizing of Li Al SiO<sub>4</sub> with subsequent devitrification yielded spheres of  $\beta$ -eucryptite. This may have advantages over vitreous silica since it has a more favorable refractive index and a lower (negative) volumetric coefficient of thermal expansion. The thermal expansions and other properties of composites prepared with these gap-graded spherical, reinforcing fillers will be investigated.

(b) Adhesion studies.

If there is bonding between a dental filling material and the cavity walls tensile forces will develop when the material shrinks on hardening. A detailed report on tensile forces developed during the hardening of filling material is appended.



#### 4.4 Zinc Oxide-Eugenol Materials

Thermodynamic ionization constants of allyl- and propenylbenzoic acids in water and 15% ethanol were determined. Based on these and previously obtained values (1) pK increases with increasing ethanol content in the 0-70% ethanol range, (2) Hammett  $\sigma$  constants change only slightly with solvent concentration reaching a maximum content 25% ethanol. However, the  $\sigma$  value of p-propenyl moiety shows a strikingly larger change with ethanol content probably due to changes in the resonance interaction. With the exception of pK values of p-propenylbenzoic acid which has to be resynthesized the measurements have been completed and a paper describing the work will be prepared at an early date.

#### 4.5 Transition Behavior of Dental Materials

The thermograms (up to 800°C) of most of the commonly used dental materials (plastics, dental cements, waxes, investments, amalgam and golds as well as components of tooth structure, (dentin enamel, hydroxyapatite and octacalcium phosphate)) were obtained. Interpretation of the peaks in terms of transitions of the known components of dental materials was usually possible. The use of differential thermal analysis (DTA) as a specification test for characterizing melting behavior of waxes and gold alloys appears to be feasible. Quantitative determination of mercury content in dental amalgam from DTA peaks proved unsuccessful. The thermograms of dentin and enamel allow rapid distinction between these components of tooth structure.

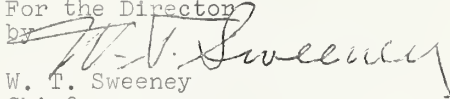
The studies will be extended in the 800-1200°C range and the temperature-weight loss relationship will be determined simultaneously. This additional information should prove most useful in the quantitative interpretation of thermograms.

#### 4.6 Evaluation of Materials

Materials evaluated for the American Dental Association by specification test methods included amalgam alloys, gold casting alloys, zinc phosphate cements, denture base resins, and a dental mercury.

#### 4.7 Specifications and Standards

Development of specifications and standards for dental materials in cooperation with the dental profession, dental manufactures and dental schools was carried on by participation in specification committee activities. Committees on which members of the Dental Research Section staff were active as member, secretary or chairman included the Federation Dentaire Internationale Commission on Dental Materials, Instruments, Equipment and Therapeutics; International Organization for Standardization Committee ISO/TC 106 Dentistry; International Association for Dental Research, Dental Materials Group Specification Committee; and Subcommittees on Amalgam, Excavating Burs and Diamond Rotary Instruments, Casting Gold Alloys, Radiographic Film, Duplicating Materials, Endodontic Files Reamers and Points, Gypsum Materials, Rubber Base Impression Materials, Toxicity Tests and Zinc Silico-Phosphate Cements.

For the Director  
by   
W. T. Sweeney  
Chief  
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