

# 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, 1966

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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

A wide range of research on dental materials and on natural tooth structure and related materials was continued during the half year ending June 30, 1966.

2. Reports Issued

- NBS Report 9360 Laboratory Tests on 13 West German Dental Silicate Cements by Methods Outlined in Fédération Dentaire Internationale Specification No. 5.  
NBS Report 9382 Solubility of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and Formation of Ion Pairs in the System  $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$  at  $37.5^\circ\text{C}$ .  
NBS Report 9390 Ionization Constants of Substituted Benzoic Acids in Ethanol-Water.  
NBS Report 9399 Segregation in Dental Gold Casting Alloys.  
NBS Report 9411 A Comparison of Brinell and Vickers Hardness Tests on Dental Gold Casting Alloys.

3. Papers Published

Analysis of the organic portion of dental calculus. J. W. Stanford. J. Dent. Res. 45:128 Jan.-Feb. 1966.

Crystal growth of bone mineral. W. E. Brown. Clinical Orthopaedics 44:205 Jan.-Feb. 1966.

Soft tissue response to implants of gallium alloys and silver amalgam alloys. H. W. Lyon, R. M. Waterstrat, G. C. Paffenbarger. JADA 72:659 March 1966.

Crystal chemistry of calcium phosphates. Walter E. Brown. Proc. 1964 Tech. Session, Cane Sugar Refining Research. Agricultural Research Serv., USDA, ARS72-44:26, March 1966.

Melting, flow, and thermal expansion characteristics of some dental and commercial waxes. M. Ohashi and G. C. Paffenbarger. JADA 72:1141 May 1966.

Dental applications of polymers: a review. G. M. Brauer. JADA 72:1151 May 1966.

Infra-red spectra of hydroxyapatite, octacalcium phosphate and pyrolysed octacalcium phosphate. B. O. Fowler, E. C. Moreno and W. E. Brown. Arch. Oral Biol. 11:477 May 1966.

4. Work in Progress

4.1 Natural Tooth Structures  
and Related Materials

(a) Solubility of Calcium Phosphates

Studies on the solubility of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  at  $37.5^\circ\text{C}$  were completed in the previous report period. Work during the present period included completion of measurements at  $25^\circ\text{C}$  and substantial completion of those at  $15^\circ\text{C}$ .

The results indicate that both the solubility and the degree of complexing are greater at  $25^\circ$  than they are at  $37.5^\circ$  and  $15^\circ$ . A detailed report is appended.

Measurements on the solubilities of  $\text{CaHPO}_4$  at  $25^\circ$  and  $37^\circ$  are almost complete. A tentative value for its solubility product at  $25^\circ$ ,  $(\text{Ca}^{++})(\text{HPO}_4^{--}) = 1.37 \times 10^{-7}$  was derived using "best-fit" values for the

complexing constants,  $(\text{Ca}^{++})(\text{HPO}_4^{--})/([\text{CaHPO}_4]^\circ) = 5 \times 10^{-3}$  and  $(\text{Ca}^{++})(\text{H}_2\text{PO}_4^-)/([\text{CaH}_2\text{PO}_4]^+) = 0.15$ . These complexing constants agree well with those derived from the data for  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  at  $25^\circ$ . The smaller solubility product constant for  $\text{CaHPO}_4$  as compared to that of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  is in accord with its known greater stability.

(b) Surface Properties of Hydroxyapatite

Requisite to these studies is a large sample of crystalline material with high specific surface, free of extraneous phases and impurities, and of sufficient stability so that changes within the crystallites will not alter the results. Such a material (specific surface  $\cong 25 \text{ m}^2/\text{g}$ ) was prepared by addition of phosphoric acid to a calcium hydroxide suspension and "annealing" the crystallites by prolonged boiling. The solubility of this material was found to be quite close to that of a hydroxyapatite annealed at  $1,000^\circ\text{C}$  in a steam atmosphere.

When this material was equilibrated with dilute solutions of phosphoric acid, the final compositions were found to be influenced by adsorption on the surfaces and by the total surface area. These results differ from those obtained with larger crystalline materials where deviations in stoichiometry of the dissolution process caused by surface effects could not be detected. Equilibrations with dilute calcium hydroxide solutions yielded similar results. Differences between the actual compositions and those predicted on the basis of congruent dissolution yielded minimum values for adsorption of phosphate and hydrogen ions.

Preliminary isotopic exchange experiments were carried out using  $\text{P}^{32}$  and  $\text{Ca}^{45}$  and solutions from the three-component system,  $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ , which were very nearly saturated with the hydroxyapatite preparation. The exchange reactions were found to be quite rapid; in the acidic range ( $\text{pH} \cong 6$ ), the reaction reached a nearly constant level in a few minutes. This is contrary to the idea that exchange reactions with the lattice (in contrast to the 'surface') proceed at a moderate rate; this suggests, also, that some of the slower reactions that have been reported relate to dissolution and reprecipitation of crystallites rather than exchange with the lattice.

In experiments carried out in the basic range, the reaction continued for a longer time, suggesting that the reactions in the two pH ranges may differ in their mechanisms as well as in the amounts that can react with the surface.

Streaming-potential measurements indicated that they may be more sensitive than electrophoretic mobilities as a means for study of electrokinetic phenomena in hydroxyapatite systems.

In an attempt to characterize further the surface properties of teeth, a sample of collagen (similar to that present in teeth) was procured which had been dried under conditions designed to prevent the collapse of the polypeptide structure. The surface area was so small that no value could be obtained using the conventional method of nitrogen adsorption at liquid nitrogen temperature. It must be concluded that collapse of the structure had, indeed, occurred.

The grinding of several hundred grams of caries-free human teeth to pass through a 120 mesh sieve was completed. The teeth were then rendered anorganic by extraction of the collagen with ethylene diamine in accordance with accepted procedure. The resultant product will be used for adsorption from solution as well as in gas systems. It is interesting that the enamel could not be separated from the dentin by the usual flotation techniques. Once the collagen had been extracted, there was no distinction between the densities of the two components each being greater than 2.70 (the density of the flotation liquid). Some fractionation may be possible based on the rate



at which the powder sinks, since the filling of the pores with solvent is a time dependent process. A water-immiscible flotation solvent ( $\rho = 2.70$ ) was prepared using 52% (by volume) Bromoform together with 48% Dibromomethane. While the dry anorganic teeth would not float in such a solvent, the addition of less than 8% water rendered the powder completely buoyant although there was no visible affect of the water on the appearance of the powder.

#### (c) Heats of Wetting of Tooth Structure

The measurement of the heat of wetting of powdered dentin under various experimental conditions, and the measurement of the effects of various ions and functional groups upon the heat of wetting of dentin have been attempted.

The values obtained for the heat of wetting of dentin are dependent on the completeness of the removal of water, that is, on the method of preparation of the sample. If the powders are conditioned over anhydrous calcium sulfate, the apparent value obtained for the heat of wetting is in the range of 8 calories per gram. Dentin samples conditioned at approximately 1 mm/Hg vacuum yield an apparent heat of wetting of 10 calories per gram. On drying of the dentin samples around  $10^{-3}$  mm/Hg, the heat of wetting is found to be on the order of 13 calories per gram.

The effects of dilute solutions of common chelating agents upon the apparent heat of wetting of dentin were also investigated. Ammonium citrate, disodium EDTA, citric acid, malonic acid and ascorbic acid increase the observed heat of wetting of dentin by a factor of four. However, sodium fluoride, and formaldehyde solutions have no effect upon the heat of wetting of dentin.

#### (d) Transport in Enamel

A valid physicochemical description of diffusion in enamel is basic to understanding the mechanism of caries formation. The diffusion phenomenon is complicated here by the fact that it involves a weak electrolyte (phosphoric acid) and it occurs in a soluble porous medium.

A comprehensive theoretical study of diffusion in the system  $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$  has been completed; if experimental tests prove its validity, it will be a significant contribution to the field of diffusion of weak electrolytes. Two models were worked out mathematically: a) the driving forces are the chemical potentials of electroneutral components; b) the driving forces are applied considering the ionic species present. Through expressions for the production of entropy, it was shown that these two models are equivalent. However, each has unique features that allow comparison of them through measurable quantities. Either model will allow tests on Onsager's reciprocal relations, and important subject in modern diffusion theory. The equations are in a form such that they may be applied to diffusion in either porous or free systems and with or without the restriction that the solutions are saturated with respect to hydroxyapatite.

#### (e) Crystallography

In a cooperative study with Tennessee Valley Authority personnel, the crystal structure of  $\text{H}_3\text{PO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$  has been determined. The calculations are being continued in an attempt to locate the hydrogen atoms.

Preparations were made of  $\text{Ca}_4\text{O}(\text{PO}_4)_2$  (tetracalcium phosphate),  $\text{Ca}_5(\text{PO}_4)_2(\text{SiO}_4)$  (sillicocarnotite), and  $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$  which contained crystals suitable for crystal-structure analysis. They were characterized optically and are now ready for use in an expanded crystal-structure program.

## 4.2 Metals

### (a) Amalgam

Additional data were collected on the effect of mercury content on the thermal expansion of dental amalgam. By electron probe and x-ray diffraction studies, crystals found on the surface of amalgam specimens which had been heated above 75°C were identified as Sn<sub>7</sub>Hg. Further studies of phase changes during the heating and cooling cycle will be made.

### (b) Gold Alloys

A study of segregation in cast gold alloys and an investigation of the relationship between Brinell hardness numbers and Vickers hardness numbers of gold alloys were completed. Detailed reports are appended.

### (c) Phase Stability in Noble-Metal Alloys.

The order-disorder reaction is of considerable importance in dental-gold alloys. To obtain fundamental information on the nature of the ordering process and the affects of various noble metal additions, a study has been in progress to determine the extent of ordering in alloy phases having the cubic A15 type structure. During this investigation a new superconductor was discovered in the chromium-osmium system. Preliminary results indicate that the ordering tendency varies with the position of the constituent atoms in the periodic table. Elements such as chromium and osmium tend to be less ordered than elements such as titanium or platinum. These results should help in designing new dental alloys having improved properties as well as in controlling the properties of alloys presently in use.

## 4.3 Resins

### Silica-Reinforced Direct Filling Resins.

Development of improved reinforced filling resins is continuing. The following monomers have been synthesized and are being evaluated as substitutes for methyl methacrylate and Bisphenol A-glycidyl methacrylate adduct in our resin formulation:

Bis( $\beta$ -methacryloxyethylene)isophthalate  
Bis( $\beta$ -methacryloxyethylene)terephthalate  
Bis(2-methacryloxypropylene)isophthalate  
Bis(2-methacryloxypropylene)terephthalate

For the purpose of improving color stability, partial substitution of benzoyl peroxide by an aliphatic acyl peroxide such as lauroyl peroxide has been successfully attempted.

## 4.4 Zinc Oxide-Eugenol Materials

### (a) Zinc Oxide-Eugenol Type Cements.

Previous studies of the setting mechanism of zinc oxide-eugenol cements and the reaction of metal oxides with chelating agents have lead to the development of a much improved dental cement containing o-ethoxybenzoic acid (EBA). This cement has become commercially available during the last year.

The incorporation of aluminum oxide of varying particle sizes including whiskers down to a particle diameter of 6  $\mu$  was investigated with the aim of further improving physical properties. The resulting cements gave a maximum compressive strength of 14,000 lb/in<sup>2</sup> that is a 10% increase over the previously developed products. Greatly reduced film thickness and improved adhesive properties of these materials would indicate their usefulness

as crown and bridge and orthodontic cements. Use of whiskers as re-enforcing agents did not yield any improvement. Apparently, complete bonding between whiskers and other components was not accomplished. The complete suspension of the whiskers in the mix also was found to be a problem since the whiskers had a tendency to conglomerate. The effect of surface active agents to improve mixing properties is being investigated.

(b) Ionization Constants of Substituted Benzoic Acids in Ethanol-Water.

The data on the ionization constants obtained in this study as well as those reported by other investigators were used to examine the validity of existing relationships between the dielectric constants of the aqueous ethanol solvent and pK values and to calculate ion size parameters. On plotting  $pK + \log [H_2O]$  versus dielectric constant a nearly linear relationship was obtained from 0 to about 45 weight percent ethanol. This relationship applied to all benzoic acids investigated as well as for nuclear substituted anilinium ions. For some solutes a plot of  $pK + \log [EtOH]$  versus dielectric constant yields a straight line at higher ethanol concentrations.

The change of the sigma and rho parameters of the Hammett equation with ethanol concentration were also studied. Up to 45% ethanol content, the product of sigma and dielectric constant is constant within 2.3%. The effect of ethanol concentration on the  $\sigma$  substituent constant was also studied for fourteen functional groups. The substituent constant is markedly dependent on solvent for the  $C_3$ ,  $H_5$ ,  $NH_2$ ,  $OH$  and  $NO_2$  groups only, where the electron distribution is altered because of solvation of the substituent. However, for none of these groups is the dependence of sigma on solvent medium as large as that found for the p-propenyl group in this study. This behavior may be indicative that the solvation shell surrounding the p-propenylbenzoic acid differed from that of other benzoic acids.

A detailed report describing this study is appended.

#### 4.6 Evaluation of Materials

Materials evaluated for the American Dental Association by specification test methods included amalgam alloys, chromium-cobalt casting alloys, gold casting alloys, hydrocolloidal impression materials, mercuries, plastic teeth, silicate cements, zinc oxide-eugenol impression pastes and zinc phosphate cements.

#### 4.7 International Standards for Dental Materials

The past year has seen considerable progress in the advancement of international standards for dental materials. The American Standards Association (A.S.A.) committee was well represented at the June-July Working Group meetings and at the July 4 Second Plenary meeting of the International Organization for Standardization (I.S.O.) in London. Eight representatives of the United States were present: Dr. G. C. Paffenbarger, Mr. E. M. Feinberg, Dr. J. F. Glenn, Colonel S. G. Gordon, USAF, DC, Dr. Gunnar Ryge, Dr. J. W. Stanford, and Mr. C. E. Hilton, also Mr. W. T. Sweeney. Dr. George C. Paffenbarger, Senior Research Associate, American Dental Association, acted as leader for the American Committee.

The participating (P) countries represented were, Australia, France, Germany, Italy (not present), Netherlands, Norway, Sweden, United Kingdom and the United States of America. The observer (O) countries were Yugoslavia, also F.D.I. and F.I.D.E. (Federation of the European Dental Industry) and the British Standards Institution who hold the Secretariat. The meeting was conducted in French and English and consisted of several days of Working Groups and Plenary meeting on July 4th. The 4 working groups discussed the working level and agreed to develop technically identical F.D.I. specifications and I.S.O. recommendations.



It was a distinct victory for our group because the nine F.D.I. specifications are almost identical with the American Dental Association's. These specifications were based on work done at the National Bureau of Standards over the last several years.

The main discussion revolved around methods for revision of old specifications and who would be responsible for initiation of the new ones. This was solved by a cooperative effort of the F.D.I. and the I.S.O. each being assigned specific subjects to prevent duplication.

Statement of Results: The second plenary meeting of ISO/TC 106 Dentistry was held in London on 4 July; meetings of the four working groups were held immediately before or after the plenary meeting. Discussions took place in an atmosphere of friendly cooperation and resulted in agreement on a procedure for developing technically identical F.D.I. (Fédération Dentaire Internationale) Specifications and I.S.O. Recommendations.

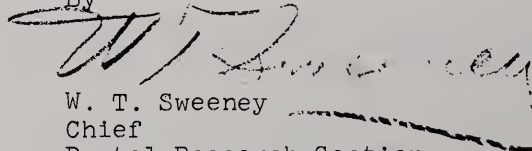
The program of work in the field of filling materials and denture materials has been agreed upon, and the Secretariat's responsibility in respect to items of work has been allocated between the F.D.I. and the two working group Secretariats concerned.

The nine published F.D.I. Specifications were accepted as Draft I.S.O. Recommendations and recommended for earliest possible I.S.O. approval and publication; these documents will at the same time become the subject of revision based on well documented technical data and in accordance with the going procedure that has been developed.

The National Bureau of Standards as part of the Department of Commerce has an opportunity through the Office of Engineering Standards to take an active part in this standardization program. Now that the committee is organized and working the American leadership in this area can be extended to the international field. Our reputation is established world-wide, and it will be to the long run advantage of American manufacturers to have standards adopted that reflect our technology as much as possible. Otherwise, they will be completely at a disadvantage in the international trade market on a technological basis that is not common to the United States. It is essential that we have strong technical representation at the ISO/TC 106 Dentistry Committee and take an active part in working groups in the future.

For the Director

By



W. T. Sweeney  
Chief  
Dental Research Section