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Report on Dental Research at the National Bureau of Standards

PROGRESS REPORT

July 1 to December 31, 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.

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 December 31, 1965.

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

2. Reports Issued

NBS Report 9039 An Evaluation of Complete Dentures Lined with Resilient Silicone Rubber

NBS Report 9049 Measurement of the Surface Area and the Heats of Wetting of Dentin Powders.

NBS Report 9060 Some Flow Characteristics at 37°C of Ternary Wax Mixtures that May Have Possible Dental Uses.

NBS Report 9078 Surface Studies of Natural and Synthetic Bone Mineral and Teeth.

NBS Report 9083 Application of Diffraction Gratings to Measurement of Strain on Certain Dental Materials.

3. Papers Published

World standards for dentistry. G. C. Paffenbarger and Marion P. Kumpula. Magazine of Standards 36:212 July 1965.

Adhesive bonding of various materials to hard tooth tissues. I. Method of determining bond strength. R. L. Bowen. J. Dent. Res. 44:690 July-Aug. 1965.

General discussion, new developments in dental materials -- A world wide survey. G. C. Paffenbarger. Internat. D. J. 15:356 Sept. 165.

Adhesive bonding of various materials to hard tooth tissues. II. Bonding to dentin promoted by a surface-active comonomer. R. L. Bowen. J. Dent. Res. 44:895 Sept.-Oct. 1965.

Adhesive bonding of various materials to hard tooth tissues. III. Bonding to dentin improved by pretreatment and the use of a surface-active comonomer. R. L. Bowen. J. Dent. Res. 44:903 Sept.-Oct. 1965.

Adhesive bonding of various materials to hard tooth tissues. IV. Bonding to dentin, enamel and fluorapatite improved by the use of a surface-active comonomer. R. L. Bowen. J. Dent. Res. 44:906 Sept.-Oct. 1965.

Restoration of complete dentures inadvertently warped by the patient: report of a case. J. B. Woelfel and G. C. Paffenbarger. JADA 71:866 Oct. 1965.

A review of zinc oxide-eugenol type filling materials and cements. G. M. Brauer. Rev. Belge Med. Dent.-Belg. Tijds. vr Tandheelk 20:323 Nov. 1965.

Crystallography of tetracalcium phosphate. W. E. Brown and E. F. Epstein. J. Res. Nat. Bur. Stds. 69A:547 Nov.-Dec. 1965.

Adhesive bonding of various materials to hard tissues. V. The effect of a surface-active comonomer on adhesion to diverse substrates. R. L. Bowen. J. D. Res. 44:1369 Nov.-Dec. 1965.

A simple device for adjusting dental interferometers. H. J. Caul and J. W. Kumpula. J. D. Res. 44:1412 Nov.-Dec. 1965.

Composition, work and interrelation of international and national organizations engaged in the standardization of dental materials. G. C. Paffenbarger and Marion P. Kumpula. Internat. D. J. 15:571 Dec. 1965.

Chemical analysis. G. M. Brauer and G. M. Kline. Encyclopedia of Polymer Science and Technology, Vol. 3. John Wiley and Sons, Inc. 1965.

4. Work in Progress

4.1 Natural Tooth Structures

(a) Structure of Calcified Tissues

Solubility of calcium phosphates: Tentative instability constants for ion-pair formation and solubility product constant for $CaHPO_4 \cdot 2H_2O$ at 37.5°, listed in the last report, have been refined. Revised values for the constants are

$$\frac{(Ca^{++})\ (HPO_4^{--})}{(CaHPO_4)} = 1.7 \times 10^{-3}$$

$$\frac{(H^+)\ (CaHPO_4)}{(CaH_2PO_4^+)} = 5.2 \times 10^{-6}$$

$$(Ca^{++})\ (HPO_4^{--}) = 2.1_9 \times 10^{-7}.$$

This completes the work on $CaHPO_4 \cdot 2H_2O$ at 37.5°; a paper covering this work has been written. Some additional work on the solubility at 25° was carried out to check points that appeared to be inconsistent with the data obtained at 37.5°. These data are being evaluated. Data at 18° reported by Bjerrum, is being reevaluated in terms of knowledge obtained at 25° and 37.5° with the hope of determining the enthalpies of ion-pair formation.

Solubility measurements on $CaHPO_4$ were initiated. Measurements at 25° are about half finished.

Transport in enamel: Study of transport in enamel was undertaken because of its importance to dental therapeutics and because of its possible importance in the mechanism of caries formation. Techniques were developed for preparation of thin sections of enamel, the diffusion apparatus was assembled, and preliminary measurements with tritiated water were carried out. The apparent diffusion coefficient through enamel is about one thousandth of that in free water. Even though the premeability of enamel is low, it appears that the radioactive techniques can be used successfully.

Surface properties of hydroxyapatite: This project includes studies of adsorption from liquid and gaseous media. The major aspects of the solution studies relate to kinetics on capacity of ion exchange; radioactive ions will be used. The equipment has been designed and assembled; measurements will be carried out on receipt of the radioactive materials. Relative to this work, exploratory electrophoretic, streaming potential, and equilibration measurements have been carried out using non-radioactive materials. The initial results on the adsorption capacity for $Ca(OH)_2$ in the high pH range of the system look promising.

Further work on pore size distribution has been done especially on synthetic preparations. The differences between "amorphous" and crystalline preparations of hydroxyapatite are impressive when compared in terms of their respective pore volume profiles. The results have been prepared for publication.

Crystal structures: It is increasingly evident that the calcium carbonates have an important role in the precipitation and properties of apatitic materials. In this connection, we have directed our attention to the possible roles of the hydrated calcium carbonates, $CaCO_3 \cdot H_2O$ and $CaCO_3 \cdot 6H_2O$; their participation in mineralization processes has been largely ignored because of their metastability. Surface energy considerations, however, suggest that they may participate in nucleation processes. Examination of the known crystallographic properties of the monohydrate revealed a structural relationship to hydroxyapatite and octacalcium phosphate which may provide an epitaxial mechanism for calcium phosphate nucleation and precipitation. Initial experimental attempts to establish the epitaxial mechanism were not successful; additional new approaches are being planned. Structural work on α-$Ca_3(PO_4)2$ is being continued in cooperation with Mr. E. F. Epstein at the University of Wisconsin. The study of the structure of $H_3PO_4 \cdot \frac{1}{2}H_2O$ in cooperation with Dr. A. Mighell of the Crystallography Section and Mr. J. P. Smith of TVA has progressed to the refinement stage.

Nucleation of calcium phosphates: The identity of the calcium phosphate that initially precipitates in tooth and bone has not been established; there are indications that it may be octacalcium phosphate. Theoretical considerations led to the conclusion that the identity of the species can be established from a plot of the

calcium hydroxide and phosphoric acid chemical potentials of nucleating solutions. In vitro data from the literature were evaluated through the use of this plot, and gave evidence that octacalcium phosphate was the nucleating substance.

Preparation of materials: The broad range of studies being carried out requires a variety of crystalline materials. About a pound of hydroxyapatite with a surface area of about 25 square meters per gram was prepared for use in the surface studies. Other materials that have been prepared include $CaHPO_4$ for solubility studies, β-$Ca_3(PO_4)_2$ and β-$Ca_2P_2O_7$ for use in thermochemical studies, and $CaCO_3 \cdot 6H_2O$ and $Ca_5(PO_4)_2(SiO_4)$ (silico-carnotite) for use in x-ray single-crystal studies.

(b) Organic Portion of Tooth Structure

After the collection and storage of numerous calculus and mucin samples, test runs of some of these showed a need for more refined techniques of demineralization. Procedures used previously (on larger samples) caused incomplete demineralization or complete loss of sample. The procedure to be used has not been completely investigated, as it is felt that our gas chromatographic studies require more attention at this time. The newer liquid phase (for gas chromatography) mentioned previously, has been more fully investigated. Separations once found difficult to achieve have now been perfected, and more detailed quantitative studies are being made on the carbohydrates of interest. For the demineralization of small amounts of calculus, a new cell is being investigated. This cell dialysis appears to remove some of the obstacles and objections connected with "bag" dialysis of micro samples.

4.2 Metals

(a) Amalgam

Study of the mechanical properties of dental amalgam by ultrasonic methods was initiated. Preliminary results of of measurements of the velocity of transverse and longitudinal waves in amalgam specimens indicate that the methods are feasible. Values near 9 or 10 x 10^{-6} psi were obtained for Young's modulus. The results appear to correlate with mercury content of the amalgam.

(b) Gallium Alloys

During this period efforts have been concentrated toward preparing significantly larger quantities of the palladium-gallium alloy powder (Pd_2Ga) in order to make a sufficient amount available for clinical and biological testing. Due to the exothermic reaction in this alloy the ingredients must be mixed very slowly or the melting operation must be performed in an electric-arc furnace. In both cases it is necessary to protect the melt by means of vacuum or an inert-gas atmosphere. No heat-treatment is necessary. The alloy ingot is converted to a fine powder by milling in a hardened-steel rod mill for 24 hours. The excellent mechanical properties previously reported have been reproduced rather well by this second lot of material. This indicates that alloy preparation will not require very critical control.

Attempts have been made to use recently publicized "whisker reinforcement" techniques in connection with the gallium alloys. This involves obtaining a uniform dispersion of very small filamentary particles (whiskers) which have extremely high strength into the matrix of the alloy. It now appears that gallium alloys are rather promising materials for "whisker reinforcement" since several percent by volume of silicon carbide whiskers can be "wetted" and incorporated into the liquid gallium solution. This liquid is then mixed with the alloy powder in the usual manner. The "whiskers" remain in suspension in the liquid for long periods of time with no apparent clustering. It remains to be seen whether the strength of these alloys may be improved by "whisker reinforcement".

(c) Gold Alloys

The x-ray emission analysis method previously reported was modified slightly to eliminate effects of overlaps between palladium and silver lines and between copper and platinum lines. After this modification the x-ray emission analyses agreed with the values determined from wet chemical methods to within approximately 0.2%. The average precisions of x-ray emission analysis of elements in duplicate samples were found to be between 0.01 and 0.11%.

Investigation of segregation in dental gold casting alloys was continued. Materials representative of four types of dental gold alloy were investigated in both the coarse and fine grained structure. The difference in grain size are very distinct and there appears to be a difference in segregation or least in type of segregation.

Variations in concentration along a 480μ were determined using the electron microprobe. Data from these scans are being examined to establish a means of defining the degree of segregation.

4.3 Resins

(a) Inorganic Fillers for Resin Composites.

A means of obtaining spheroidal particles of fused silica and β-eucryptite glass was found in the use of the oxygen-acetylene flame of a ceramic powder gun, making the use of a plasma jet unnecessary. With the oxygen-acetylene flame, quartz particles smaller than about 20μ were vitrified; those smaller than 5-10μ were converted into spheres. Larger particles of β-eucryptite and its solid solutions were spheroidized readily in the flame. It was found necessary to remove surface alkali to obtain optimum silane treatment of the β-eucryptite particles. A composite prepared with about 78 weight percent of gap graded fused silica spheres together with 22 weight percent of a polymerizable organic resin binder had a coefficient of thermal expansion of about 17 parts per million per degree C from 25 to 48°C. A composite prepared with only 74 weight percent of gap graded β-eucryptite spheres together with 26 weight percent of the same polymerizable organic resin binder had a coefficient of thermal expansion of about 18 parts per million per degree C over approximately the same temperature range.

4.4 Zinc Oxide-Eugenol Materials

Ionization constants of substituted benzoic acids: The ionization constants of p-propenylbenzoic acid in various ethanol-water mixtures have been determined. On changing the solvent concentration the relative acidic strength of the allyl and propenylbenzoic acids show inversions. The Hammett σ constant of the p-propenylbenzoic acid changes markedly with the solvent medium whereas the other substituted benzoic acids show only a slight variation with changes in solvent composition. Statistical analysis of the σ-solvent composition relationship was carried out.

4.5 Transition Behavior of Dental Materials

Thermogravimetric techniques (TGA) were found to be very useful as replacement for the much more time consuming gravimetric procedures. Among the problems to which the technique which requires only a few milligrams of sample has been applied successfully are (1) residue in dental mercury and waxes, (2) loss in volatiles and amount of organic constituents in components in tooth structure, (3) loss in weight of dental cements which show phase transitions, but a weight loss of only 1% on heating to 900°C and (4) weight changes of dental resins on heating. By using a specially designed quartz sample probe DTA thermograms of the transition points of gold alloys reproducible within ± 0.5°C have been obtained.

4.6 Evaluation of Materials

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

For the Director
By

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