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NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1960

Dental Research Laboratory

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

Publications

The results of the Bureau's work take the form of either actual equipment and devices or published papers. These papers appear either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau itself publishes three periodicals available from the Government Printing Office: The Journal of Research, published in four separate sections, presents complete scientific and technical papers; the Technical News Bulletin presents summary and preliminary reports on work in progress; and Basic Radio Propagation Predictions provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: Monographs, Applied Mathematics Series, Handbooks, Miscellaneous Publications, and Technical Notes.

Information on the Bureau's publications can be found in NBS Circular 460, Publications of the National Bureau of Standards ($1.25) and its Supplement ($1.50), available from the Superintendent of Documents, Government Printing Office, Washington 25, D.C.

NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1960

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 Army Dental Corps, the Dental Sciences Division of the School of Aviation Medicine, USAF, the Navy Dental Corps, and the Veterans Administration.

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Research on a wide variety of dental materials and equipment and on natural tooth structure has continued at the National Bureau of Standards during the half year ending June 30, 1960.

Summaries of results obtained on work in progress, a list of reports issued and a list of papers published during the period are given below. Copies of reports are appended.

2. REPORTS ISSUED

NBS Report 6826 A Procedure for the Determination of the Noble Metal Content of Dental Gold Alloys.

NBS Report 6853 Analysis of Pyrolyzates of Polymers by Gas Chromatography
I. Pyrolysis of Polystyrene and Poly(methyl methacrylate) at 400 to 1100 °C

NBS Report 6946 Some Tensile Properties of Amalgam

3. PAPERS PUBLISHED

American Dental Association Specifications for Dental Materials 1960-1961. Fourth Edition. G. C. Paffenbarger, J. W. Stanford and W. T. Sweeney. American Dental Association, Chicago, Ill. Jan. 1960.

Teeth: Artificial. G. C. Paffenbarger. Encyclopedia Britannica 21:878, Jan. 1960.

Physical Properties of Synthetic Rubber-Base Dental Impression Materials. W. A. C. Miller, Jr., W. C. Hansen and George Dickson. J. A. D. A. 60:211, Feb. 1960.

Proposed Specification for Impression Materials, Synthetic Rubber-Base, Dental. W. A. C. Miller, Jr., W. C. Hansen and George Dickson. J.A.D.A. 60:225, Feb. 1960.

Opportunities in Dental Research. G. C. Paffenbarger. J.A.D.A. 60:268, Feb. 1960.

Low Angle Diffraction of Fibrous Polyethylene. A. S. Posner, L. Mandelkern, C. R. Worthington and A. F. Diorio. J. Applied Physics 31: 536, March 1960.

Analysis of Methyl Methacrylate Copolymers by Gas Chromatography. J. Strassburger, G. M. Brauer, M. Tryon and A. F. Forziati. Analytical Chem. 32:454, April 1960

Dental Materials 1956-1958. G. C. Paffenbarger. J.A.D.A. 60:600, May 1960.

Cements from Metal Oxides and Chelating Agents. G. M. Brauer. U. S. Patent No. 2,936,242, May 1960.

Radial Distribution Study of Vitreous Barium Borate. A. Bienenstock, A. S. Posner and S. Block. J. Res. NBS 64A: 229, May-June 1960.

Compressive Properties of Hard Tooth Tissues and Some Restorative Materials. J. W. Stanford, K. V. Weigel, G. C. Paffenbarger and W. T. Sweeney. J.A.D.A. 60:746, June 1960.

The Nature of the Inorganic Phase in Calcified Tissues. A. S. Posner. Calcification in Biological Systems, p. 373. Am. Assn. Advancement Sci., Washington, D. C., July 1960.

4. WORK IN PROGRESS

4.1 Human Tooth Enamel and Dentin

(a) Fluorescence Studies.

Isolation and Identification of the Fluorescent Components of Tooth Structure.

The protein complexes extracted from dentin were treated with trypsin, chymotrypsin, pepsin, papain and collagenase. Although a number of peptides were liberated by these enzymes, only papain released even a small amount of fluorescent material from the protein complexes. Accordingly, a more vigorous hydrolysis with 6N HCl was employed. Subsequent paper electrophoresis showed that considerable degradation of the fluorescent material had occurred. Two fluorescent peptides containing a pyrimidine derivative were found among the many breakdown products.

(b) Crystallographic Studies.

Low angle X-ray diffraction studies of long chain polymers were continued. Particular attention was given to long range periodicity in fibrous and bulk polyethylene because of the resemblance of this comparatively simple polymer to collagen of dentin and bone.

Studies of phase changes in polymers such as myosin, muscle, and polyethylene were continued employing wide angle X-ray diffraction techniques.

Work also continued on the analysis of X-ray diffraction line broadening as a method of investigating the misalignment of the atoms of hydroxyapatites and determining the role of this misalignment in calcified tissue metabolism.

A new study was begun in cooperation with the National Institute of Dental Research on the comparative uptake of Ca^{45} and Sr^{89} by certain snails. A similar study is being carried out on the comparative metabolism of these ions in the enamel and dentin of laboratory rats. The snails are of particular interest because their exoskeletons are composed of $CaCO_3$ of the aragonite phase unlike the hydroxyapatite skeleton of higher animals.

An infra-red absorption study of the nature of hydrogen-bonding in calcium phosphates was initiated. Synthetic hydroxyapatites deficient in calcium have been shown to contain hydrogen in hydrogen bonds replacing the lost positive charge.

(c) Dental Calculus Studies.

Infrared studies have shown that the lipide content of dental calculus appears to be a neutral fat. Application of different methods of decalcification or extraction to separate the mineral portion from the organic continues. Eighteen amino acids have been shown to be present in the protein of portions of the organic matrix which have been hydrolyzed. To determine the acids quantitatively, standard calibration curves are being prepared for each amino acid which has been identified. Identification is being done by paper chromatography using two dimensional runs as follows:

First solvent: EtOH/Tert. Butanol/NH_4OH/H_2O;

Second solvent: Phenol/H_2O/NH_4OH in atmosphere of cyanide. Spots are developed with 2% alcoholic ninhydrin and color is eluted with 50% aqueous n-propanol. Optical densities are being measured on a spectrophotometer

4.2 METALS

(a) Amalgam.

Constitution of the Silver-Tin-Mercury System.

More than fifty specimens covering the majority of the ternary system have been prepared and are being annealed for subsequent metallographic and microhardness examination. Study of the tin-mercury portion of the system was continued by a

combination of diffusion, thermal analysis, and x-ray diffraction techniques.

Analyses of sections of diffusion specimens indicated the existence of three intermediate phases at temperatures near 37°C. Maximum mercury contents of the three phases are approximately 19.2, 20.1 and 22.3 wt. %. X-ray diffraction results confirm a structural difference between the 20.1% and 22.3% mercury phases. Thermal analysis studies indicate that the 20.1% phase is associated with the 90°C thermal arrest reported by M. L. V. Gaylor. It is anticipated that, as the ternary specimens become available, these structures can be traced into the adjoining ternary regions. The data to date indicate the need for considerable revision of the published diagrams.

Particle Size.

An investigation of the effect of particle size on the properties of dental amalgam was started. For this purpose an alloy containing 71%Ag, 26% Sn, 2.5% Cu and 0.5% Zn prepared at NBS was "atomized" into powder of spherical form by a commercial laboratory (Federal-Mogul Co.). The particles are being separated by sieving and elutriation into 8 sizes ranging from a minimum size of less than 4 microns diameter to a maximum of 150 microns. Physical properties including dimensional changes in setting, compressive strength, tensile strength and flow will be determined on amalgams made from the experimental alloy.

(b) Gold Alloys.

A report on the improved wet analysis method for the noble metal content of gold alloys is appended. Investigation of rapid analysis of gold alloys by fire assay and by x-ray fluorescence methods is now in progress.

(c) Chromium-Cobalt Alloys

The effect of remelting on the properties of chromium-cobalt casting alloys was investigated. Tests of the effect of remelting upon tensile properties were made on two lots of Ticonium and one lot of Cannon Muskegon No. 2 chrome-cobalt alloys. Patterns were molded at the National Bureau of Standards while all castings were made at the Central Dental Laboratory, Walter Reed Army Medical Center. Normal laboratory routine was followed as far as possible. Each series of castings was made in the following manner. A set of six or eight patterns were invested two to a mold. The castings were made from new metal. The castings were separated from the investment, cleaned by sandblasting, and the sprues and buttons

removed. The specimens, containing metal melted once only, were reserved for testing. The scrap, combined with an equal weight of new metal, was used to cast a second set of specimens. The process of casting, cleaning, separating and adding 50% new metal was repeated until specimens were made containing metal cast one, two, four and eight times. This procedure was repeated on each lot of alloy to provide an independent check on possible depletion or contamination of the alloy.

The repeated reuse of scrap as a portion of the metal melted caused a definite decrease in the numerical values for all properties (tensile strength, yield strength, modulus of elasticity and elongation) for the first lot of Ticonium. The second lot of Ticonium showed a smaller decrease while the Cannon Muskegon alloy showed no statistically significant decrease at all. Much of the difference between lots appears due to increased experience on the part of the melter, although the results on the Cannon Muskegon alloy may also reflect a lower sensitivity to remelting. With the exception of the elongation values, the properties of all three lots of alloy, even after eight meltings, would meet the present A.D.A. and Federal Specifications for these alloys. The cause of the low elongation values for the two lots of Ticonium was not determined Only those for new metal will pass the specification, but these also are much lower than previous results for this alloy. The low elongation values found here appear due mainly to the effect of some other factor than remelting.

On the basis of these results the reuse of 50% scrap metal appears both safe and immediately practical. It is further indicated that, as the laboratory personnel become more experienced in the reuse of scrap metal, progressively less difference is observed between the properties of new and reused metal. Results to date, on a total of something over 3000 clinical cases, support this conclusion. Additional work is still in progress on this project. In particular, a series of specimens is being made from 100% scrap metal in order to determine the necessity of limiting the quantity of scrap used to 50%.

(d) Gallium Alloys

Investigation of the possibility of gallium alloys for use as a dental restorative material has been resumed. Previous experimental work indicated that gallium will combine with certain powdered face-centered-cubic metals and that the gallium-tin eutectic (89 weight % Ga- 11 weight % Sn) will combine with powdered face-centered-cubic metals and binary intermetallic compounds of these metals with tin as the second component. The

face-centered-cubic metals with which gallium combines have atomic radii between 1.25 and 1.28 Å. Copper and nickel are the only metals which meet this requirement. Since copper has poor corrosion resistance in the presence of the oral fluids, work has been concentrated on nickel and nickel-tin alloys.

The two most promising alloys developed thus far are 55 weight % monel-45 weight % gallium-tin eutectic and 60 weight % β-nickel-tin (60 weight % Ni-40 weight % Sn) - 40 weight % gallium-tin eutectic. The monel base alloy has a seven day compressive strength of 33,000 psi and a setting expansion of 5 μ/cm. The addition of 10 weight % chromium powder to the powdered monel increased the seven day compressive strength to 43,000 psi and the setting expansion to 12 μ/cm. The β-nickel-tin alloy has a one hour compressive strength of 11,000 psi. After one day the compressive strength is 31,000 psi and it does not increase after this time. The setting expansion of this alloy is 20 μ/cm after one day and 45 μ/cm after seven days. Combinations of gallium with powdered monel and powdered β-nickel-tin did not harden to any extent.

4.3 RESINS

(a) Denture Base Resins.

Dimensional changes across the posterior parts of thick technic dentures were measured at 18, 24 and 30 months. All of these dentures which were made of 12 different types of resins are almost in equilibrium except those made of an epoxy-type resin. On these, the expansion caused by water sorption over 18 to 24 months ran 0.11% for the upper and 0.09% for the lower dentures. During the next six months the values for the epoxy dentures were + 0.03% and + 0.06% respectively. Anterior-posterior measurements on each side were of a similar order and show the epoxy dentures are expanding equally in all directions. Generally the anterior-posterior changes are only a fraction of the molar-to-molar changes on other types of resins.

(b) Silica-Resin Direct Filling Material.

Water sorption and solubility of the previously developed experimental direct filling material as determined in accordance with methods described in American Dental Association Specification No. 12 were well within the limits specified for denture base resins.

A test method is being developed to gain information on the nature of dental solid surfaces. At present it utilizes a system of n-butanol, water and finely divided powders of dentin,

enamel, bone ash, anorganic bone, precipitated tricalcium phosphate and, for comparison and contrast, ferric oxide and silica. These powders are normally hydrophilic (stay in aqueous phase), but when certain ionic surface active agents are added to the system, some of the powders are preferentially wetted by the n-butanol (become organophilic).

(c) Chromatography

The volatile pyrolyzates of polystyrene and poly (methyl methacrylate) were studied at temperatures ranging from 400 to 1100 °C. The degradation products were identified and the quantitative composition of the volatile pyrolyzate was determined with a reproducibility of better than 1%. Details of this work are given in an appended report.

The composition of the pyrolyzates of polytetrafluoroethylene and linear and branched polyethylene has also been investigated. Whereas tetrafluoroethylene monomer was the only identifiable product in the degradation of Teflon, a large number of compounds have been detected in the pyrolyzates of the various polyethylenes. A considerable amount of the less volatile decomposition products are not eluted from the chromatographic column. Hence, measurements to determine the percentage of the pyrolyzate detected under the experimental conditions used are being conducted.

Liquid fractions of poly (methyl methacrylate) and polytetrafluoroethylene, degraded in pyrolysis apparatus at various temperatures, have been analyzed by gas chromatography. Preliminary results indicate good agreement with mass spectrometric analyses of the same fractions.

4.4 Synthesis of Isomers of Eugenol

The synthesis of 2-methoxy-3-allylphenol was completed. A new route for the synthesis of chavibetol was unsuccessful. Efforts were made to separate eugenol-chavibetol mixtures which are obtained on partial demethylation of methyleugenol. The use of column chromatography and ion exchange resins is being explored.

Salicylic acid derivatives containing long side chains are likely to form with metal oxides hard cementious chelates having lower water solubility than those obtained with o-ethoxybenzoic acid. The synthesis of a typical liquid alkoxy methylbenzoic acid, 2-propoxy-5-methylbenzoic acid has been initiated.

These studies will contribute to the better understanding of the ZnO-Eugenol type of dental cements and point out methods of improvement of properties.

4.5 Silicate Cement

An investigation of the relationship between the clinical solubility of silicate cements and solubility as determined by American Dental Association and Federal Specification methods has been started in cooperation with the National Training School for Boys. Matched cavities were prepared and pairs of silicate cement restorations were placed, one of each pair having approximately twice the solubility of the other according to the specification test. Photographic, written and stone cast records are being utilized to follow changes in the restorations during clinical service.

4.6 Evaluation of Materials

Materials evaluated for the Federal dental services and the American Dental Association by specification and other test methods included acrylic teeth, amalgam, artificial stone, base plates, base plate wax, chromium-cobalt alloy, chromium-cobalt alloy investment, denture base resin, denture base relining resin, denture base repair resin, silicate cement, and wrought gold wire.

For the Director
By

W. T. Sweeney, Chief
Dental Research Section

USCOMM-NBS-DC