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REPORT ON DENTAL RESEARCH

AT THE

NATIONAL BUREAU OF STANDARDS

Progress Report

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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

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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, 1964.

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 8636 Pertinent Data on some Physical Properties of Different Investment Used in the Casting of Gold Alloys.

NBS Report 8639 Analysis of Gold and Platinum Group Alloys by X-ray Emission.

NBS Report 8647 A Review of Zinc Oxide Type Filling Materials and Cements.

NBS Report 8654 The Definition of Alginate Impression Materials by a Specification.

3. Papers Published

Gallium-Palladium alloys as dental filling material. R. M. Waterstrat and R. W. Longton. Public Health Reports, 79:638 July 1964.

Phosphorescence of calcified tissues. K. C. Hoerman and S. A. Mancewicz, Arch. Oral Biol. 9:517 Sept.-Oct. 1964.

Characteristics of insoluble protein of tooth and bone -- I. Fluorescence of acidic hydrolytic fragments. S. A. Mancewicz and K. C. Hoerman, Arch. Oral Biol. 9:535 Sept.-Oct. 1964.

Effect of particle shape and size distribution in a reinforced polymer. R. L. Bowen. JADA 69:481 Oct. 1964.

Plastics and the dental market. G. M. Brauer. Plastics World 22:12 Oct. 1964.

Ionization constants and reactivity of isomers of eugenol. G. M. Brauer; H. Argentar and G. Durany. J. Research NBS 68A:619, Nov.-Dec., 1964.

Early strength, flow and dimensional changes obtained on amalgam prepared with a standardized mechanical technic. H. J. Caul; W. S. Crowell; W. D. Kimmel and G. C. Paffenbarger JADA 69:742 Dec. 1964.

4. Work in Progress

4.1 Natural Tooth Structure

(a) Structure of Calcified Tissues.

Solubility of hydroxyapatite: Solubility measurements over about a 30-fold range of concentrations were made on three samples of a single preparation that had been treated as follows:

Sample 1: As precipitated, dried at 200°C.
Sample 2: Heated 5 days at 1,000°C in room atmosphere.
Sample 3: Heated 5 days at 1,000°C in steam atmosphere.

Contrary to experiences of others, all three samples dissolved congruently and samples 2 and 3 yielded solubility products that were constant within experimental error. Sample 3 was the most insoluble ($K_{sp}=3.8 \times 10^{-58}$) and sample 2 was the most soluble ($K_{sp}=4.1 \times 10^{-55}$) of the three. Sample 1 equilibrated slowly and did not give a reliable solubility constant. The solubility constant obtained from sample 3 is the most reliable yet obtained because the treatment in a steam atmosphere is believed to remove lattice defects which decrease the stability of the crystals.

The study will be extended to the hydroxyapatite annealed in a hydrothermal bomb. When this is completed, the results will be ready for publication.

Pyrolysis of octacalcium phosphate: Recent studies have revealed that phosphate enters tooth and bone crystallites in an acid form which is believed to be octacalcium phosphate. Its presence there is indicated by the partial conversion to pyrophosphate on heating. As part of the study of the pyrolysis reactions, the absorption peaks in the infrared spectra of hydroxyapatite, octacalcium phosphate, and the pyrolysis products have been investigated and characteristic normal vibrational modes have been assigned to the peaks. A paper has been prepared for publication.

Mechanism of growth of apatitic crystals: A consideration of the structural and chemical properties of octacalcium phosphate led to a proposed growth mechanism for hydroxyapatite in which octacalcium phosphate is an intermediate. This was described in a paper that is now in press. Additional evidence supporting the mechanism was obtained in the laboratory; the results also indicated that there may be another, as yet undescribed, intermediate salt. This complication necessitates additional study of the growth process.

A new caries mechanism: The generally accepted theories on mechanism of caries formation depend on the action of acids or complexing agents to dissolve the apatite crystals in tooth. A new mechanism has been proposed which is based on the solubility diagram for hydroxyapatite and on the relative rates of diffusion of calcium and phosphate ions in enamel. The new mechanism is consistent with earlier theories, but introduces other new and important considerations. A paper on this subject is in press. Experiments are being designed to measure the relative rates of diffusion of calcium and phosphate ions in enamel.

Surface area of tooth mineral: The work on surface area by nitrogen gas adsorption as a tool in the characterization of tooth mineral has progressed considerably. Samples of human dentin, human enamel, and animal bone as well as synthetic calcium phosphate preparations have been studied. While surface areas of the order of magnitude of 10 square meters per gram or less were found for dentin and Bovine femur whether dried or fat-extracted only; areas in excess of 100 m^2/g were obtained after extraction of virtually all of the organic matter. These collagen-extracted (anorganic) samples were temperature stable insofar as their surface areas were concerned up to 300°C. The area of dentin, in fact, increased to about 150 m^2/g when its temperature of preheating was raised to 200°C after which it leveled off. (This conforms qualitatively to the trend which others have found for bone.)

A sample of raw human enamel (loaned temporarily through the courtesy of Mr. Bruce Fowler of NIDR) of finely ground powder (325 mesh) exhibited an area of 1 1/2 m^2/g. A sample of synthetic octacalcium phosphate had a surface area of 4.3 m^2/g. The same sample after hydrolysis to the extent of 47.75% into hydroxyapatite yielded virtually an unchanged area (4.0 m^2/g). In view of the above findings, it is planned to measure other preparations of synthetic hydroxyapatite after attempts have been made to "open up" the areas by various water-treatments.

Work has begun on pore size distribution determinations in order to give greater insight into the internal submicroscopic structure of tooth-mineral.

Heats of wetting of dentin: Due to loss of personnel only a few measurements were made during this period. Addition of LiCl, LiBr or stearic acid to water does not appreciably change the apparent heat of wetting.

(b) Organic Portion of Tooth Structure

Chemical studies of dental calculus: Since electrophoretic studies have confirmed the presence of a glycoprotein in the organic portion of dental calculus, efforts have been concentrated on the analyses of the carbohydrate fractions of calculus and mucin to determine if differences can be observed in mucins and in calculi from heavy formers and from light formers.

A Micro-Tak GC-2000R gas chromatograph with dual columns and dual hydrogen flame ionization detectors was recently purchased. Separation of the carbohydrate derivatives has been achieved on polar and non-polar liquid phases in columns of varying length and diameter. The method is being extended to a complete analysis of the hydrolysis products of mucopolysaccharides, that is, from deoxy sugar to sialic acids. Identification of the volatile derivatives is made by retention time and quantification is being achieved by determination of the peak areas.

A limited number of mucin samples have been analyzed yeilding only qualitative data. These analyses showed a need for extension of the method to sub-micro technique since it is realized that, at times, only limited amounts of sample will be obtainable.

4.2 Metals

(a) Amalgam: Utilizing a technique developed for preparing cylindrical specimens of dental amalgam at a constant packing pressure, data have been obtained for the tensile strengths of dental amalgams as a function of packing pressures between 95 psi and 2140 psi. A statistically significant number of amalgam samples were prepared from spherical alloy powders in various particle-size ranges. The results indicate that at the lowest packing pressures the spherical amalgams retain a greater percentage of their tensile strength than is the case for several commercial alloys. It has also been demonstrated that at the lowest packing pressures the spherical amalgams exhibit a remarkable ability to adapt to the shape of the cylindrical mold while the commercial alloys exhibited a very poor adaptability at these low pressures. The results provide confirmation of previous clinical data on the behavior of the spherical amalgams. It is indicated that much lower packing pressures may be used during condensation of the spherical amalgams. A long-range clinical study of spherical amalgams is now in progress.

Studies were made of the flow or viscous strain rate of dental amalgam in tension under various stresses at temperatures from 23°C to 52 C. The data indicate that the viscous strain rate can be described by an equation of the form $\dot{\epsilon}_v = K\sigma^m e^{-\frac{E}{RT}}$ where

$\dot{\epsilon}_v$ is the viscous strain rate

K and m are constants

σ is the stress

E is the activation energy for self diffusion

R is the gas constant

T is the absolute temperature

The value for E was found to be 35,000 cal/mole. The wide variation in viscous properties of amalgam under clinical conditions is evident since m was found to be approximately 3.4 (indicating that the viscous strain rate is proportional to the third or fourth power of the stress) while at constant stress the viscous strain rate increased by a factor of approximately 100 when the temperature was raised from 25 to 50°C.

(b) Gallium alloys: A program to investigate the behavior of gallium alloys in vital human teeth is being continued in cooperation with biological laboratories. In a concurrent investigation, the tissue reactions of these alloys are being studied using sub-dermal implants in rats. The results of these investigations must be evaluated over long time intervals using a statistically significant number of samples.

(c) Analysis of alloys: The work on the analysis of dental gold alloys by x-ray emission methods has been completed. A detailed report is appended.

The x-ray emission analysis of dental silver alloys is nearing completion. The main problem here has been the determination of tin. This has been resolved by obtaining a straight analytical line when the ratio of %Ag to % Sn is plotted against the ratios of the intensities of Ag and Sn. Also, the specimen preparation has been solved by making brickettes at 20,000 psi. Some more data must be collected on reproducibility before this project is completed.

4.3 Resins

(a) Silica-reinforced direct filling resins: Information from the fields of dyestuff technology and free radical polymerization were applied to the problem of discoloration in "self-curing" methacrylates. The information suggests that color results primarily from the effects of planar, conjugated double bonds, especially those associated with auxochromic groups. Free radical reactions (such as radical combination and others) can produce such colored systems. Certain configurations of the molecules in a formulation can reduce the intensity of the color that develops by steric restrictions on coplanarity of the conjugated systems that may form.

A compound (N,N-dimethyl-3,5-dimethylaniline) was synthesized which was an effective polymerization accelerator and which produces less discoloration than did N,N-dimethyl-p-toluidene.

Furthermore, the study led to the use of BHT (2,6-di-tert.-butyl-p-cresol) as a replacement for the stabilizer hydroquinone, and to other modifications of conventional formulations, resulting in considerable reductions in polymer discoloration.

(b) Adhesion studies: Tensile forces develop when dental filling materials harden within a cavity if there is bonding to the cavity walls. Data on these forces were obtained and prepared for publication.

It was estimated that the development of a tensile stress of 49 kg/cm^2 (700 psi) at the walls of a cavity might be typical during the hardening of a methacrylate filling resin. The other direct filling materials showed stresses of lower magnitude. The stress depended on the exact test method, the material, and other factors.

The strength of adhesive bonding between a direct filling material and the cavity walls of a tooth must exceed the tensile stresses that develop during the hardening of the filling material, if the bonding is to remain intact.

4.4 Zinc Oxide-Eugenol Materials

Polarographic studies clearly indicate complex formation takes place when Zn^{++} reacts with eugenol or o-ethoxybenzoic acid. Some difficulties were encountered in obtaining values for the complex stability constants perhaps due to the high internal resistance of the cell. To obtain a better understanding of the zinc oxide-eugenol type materials, their physical, histological and clinical properties were reviewed. It is hoped that the detailed report will stimulate interest to conduct research in this field. The report is appended.

4.5 Waxes

The determination of the flow of binary mixtures of wax was continued. The flow of 10 and sometimes 20 percent composition increments was determined at 30°C, 37°C, 40°C and 45°C. In binary compositions of Spermaceti wax with Paraffin wax 124, Ceresine #1573/1, Paraffin wax 138/141, Beeswax, Ultraflex, Flexowax C light, C-905 wax, Be Square 170/175 and Rosin, and of Rosin with Paraffin 124, Ceresin #1573/1, Beeswax, Ultraflex and Flexowax C light the flow of some proportions was greater than the flow of either of the individual constituents.

The flow of 11 ternary mixtures that appeared to have the most promising flows, as far as a functional dental impression material is concerned, were determined at 30°C, at mouth temperature, at 40°C, and 45°C. Even though these 11 ternary mixtures had little difference in flow at 37°C (88.9 to 95.4%) they had different working characteristics. Some of the combinations were more brittle than others. Some had a tendency to flake or layer. Clinical tests are in process.

4.6 New Research and Test Methods

(a) Diametral compression test: Investigation of the diametral compression test as a method for determining the tensile strength of dental materials was continued. Results on dental amalgam, given below, indicate that the padding material placed between the specimen and the testing machine platen is the largest source of variations in results. Loading rate and specimen size appear to have some effect on the results, but the variations do not greatly exceed variations observed when loading rate and specimen size are held constant. The method shows a consistent change in tensile strength as the amalgam ages.

Effect of head speed and padding material on tensile strength:

Head Speed	Padding				
	None	1 layer foil	2 layers foil	4 layers foil	blotter
	psi*	psi*	psi*	psi*	psi*
0.02 in/min	7450	8250	8450	8350	10,950
0.2 in/min	7000	7450	8650	10,750	9650

4 x 8 mm specimens; * average of 6 specimens.

The lower head speed gave cleaner breaks than the higher one, although all were tensile breaks.

Effect of specimen size on tensile strength: Head speed of 0.02"/min; 2 layers of foil. Results are average of 6 specimens.

Diameter \ Length	4 mm	6 mm	8 mm	10 mm	Average
	psi	psi	psi	psi	psi
4 mm	7400	7100	8450	6650	7400
6 mm	8100	7950	7800	7350	7800
8 mm	8200	8300	8150	8100	8190
Average	7900	7780	8130	7370	7800

The 6 and 8 mm diameter specimens appear to give slightly higher values but tend to give a "triple-"cleft" rather than a "true" tensile break.

Effect of age on tensile strength: 4 x 8 mm specimens; 2 layers foil; 0.02 in/min headspeed; average of 6 specimens.

Age*	Tensile Strength psi	σ psi
5 min	145	15
10 min	205	10
15 min	270	10
30 min	485	35
1 hour	1160	70
2 hours	2680	150
4 hours	6050	700
6 hours	6800	450
24 hours	6850	550
7 days	8400	450
14 days	8450	600

* Age determined from end of trituration.

(b) Diffraction grating strain gages: Diffraction gratings ruled on small specimens are being used to determine strain during compression. Gratings have been ruled on aluminum, brass, gold and dental amalgam. Small specimens have been subjected to compression; the results measured photo electrically and recorded on an oscillograph. Preliminary data indicate that the test method is accurate within acceptable tolerances and that the following advantages may be expected:

1. Very short gage lengths (0.01 in) have been used.

2. Responses are measured rapidly and recorded immediately.

3. No devices need be attached to the specimen.

Data for verification of the results are being taken and modifications to simplify the measurement operation are being accomplished.

(c) Applications of the electron microprobe to dental research: The electron microprobe allows point by point chemical analysis at the microscopic level. This technique is very useful in characterizing both biological and non-biological specimens of interest to dental research. Work has been initiated to determine the uniformity of amalgam specimens, especially possible variations in composition near the margins that may be responsible for failures of this type of restoration. Studies of the diffusion of constituents of amalgam into tooth structure have also be started. Teeth specimens containing sound and unsatisfactory restorations have been embedded and metallized subsequent to electron microprobe analysis.

4.7 Transition Behavior of Dental Materials

Many dental materials break down or show undesirable properties due to phase transitions. This phenomenon applies to precious metals, amalgams, direct filling resins, denture base materials, dental gypsums, investment materials and ceramics. The proper performance of some products such as dental waxes or impression materials is dependent on the occurrance of phase changes in the proper temperature region. The objective of this investigation is to determine physical transitions (such as glass transitions, crystalline disorientation and melting) and chemical reactions and melting (such as dehydration, decarboxylation and crosslinking) occuring in dental materials and components of tooth structure using differential thermal analysis techniques.

The data obtained so far from the thermograms of a number of dental materials indicate that this technique is useful for (1) identifying differences in compositions, (2) determination of heat stability of these materials, and (3) aiding in establishing the phases present at a certain temperature. The technique may also be useful as a test for future specifications.

4.8 Evaluation of Materials

Materials evaluated for the American Dental Association by specification test methods included amalgam alloys, gold casting alloys, denture base resins, zinc oxide-eugenol impression paste, a zinc phosphate cement, casting investments for dental gold alloys, and a dental inlay casting wax. The method of X-ray emission analysis as described in NBS Report 8639, Analysis of Gold and Platinum Group Alloys by X-ray Emission,(appended) is being employed to analyze, in duplicate, over one-hundred and thirty commercial dental gold casting alloys.

4.9 Specification and Standards

American specifications for dental materials have set the pattern for the first eight international specifications of the Federation Dentaire Internationale. In turn, these FDI specifications have been or are being adopted as national standards by the dental associations of Canada, Argentina, Denmark, Korea, Japan, Malaya, New Zealand, Norway, Switzerland the the United States of America. The Dental Research Section has played an important part in the internationalization of American dental specifications.

For the Director
By W. T. Sweeney
W. T. Sweeney
Chief
Dental Research Section

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