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Report on Dental Research at the National Bureau of Standards

PROGRESS REPORT

January 1 to June 30, 1967

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

TABLE OF CONTENTS

REPORT ON DENTAL RESEARCH
at the
NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Progress on dental research conducted at the National Bureau of Standards during the period from January 1 through June 30, 1967, is summarized in this report. More detailed information on several phases of the work is given in the appended reports and in papers published during the period. Both the reports and papers are listed below.

In the summaries of work now in progress, sponsors of individual projects are identified. However, the projects are so closely interrelated, both technically and administratively, that reports of activities on all projects are presented for the information of all cooperating agencies.

2. REPORTS ISSUED

NBS Report 9568	Apparent Heats of Wetting and Heats of Reaction of Components of Tooth Structure.
NBS Report 9594	X-Ray Fluorescence Analysis of Silver Dental Alloys with Correction for a Line Interference.
NBS Report 9611	A Laboratory and Clinical Comparison of Silicate Cements and a Direct Filling Resin, With and Without Fused Silica.
NBS Report 9620	Elastic Constants of Dental Amalgam.

3. PAPERS PUBLISHED

Adhesive Bonding of Various Materials to Hard Tooth Tissues. VI. Forces developing in direct-filling materials

during hardening. R. L. Bowen. JADA 74:439 Feb. 1967.

The Relationship Between Laboratory Tests on Solubility of Zinc Oxide-Eugenol Type Cements and Their Behavior in the Mouth. G. M. Brauer. N. Y. J. Dentistry 37:146 Apr. 1967.

Bonding Porcelain Teeth to Acrylic Resin Denture Bases. G. C. Paffenbarger, W. Timothy Sweeney and R. L. Bowen. JADA 74:1018 Apr. 1967.

Effects of Packing Pressure on the Properties of Spherical-Alloy Amalgams. G. T. Eden and R. M. Waterstrat. JADA 74:1024 Apr. 1967.

4. WORK IN PROGRESS

4.1. Crystallography of Calcium Phosphates and Calcium Carbonates

Sponsor: NIDR, ADA

4.1.1. Crystal-Structure Analysis

In general, two classes of compounds are of primary interest in mineralization phenomena - the calcium phosphates and the calcium carbonates. Our objectives are to increase the understanding of how the ions are arranged in ideal structures so as to provide a basis for models for describing chemical reactions such as dissolution, crystallization and the incorporation of carbonate, fluoride and other impurities in bone mineral. Some of the projects described below involve the growth of crystals suitable for single-crystal X-ray studies. The timing of the structure determination in these instances depends on the success of our efforts to grow crystals.

4.1.2. Calcium Carbonates

Work on the determination of the structures of five calcium carbonates is in various stages of progress. Knowledge of how calcium and carbonate ions and water molecules can arrange themselves about one another is still very incomplete. To provide such knowledge we are studying various hydrates of calcium carbonates.

4.1.3. $CaCO_3 \cdot 6H_2O$

Farthest along is the work on $CaCO_3 \cdot 6H_2O$. Intensity films have been collected which contain roughly 5000 unique reflections. The intensities of approximately 1/6 of these have been estimated visually, and estimation of the remaining reflections is continuing. Once these are on hand, atomic positions in the unit cell will be calculated. Because of the instability of the compound, the data were collected at low temperature using the oscillation technique. Most of the programs for processing data from this type of film have now been written by us and are being tested.

4.1.4. $CaCO_3 \cdot H_2O$

This salt is the only other known hydrated calcium carbonate. It is believed that the two hydrated salts may have much more importance in mineralization than is presently recognized. Their importance may have been overlooked because of their metastable character. Experiments in which we are attempting to grow single crystals of $CaCO_3 \cdot H_2O$ have been in progress for about three months. If these prove successful, we propose to verify the correctness of the unit-cell data in the literature and to proceed with a complete structure determination.

4.1.5. $Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$ and $Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$

These two salts provide further examples in which calcium and carbonate ions are coordinated by water molecules. Crystals of both have been prepared, collection of three-dimensional intensity data on the pentahydrate has been started. Data on the dihydrate will be collected when feasible.

4.1.6. Vaterite, $CaCO_3$

This is the only well known anhydrous calcium carbonate for which the complete structure is not known. This is due to the fact that good single crystals have been impossible to grow. We are continuing attempts to grow single crystals,in various ways,which would be suitable for a structure determination.

4.1.7. Calcium Phosphates

The calcium phosphates as a group comprise the most important inorganic compounds of physiological interest.

4.1.8. Orthophosphates

Three of these have not had their structures determined, and of these three we plan to study tetracalcium phosphate, and β-tricalcium phosphate, and we will determine the structure of a tricalcium phosphate analog, $Ca_4Mg_5(PO_4)_6$ if time permits.

4.1.9. Hydroxyapatite Analogs

Two other compounds, believed to be related to hydroxyapatite, $Ca_5(PO_4)_2SiO_4$ and $NaLa_9(SiO_4)_6O_2$, are of interest because of the information they may reveal about the structure of tooth and bone mineral. In $Ca_5(PO_4)_2SiO_4$, one PO_4^{---} and one OH^- group have been replaced by an SiO_4^{----} group, leading to pronounced changes in the structure. Since similar substitution may occur in tooth and bone mineral, the convenient way to study such substitutions is through the structure of $Ca_5(PO_4)_2SiO_4$. The sodium-lanthenum silicate is isostructural with hydroxyapatites, but it has a considerably different charge distribution. A determination of its structure will reveal how these changes in charge affect the details of the atomic coordination.

4.1.10. Condensed Phosphates

We have shown that $CaMgP_2O_7$ is probably isostructural with $Mg_2P_2O_7$. There is still uncertainty as to the configuration of the pyrophosphate ion in $Mg_2P_2O_7$. We plan to study the extent of solid solution between these two compounds, and to make a precise determination of the structure of one of these salts to resolve the question about the pyrophosphate configuration. The configuration and intraionic bonding of the pyrophosphate ion is a matter of considerable interest because of the occurrence of the pyrophosphate moiety in metabolically active compounds.

4.1.11. Petrographic Microscopy

With the addition to our staff of a research associate with experience in petrographic microscopy, we are increasing our activities which can take advantage of this technique. The initial emphasis will be on the study of dental calculus. The direction of this research will depend on evaluation of the initial results, but it probably will relate to the transformations that occur between solid phases $CaHPO_4 \cdot 2H_2O$, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, β-$Ca_3(PO_4)_2$ and $Ca_5(OH)(PO_4)_6$. The technique will also be used to study other dental materials and as an adjunct to our crystal-structure determinations.

4.2. Solubilities of Calcium Phosphates

Sponsor: NIDR, ADA

The solubilities of five calcium phosphates, $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, β-$Ca_3(PO_4)_2$, and $Ca_5(OH)(PO_4)_3$, are of direct interest to the understanding of calcification and decalcification processes in biological systems. In addition to these five, $Ca_5F(PO_4)_3$ and what appear to be solid solutions between $Ca_5F(PO_4)_3$

and $Ca_5(OH)(PO_4)_3$ have a direct bearing on the properties of enamel, particularly as they relate to caries. In the past, we have intensively studied the solubilities of $CaHPO_4 \cdot 2H_2O$ and $CaHPO_4$ at four temperatures and that of $Ca_5(OH)(PO_4)_3$ at 25°C in the three-component system, $Ca(OH)_2$-H_3PO_4-H_2O.

In our continuation of these studies, we plan to extend the work on $Ca_5(OH)(PO_4)_3$ to 37°C and subsequently to other temperatures. We are initiating work on $Ca_5F(PO_4)_3$ which will be extended to include solubility studies of the solid solutions between $Ca_5F(PO_4)_3$ and $Ca_5(OH)(PO_4)_3$. A major emphasis of the latter study will be an attempt to test several thermodynamic and mathematical models describing the solubility behavior of the solid solutions. It is believed that an understanding of the physical chemical behavior of these solid solutions will provide a better understanding of how fluoride is effective in preventing caries.

Work on the solubilities of β-$Ca_3(PO_4)_2$ and $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, both of which are constituents of dental calculus, will be initiated as soon as time permits.

In the last two years there has been considerable interest in the use of calcium electrodes to measure calcium-ion activities in solutions. All of the calcium-ion electrodes available commercially are empirical in their operation and our experience with them is somewhat disappointing from the standpoint of their accuracy. We are, therefore, working on a calcium-amalgam electrode with the hope of eliminating the shortcomings that they have had in the past and establishing conditions under which their operation would be reversible.

Our theoretical examination of the diffusion of calcium and phosphate ions in aqueous systems has shown

that the phenomenon is much more complex than is normally assumed, and our experimental tests have borne this out. Experimental work is continuing employing two types of diffusion cells. In one, the membrane is so thin that surface transport is essentially eliminated. This will give us information on the transport of free calcium and phosphate ions. In the other, with which we already have experience, a thicker membrane is employed so that surface transport is important. The latter is more in line with what occurs in dental enamel. An investigation of both types of cells is necessary to get a more complete understanding of the diffusion phenomena and to provide a true test of the theory.

4.3. Adsorption Studies

Sponsor: NIDR

4.3.1. Surface Area and Pore Size

The low-temperature gas-adsorption technique provides a unique way to characterize the surfaces of finely divided solids. Most research using this technique concerns itself with measurement of surface area; we are concerned, however, more with use of this method to characterize the pore-size distribution. The chief shortcoming of the method was the time-consuming nature of the treatment of experimental data, but this has now been overcome with a new program for translating adsorption data into pore-size distributions. This method will now be used to characterize the pores and defects in hydroxyapatite crystals. The crystalline defects in hydroxyapatite undoubtedly have important bearing on its chemical properties and may give clues as to the mechanism of crystal growth. One feature of the study will be thermal treatment of the crystals to determine if pores are produced by driving out volatile constituents. Once we have experience with relatively pure synthetic

samples, the study will be extended to tooth mineral.

4.3.2. Adsorption from Solution

Interreactions of ions with the tooth mineral surfaces are complex. For example, fluoride appears to react in at least two ways, one of which has the characteristic of being reversible in the sense that the fluoride can be removed by washing and the other appears to be irreversible. For this reason we are developing kinetic equations to describe the adsorption of ions on apatite surfaces which simultaneously include expressions for two independent processes. These processes may be both reversible, both irreversible, or one of each. These equations have been programmed for the computer and are being tested using isotopic-exchange data collected by using Ca^{45} and P^{32} in saturated solutions. They will be extended to other systems after we have more experience with their validity.

4.4. Reactivity of Components of Tooth Structure

Sponsor: NIDR, U. S. Army

The reactivity of tooth surface and components of tooth structure has not been investigated in detail. Results of such a study should demonstrate ways to obtain a modified tooth surface that may improve chemical bonding with an adhesive resin.

The apparent heats of wetting of dentin, enamel, anorganic whole tooth and fluoroapatite have been determined. The heat of reaction, ΔH_R, is obtained by subtracting the observed heat of wetting in water from the measured heat of wetting in the respective solution. Dry dentin was found to react with organic acids. This interaction is primarily with the organic constituents of dentin since the ΔH_R values for anorganic whole tooth tissue enamel and fluoroapatite are much smaller. Enamel

and, to a much larger extent, dentin react with aqueous stannous fluoride, but apparently no reaction takes place with anorganic whole tooth tissue. Thus, stannous fluoride reacts entirely with the organic constituents of powdered tooth tissue.

A literature survey of compounds that react with collagen has been completed. The reactivity of representative compounds of this group with components of tooth structure is now under active investigation. The reactivity towards (1) acids, (2) various ions, (3) reducing agents, (4) oxidizing agents, (5) tanning agents, and (6) specific amino acid reagents, will be studied. The results obtained so far indicate that compounds such as formaldehyde and glutaraldehyde that react with free collagen show little or no reactivity with dentin. Future work will attempt to pinpoint the reaction site, to ascertain which amino acid is responsible for the reactivity with a particular compound. Blocking off reactive -OH, COOH or NH_2 groups may assist in solving this task. Another approach, that is, synthesis of phosphorous-containing chelating agents that are likely to react with calcium, will also be attempted. If these compounds modify tooth surface,polymerizable derivatives containing vinyl or acryl groups could be synthesized.

The resulting monomer should not only bond to tooth structure, but will also be compatible with dental resins.

4.5. Characterization of Components of Tooth Structure and Dental Materials by Differential Thermal Analysis

Sponsor: NIDR

Differential thermal analysis (DTA) measures the heat-energy changes associated with physical and chemical transformations as a function of temperature or time. The number, shape and position of peaks of the differential

temperature curve or thermogram can be used for the qualitative identification of a substance as well as for the determination of the physical properties of the material such as its transition temperatures and its chemical reactions. In the present study, the thermograms of many dental restorative materials and components of tooth structure were investigated with special emphasis on (1) evaluating this technique for characterizing similar, but not identical, materials (2) purity of raw materials and quality control of products, (3) determination of transition and melting point ranges of many dental materials such as waxes or casting golds, and (4) determination of the degradation parameters that are of greatest importance for the proper functioning, behavior and stability.

Work to study the melting behavior of dental gold alloys was initiated. The melting points of several substances were determined to calibrate the equipment in the 600 to 1200°C range. Samples of human and beagle calculus subjected to DTA and thermogravimetric analysis (TGA), showed greatly differing thermograms.

Because of breakdown of the 1200°C furnaces, these studies were temporarily interrupted. Efforts are being made to rebuild the furnaces. When these repairs are completed, the melting point ranges of dental golds, which otherwise are located by time-consuming freezing point curves, will be determined. Studies of anorganic whole teeth, dentin, enamel and certain phosphates using DTA and TGA techniques will be undertaken. If a furnace can be procured, the DTA work will be expanded to 1600°C. This will allow rapid determination of the melting point ranges of base metal alloys used in dentistry.

4.6. Thermal Expansion of Enamel and Dentin

Sponsor: NIDR, USAF

An investigation of the thermal expansion characteristics of tooth enamel and dentin is in progress. Since one of the problems of major interest in the area of restorative materials is the development of a material that will adhere to tooth structure, information on the relative dimensional changes of natural tooth and restorative material when heated or cooled is needed. The generally quoted values for thermal expansion of tooth structures were obtained about 50 years ago at NBS on a limited number of specimens. Although there is no reason to doubt these data, a verification using a wider range of specimens is desirable. Problems involved include the small size of available specimens of enamel and dentin, and the necessity for keeping the specimens in water during the period of measurement. Factors to be investigated include the effect of orientation of enamel rods and dentinal tubules on expansion, the effect of combinations of enamel and dentin on the composite expansion and the relationship, particularly in dentin, between thermal expansion and the characteristics of the organic portion of the material.

4.7. Mechanical Behavior of Skin

Sponsor: NIDR

Using the model system of rat skin to gain insight into the mechanical behavior of the mucous membrane of the oral cavity, a study is being carried out on the thermodynamic and viscoelastic properties of rat skin under various mechanical conditions and at various temperatures. A number of mechanical phenomena have been found to exist in skin simultaneously, some of which are thermodynamic in character and others viscoelastic in character. It has been found to be necessary to conduct

a number of different types of mechanical and thermal tests on skin in order to separate these different phenomena.

An attempt has been made to evaluate the relative contribution of each phenomenon over the temperature range from 25°C to about 70°C. It has been found that viscoelastic behavior is the dominant behavior at room temperature and at physiological temperatures, as opposed to thermodynamic governed behavior. However, at temperatures above 56°C, at approximately 57°C to 59°C, the thermodynamic controlled collagen → gelatin transition becomes the dominant behavior up to 65°C to 70°C and above, depending on the age of the animal and the location from which the skin was obtained, dorsal or vestral. The transition was measured in terms of the force of contraction as a function of temperature. For example, it has been found that the stomach skin from a 530 gm animal gives a force of contraction 5 to 10 times as great as that from a 200 gm animal at a temperature of 61°C.

The first thing that must be completed in this study is the development of sufficient methodology and the demonstration that these methods and tests will in combination separate the various phenomena contributing simultaneously to the gross mechanical behavior of skin. Once each phenomena contributing to the mechanical behavior of skin has been well characterized over the temperature range from 0°C to about 90°C, these phenomena can be related to the behavior of the molecular components of skin, for example, collagen. These separate phenomena will then be assessed in terms of various metabolic, physiological, pharmacological and pathological factors that affect the mechanical behavior of skin.

4.8. Elastic and Rheological Properties of Materials

Sponsor: NIDR

In addition to the determination of mechanical properties of skin as described above, the development of new and improved methods for measuring the mechanical characteristics of both biological and other materials will be continued. At the present time, rheological studies of materials are concentrated on resolving apparent differences between experimental behavior of dental amalgam and accepted rheological theory. It appears that revisions in some of the approximations involved in the theory may reconcile theory and experimental results.

The ultrasonic method previously employed for determination of the elastic constants of amalgam will be extended to other materials and made more precise. Application of ultrasonic interference methods will be investigated as a means of accurate determination of change in properties of a material as a result of changes in temperature, for example, or changes with age of specimen. The possibility of using ultrasonic methods for investigation of natural teeth will continue to be studied, although there are many difficulties to overcome in obtaining the required combination of small transducers and suitable frequency and in interpretation of results obtained on an irregularly shaped non-homogenous specimen.

4.9. Stress Analysis

Sponsor: NIDR

A study of stress distributions in oral structures is in progress. Knowledge of the distribution of mechanical stresses is important for both natural structures and their artificial replacements. A thorough understanding of the stresses involved should make possible better

utilization of materials both for increasing the life of the replacements and preserving the remaining natural structures. The relationship of mechanical forces to tooth movement, either intentional or otherwise, is perhaps the most obvious example of an opportunity for direct application of stress analysis to dental problems.

Both theoretical and experimental methods have been initiated. Two phases are included in the theoretical studies; first, application of new methods to the solution of problems in stress analysis and, second, the application of existing methods to the solution of dental problems. The first phase is concerned with the development of general procedures for the solution of problems involving complicated boundaries by means of Airy's stress function. Efforts are being made to apply this to a relatively simple idealized problem. If useful results can be obtained here, attempts will be made to extend the idea to more complicated geometries and to three-dimensional stress functions.

In order to apply present numerical methods in stress analysis to some dental problems, a computer program was obtained from the Rohm and Haas Company which can be used to solve problems involving plane stress, plane strain, and axial symmetry. A cuspid was selected to be analyzed under a point load, since this tooth is the closest to axisymmetric of all human teeth. The cuspid was idealized so that it would be axisymmetric. This shape will be analyzed in three steps:

1. Assume axial symmetry does exist and determine the stress distribution for the assigned boundary conditions, assuming the tooth is made of two materials (enamel and dentin) both being homogenous and isotropic.

2. Assume the problem is one of plane stress and determine the stress distribution for the same boundary

conditions as above, and making the same assumption concerning the material.

3. Conduct the same analysis as in part 2, with non-homogenous materials. Since the programs allow us to vary the material properties from point to point, we can try to reproduce the best known distribution of material properties.

The results of the three parts will then be compared in order to gain an insight into the accuracy of the second step in representing the true nature of the stress distribution. This is important since all experimental work which has been done has assumed plane stress, isotropy, and homogeneity.

The computer programs for the analysis, which were written for the IBM 7094, are being adapted for use on the UNIVAC 1108. This has revealed the need for some debugging of the compiler of the new UNIVAC computer. When this has been done, it will then be possible to apply the programs to the three-step program outlined. In addition, these programs may at times be used to verify certain results obtained experimentally. Also, they could be used to determine stresses for any plane shape once the boundary conditions are determined.

The experimental phase of the research involves the application of photoelasticity to the solutions of problems in dentistry. At present, procedures are being developed for casting plane stress analysis models which are composed of several different materials (representing enamel, dentin, and periodontal membrane). Although it is difficult to find materials which have approximately the same ratiosof moduli of elasticity as the materials we are trying to represent, two materials have been obtained which have appreciably different moduli of elasticity and which exhibit little shrinkage when cured

at room temperature. This cure takes about 10 days, and since we are dealing with composite models, each one takes over a month to prepare. To date, no model has been obtained which is worth the time it would require to analyze the stresses in it when it is loaded. However, it should not be much longer before a suitable model is obtained.

The shape of the model is the same symmetric cuspid shape which will be solved on the computer. The results from the experimental analysis will be used to determine the boundary conditions which will be fed into the computer.

The next steps as planned are:

(a) Another symmetric, but two-rooted, tooth will be analyzed using plane stress approach.

(b) A non-symmetric tooth will be attempted using the same approach.

(c) The production of three-dimensional models will be investigated.

As a practical application of the two-dimensional manufacture and analysis of models, a photoelastic model of a section of a full denture is being produced so that an analysis of the stress distribution in the denture may be made and an optimum design of the cross section found. An improved design could result in a better distribution of loads, so that dentures could become more comfortable and have less chance of fracturing.

4.10. Dental Amalgam

Sponsor: ADA, USAF, USA, VA

4.10.1. Setting Rate

The setting rate of amalgam was studied using tensile strengths, as determined by the diametral compressive test method, as a criteria. Strength of amalgams was determined at various time intervals from 5 min. to 24 hrs.

on 4 alloys. In addition, 28 alloys were studied at 15 min., 3 hrs., and 24 hrs. These times were chosen as representative of when a dentist would finish placing a restoration, the length of time a patient might be expected to refrain from biting on a restoration, and the time final finishing and polishing would be done. The strength at 15 min. ranged from 225 to 950 psi; at 3 hrs. from 1600 to 5600 psi; and at 24 hrs. from 5600 to 8400 psi. Six alloys with a wide spread of setting times were used in a blindfold carving test by 6 dentists at Walter Reed Army Medical Center. These alloys were designated as slow, medium or fast depending on their strength at 15 min. The fast alloys had a strength of approximately 800 psi and the slow only 200 psi. The dentists were asked to designate the alloys as fast, medium or slow. Each dentist carved a set of 6 specimens. Each set of specimens contained a duplicate. There was no correlation between the judgment of the dentists and laboratory results. To further investigate the clinical judgment of alloys, 125 questionnaires were sent to practicing dentists throughout the country, requesting information on the brand of alloy they used and whether they considered it a fast, medium or slow setting alloy. Again, the results of this survey did not correlate with laboratory findings. The problem seems to be complicated by the fact that a dentist's judgment of the setting rate of an alloy is probably related to the speed at which he works and the technique he uses.

Work has been initiated on the effect of some manipulative variables on the residual mercury content and tensile strength of amalgam. Variables to be studied are initial Hg to alloy ratio, trituration time and packing pressure. To date, two alloys have been studied using

1:1, 1 1/2:1, and 2:1 Hg alloy ratios; 15, 30, 40, 60, and 90 sec. trituration times, and a 2000 psi packing pressure. Tensile strengths at 24 hours have been determined for these variables. Results are given in the following table.

1:1 Ratio - 2000 psi packing pressure

	Alloy A		Alloy B	
Trit. time Sec.	Ten. St. psi	Hg. Cont. %	Ten. St. psi	Hg. Cont. %
15	2950	--	3575	48.0
30	2850	49.2	3975	47.0
40	2675	49.1	4700	45.6
60	3350	48.0	6325	44.2
90	4550	46.8	6750	43.4
1 1/2:1 Ratio				
15	6325	51.1	5900	49.1
30	6225	50.5	6925	47.6
40	7825	50.0	7400	47.1
60	8075	49.4	7150	47.1
90	7625	50.0	7275	47.2
2:1 Ratio				
15	7625	52.6	6875	50.2
30	7725	51.8	6350	49.1
40	7900	51.8	6875	48.5
60	8000	52.0	6625	48.2
90	7525	52.4	6625	48.1

There appears to be a tendency for maximum tensile strengths to occur with higher Hg to alloy ratios and long trituration times. Further work on the manipulative effect will include 15 min. strength and the investigation of other alloys.

4.10.2. Revision of Amalgam Specification

As part of the specification development program,

work is nearly complete on testing 50 amalgam alloys against the proposed A.D.A. revision of the amalgam specification. Data are complete on particle thickness, 24-hour setting change (as received and aged) and foreign material. The tests on diametral tensile strength at 15 mins. are nearly complete, while the 24-hour tests are finished. The % Hg. has been determined as a sidelight on this procedure.

4.11. Dental Metallurgy

Sponsor: ADA, USAF, USA, VA

4.11.1. Amalgam Alloys

Measurements have been completed on the relative quantities of voids and of constituent phases in dental amalgam. The data obtained is being evaluated statistically in order to determine whether these measurements can be correlated with the observed mechanical properties.

The mechanical behavior of dental amalgams prepared from spherical-particle alloys in various particle size ranges has already been investigated by rheological methods. In some cases, similar data are available for the individual phases present in dental amalgam, such as the gamma phase (Ag_2Hg_3), and as these data are accumulated, it appears that the basic mechanisms involved in the deformation and fracture of dental amalgam will be revealed.

4.11.2. Gallium Alloys

A final report is being compiled on all of our research on gallium alloys as potential dental restorative material. A limited amount of experimental work is being done on these alloys to determine

(a) whether "delayed expansion" occurs in these alloys,

(b) whether more effective marginal sealing is obtained, and

(c) thermal expansion coefficients and elastic constants.

The final report on this project is expected to be completed by March 1968, but the question of whether these alloys are suitable for actual clinical use will not be answered until extensive biological and clinical tests can be made. This type of work cannot be done in our laboratory since the required facilities and personnel are not available. It is hoped that our report will stimulate interest in gallium alloys by other organizations and individuals so that the use of this interesting material can be adequately investigated.

4.11.3. Noble Metals

The program on alloy systems involving the noble metals is proceeding. A series of platinum-chromium alloys have been prepared and are now being analyzed. The basic data obtained thus far, although very preliminary in nature, have suggested several interesting possibilities for developing new and improved alloys for partial dentures. Although these possibilities are being explored, it is essential that the work on phase diagrams be completed so that more systematic methods can be applied in designing future alloys.

4.12. Development of an Adhesive Dental Restorative Material

Sponsor: ADA, USAF, USA, VA

Special barium-fluoride glasses were prepared for use as part of the reinforcing filler in the composite dental restorative material. These glasses have high x-ray opacity and relatively low refractive indexes for visible light. The refractive indexes approach those of the polymeric matrix materials and thus minimize light scattering. Use of these fillers will give suitable x-ray opacity to the filling material which should provide

easier detection of recurrent caries by the use of roentgenograms.

Requests for bids were submitted to approximately 18 companies for synthesis of the monomers in the ternary eutectic system (HEMA-Isophthalate, HEMA-Terephthalate and HEMA-Phthalate). We have received some favorable replies, with prices in a feasible price range, making these materials commercially available.

Synthesis of the adduct of p-dimethylaminoacetophenone and 3-mercaptopropionic or thioglycolic acid was attempted to yield a compound which would be an accelerator with better color stability than the previously discussed adduct of p-dimethylaminobenzaldehyde and 3-mercaptopropionic acid (DABMA). However, the synthesis failed.

A quantitative evaluation of the effectiveness of DABMA as an amine accelerator was made. The compound proved to be comparable to N,N-dimethylaniline as a polymerization accelerator of hydroxyethyl methacrylate monomer using benzoyl peroxide.

N,N-dimethyl-p-dodecylaniline was synthesized. This compound is predicted to be comparable to dimethyl-p-toluidine in its rate of accelerating the decomposition of peroxide initiators. Because of its higher molecular weight (about 289 vs. 135) the toxicity would be expected to be lower than that of dimethyl-p-toluidine, and its solubility in the aqueous fluids of the dentinal tubules should be appreciably reduced.

Approximately 25 patients have been examined for the purpose of expanding the clinical projects. These patients have volunteered to participate; we will place our new composite materials,once they are deemed safe for human use according to toxicity tests performed at Hazelton Laboratories,and once we receive approval from the Committee of Institutional Associates at the American Dental

Association. A formulation utilizing the ternary eutectic monomer system was forwarded to the laboratories for acute oral toxicity and eye irritation tests.

We have started taking x-rays of some of the above patients, when indicated, and at the same time have examined patients for posterior caries to be utilized in projects involving other materials.

4.13. Zinc Oxide-Eugenol Cements

Sponsor: USAF, USA, VA

Investigations of improved zinc oxide o-ethoxybenzoic acid (EBA)-eugenol cements containing aluminum oxide as a reinforcing agent, were continued. These cements have compressive strengths up to 14,000 psi, and have lower film thickness and better mixing properties than the commercial cements originally developed in this laboratory.

At present, the following parameters are being investigated: (1) optimum percentage of reinforcing agent, (2) most suitable rosin derivative and its proper concentration, (3) replacement of rosin by abietic acid, and (4) improved mixing procedures using a capsule attached to a mechanical mixing device. Possible studies using spherical or micro particle size aluminum oxide are contemplated.

Another objective of this project is the development of a longer lasting temporary zinc oxide-eugenol type filling material that will yield sedation and protection of the tooth from irritants and decay. Since the EBA type cements have been shown to have even better tissue tolerance than ZOE cement, they should be eminently qualified for this purpose provided that solubility and disintegration by mouth fluids is kept to a minimum. A filling material containing zinc oxide, aluminum oxide, hydrogenated rosin and stearic acid in the powder and EBA

and eugenol as liquid appears to have promise for such application. Limited clinical evaluation of this material has been initiated. One, two, and three surface cavities (about thirty) have been restored with this material to compare its serviceability with zinc phoshate and ZOE type fillings placed in equivalent locations. The newly developed product is more manageable than ZOE and zinc phosphate and in its plastic state adheres better to the dentinal walls.

4.14. Ionization Constants in Ethanol-Water Mixtures

Sponsor: ADA, USA, USAF, VA

This study has,as its aim,to determine the reactivity constants of allyl and propenyl groups present in eugenol and its isomers. A knowledge of these constants may allow prediction of the setting reaction and the stability of the resulting metal chelates. To round off previous work, the ionization constants of benzoic and p-propenylbenzoic acid in 70% by volume ethanol were measured.

An attempt was made to derive an equation relating the negative logarithm of the ionization constants (pK) and solvent medium. From theoretical considerations and by making certain assumptions, the following equation was deduced

$$\mathrm{pK} = \frac{c}{D} - \log \frac{[\mathrm{H_2O}]D_{HA}B_H([\mathrm{H_2O}]+[\mathrm{EtOH}])+[\mathrm{EtOH}]B_R(D_A-[\mathrm{H_2O}]+[\mathrm{EtOH}])}{[\mathrm{EtOH}] + [\mathrm{H_2O}]D_{HA}}$$

where D = dielectric constant of the medium; and C, D_{HA}, B_H, B_R and D_A are parameters that have physical significance.

A computer program was developed that made it possible to check the validity of the equation. Using experimental data for benzoic acid, substituted benzoic acids as well as aliphatic acids, the equation allowed estimation of the pK within ± 0.03 of the actual value. Unfortunately, most of the experimental data for the pK

of the respective compounds in ethanol-water mixtures were made nearly thirty years ago when the measurement techniques for determining pK were not as sophisticated and accurate as those presently employed. Future efforts will be directed to determine whether the experimental pK values in the mixed solvent are dependent on the method used (for instance, spectroscopic or potentiometric technique), and to study water-methanol mixtures for which more accurate pK values are available.