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REPORT ON DENTAL RESEARCH
AT THE
NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 – June 30, 1971

The dental research program at the National Bureau of Standards is carried on in cooperation with the American Dental Association- the National Institute of Dental Research; the Dental Research Division of the U. S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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NBS Report 10533	Dental Cements, Direct Filling Resins, Composite and Adhesive Restorative Materials: A Resume.
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REPORT ON DENTAL RESEARCH
at the
NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Dental research at the National Bureau of Standards during the half year ending June 30, 1971 included investigations of a wide range of materials used in restorative dentistry and of hard and soft natural tissues. The research program is supported by the Council on Dental Research of the American Dental Association, the Collaborative Research Office of the National Institute of Dental Research, the Dental Research Division of the U. S. Army Medical Research and Development Command, the Dental Sciences Division of the U. S. Air Force School of Aerospace Medicine, and the Veterans Administration. Support from the National Institute of Dental Research is also provided in the form of grants to Research Associates sponsored by the American Dental Association. This support is designated NIDR (Grant) where reference to it is made. In the summaries of work in progress, sponsors of various projects are identified. However, since most of the projects are closely related both technically and administratively, reports on all projects are presented for the information of all sponsors. Detailed reports issued during the period on some phases of the research are listed and are appended to this report.

2. REPORTS ISSUED

NBS Report 10421	Research Technics Used in Evaluating Dental Materials.
NBS Report 10422	Determination of the Degree of Polymerization of a Polymeric Aromatic Amine from NMR Data Using a "Least-Squares" Approach.
NBS Report 10441	The Crystal Structure of $CaKAsO_4 \cdot 8H_2O$.
NBS Report 10442	A Stabilizing Comonomer: I. Synthesis and Confirmation of Structure.
NBS Report 10521	Influence of Alloy Particle Size and Shape.
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NBS Report 10598	Adhesive Restorative Materials.
NBS Report 10599	Solubilities of Phosphates and Other Sparingly Soluble Compounds.

3. PAPERS PUBLISHED

Woelfel, J. B. and Paffenbarger, G. C. Expanding and Shrinking 7-Year Old Dentures: Report of Cases. JADA 81:1342-1348, No. 6, December 1970.

Bardos, D. I.; Waterstrat, R. M.; Rowland, F. J.; and Darby, J. B., Jr. The Magnetic Susceptibility of Transition-Metal A15-Type Phases. J. Low Temp. Phys. 3:509-518, November 1970.

Dickens, B. and Bowen, J. S. Refinement of the Crystal Structure of the Aragonite Phase of $CaCO_3$. J. Res. NBS 75A:27-32, Jan.-Feb. 1971.

Chandler, H. H.; Rupp, N. W.; and Paffenbarger, G. C. Poor Mercury Hygiene from Ultrasonic Amalgam Condensation. JADA 82:553-557, March 1971.

Wallace, Betty M. and Brown, W. E. Stoichiometric Composition of Whitlockite. J. Dent. Res. 50:343-346, March-April 1971.

Dickens, B.; Hyman, A.; and Brown, W. E. Crystal Structure of $Ca_2Na_2(CO_3)_3$ (Shortite). J. Res. NBS 75A:129-135, March-April 1971.

Chandler, H. H.; Bowen, R. L.; and Paffenbarger, G. C. The Need for Radiopaque Denture Base Materials: A Review of the Literature. J. Biomed. Mat. Res. 5:245-252, May 1971.

Chandler, H. H.; Bowen, R. L.; and Paffenbarger, G. C. Development of a Radiopaque Denture Base Material. J. Biomed. Mat. Res. 5:253-265, May 1971.

Feagin, F.; Patel, P.; Koulourides, T.; and Pigman, W. Study of the Effect of Calcium, Phosphate, Fluoride and Hydrogen Concentrations on the Remineralization of Partially Demineralized Enamel Surfaces. Arch. Oral. Biol. 16:535- , May 1971.

Huget, E. F. and Brauer, G. M. Heats of Immersion of the Components of Tooth Structure (Research Annotation). J. Dent. Res. 50:776, May-June 1971.

Means, C. R.; Rupp, N. W.; and Paffenbarger, G. C. Clinical Evaluation of Two Types of Resilient Liners on Dentures. JADA 82:1376-1380, June 1971.

Dickens, B. and Brown, W. E. The Crystal Structure of $Ca_5(PO_4)_2SiO_4$ (S-Phase or Silicocarnotite). Tschermaks Mineralogische und Petrographische Mitteilungen (TMPM) 16:1-27, June 1971.

Dickens, B. and Brown, W. E. The Crystal Structure of $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$. TMPM 16:79-104, June 1971.

Rupp, N. W. and Paffenbarger, G. C. Significance to Health of Mercury Used in Dental Practice: A Review. JADA 82:1401-1407, June 1971.

Loebenstein, W. F. The Exchange of ^{45}Ca and ^{32}P with Hydroxyapatite as Interpreted by Adsorption from Solution. J. Colloid Interface Sci. 36:234-246, June 1971.

4. WORK IN PROGRESS

4.1. Determination of Crystal Structures

Sponsor: NIDR, NIDR (Grant), ADA

The objective of our research program is to secure structural data on biologically important inorganic substances so as to evolve a better understanding of processes such as mineralization and demineralization and to assist in a systematic approach to the development of adhesion between restorative materials and tooth structure.

Crystals are grown of pure compounds or of compounds with predetermined amounts of selected impurities. Their crystal structures are determined by X-ray and/or neutron diffraction. The structural parameters give the overall arrangement in the solid phase. The sites of the impurities are usually obvious from these parameters. The reason for the choice of a particular atomic site by an impurity is often apparent. From the structural parameters, much crystal chemistry can be inferred.

Papers have been written on the crystal structures of $CaHPO_4$ (monetite) and $CaKAsO_4 \cdot 8H_2O$. Papers on $Ca(H_2PO_4)_2 \cdot H_2O$, $CaCO_3$ (aragonite), $Ca_2Na_2(CO_3)_3$ (shortite), $BaCa(CO_3)_2$ (barytocalcite), $Ca_5(PO_4)_2SiO_4$ (silicocarnotite) and $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ have been published in journals during the report period, or are in press.

β-$Ca_3(PO_4)_2$

β-$Ca_3(PO_4)_2$ is found in salivary ducts and glands in areas where the drinking water contains magnesium ions, and is also found in carious materials. It is stabilized by small cations, and in the presence of such cations is produced *in vitro* under conditions where the pure compound decomposes into OHAp and monetite. The material found *in vivo* invariably contains magnesium.

To investigate the stabilizing role of the magnesium impurity, we have prepared at about 1350°C samples of β-$Ca_3(PO_4)_2$ which contain various amounts of magnesium as an impurity. The crystal structures of two of these samples have been determined and the locations of the impurity have been found. Presently, we are trying to obtain a good electron-microprobe analysis to use as an overall constraint on the amount of impurity in the specific crystals which were used in the structural analysis. We will then attempt to obtain, by least squares treatment of the diffraction data, the distribution of these amounts of impurities over the possible places in each structure. At this stage, we know the approximate distributions of impurity in samples of β-$Ca_3(PO_4)_2$ containing approximately 10% and 4%, respectively, of the cations as magnesium. In the 10% Mg sample, the Mg impurity is concentrated into one crystallographic site (the total amount of the impurity present was constrained in the least squares analysis to that introduced in the preparation). One cation site in the crystal structures appeared to be only partially occupied; actually, only one-half of these sites in the crystal structure were occupied. In the 10% Mg sample of β-$Ca_3(PO_4)_2$, no magnesium was found in this site which, therefore, had a total occupancy of 0.5 Ca. A second sample of β-$Ca_3(PO_4)_2$ came from a preparation in which 4% of the cations were magnesium. In the second sample, the occupancy by calcium was about twice as high as by magnesium in both these sites.

The occupancy parameters are only approximate at this time and will be revised after we have determined the composition of the crystals by electron microprobe analysis and after we have evaluated our data and processing procedure using the error analysis program which is being written and which will be described later. An earlier microprobe analysis was unsuccessful because flat surfaces were not ground on the specimens. The specimens have been remounted and flat surfaces have been ground.

Comparison with other recent research now suggests that β-$Ca_3(PO_4)_2$ exists in two slightly different arrangements, one when formed at higher temperatures (~1000°C) and the other formed from an aqueous system (i.e., *in vivo* or hydrothermally). The material formed *in vivo* is too fine grained for single crystal work, but it probably can best be simulated by materials synthesized hydrothermally in crystallization chambers at about 200°C. We have, therefore, been preparing to grow samples of β-$Ca_3(PO_4)_2$ hydrothermally with different amounts of magnesium present. Their crystal structures will then be determined. We have recently repaired the inert liner in our crystallization chamber. The old liner was cracked and introduced impurities from the chamber wall, and the seal leaked.

$Ca(H_2PO_4)_2$

The previously unknown crystal structure of $Ca(H_2PO_4)_2$ has been determined by X-ray and neutron diffraction. The X-ray structural determination proceeded reasonably well, but as is unavoidable in X-ray crystallography, gave fairly imprecise locations for the hydrogen atoms. Neutron diffraction work was undertaken because it provides structural parameters for hydrogen atoms which are essentially as precise as those of heavier atoms. However, the structural analysis did not proceed as well as the X-ray analysis because the neutron data were more widely affected by extreme secondary extinction. This extinction must be corrected before fine details of the hydrogen atoms may be discerned. Isotropic secondary extinction corrections did not prove satisfactory. As a preliminary to more complicated extinction corrections, an error checking program is being written.

The results of the neutron structural determination at this stage show that at least two of the five crystallographically distinct hydrogen atoms in the structure of $Ca(H_2PO_4)_2$ may be centrosymmetrically disposed between the two oxygen atoms coordinated to each hydrogen atom. Centrosymmetric hydrogen bonds are very rare and poorly understood. We hope to elucidate the hydrogen bonds in $Ca(H_2PO_4)_2$ by (i) further refinement after a good extinction correction has been applied to the neutron diffraction, and (ii) use of data from spectral techniques such as IR.

α-$Ca_3(PO_4)_2$

The structure of α-$Ca_3(PO_4)_2$ is probably related to those of $Ca_5(PO_4)_2SiO_4$, $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$, and $K_3Na(SO_4)_2$, with systematic cation vacancies present in the first two materials and in α-$Ca_3(PO_4)_2$. α-$Ca_3(PO_4)_2$ contains a pseudo-cell which is expanded by a factor of three into the real cell, presumably by slight differences in the positions of atoms in different pseudo-cells. These differences, and hence the real structure, may be difficult to find but an attempt to determine the crystal structure of α-$Ca_3(PO_4)_2$ will be made. The structure is needed to shed light on several anomalies in the β-$Ca_3(PO_4)_2$ structure and to help complete the correlation of the roles played by systematic cation vacancies in calcium phosphates. Over 12,000 X-ray diffraction intensities have been measured from a single crystal of α-$Ca_3(PO_4)_2$. About 3,000 more are needed to complete the measurement of the unique set of data (i.e., because of the large amount of data, no data have been measured twice or more, as is our usual custom to track down measurement error). Work on the solution of the crystal structure of α-$Ca_3(PO_4)_2$ will commence when the measurement of the data is complete.

Computer Programs

The site occupancy parameters, which lead directly to the position and extent of impurity substitution in crystal structures, are the least precisely determined structural parameters. The parameters representing apparent atomic motion are likewise among the more poorly determined quantities, yet provide important indications of the forces in the solid state and of the mechanisms by which substitution of impurities which differ in size from the constituent atoms is achieved. Thus, we have a general concern about improving the already high quality of our crystallographic data.

The X-ray diffractometer programs have been modified to allow output of the X-ray intensity data directly onto magnetic tape. Another modification allows automatic realignment of the crystal at well-defined intervals under local computer control. The Univac 1108 computer program which was used to process the data as output on paper tape has been rewritten to process the magnetic tape and has been further extensively modified in several ways, which include (i) better corrections for unavoidable fluctuations in intensity of the X-ray beam due to air scattering, (ii) an estimate of the importance of short term and long term fluctuation in beam intensity, and (iii) greatly improved computing speed.

Because of the need to elucidate the nature of the severe secondary extinction in the neutron data obtained from a crystal of $Ca(H_2PO_4)_2$ and because of its general applicability, a program has been written to evaluate the standard deviations attached to measured intensities and refined structural parameters. This program is currently being tested. Basically, it computes the ratio of the actual difference between two equivalent but independent quantities to the uncertainties in these quantities as estimated from statistical procedures and compares the distribution of these ratios with the normal probability distribution. The fit should be good if the errors present in the quantities are random and if the scales of the standard deviations are approximately correct. Misfits will occur if systematic error is present or if the standard deviations are all too high or too low.

4.2. Physicochemical Studies of Apatite and Related Inorganic Substances

Sponsor: NIDR (Grant), ADA

4.2.1. Crystal Chemistry

A new method was described in the previous report for the preparation of hydroxyapatite and other calcium phosphates. The hydroxyapatite crystals produced by this method are relatively large and are especially suitable for use in studies in which synthetic crystals that mimic those in enamel are needed. One feature of the product formed by this process is an apparent low Ca/P ratio. Since the crystals formed by this process are unusually well formed for a "non-stoichiometric" hydroxyapatite, their physical and chemical properties are being investigated in the hope that an answer can be found to the old question of what causes the apparent non-stoichiometry in apatites. The cause may have an important bearing on two other important questions: (1) What is the reason that the carious lesion forms under the surface of the enamel rather than forming an eroded spot, and (2) Why do individuals differ in their caries susceptibility?

It was found that by continued washing of the non-stoichiometric product, the composition would slowly approach the ideal composition without the crystals changing significantly in morphology or optical properties. A series of products derived from the original precipitates have now been prepared; these vary in Ca/P ratio from about 1.59 to 1.67. Pyrolysis of some of these products show that they behave in a way that is normal for "non-stoichiometric" apatites -- the greater the deviations in Ca/P from the ideal value, the greater the amount of $P_2O_7^{4-}$ that is formed. On the assumption that the low Ca/P ratio was due to the presence of $CaHPO_4$ which decomposes under pyrolysis according to the reaction

$$2\ CaHPO_4 \longrightarrow Ca_2P_2O_7 + H_2O \quad ,$$

it was found that the P_2O_7 formation could be used to show that the apatite portion of the sample had the theoretical Ca/P ratio of 1.67. This view is in accord with (i) the X-ray diffraction and infrared absorption results that show no significant change although the gross Ca/P ratios of the preparations varied considerably, and (ii) evidence obtained subsequently with the polarizing microscope showing the presence of significant amounts of divided birefringent crystallites of $CaHPO_4$; the latter were not given adequate recognition in the initial examinations. Thus, although we initially thought we had prepared a material that might have bearing on "non-stoichiometric apatites", careful investigation revealed that the cause of the apparent anomaly was the presence of a secondary phase of acid calcium phosphate. We believe this has bearing on many other reported cases of non-stoichiometric apatites in which adequate efforts were not made to detect the presence of such phases.

Modifications of the crystal-growth procedure have been used to produce several other products.

(1) Fairly large amounts of octacalcium phosphate were prepared for use in a solubility study.

(2) Chlorine-containing hydroxyapatites were prepared for study by X-ray diffraction and infrared spectroscopy.

(3) Chlorapatite, $Ca_5(PO_4)_3Cl$, was prepared, possibly for the first time, from an aqueous system.

Relatively small amounts of Cl^- were found to disrupt the structure to the extent that the 638 cm^{-1} peak caused by the librational motion of the OH^- hydrogen was not detectable, and the OH stretching peak was considerably broadened. This effect may signify that Cl^- in the structure may alter the lattice energy and thereby significantly increase the solubility of the hydroxyapatite. This may have an important bearing on how Cl^- in enamel may affect its solubility and on the formation of caries.

The major drawback of our procedure for growing hydroxyapatite is the difficulty in removing the last traces of $CaHPO_4$. Continued washing for several weeks, although successful, precludes preparation of large amounts. We have tried several methods to accelerate removal of $CaHPO_4$ without significant success. This phase of the work is being given special attention; neutral ammonium citrate solution, which is used for this purpose in the fertilizer industry, is being tried under various conditions.

4.2.2. Solubility Studies

Solubility of tooth enamel

A primary objective of this part of the project was to explore solubility behavior of important biominerals by utilizing the techniques applied to the synthetic calcium phosphates in our previous studies. We have made considerable progress with pooled samples of powdered human tooth enamel. The method of approach involved successive batchwise extractions of a powdered enamel sample with a given phosphoric acid solution in the concentration range $1.7 \times 10^{-2} - 1.5 \times 10^{-4}$ molar. Each extraction was carried out until apparent equilibrium between the solid and liquid phase was reached. By choosing phosphoric acid as the extracting solvent, we were able to restrict the foreign ions to only those coming from the enamel mineral. This simplified the interpretation of data.

The equilibrium measurements (pH, calcium concentration and phosphorus concentration) were interpreted through the use of considerations such as ion-activity products for the various calcium phosphates, the stoichiometry of the dissolution reaction, the electroneutrality unbalance, cumulative amounts (wt%) of calcium dissolved, and "potential diagrams". The ion-activity products $(Ca^{2+})^5(PO_4^{3-})^3(OH^-)$, (a_{OHAp}), derived from the results of extractions indicate that the enamel sample contained appreciable amounts of calcium phosphate more soluble than the pure, crystalline $Ca_5(PO_4)_3OH$, (OHAp). In an equilibration with a pH value of about 4.8, large crystals of $CaHPO_4 \cdot 2H_2O$ (DCPD) were observed, whereas in synthetic mineral systems the invariant point between DCPD and OHAp is about pH 4.3, again suggesting that the tooth mineral contained a fraction that is more soluble than synthetic OHAp. The ion-activity products, a_{OHAp}, showed a strong dependence on the cumulative amount of solid extracted; the greater the amount of solid extracted, the smaller was the ion-activity product. The smallest value of the activity product after about 30% extraction of the solid was about 1×10^{-57}; this value is still significantly larger than the solubility product constant of synthetic OHAp, 3.7×10^{-58}. The electroneutrality unbalance contributed by the dissolution of foreign ions from the enamel mineral was large and cationic in nature in the first extractions; it dropped off to an insignificant amount in the subsequent extractions when about 5% of the solid phase had dissolved. This suggests that the more soluble foreign cations are dissolving in the initial extractions.

From the plots of quantities proportional to the chemical potentials of $Ca(OH)_2$ and H_3PO_4 for enamel solubility data and the previous synthetic calcium phosphate solubility data, it was apparent that the enamel samples were more soluble than hydroxyapatite but less soluble than other calcium phosphates. The negative reciprocal of slopes of the lines for synthetic minerals in such plots represent the Ca/P ratios of the respective solid phases; we cannot apply this criterion to the enamel data because in each group of points for enamel solubility we find varying ion-activity products due to changing solubility. Potential diagrams have limited use for establishing the stoichiometry of the equilibrating solid phase in tooth and bone mineral because the slope of the line may be affected by how much of the mineral has dissolved.

The results obtained in the batch-wise equilibrations require considerable care in their interpretation because the presence of impurity ions and sometimes the precipitation of acidic calcium phosphates altered the apparent stoichiometry of the dissolution reaction. The results obtained in the continuous, titration-type equilibrations, which were initiated near the end of this report period, were more consistent and less affected by the above factors. Although the equilibration times were shorter than those used in the batch-wise experiments, the indicated solubilities were greater, suggesting that reprecipitation was minimized and that the results are more indicative of the solubility characteristics of the original enamel mineral.

Solubility of dicalcium phosphate dihydrate

Solubility measurements on $CaHPO_4 \cdot 2H_2O$ in the presence of various concentrations of NaCl, described in the report for the previous periods, were completed. A manuscript for publication is in preparation.

Efforts were made to extend the solubility measurements on $CaHPO_4 \cdot 2H_2O$ into the range of pH's above 7 with the objective of collecting information on the stability of the ion pair $CaPO_4^-$. The procedure involved the use of disodium ethane-1-hydroxy-1,1-diphosphonate to prevent the precipitation of hydroxyapatite. Although this method has prevented the crystallization of hydroxyapatite in many other situations, it was not successful in this instance. The possible reason for this is that the times required for our equilibrations were much longer than for the other studies in which the diphosphonate has been used.

Future work on solubility of calcium phosphates relates to the effects of NaCl on the solubility of hydroxyapatite and $CaHPO_4$. The measurements will be made on solutions in equilibrium with both solids (i.e., at the singular points) and at the temperatures, 25°C and 37°C. In this way, we will be able to use the hydroxyapatites prepared by the method described above without being concerned about the presence of unreacted $CaHPO_4$. Measurements made at the singular points are governed by an additional constraint on the system that should be of considerable value in the theoretical treatment of the data. These equilibrations should also give us a unique means of testing the reliability of the calcium and hydrogen electrodes.

Solubility of octacalcium phosphate

From the stability point of view, in physiological pH ranges (6.4 to 7.5), octacalcium phosphate (OCP), $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, is in the center among various calcium orthophosphate compounds; hydroxyapatite, $Ca_5(PO_4)_3OH$, and β-tricalcium phosphate, $\beta\text{-}Ca_3(PO_4)_2$, are more stable, and anhydrous dicalcium phosphate, $CaHPO_4$, and dicalcium phosphate dihydrate, $CaHPO_4 \cdot 2H_2O$, are less stable. Although it has not been proven that OCP participates either as a precursor in tooth and bone mineralization or as a more or less permanent component (as it is in calculus), there is considerable evidence to support this view. Thus, its solubility is important because it would define minimum levels at which it can form.

A large batch of OCP was prepared by utilizing a new method which was described in a previous report. We are presently continuing solubility measurements on the new preparation of OCP over a range of solution compositions. Initial results indicate that the measurements are satisfactory; however, the conversion of OCP to $CaHPO_4 \cdot 2H_2O$ is quite rapid in the pH range below that of the singular point for these two compounds. This will restrict the range of compositions that can be studied, thereby precluding an independent check of the ion-pair formation constant for $CaH_2PO_4^+$ derived in studies of the other salts. However, we do not anticipate that this difficulty would prevent us from improving the existing value of the solubility constant at 25°C and establishing values for the constant at 5, 15, and 37°C.

Additional experiments are being carried out on aqueous mixtures of OCP and $CaHPO_4 \cdot 2H_2O$ to check the singular point composition.

4.2.3. Topical Fluoridation

Thermodynamic and kinetic considerations have led us to propose that fluorapatite (FAp) might be formed from hydroxyapatite (OHAp) in tooth enamel through the following path,

$$\text{OHAp} \xrightarrow{\text{DCPD soln*}} \text{DCPD} \qquad [\text{I}]$$

$$\text{DCPD} \xrightarrow{F^-} \text{FAp} \qquad [\text{II}]$$

* A pretreatment solution that is saturated with respect to DCPD but is undersaturated with respect to OHAp. [DCPD = $CaHPO_4 \cdot 2H_2O$]. These solutions range in composition from those saturated with respect to DCPD and OHAp (pH $\approx$ 4.3) to those saturated with respect to DCPD and $Ca(H_2PO_4)_2 \cdot 2H_2O$ (pH < 2).

Preliminary studies on synthetic OHAp and DCPD indicated that this proposed path is feasible. Studies were also made on extracted human teeth; some representative results were presented in the last report.

Although fluoride is known to react rapidly with DCPD in aqueous solutions, there is great uncertainty as to the nature of the product formed. CaF_2, OHAp, FAp and unreacted DCPD are among the compounds that have been observed as the product of such a reaction. Because of its complexity, it is necessary to study reaction [II] in more detail.

When DCPD was immersed in 0.1 wt% F solution, near complete conversion of DCPD to FAp was obtained after 24 hours reaction time. This indicates that the rate and yield of this reaction are many orders of magnitude greater than those for the reaction of OHAp with F to form FAp. The optimum F concentration for this reaction appears to be somewhere around 0.2 wt%. Too high an F concentration resulted in large amounts of CaF_2, while too low an F concentration did not provide enough F for the reaction to proceed to the right. DCPD did not hydrolyze in significant amounts to form OHAp (or an OHAp-FAp solid solution) with F concentrations below 0.05 wt%.

In line with the study of the reaction of DCPD with F, it was also found that DCPD would react with CaF_2 to form FAp. The rate of this reaction was greatly enhanced in the presence of OHAp, indicating that the OHAp acted as a template for the formation of FAp. This result encourages us to believe that we may have found a way to overcome one of the major limitations (the slowness of solid state reactions) to the efficacy of the FAp reaction. By forming CaF_2 and DCPD within the enamel, we hope that these will then react to form FAp layers on the OHAp crystals. The thickness of these layers would not be limited by the slowness of a solid state reaction and the acid produced in the reaction would tend to facilitate its rate.

4.2.4. Calorimetry

We have been setting up calorimetry facilities for measuring the heat given off when calcium phosphates dissolve. This information is needed to characterize fully the thermodynamic properties of these compounds. Since this work is being carried out in close cooperation with the Thermochemistry Section of the National Bureau of Standards, it has been possible to develop our capability in this field to a very high level of accuracy. During calibration and testing of our calorimeter, measurements have been made on the heat of dissolution of tris(hydroxymethyl) aminomethane (tris) in hydrochloric acid. This is the standard reference material distributed by the National Bureau of Standards for calibration of solution calorimeters. As an indication of the quality of calorimetry we are now able to perform, these measurements on the heat of solution of tris are to be reported at the international calorimetry conference, July 1971, and will be incorporated into the value that will be used to support the certification of this material as a standard reference. As part of this development, we participated in a thorough analysis of the sources of errors involved in calorimetric measurements and contributed to improving the automation of data collection.

Work on the heats of dissolution of calcium phosphates has been initiated; a reference material for these studies will be CaO. This material was chosen because it will be used to adjust the final solution compositions so that they will be the same irrespective of the calcium phosphate salt which is being measured. Preliminary measurements have been made on the heat of dissolution of hydroxyapatite; these will permit us to establish the most propitious conditions for the final measurements.

A National Bureau of Standards report, "Digital Data Acquisition and Computer Computation Applied to Calorimetric Experiments", has been written.

4.3. Surface Characterization Through Adsorption Studies

Sponsor: NIDR

Water Adsorption

The work involved in the water vapor adsorption and desorption on collagen, dentin, enamel, anorganic whole teeth, polymethyl methacrylate, and investment compound is being prepared for publication.

Additional work along these lines is being extended to include dental cements and other restorative materials inasmuch as they come in direct contact with the teeth. These materials will include zinc phosphate cement, polycarboxylate cement, zinc oxide-eugenol, a composite (filled resin), and an amalgam. Also, a sample of anorganic dentin is included to complement the earlier series.

High Temperature Water Adsorption

A preliminary experiment has been performed to determine the feasibility of higher than room temperature water adsorption at humidities approaching saturation. This was carried out with dentin using a conventional "desiccator method". It was found that at 96% relative humidity and 50°C (where the vapor pressure of water is 92.5 torr), dentin contained 24% water. This may be compared with 13.5% water when saturated at 23°C where the vapor pressure is 21.1 torr. It is significant that while the vapor pressure of water is more than four times greater at the higher temperature, the water content of dentin is barely double.

Hysteresis Theory

Some progress has been made in this laboratory in advancing the theory of adsorption hysteresis. These developments are being tested by applying them to water-on-dentin data in an attempt to account for the course of adsorption within the region contained in the hysteresis loop.

Indirect Determination of Dry Wt.

Data points (as fast as they are obtained) are being checked against this original theory to compare them with actual drying experiments. An understanding of adsorption hysteresis is necessary in order to eliminate anomalous results. Preparation for publication will be deferred until after a Hysteresis Theory paper has been submitted, in order to follow a logical sequence.

4.4. Mechanical and Physical Properties of Oral Structures and Restorative Materials

4.4.1. Dimensional Changes in Teeth Components

Sponsor: NIDR, USAF, VA

Studies of the dimensional changes of tooth structure were concentrated on dentin, particularly on the time dependence of the "thermal expansion" of dentin. All evidence obtained so far is consistent with the hypothesis that in addition to the thermal dimensional change when dentin is heated or cooled in water, there is also a dimensional change due to water movement in and out of the material. Water content, which comes to equilibrium slowly, is apparently reduced as temperature is raised. Thus, the heating or cooling of dentin in water is accompanied by two dimensional change phenomena, opposite in direction, one of which is time dependent. The range of dimensional change when a specimen at equilibrium at a temperature, t_1, is raised to a higher temperature, t_2, and then brought back to t_1 appears to be limited by two parallel curves - one representing the "instantaneous" thermal expansion from t_1 to t_2 with t_1-equilibrium water content, and the other representing the "instantaneous" thermal contraction from t_2 to t_1 with t_2-equilibrium water content. The experimental temperature-ΔL curve may fall anywhere within these limits depending upon the time-temperature history of the specimen.

In addition to the time dependence of the "thermal expansion" of dentin, there also appear to be anisotropic variations as well as tooth-to-tooth and location-in-tooth variations. Preliminary data suggest that the anisotropic effects are not present in anorganic dentin, but further verification of this observation is needed.

Measurements of the rapid heating or cooling coefficient on about 30 dentin specimens gave an average value of 7.5×10^{-6}/°C (S.D. = 1.0) for specimens in which the direction of the dentinal tubules was generally perpendicular to the direction of measurement. The coefficient with tubules more nearly parallel to the direction of measurement was 5.4×10^{-6}/°C (S.D. = 0.7). Measurements made in three directions on two rectangular-prism specimens of root dentin gave the following results:

	Specimen	
Direction	A	B
Perpendicular to tubules	7.2×10^{-6}	7.6×10^{-6}
Parallel and perpendicular (1)	6.4	5.3
Parallel and perpendicular (2)	4.9	4.9
Volume	18.5	17.8

The overlapping of ranges may result from difficulty in obtaining specimens with tubules aligned uniformly in the desired direction, as well as from other specimen-to-specimen variations.

4.4.2. Mechanical and Electrical Properties of Hard and Soft Tissues

Sponsor: NIDR, VA

A new experimental program is being developed to study the physical properties of hard and soft tissues. A varied experimental approach involving piezoelectric, dielectric, mechanical, x-ray, dilatometric, NMR and other observations will be employed in accordance with the demands of the problem. The phenomena to be investigated include viscoelastic effects, relaxation times, crystalline and amorphous phase transitions and molecular structure. In order to obtain a broad view of these phenomena, observations as a function of temperature will be emphasized. Information about molecular structure and the molecular origins of the observed phenomena will be sought.

Initial attention will be given to the electrical and mechanical measurements of collagen and bone as a function of temperature. Most published data in this area have been confined to observations at a constant temperature, so that a limited physical picture exists. For example, the molecular changes which occur in collagen near 40°C can be studied in detail with dynamic mechanical, piezoelectric, and x-ray measurements using temperature as a variable. The piezoelectric effect has its origin in the oriented crystalline regions of the sample. With x-rays, the oriented and unoriented crystalline regions are observed. The dynamic mechanical measurements are used to examine the viscoelastic properties involving both amorphous and crystalline regions. With these experiments, it will be possible to isolate the origins of the observed phenomena in the oriented crystal, randomly oriented crystal, or amorphous phase. A molecular description of the observed phenomena will be pursued, and may require data from other experiments.

The physical properties of the dentin and enamel components of tooth structure will be studied using mechanical and viscoelastic measurements. These materials can be viewed as a composite, and the interpretation of the experimental data will rely on recent advances in the understanding of the mechanical behavior of composite materials. This work will be correlated with thermal expansion measurements now being made.

In the area of dental materials, consideration will be given to the problem of stress distribution, stress corrosion, and fatigue in dentures. A study will be made of the feasibility of using thin piezoelectrically-active polymer films as stress-strain detectors. This work would rely on an already existing piezoelectric program in the polymers and electronic technology divisions of NBS.

An immediate undertaking will be the construction of appropriate experimental equipment. A piezoelectric measurement system will be developed and the possibility of making viscoelastic measurements with same system will be considered. Temperature control over a suitable temperature range and the capability of _in vivo_ measurements will be incorporated in the apparatus.

A rough draft of the second part of a paper on viscoelastic properties has been completed and is being edited for inclusion in the Proceedings of the 50th Anniversary Symposium.

4.5. Collagen-Water Interaction

Sponsor: NIDR

Calorimetry

The effort to definitively characterize the dimensional changes of tooth structure which occur as the temperature of a bathing medium is varied (e.g., see 4.4.) has resulted in an intensive study of possible changes in dentin which are responsible for its anomalous behavior at temperatures as low as seven degrees above normal mouth temperature. To ascertain whether the anomalous behavior involved a phase transition in the collagenous component of dentin, experiments were conducted with a differential scanning calorimeter. Typical endotherms were observed in the expected temperature range with commercial Perkin-Elmer equipment when specimens of collagenous tissues such as bovine hide, rat-tail tendon, kangaroo-tail tendon and demineralized bovine dentin were examined in water. However, the noise level of the instrument was not sufficiently low to permit investigation of mineralized dentin, the collagenous component of which accounted for only 20% of its weight. The microcalorimetry section of NBS was approached and with equipment utilizing 500 thermocouples around the reaction vessel rather than the usual single thermocouple and into which numerous additional features have been incorporated to give an overall sensitivity of 60 microvolts, samples of collagen and dentin in water were again examined for heat absorption or evolution. In addition to some intriguing additional information on tendon collagen, the instrumentation has clearly shown the absence of an endothermic transition in dentin over a temperature range 35°C - 90°C. The collagen component of dentin, when not confined by the mineral hydroxyapatite, however, shows a normal first order melting phenomena, melting a few degrees less than 60°C. The microcalorimetric measurement of dentin provides very strong evidence for the true composite nature of dentin and clearly indicates that its mechanical properties must be analyzed from this point of view.

NMR and IR Studies

Further experimental studies of the water of hydration in collagenous tissue were obtained using near-infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, in combination with differential scanning calorimetry (DSC). The results can be roughly grouped into two categories, as follows:

A. Nature of Bound Water in Helical vs. Denatured Collagen.

When wet animal tendon is heated above about 55°C, the hydrogen-bonded helical molecular conformation of the collagen breaks down into a random-coil structure, with some reforming of hydrogen bonds between the chains. However, one would expect a net change (probably loss) in the number of intramolecular hydrogen bonds after the helix-coil transition. This should lead to a like change in the number of hydrogen-bonding sites on the protein available to water, and therefore might be epxected to produce a change in the amount of unfreezable water in the system. In order to test this hypothesis, the amounts of unfrozen water in native and denatured collagen were measured by DSC. Samples of wet KTT (kangaroo-tail tendon) were each sealed in small aluminum pans to prevent evaporation during the experiment. Each was frozen below -40°C and scanned through the melt. From the calibrated melt endotherm, the weight of ice in the "frozen" collagen was calculated. Each sample was then heated above 60°C, through the helix-coil endotherm. The samples were then refrozen and the ice melt endotherm was again recorded. The observed changes in the amount of unfrozen water after vs. before denaturation for the three samples were -1.2%, -6.7%, and +0.8%. Two of these values are within the replicate reproducibility of this type of experiment, and the third is only outside this value by a small amount. It would, therefore, appear that any changes in the availability of hydrogen-bonding sites to water before and after denaturation are so small as to be impossible to detect with this technique.

A full discussion of the NMR experiment is beyond the scope of this report. Briefly, it consisted in recording the shape and width of the NMR spectrum of D_2O in a sample composed of small segments of randomly oriented KTT, before and after heat denaturation of the collagen. The observed narrowing of the NMR line after heat denaturation is consistent with rotational diffusion of the water in the collagen matrix, and not with *in situ* rotation of the water molecules at their hydrogen-bonded sites on the collagen. The latter effect would likely have produced a spectrum very much like that of undenatured collagen. Although the result is only qualitative, it is a further indication that the water in the collagen matrix is not at all "icelike", but is rather a fluid with considerable translational mobility. (It should be possible to measure the self-diffusion coefficient directly by another NMR technique, which is not presently available here).

B. IR Spectra of Water in KTT.

Infrared spectroscopy offers a few additional advantages in studying the nature of water and ice in collagen. Briefly, they may be summarized as follows:

(1) Very high sensitivity. Two water bands in the near-IR spectrum of hydrated collagen at 1.45μ and 1.94μ are almost completely unobstructed by the collagen spectrum. They are the same wavelengths as the bands of pure water, and do not indicate the high-frequency shifts observed for ice, again indicating the liquid-like nature of the water. We have observed concentrations of water as low as about 0.1 water molecule per amino acid, which is well below the concentration observable by the present wideline NMR spectrometer.

(2) Very fast measurement. The timescale of the IR measurement is so short ($\sim 10^{-12}$ sec) that the water molecules are not able to diffuse measurably or rotate by more than a fraction of a complete revolution during the time in which they are absorbing IR energy. This is in contrast with the very long NMR timescale, in which the molecules diffuse at least several hundred molecular diameters during the measurement. The IR bands are dichroic, indicating anisotropic distribution of water molecule orientations.

(3) Direct observation of all the water in "frozen" collagen. NMR spectroscopy sees only the unfrozen water in collagen, since the ice spectrum is too broad to detect. Calorimetry only detects the melting of the frozen water component. The IR bands, which arise from all the water in the frozen collagen, show frequency shifts which must correspond to an overlap of water and ice bands.

4.6. Dental Metallurgy

Sponsor: NIDR (Grant)

Binary Noble Metal Constitution Diagrams

The existing metallurgical literature concerning binary or ternary constitution diagrams contains only a relatively small percentage of alloy combinations involving the noble metals (i.e., those metals which are exceptionally resistant to chemical corrosion or oxidation, such as gold and metals of the platinum group). To help fill this gap, a report (see Appendix) has been published which presents four new binary constitution diagrams. These diagrams include the Cr-Pt, Cr-Ir, Cr-Rh and V-Pt alloy systems. In this research, all experimental alloys were prepared from starting materials having a nominal purity of at least 99.9% and precautions were taken to insure that no significant contamination was introduced during alloy preparation and heat-treatment.

The program is being continued with the current effort centered on the vanadium-ruthenium and vanadium-rhodium systems.

Gallium-Palladium Alloy

Previous research in this section pointed up the potential of a gallium-palladium-tin alloy in dental restorative work. At the most recent IADR meeting, some German researchers presented data confirming and supplementing these studies. The need for clinical examination of the alloy has long been stressed by members of this section and recent clinical studies at the University of Alabama now suggest that there are some serious stress corrosion problems with these materials which must be taken into account in the future. Corrosion studies are, therefore, being undertaken in cooperation with other laboratories. These studies will investigate both the gallium-palladium-tin alloy and also a gallium-copper-tin alloy for which satisfactory clinical results have been claimed in some recent Russian publications.

Amalgam Research

A development in amalgam research at the University of Virginia, and thought by some to be a major breakthrough, involves incorporation of gold into the alloy. This is believed to cause elimination of the so-called γ_2 phase (tin-mercury phase) which is considered to be the weakest mechanically and least corrosion resistant of the phases that are formed in amalgam.

A cooperative program to test if indeed the γ_2 phase has been eliminated has been initiated between this section, the reactor group with their neutron diffraction capability at NBS, and the University of Virginia group. The indications are that the phase is absent, although some questions remain to be answered.

Nitinol Alloys

A research proposal has been prepared to explore the possible uses of Nitinol alloys in dentistry. These alloys are quite unique in their ability to "remember" a pre-determined shape. Any arbitrary shape may be pre-selected simply by shaping and constraining the metal mechanically and then heating it to a dull red heat. The metal may then be cooled to room temperature (i.e., below mouth temperature), and if it is now rather severely bent or deformed, it can be restored to its pre-selected shape merely by heating it to a temperature which lies between mouth temperature and boiling water temperature, depending on the alloy composition. In returning to its pre-selected shape, the metal exerts considerable force, comparable to its tensile strength of about 100,000 psi. It is quite pliable below the transition temperature, however, and this suggests a possible dental application as clasp wires in cases where a large undercut is needed. The clasp could, for example, be rendered pliable by placing it in ice water and subsequently replacing it in the mouth. Upon warming to mouth temperature, it would restore itself to a pre-selected shape and grasp securely to a tooth. This method is impossible with present alloys since they are incapable of undergoing such large strains without being permanently deformed.

The Nitinol alloys are composed mainly of nickel and titanium in equi-atomic proportions. It is expected that they will be quite corrosion-resistant in an oral environment and will be biologically inert. They were discovered at the Naval Ordnance Laboratory at White Oak, Maryland several years ago, but only recently have the "memory transition temperatures" been adjusted so as to be sufficiently low to enable its use in the human body.

Borazon

The use of cubic boron nitride, Borazon, as a possible dental grinding material to replace diamonds is being considered. The General Electric

Company has recently begun to market this material. It possesses the same atomic structure as diamond, and is nearly as hard, but unlike diamond, it can be heated to high temperatures without decomposing. Furthermore, it appears to cut hard material more efficiently than diamond. Its possible use in dentistry for cutting or grinding tooth structure ought to be explored and preliminary negotiations are now under way to investigate this possibility in cooperation with the General Electric Company.

4.7. Dental Ceramics

Sponsor: ADA

In cooperation with the Navy Bureau of Ships, several graphite crucibles were vacuum-impregnated with zirconium-acetate solutions, heat cured and dried. Titanium alloy was then melted in them. Carbon pickup from both the unimpregnated and impregnated crucibles was large. Tests suggest that the zirconium-acetate impregnated crucibles might prove to have slightly greater stability upon prolonged use. However, carbon pickup by the molten metal was so high that no further work appears merited.

Work continues on the development of porcelain "frits" prepared by the gelling of inorganic-polymer solutions. By this procedure, all constituents of the porcelain are mixed as liquid solutions and gelled. The air-cured and hardened gels are then calcined at a suitable temperature. Calcination temperature controls "frit" porosity and density. A nearly pure mullite porcelain has been prepared by this procedure. However, the firing shrinkage was greater than 50%.

Work is now being directed toward developing "frits" with suitable densities and wetting properties. If this is successful, attempts will be made to spherulitize these gels and thus control "frit" particle size and shape. It is hoped that porcelains made out of these "frits" may show reduced firing shrinkage due to better control of particle size and more localized and restricted flux action.

Dilute chloride-stabilized-alumina and ammonium-stabilized-silica water solutions were substituted for distilled water in the fabrication of low-and-high-fusing straight-dental-porcelain bodies. Alumina solution additions had too refractory an effect on the porcelains and severely retarded their maturation. Preliminary tests using silica solutions appear to hold promise wtih regard to greatly reducing balling during firing and increasing green porcelain strength.

Extensive tests are being performed on small cylindrical pellets of a low fusing (Apco) porcelain. Pellets were prepared using 1.0 to 15% SiO_2 water solutions. These were fired with identically prepared controls in which only distilled water was added. Results show that the silica solution additions greatly reduced balling during firing, thereby increasing the sharpness of prepared edges and, due to restricted flow, decreased disproportionation in the porcelain body form. Increase in the green strength of the dried porcelain body was noted. In the 1.0 to 5.0% SiO_2 solution additions, translucency appeared unaffected and only a slight change in the Gardner tristimulus color values was noted. Gloss was reduced, but, in all cases, was adequately compensated for by the addition of Superglaze enamel coats. Firing shrinkage was appreciably reduced only in bodies in which solution additions with greater than 5% SiO_2 were used. Pronounced decrease in edge strength was noted when using solution additions having SiO_2 concentrations in excess of 8%. Extensive tests are now underway to assess the significance of any strength decline.

The mapping out of firing shrinkage, firing color and tensile strength stability diagrams for the various porcelains is underway. The effects of firing rate and temperature are being assessed. Detailed petrographic studies are to be made of reaction mechanisms.

4.8. Dental Investment Studies

The thermal expansion compensation technique has been used extensively in the casting of dental restorations. That additives such as NaCl and H_3BO_3 influence the thermal expansion of dental investments has been known for a long time. However, the nature of the phenomenon by which these and other additives influence thermal expansion has not been adequately explained, although the evidence points to reaction with the gypsum binder component of the investment. As a part of a one-year guest worker program at NBS, Dr. S. Nomoto, Professor of Dental Materials at Tokyo Medical and Dental University, has begun a study of the thermal expansion (ADA Specification No. 2 for casting investment for dental gold alloy) of investment materials with various amounts of additives and of the effect of wax dipping on the thermal expansion of such materials. Petrographic analysis will be employed to correlate structure and the physical properties observed.

4.9. Grafting of Monomers to Collagen and Soft and Hard Tissues

Sponsor: U. S. Army, NIDR

The aim of this study is to modify the surface of the proteinaceous material by chemical attachment (grafting) of polymeric side chains to soft and hard mineralized tissues containing a collagenous or keratinous component. Previous studies in this laboratory have shown that a variety of monomers can be grafted to these substrates. It therefore appears possible that surfaces with the desired degree of hydrophilic to hydrophobic balance to suit specific applications can be obtained.

During this period, the main emphasis was placed on (a) grafting of monomers to ratskin, and (b) studying the mechanism of the grafting of methyl methacrylate onto an insoluble collagen substrate.

(a) Grafting of Monomers to Soft Tissues (U. S. Army)

The ratskins were prepared by the procedure previously developed. In some experiments anionic and non-ionic emulsifiers were added to the reaction mixture. Soluble homopolymers in the specimens were removed from the products by subsequent extraction with acetone and ethanol for at least 24 hours. The treated skins were then dried in a vacuum and weighed. Significant weight increases were obtained with a variety of monomers such as methyl-, isodecyl- and glycidyl methacrylate, cyanoethyl acrylate, ethylene dimethacrylate and ethylene glycol monomethacrylate. Furthermore, use of comonomers such as ethylene dimethacrylate-methyl methacrylate or maleic anhydride-methyl methacrylate increased the yield as compared to the use of a single monomer. Increase in weight (based on the weight of the original material) of up to 48% was obtained on grafting monomers to ratskin, although the average increase in weight ranged from 8 to 20%, as compared to an increase of 4% for a blank run in which addition of monomer was omitted. Visual inspection of some of the graft products showed profound surface changes. For instance, the isodecyl acrylate graft yielded a highly tacky surface.

Additional studies with collagen films gave considerable weight increases, indicative of successful grafting, with the following monomers: butenediol, isodecyl-, cyanoethyl- and cellusolve acrylate, diallyl phosphite and triallyl phosphate. Further investigations using fluorine containing monomers to obtain surfaces that are not readily wetted in an aqueous environment are being initiated. Another aspect of assessing the efficiency of certain co-initiators to increase the rate of grafting will be explored.

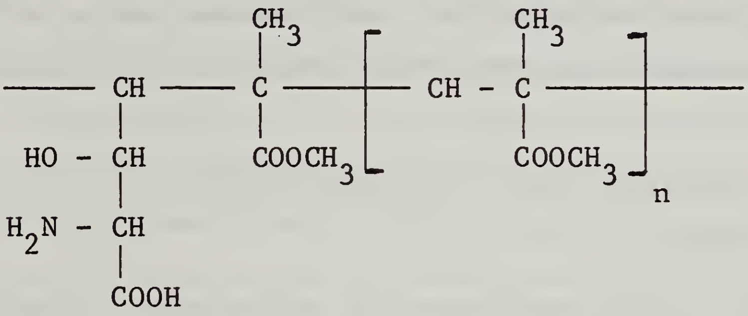
(b) Characterization of the Bonding Site of the Grafted Side Chain (NIDR)

The previous results indicate that a chemical bond is formed between the collagen backbone and the graft polymer. Since the strength of this bond should be high, it may be possible to utilize the grafting technique to obtain improved adhesion. This grafting reaction may, therefore, be of clinical usefulness in a variety of applications. Little is known, however, of the type of attachment and location of the bonding site of the side chain polymer on the substrate. An investigation has been initiated to obtain a better understanding of the mechanism of grafting to a collagen backbone and the mode of attachment of the side chain.

Methyl methacrylate was grafted in nearly quantitative yield (94.6% after removal of soluble homopolymer) onto steer hide collagen powder. The product was refluxed with 6N HCl for 24 hours to hydrolyze the protein backbone. The insoluble residue was washed with dilute acid, base and water to remove any aminoacid. Most of the grafted polymethyl methacrylate (70%) was recovered.

The water insoluble hydrolyzate showed a solubility behavior (soluble in acetone, chloroform, methylene dichloride, benzene and dioxone) similar to that of poly(methyl methacrylate). Its infrared spectrum is also nearly identical with this polymer.

The insoluble hydrolyzate gave a positive protein test with ninhydrin. It gave a negative test with o-phthaldehyde for glycine residues, a negative test with 1,2-naphthoquinone-4-sulfonate, vanillin and isatin-ninhydrin reagents for proline or hydroxyproline, a negative test for tyrosine with 1-nitroso-2-naphthol. It gave a positive test for serine or threonine (no ninhydrin color formation after treatment of the spot with $NaIO_4$). Serine is the only amino acid present in collagen containing a primary alcohol group. This group is much more likely to react with ceric initiator than the other amino acids containing secondary alcohol groups (threonine, hydroxyproline, hydroxylysine). Furthermore, serine residues are more abundant in the collagen backbone (3.1% of total residues) than those of threonine (1.9%). Based on these preliminary studies, it is postulated that the insoluble hydrolyzate has the following structure:



Further confirmation of this structure for the isolated graft is now being sought by (1) elementary analysis, (2) dinitrophenylation, (3) additional spot tests, and (4) positive identification of glyoxylic acids which should be one of the oxidation products when this serine derivative is treated with periodate. The polymer chain will also be characterized. This will include determination of the viscosity molecular weight and presence of any stereoregular polymer by NMR techniques. Preliminary data indicate that characteristic 60 Mc/sec NMR spectra of the polymer cannot be obtained at room temperature because of its relatively low solubility. However, it is anticipated that spectra run in suitable solvents at 150°C or above will increase resolution by minimizing dipolar broadening.

Another approach to establish the structure of the polymer will be explored. Methyl methacrylate or other suitable monomer will be grafted to the amino acids or poly(amino acids) present in collagent. From the rate of grafting and the yields obtained in these reactions, the site of the attachment of the monomer to the amino acid residue in collagen should be established.

4.10. Centrifugal Tensile Strength Testing

Sponsor: NIDR

A collaborative study employing the centrifugal tensile strength testing procedure was initiated with Dr. Forsten, School of Dentistry, S.U.N.Y. at Buffalo, and Institute of Dentistry, University of Turku, Finland. The measurements are designed to aid in a study of the effects of manipulation variables on the strength of amalgam. Centrifugal tensile strength testing data is to be compared with a transverse specimen testing procedure. Particular emphasis is being placed on determining the decrease in final transverse strength of amalgams caused by delayed condensation and the relation of this decrease in strength to the one-hour strength and manipulation technique. Preliminary measurements indicate that the two strength tests similarly evaluate or correlate manipulation variables.

4.11. Adhesive Direct Filling Materials

Sponsor: ADA, NIDR (Grant)

Work has continued in the development of an esthetic, composite dental material that can be used for both restorative and preventive dentistry. The endeavors have been centered on optimizing the chemical and physical properties of the material itself, and on improving means of chemically bonding the material to hard tooth tissues. The composite material itself consists of (a) reinforcing filler, (b) polymethacrylate monomers, (c) stabilizers, (d) tertiary aromatic amine polymerization accelerators, and other necessary additives.

Improvement, if not perfection, of composite dental materials is incumbent upon the Dental Research Section since it was primarily responsible for the invention and development of this kind of restorative material. According to the latest estimate, something like 250 million of these restorations have been placed, about 50% of all esthetic restorations.

(a) A necessary requirement of the reinforcing filler particles is that they match the refractive index of the polymeric matrix rather closely, and a desirable feature is that they contribute to the composite material sufficient x-ray opacity for radiographic diagnosis of secondary or underlying decay should this occur. Consequently, during this period, a glass formulation containing 16.5 mole percent (31.9 wt.%) barium oxide as the constituent contributing both the x-ray opacity and a predicted refractive index that is desired for this application (n_D about 1.548) was ordered and obtained from a commercial company. The formulation, developed here and described in previous reports, theoretically takes advantage of the "aluminoborate anomaly" that should give minimal coefficient of thermal expansion. Preliminary studies of methods of silane treatment and composite preparation were made.

A manuscript describing "A New Series of X-Ray-Opaque Reinforcing Fillers for Composite Materials" was submitted to the Journal of Dental Research.

A project was initiated to determine the feasibility of making a composite material with a metal powder reinforcement. It is possible that the malleability of the metal reinforcing filler would result in a composite with greater resistance to wear and attrition than the present glass-filled composites. Various metals will be used and initial testing will be to determine if the metals can be bonded to the resin matrix with appropriate coupling agents. If such bonding is successful, physical properties testing will be completed.

(b) The phthalate dimethacrylate monomers reported during previous periods were the subject of U. S. Patent No. 3,539,526: "Ternary Eutectic Dimethacrylate Monomer System and Restorative Dental Material Prepared Therefrom", Rafael L. Bowen, Nov. 10, 1970. Dental manufacturers have commenced to utilize these resins in some of their products.

The phthalate monomers have Π-acid characteristics; work was commenced this period on the synthesis of monomers with Π-base characteristics. (See Synthesis of Monomers with Π-base characteristics).

(c) Sterically hindered phenols are used as antioxidants and as stabilizers for monomers that polymerize by way of free radicals. 3,5-Di-t-butyl-4-hydroxybenzyl methacrylate (BHM) was synthesized. This compound was demonstrated to be an effective stabilizer that contains, in the same molecule, a methacrylate moiety capable of copolymerization in the methacrylate monomer system. This would be expected to have advantages both with respect to polymerization kinetics and also from a toxicological viewpoint since BHM or its decomposition products would become part of the polymeric network.

The manuscript describing the synthesis of BHM was approved for publication by the National Bureau of Standards (WERB).

(d) Tertiary aromatic amines such as N,N-dimethyl-p-toluidine and N,N-dimethyl-3,5-xylidine are currently used as polymerization accelerators in dental direct filling resins and in the commercial composite direct filling materials. Since the lower-molecular-weight aromatic amines are capable of skin penetration and are systemically poisonous, it is conceivable that they might contribute to the pulpal irritation that is currently being reported by various investigators.

Hence, novel tertiary aromatic amines were synthesized, having high molecular weights. The latest of these N,N-Bis(3-p-n-butylphenoxy-2-hydroxypropyl)-p-n-butylaniline, a white crystalline solid (m.p. 98-103°C) was prepared by custom synthesis by a chemical supply company. This and other similar amines, prepared in the Dental Research Section previously are currently being evaluated.

A manuscript entitled, "Tertiary Aromatic Amine Accelerators with Molecular Weights Above 400", describing these compounds has been accepted for publication in the Journal of Dental Research.

These amines are examples of a more general scheme to provide the required ingredients with optimum functionality, utilizing maximum feasible molecular weights ("bulkiness") of the organic compounds so as to minimize undesired tissue penetration and untoward side effects in biomaterials formulations.

A summer student was trained in the procedures of testing adhesion between dental materials and hard tooth tissues. He is helping evaluate surface-active coupling agents, synthesized during previous periods. One compound, NPG-CGE (the addition product of N-phenylglycine and p-chlorophenyl glycidyl ether) was compared with NPG-GMA (the reaction product of N-phenylglycine and glycidyl methacrylate) for relative efficacy in mediating adhesive bonding. The purpose of this comparison was to evaluate the relative importance of dispersion-force interactions versus copolymerization between such primers and polymeric materials. These two compounds were comparable (within the precision of the test method) and appeared to give significantly stronger bonds compared with the controls (no coupling agents).

As a prototype of adhesive varnishes or lacquers, a compound derived from the diglycidyl ether of bisphenol A and N-phenylglycine was prepared.

This compound has two of the monovalent, tridentate chelate moieties on the same molecule (in contrast to the compounds mentioned in the previous paragraph which have only one such chelate group). Preliminary adhesion tests were encouraging. Subsequent compounds in this series will have more than two such chelate groups and will have higher molecular weights, increasing until solubility limitations are encountered.

To obtain increased information on adhesive bonding mechanisms so as to obtain improved adhesion of the restorative and preventive materials to the hard tooth tissues, preliminary or exploratory attempts were made to synthesize eight new organic compounds. These included a methacrylate monomer containing a urethane moiety, as a model compound to study the mechanism of adhesion in polyurethanes, and various methacrylate monomers, each containing a free carboxyl group, for the continuing study of surface active comonomers. One methacrylate monomer contains an amine-BF_3 complex, for possible use in preventive dentistry.

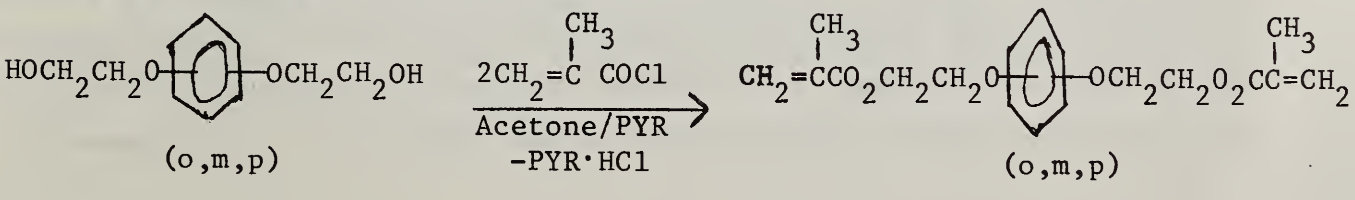
4.12. Synthesis of Monomers with Π-Base Characteristics

Sponsor: NIDR

Previously, it had been shown that the isomeric crystalline dimethacrylate monomers derived from 2-hydroxyethyl methacrylate and the corresponding acid chlorides of phthalic, isophthalic and terephthalic acid, respectively, formed a ternary eutectic that is a liquid at room temperature.

Although this colorless, slightly viscous liquid appears to offer many advantages as a binder material for composites, it does suffer from the fact that one or more of the isomeric monomers forms a yellow charge transfer complex with tertiary amines (frequently used as polymerization accelerators for such systems).

A way to circumvent the charge transfer complex problem is to employ similar isomeric crystalline monomers that possess diminished Π-acid character. Three such monomers should be the bis(2-methacryloxyethyl) ethers of hydroquinone, resorcinol and catechol, respectively. These may be prepared by the following reaction scheme:



Thus far, both the para isomer, bis(2-methacryloxyethyl) ether of hydroquinone and the meta isomer, bis(2-methacryloxyethyl) ether of resorcinol have been successfully synthesized by this procedure. The para isomer appears to have a melting point of 69-70°, whereas the meta isomer has a melting point just above room temperature (m.p. 31-33°C). In view of the favorable melting point relationship of the para/meta isomers, it may be possible to prepare a liquid binary eutectic by the proper admixture of the two isomers. If this is not possible, then the ortho isomer derived from catechol will be synthesized and, hopefully, a liquid ternary eutectic of the three isomers may be prepared.

4.13. Three-Dimensional Panoramic Dental X-Ray

Sponsor: ADA, NIDR

Various modifications to the original panoramic x-ray unit are being made to make the best possible stereo pair. An improved viewing device is being developed to observe the results of the changes on the depth of field in individual roentgenographs and the effect this has on the stereo viewing.

Associated with the viewing device is the design and construction of the camera (the film carrier and image former). This will begin as soon as the best system of optical grid or lenticular plate is selected. This system will form the image on the film emulsion from the intensifying screen. The thin lines formed on the film will be viewed through the lenticular grid or plate to give some spatial relationship or stereo effect.

4.14. Correlation of Dimensional Change on Hardening in Amalgam Restorations with Marginal Leakage

Sponsor: ADA

The laboratory phase of the project continues as the quantity of space is being determined between the tooth and the various dental amalgams being used. Clinical restoratives are being placed to correlate laboratory findings and long term clinical experience (3-5 yrs.). The various alloys being used include those with extreme (60 μm/cm) dimensional change during hardening and two commonly used alloys, Spheralloy and Dispersalloy.

Also, we have begun laboratory testing of a recently developed alloy with 10% gold as a replacement for a portion of the silver in dental amalgams. Should this material give satisfactory tensile and compressive strengths and acceptable dimensional changes during hardening, then it will be included in the clinical testing program.

4.15. Clinical Research

Sponsor: ADA, NIDR (Grant)

Clinical evaluations of the composite restorative materials, the effects of the adhesion-promoting coupling agent (NPG-GMA), and of various methods of polishing composite materials have been continuing.

Sixty amalgam restorations have been placed in the investigation of the correlation between dimensional change on hardening of five amalgam types and clinical and laboratory (air pressure) observation of marginal leakage.

4.16. Specifications and Related Activities

Sponsor: ADA

A re-examination was made of the physical property tests currently prescribed in ADA Specification No. 1 for alloy for dental amalgam. Five currently approved alloys were subjected to the tests in order to evaluate the test methods. This is part of a series of tests on which to base recommendations for future revisions.

A draft of the revised Denture Base specification was re-written, incorporating the comments received by "all interested parties". Completion of this specification will require acquisition of data on the properties of pour-type resins and a study of the substitution of alginates for tin foil in processing.

G. C. Paffenbarger attended meetings of two Joint FDI-ISO Working Groups (Secretary), two sessions of ISO/TC 106 Working Group 3, and the Plenary Session of the International Standards Organization Technical Committee 106 for Dentistry, June 6-11, Munich, Germany.

G. C. Paffenbarger presided as chairman of the FDI Commission on Dental Materials, Instruments, Equipment and Therapeutics, June 16.

4.17. Fiftieth Anniversary Symposium Proceedings

Sponsor: ADA

Twenty-four of the papers presented at the Symposium have been edited and turned in to the NBS publications section for preparation of the bound copy of the written proceedings of the symposium.