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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1970

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 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. During this report period, funding support was also provided by the Research and Education Foundation of the American Dental Association.

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U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS



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NBS Report 19272	Development of a Radiopaque Denture Base Material.
NBS Report 10273	Physical Properties of a Radiopaque Denture Base Material.
NBS Report 10274	Radiopaque Denture Base Materials - Technic Dentures.
NBS Report 10275	Heats of Adsorption of Ammonia and Carbon Dioxide on Tooth Components.
NBS Report 10276	The Crystal Structure of the Aragonite Phase of CaCO_3 .
NBS Report 10277	Tertiary Aromatic Amine Accelerators with Molecular Weights Above 400.
NBS Report 10278	A Method for Finishing Composite Restorative Materials.
NBS Report 10294	Mechanical Properties - Viscoelastic Methods. Part I - Creep, Relaxation and Stress-Strain Methods.



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, 1970 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 Institutes 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 10271 Aggregation Phenomena of Collagen.
- NBS Report 10272 Development of a Radiopaque Denture Base Material.
- NBS Report 10273 Physical Properties of a Radiopaque Denture Base Material.
- NBS Report 10274 Radiopaque Denture Base Materials - Technic Dentures.
- NBS Report 10275 Heats of Adsorption of Ammonia and Carbon Dioxide on Tooth Components.

- NBS Report 10276 The Crystal Structure of the Aragonite Phase of CaCO_3 .
- NBS Report 10277 Tertiary Aromatic Amine Accelerators with Molecular Weights Above 400.
- NBS Report 10278 A Method for Finishing Composite Restorative Materials.
- NBS Report 10294 Mechanical Properties - Viscoelastic Methods. Part I - Creep, Relaxation and Stress-Strain Methods.

3. PAPERS PUBLISHED

- Moreno, E. C.; Patel, P. R.; and Brown, W. E. Isothermal Diffusion in the Dilute Range of the System $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$: Theory. J. Res. NBS (Physics & Chemistry) 74A, No. 1:55-63, January-February 1970.
- Blaugher, R. D.; Hein, R. E.; Cox, J. E.; and Waterstrat, R. M. Atomic Ordering and Superconductivity in Al5 Compounds. J. of Low Temp. Physics 1:539-561, No. 6, December 1969.
- Dickens, B. and Brown, W. E. The Crystal Structure of Calcium Carbonate Hexahydrate at $\sim -120^\circ$. Inorganic Chemistry #3, 9:480-486, March 1970.
- Brauer, G. M.; Termini, D. J.; and Burns, C. L. Characterization of Components of Dental Materials and Components of Tooth Structure by Differential Thermal Analysis. J. Dent. Res. 49:100-110, No. 1, January-February 1970.
- Brauer, G. M. Pyrolysis-Gas Chromatographic Techniques for Polymer Identification. Techniques and Methods of Polymer Evaluation, Vol. II entitled Thermal Characterization Techniques, pages 41-105, Ed. P. E. Slade and L. T. Jenkins, Marcel Dekker, N. Y., Publisher, 1970.

4. WORK IN PROGRESS

4.1. Determination of Crystal Structures

Sponsor: NIDR, NIDR (Grant), ADA

The objectives of the crystallographic studies are to increase our understanding of ionic arrangements and to provide us with structural experience, so that models can be postulated for (a) groups of ions present in aqueous solution, (b) phenomena important in nucleation and crystal growth from aqueous solution, and (c) the incorporation of 'defects', impurities, vacancies and nonstoichiometry into tooth and bone mineral.

Automatic X-ray Diffraction:

A magnetic disc for the rapid storage and retrieval of computer programs and associated data has been added to the computer-automated Picker X-ray single-crystal diffractometer. Programs are now kept on the disc and the error-prone and time-consuming process of reading these programs from paper tape has been by-passed. An improved version of the operating programs has been received from Dr. Galen Lenhert of Vanderbilt University and will be tried out soon. This is another step towards more automatic operation.

Crystal Structure:

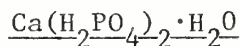
Aragonite, CaCO_3

The crystal structure of aragonite, an important biomineral, has been refined to $R_w = 0.024$ using new X-ray data collected from an irregularly shaped fragment. Absorption corrections were applied using the recently written absorption program. The general features of the aragonite structure were already well known. The new refinement reveals that the CO_3 group appears to be slightly non-trigonal with O-C-O angles of $119.62(4)^\circ$, $120.13(8)^\circ$ and $120.13(8)^\circ$ and C-O distances of $1.288(2) \text{ \AA}$, $1.283(2) \text{ \AA}$ and $1.283(2) \text{ \AA}$.

$\text{BaCa}(\text{CO}_3)_2$ (alstonite phase)

The crystal structure of the barytocalcite phase of $\text{BaCa}(\text{CO}_3)_2$ was included in the report July-December 1969. Work on the chemically related phase, alstonite, of $\text{BaCa}(\text{CO}_3)_2$ has been started. Thus far, the progress has been good. The fact that the monoclinic unit cell of

alstonite $\underline{a} = 30.163(9)\text{\AA}$, $\underline{b} = 17.413(5)\text{\AA}$, $\underline{c} = 6.110(1)\text{\AA}$, $\beta = 89.91(1)^\circ$ is essentially rectilinear makes twinning very likely. Most samples of alstonite are twinned; an apparently untwinned crystal was used to collect the X-ray data. The least squares refinement showed that β is significantly different from 90° . The cation positions in alstonite have been located although the identities of one or two have not been resolved definitely at this time. The cation positions in alstonite, as was suspected, are related to those in aragonite. Work is still in progress.

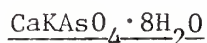


The structure of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ contains corrugated sheets, made up of $\text{Ca} \dots \text{PO}_4$ chains, as do the structures of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)\text{Cl} \cdot \text{H}_2\text{O}$ and several other related compounds. The existence of this structural feature in several compounds speaks for its stability. Interlayering between these compounds could account for variability in stoichiometry.

Two sets of workers have published papers on the structure of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, but the fine details of the structure and the positions of the hydrogen atoms were not known, although positions for the latter and a hydrogen bonding scheme had been suggested. We have collected new X-ray data from a plate-shaped single crystal of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and these data were corrected for absorption. Refinements revealed the fine details of the structure, and decreased the previously published standard deviations by a factor of 10. The hydrogen atoms were located, and their positions were corroborated by the fine structural details. Part of the hydrogen bonding scheme reported in the literature was shown to be incorrect.

The previously reported close approach $0(1) \dots 0(1')$, $2.67(5) \text{\AA}$ across a center of symmetry, has now been shown to be $2.855(3) \text{\AA}$. Since this is greater than the sum, 2.75\AA , of the van der Waals radii of the two oxygens, no attractive force between the two atoms needs be postulated and, in particular, there is no need for a hydrogen to be disordered about the center of symmetry in a hydrogen bond $0(1) - \text{H} \dots 0(1')$. The hydrogen bonding scheme is now $0(3) - \text{H} \dots 0(5)$, $0(4) - \text{H}(2) \dots 0(9)$, $0(6) - \text{H}(3) \dots 0(8)$, $0(7) - \text{H}(4) \dots 0(8)$, $0(9) - \text{H}(5) \dots 0(8)$ and $0(9) - \text{H}(6) \dots 0(6,7)$.

Two unusual features in this scheme, which is supported by the P-O distances, the O...O distances and the Fourier electron density difference synthesis, are (1) the formation of three hydrogen bonds to one oxygen atom, O(8), and (2) a bifurcated hydrogen bond from hydrogen atom H(6), on the water oxygen O(9), simultaneously to oxygens O(6) and O(7) in different phosphate groups. The present hydrogen bonding scheme is less complex than the previously suggested one.



The crystal structure of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ has been determined from a plate-shaped single crystal and has been refined to $R_w = 0.045$. The data were corrected for absorption. The compound was previously thought to be $\text{CaKAsO}_4 \cdot 7\text{H}_2\text{O}$, but the suggestion by the X-ray analysis of eight waters of hydration was confirmed in a thermogravimetric experiment. The crystal was thought by us to be one where it was likely that the Ca ion would be completely hydrated, and this turned out to be the case. No other example is known at the present time. The overall structural arrangement has a strong resemblance to that of the bio-mineral $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite), although the details are different in the two cases. The existence of the compounds $\text{CaKAsO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MgKH}(\text{PO}_4)_2 \cdot 15\text{H}_2\text{O}$, which have unit cells related to the unit cells of $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, suggests that this structural type may be wide spread and important. The fact that the relatively large K ion is also completely hydrated in the $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$ structure gives some idea of the stability of the overall structural arrangement.

Computer Programs:

A computer program to correct X-ray intensities for the absorption

of the X-ray beam by the crystal has been written using subroutines adapted from a program written by C. W. Burnham of Harvard University. This program has been used to correct the intensities of the X-ray reflections of aragonite, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{CaKAsO}_4 \cdot 8\text{H}_2\text{O}$. The collection of data from the very important compound $\text{Ca}_8\text{H}_2\text{PO}_4 \cdot 5\text{H}_2\text{O}$, octacalcium phosphate, is now feasible, since it will be necessary to correct these data for considerable absorption. For the absorption correction program, the shape of the crystal must be expressed by giving the coordinates in three dimensions of three points, usually the corners of the crystal, for each of the limiting planes (assumed to be planar) which define the outside of the crystal. A program to check whether the planes specified are indeed on the outside of the crystal has been written and is now being used routinely. Some crystal shapes involve nearly parallel planes which are difficult to separate by other methods.

4.2. Physicochemical Studies of Apatite and Related Inorganic Substances

Sponsor: NIDR (Grant), ADA

4.2.1. Crystal Growth

A major goal of research on tooth and bone mineral for many years has been the growth of larger and purer hydroxyapatite crystals so that more powerful physical methods can be employed in the study of their properties. A major step was made during the report period when a new method was developed for controlled growth of hydroxyapatite crystals.

The procedure is based on the fact that in the ternary system, $\text{Ca}(\text{OH})_2\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$, at a given temperature and pressure, a solution saturated with respect to two calcium phosphates has a fixed composition. The conversion of an acid calcium phosphate (e.g., CaHPO_4) into a more basic calcium phosphate (e.g., $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) can be effected by slowly titrating a mixture of the two solids with water. The yield is fixed entirely by the Ca/P ratio in the solution. For the two salts listed above, since the Ca/P ratio for the singular point is about 1/2, the yield is about 3 moles of PO_4 , as $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, for each 7 moles of CaHPO_4 used in the hydrolysis reaction. The major advantages of this

procedure are its simplicity, good yields, precise control of conditions, avoidance of conditions of local supersaturation and the ability to continue the crystal growth indefinitely.

The properties of the hydroxyapatite crystals produced by this technic more nearly resemble those in enamel than do the crystals that have been obtained heretofore at higher temperatures. They should prove to be of great value, therefore, in providing information on how the imperfect crystals in tooth and bone deviate from the more nearly ideal crystals that are formed at higher temperatures. In particular, the hydroxyapatite crystals produced thus far are fibrous bundles, often exceeding 100 μ in length. They apparently are the longest hydroxyapatite crystals that have been grown at atmospheric pressure. These bundles display anomalous optical properties, appearing optically positive in water media and optically negative in index of refraction oils. The thicker crystals lose the anomalous optical character, indicating that the abnormal optical properties relate to form birefringence. Differences in form birefringence, known to be present in carious vs. non-carious enamel, can be evaluated more readily through the use of crystals synthesized by the above procedure.

The procedure has also been used to prepare octacalcium phosphate. Previous efforts to measure the solubility of this salt have failed because of the instability of the octacalcium phosphate, which caused it to hydrolyze during equilibrium, and because of our inability to make a preparation free of impurities. The new procedure appears to have overcome both of these difficulties, and we are optimistic that our renewed efforts to measure the solubility of this compound will be successful.

4.2.2. Solubilities of Calcium Phosphates

(a) Solubilities of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the presence of NaCl:

In the previous report, it was mentioned that solubility studies of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were being extended to include sodium chloride as an additional component to the ternary system $\text{Ca}(\text{OH})_2$ - H_3PO_4 - H_2O employed previously. The objective is to test the applicability of the solubility-product equations to more concentrated solutions resembling biological fluids. A series of solubility data for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ has

been obtained in the pH range of 4.3 to 6.8. Solubility product constants for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were calculated with the Debye-Hückel equation (without a linear correction term) for calculating activity coefficients. Because this equation is only useful for ionic strength values below 0.1, we did not expect to obtain K_{sp} values independent of ionic strength. Instead, a linear relationship was revealed between $\text{p}K_{\text{sp}}$ and the ionic strength (for ionic strengths in the range 0.05 to 0.59); the value of $\text{p}K_{\text{sp}}$ extrapolated to zero ionic strength was 6.599 and compares well with the thermodynamic $\text{p}K_{\text{sp}}$ value 6.592 reported previously by this laboratory for $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in systems which did not contain NaCl. When a linear correction term containing a parameter obtained from the least squares regression of this line was included in the Debye-Hückel equation, the new set of calculated $\text{p}K_{\text{sp}}$ values did not vary with ionic strength. It remains to be determined if the Debye-Hückel equation with this linear correction term will be applicable for calculating accurate activity coefficients of other calcium phosphates and in other solutions, including those of biological origin, having ionic strength values in the range 0.1 to 0.5.

(b) Solubility of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in more basic solutions:

$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ is known to hydrolyze into more basic calcium phosphates (octacalcium phosphate and hydroxyapatite) above about pH 6.4. It should be possible to avoid this hydrolysis through use of a growth poison which would inhibit formation of the more basic calcium phosphates. The growth inhibitor (disodium ethane-1-hydroxy-1, 1-diphosphonate) for hydroxyapatite reported in the literature is being tested. If this method proves to be successful in preventing this hydrolysis, then it should be possible to study the solubility of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ in the basic pH ranges and thus would allow determination of stability constant of the ion pair $(\text{CaPO}_4)^-$.

(c) Solubility of human tooth enamel:

The work carried out in the past few years has shown that it is now possible to measure reliably the solubility of synthetic hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. We have initiated a project in which we are trying to determine the suitability of these techniques for the study of powdered samples of human tooth enamel. If this project is

successful, it would be the first time that reliable solubility measurements would have been made on a calcified tissue. The knowledge gained from this work will be valuable in interpretation of the topical fluoride experiments and should be of great value in establishing distinguishing characteristics between enamel varying in caries resistance.

Preliminary experiments have been carried out with a powdered enamel sample which contained some dentin. The ion-activity products derived from the results indicate that this sample contained appreciable amounts of calcium phosphate more soluble than the pure, crystalline $\text{Ca}_5(\text{PO}_4)_6\text{OH}$ used in our previous solubility measurements. In an equilibration with a pH value of about 4.8, large crystals of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ were observed. In synthetic mineral systems the invariant point between $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{Ca})_5(\text{PO}_4)_3\text{OH}$ is at about pH 4.3, again showing that the tooth mineral contained a fraction more soluble than synthetic $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.

We are in the process of collecting enamel samples completely free of dentin to eliminate the possibility that dentin is the cause of the greater solubility. To achieve this, it is necessary to follow a laborious procedure. Freshly extracted teeth stored in water containing antibacterial agents are cut to remove the roots and then the dentin portion is carefully drilled out using dental burrs of various sizes to reach all the crevices. After enough enamel crowns are collected, they will be pulverized to a fine powder in a Wiley Mill. Precaution will be taken to cool the material with liquid nitrogen while pulverizing so that undue irreversible chemical damage is not done to the enamel materials. Material derived from carious teeth is kept separate from that of non-carious teeth. Processing of teeth for this purpose is nearly completed, and it is expected that the equilibration can be started soon.

4.2.3. Generalized Least Squares Calculations

While collecting solubility data on the compounds $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, CaHPO_4 , $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\beta\text{-Ca}_3(\text{PO}_4)_2$, we have been developing an adjustment procedure for statistically treating the data which would give the most reliable values for the derived constants, would realistically assess the errors in these constants, and would explicitly take into account the chemical model used to describe the system. We believe this procedure

has great merit for treating physicochemical data and warrants widespread use. As the solubility data for each of the above compounds became available, the set of data was processed by this procedure. Separate treatment of the data does not, however, give a test of possible inconsistencies between sets. We have, therefore, modified the procedure to permit processing of the combined data. At the same time, we are re-evaluating the data on the dissociation constants of H_3PO_4 since these constants are basic to treatment of the solubility data. These data on the dissociation constants of H_3PO_4 are considered to be highly precise, but the chemical models used in describing the systems differed somewhat from ours and the data were treated by procedures less powerful than the one discussed above. Recognizing that any procedure for treating data on ionic solutions involves arbitrary assumptions and somewhat unrealistic models, we are trying to achieve maximum internal consistency by treating the combined solubility data and by re-evaluating the dissociation constants for H_3PO_4 .

Provisional results have been obtained from the combined data on $CaHPO_4 \cdot 2H_2O$ (DCPD), $CaHPO_4$ (DCPA), β - $Ca_3(PO_4)_2$ (TCP), and two preparations of hydroxyapatite, $Ca_5OH(PO_4)_3$, HA-1 and HA-2, the first of which had been heat-treated prior to the solubility study. The association constants K_x and K_y for the species $[CaHPO_4^\circ]$ and $[CaH_2PO_4^+]$ were included in the calculation scheme. The input is summarized in the following table:

Compound	No. of Systems and Condition Functions		Experimental Temperatures °C	Adj. Parameters in log K (A + B/T + CT)
	2 C.F.	3 C.F.		
DCPD		35	5, 15, 25, 37.5	3
DCPA	11	46	5, 15, 25, 37	3
TCP		35	5, 15, 25, 37	3
HA-1	8	27	5, 15, 25, 37	3
HA-2		10	25	1
Sub-totals	19	153		13
$[CaHPO_4^\circ]$				3
$[CaH_2PO_4^+]$				3
Totals		172		19

The results may be stated; (1) K_y exhibits a maximum near 15° , whereas previous calculations on DCPD alone produced a monotonic decrease; (2) the maxima in the K_{sp} 's of DCPD and TCP, and the minimum in K_x , all of which occur between 15 and 25° , were confirmed; (3) the monotonic decrease in K_{sp} (DCPA) was confirmed; (4) for the heat-treated apatite, HA-1, K_{sp} decreased monotonically with temperature; and (5) the second apatite preparation, HA-2, appears to be slightly more soluble at 25° than HA-1. It is expected that additional data on DCPA and on a steam-heated apatite will be included in the final calculation.

The data on dissociation constants of H_3PO_4 , obtained by Bates and Acree (1943 and 1945) with the Ag/AgCl electrode, and those of Grzybowski (1958) with the calomel electrode, have been re-evaluated. Although only the customary single condition function per system was imposed, the present calculations are novel in the following respects: (1) the relatively small errors in the salt solution concentrations were incorporated in the treatment; (2) the resulting non-identity covariance matrix for the EMF measurements made on a single solution at a series of temperatures was made explicit in the calculations; (3) the "distance of closest approach" parameter, \hat{a} , was treated as an adjustable parameter for the first time, so that a least-squares estimate could be obtained. Its value was arbitrarily represented in these calculations by the equation $\log \hat{a} = A + B/T$, with A and B adjustable. It should be mentioned that the "observed" pK_2' values are actually functions of this parameter; and (4) the customary smoothing function, $pK_2^\circ = A + B/T + CT$, has heretofore provided merely a least-squares estimate of the best curve through the final set of pK_2° 's. In the present calculations, the parameters A, B, and C were estimated directly as a part of the adjustment procedure applied to the raw data.

The results to date are as follows: (1) the parameter \hat{a} has been satisfactorily determined as a temperature-dependent constant. The numerical values are comparable to those previously estimated by graphical means. A more precise estimate of its errors at the several temperatures is now available; and (2) the final smoothed values of pK_2° are quite similar to the previous results, but there is a marked difference in the distribution of the individual points. Whereas the individual

pK_2° values at each temperature, as determined by the previous investigators, tend to cluster uniformly about the average for that temperature, they are markedly skewed in distribution about the smoothed value. In contrast, the present calculations produced a fairly uniform distribution about the values given directly by the equation $pK_2^\circ = A+B/T+CT$.

4.2.4. Calorimetry and Electro-chemistry

Combined with good heat capacity measurements in the literature, the solubility data collected in these laboratories are a major step in defining the thermodynamic properties of the biologically important calcium phosphates. One of the major remaining deficiencies is the lack of accurate data on the standard heats of solution for these compounds. For example, the preferred value was obtained from a sample which undoubtedly lacked in purity because it was prepared by calcining the root of a tooth. We have undertaken a program in solution calorimetry to fill this void in the thermodynamic data on calcium phosphates.

The temperature sensing unit (the quartz thermometer) for the solution calorimeter has been received and extensively tested for accuracy and stability. Minor circuit modifications have successfully reduced short-term temperature drift and improved the precision to a very satisfactory level.

Delays in the shipment of other components of the solution calorimeter have slowed progress in the program; however, completion of the calorimeter is anticipated in the near future.

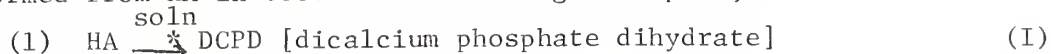
The Bureau's Thermochemistry Section has invited us to participate in a cooperative program. Their interest and cooperation, together with their extensive and highly specialized facilities, are expected to considerably enhance our capabilities and progress in this area while minimizing equipment redundancy.

Work is continuing on the properties of the mercury-based phosphate-electrode system $Hg(1)/HgH_2PO_4$ referred to in the previous report. Results to date are incomplete.

4.2.5. Topical Fluoridation

In the last report, it was noted that the reaction of hydroxyapatite (HA) with a fluoride solution to form fluorapatite (FA) proceeds very

slowly with poor yields. As a result, the amount of F uptake after the topical F treatment is very low and the penetration of F into the enamel is extremely small (usually less than 5 μ). Thermodynamic and kinetic considerations of the HA-FA system have led to the proposal that FA may be formed from HA in tooth enamel through the path,



* A treatment solution which is saturated with respect to DCPD, but is undersaturated with respect to HA.

During the past six months, the yields and rates of these two reactions have been investigated using synthetic HA and DCPD. In accordance with equation (I), when HA was treated with a solution having an initial pH value of 1.8, the following typical results were obtained:

<u>Reaction Time (hr.)</u>	<u>DCPD in Product (wt%)</u>
1	19
4	67
7	88

Regarding equation (II), it was found that DCPD was nearly completely converted to FA in 5 hours after treatment with a solution containing only 0.54 wt%. These results on synthetic HA clearly indicate that the proposed path, as indicated in equations (I) and (II), to form FA from HA in tooth enamel, is indeed feasible.

Some preliminary studies on enamel were made using extracted human teeth. Following essentially the same procedure, the teeth were treated with the acidic solution before being exposed to the F solution. Each tooth was washed after the F treatment with 100 ml of distilled water for 24 hours. The F uptake in the outer 25 μ layer of the enamel after this treatment averaged to approximately 6,600 ppm. This value is 2 1/2 times greater than the highest F uptake that has been reported. In addition, the enamel at the 20 to 25 μ region had a sixfold increase in F as compared to the less than two-fold increase obtained by previous methods.

Currently, we are proceeding with a more systematic study on tooth enamel. In order to further decrease the time required for the treatment, a more concentrated F solution may prove beneficial. Another

important objective is to further increase the depth of F penetration. In this regard, several mechanical and chemical techniques are being investigated.

4.3. Gas and Vapor Adsorption Measurements on Dentin and Enamel; Dentinal Collagen Solubilization Studies

Sponsor: NIDR

Heats of Adsorption Project

This aspect of the surface chemistry program which dealt with the adsorption of CO_2 and NH_3 on dentin and anorganic whole teeth has been completed. It was reported in a talk given at the New York meeting of the IADR in March. It has since been written up and submitted for publication in a paper entitled "Heats of Adsorption of Ammonia and Carbon Dioxide on Tooth Components". The unusually high capacity for the adsorption of ammonia by dentin (indicating a surface area of about $160 \text{ m}^2/\text{g}$) raised the question as to what might be expected for the adsorption of methylamine, the next higher member of the homologous series. Accordingly, duplicate adsorption runs were made at zero degrees C. on dentin. The results were 86.2 and $84.7 \text{ m}^2/\text{g}$ showing good reproducibility. These values are still very high compared to nitrogen ($7.5 \text{ m}^2/\text{g}$), but slightly more than half that of ammonia.

Water Adsorption

Much fundamental knowledge can be gained from a study of the adsorption of water vapor on bone, dentin, enamel and collagen. Brunauer, et al (Hagymassy, Brunauer and Mikhail, J. Colloid and Interface Science 29, 485, 1969), have recently pointed out that there are many important adsorbents that have part of their pore systems, often the major part, inaccessible to nitrogen but accessible to water vapor. The authors go on further to say that certain clays, soils and especially biological systems, should be investigated by water adsorption. Inasmuch as the work just completed on CO_2 and NH_3 adsorption demonstrated the profound influence of polar groups on the capacity for adsorption by dentin, as well as the fact that water is the most abundant component of all biological systems, the water vapor adsorption project was initiated.

Other reasons exist for investigating the water adsorption characteristics of dental materials. Dimensional changes in dentin as a function of temperature and humidity are being investigated by Barton and Dickson of this laboratory. These studies will be aided by a thorough understanding of the water vapor adsorption-desorption isotherms together with their hysteresis effects.

A careful study was made of the various methods in practice for measuring water adsorption at room temperature. No method was considered completely satisfactory either because of the complexity of the system or because of the long time intervals required for attaining equilibrium.

A circulating closed system was finally decided upon utilizing a peristaltic type ("Sigma-Motor") pump to control the rate of circulation of air saturated with water vapor. The adsorbent was contained in a weighing tube mounted vertically with openings at each end. Ground glass caps were fitted over the openings during weighing after attainment of equilibrium at each adsorption point. Either an analytical balance or a micro balance could be used to measure the water adsorbed gravimetrically, depending upon the size of the sample and the expected changes in weight. During the adsorption process, the tube is mounted up stream from the pump and saturator with the effluent connected back to the pump to complete the circuit. All connections were made with Tygon tubing. More than a dozen gas saturators were fabricated according to the design of Bichosky and Storch (J. American Chemical Society 37, 2695, 1915). Each was filled with a different saturated salt solution and used, one at a time, to obtain the different relative humidity points that would comprise the abscissas of the resultant adsorption isotherm. Relative humidities ranged from less than 10% to greater than 97%. Approximately two days of cycling were required for attainment of equilibrium except at the higher end of the curve. Several experiments could be performed simultaneously, resulting in further economy of time. Dead volume of the system is very small compared with other systems. This, together with a minimum of dependence on diffusion, contribute appreciably to the superior performance of the apparatus.

A striking observation of the water adsorption characteristics of

collagen-containing adsorbents is the large hysteresis loops which persist over the entire range of humidities. These properties are being studied carefully in the hopes that they may throw light upon anomolous results of other investigators.

The water adsorption isotherms of dentin, disclosed a surface area of $129 \text{ m}^2/\text{g}$ in reasonably good agreement with the ammonia results of $160 \text{ m}^2/\text{g}$; but considerably different from the nitrogen adsorption areas ($7.5 \text{ m}^2/\text{g}$). These findings give credence to the statements of Brunauer et al referred to earlier regarding biological systems.

Water adsorption measurements have been made on specimens of collagen because collagen comprises approximately 50% by volume and 20% by weight of dentin. Well characterized linear collagen (rat tail tendons) was selected for the initial series of measurements. Surface areas of the order of $400 \text{ m}^2/\text{g}$ have been obtained which are in agreement with published values of hide collagen (Kanagy, J. American Leather Chemists' Assn. 45, 12, 1950). These experiments are still in progress.

Collagen Extraction

Some preliminary experiments for the solubilization of collagen from tissues in which it is normally insoluble have been performed based on a suggested procedure described by Veis and Katz (Biochem. Biophys. Acta 22, 96, 1956). It involves the use of NH_4SCN saturated solution in liquid ammonia. This procedure appears to hold promise for the extraction of dentinal collagen. A fluffy precipitate has been isolated which resembles other collagen preparations. The procedure may have further possibilities if the undissolved dentin can be completely rid of its collagenous component in that preparations of anorganic samples would then be possible without requiring heating above room temperature.

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

4.4.1. Dimensional Changes in Teeth Components

Sponsor: NIDR, USAF, VA, REF (ADA)

Studies of the thermal and hygroscopic dimensional changes of human tooth structure have continued with particular emphasis on the time dependent dimensional changes in dentin. As indicated previously,

when dentin is heated to temperatures above about 35°C, there is an "immediate" expansion followed by a delayed contraction, and on cooling from elevated temperatures an "immediate" contraction is followed by a delayed expansion. Results so far are consistent with the hypothesis that the "immediate" dimensional changes are produced by the mineral portion of the dentin while the delayed effects are produced by the collagen content. The results suggest that the structure of dentin is such that the tensile stresses produced by the longitudinal shrinkages of the collagen on melting produce a bulk shrinkage of the dentin.

The dimensional changes which occur in enamel and dentin equilibrated at different relative humidities were determined using the interferometer. The dimensional change of dentin when changing the relative humidity from 10 to 40% is considerably larger than that observed on changing from 40 to 80%. These changes, significantly larger than those induced thermally are presumed to relate to the moisture gain by the dentin specimen. Comparison of the dimensional changes of whole dentin, anorganic dentin and enamel indicates that the hygroscopic dimensional changes depend on collagen content.

The measurements of the thermal expansion of tooth structure have been made using an interferometer which presents some difficulties since the specimen and the interferometer must be in water to prevent drying out of the tooth specimen. To overcome these difficulties, a miniature fused-quartz dilatometer has been designed and built. Preliminary testing of small samples of tooth structure using the miniature quartz tube dilatometer show similar results are obtained with greater ease than when using the interferometer technique. No interference due to accumulation of air bubbles has been observed using this procedure. Automatic recording of the dimensional change and temperature is an improvement over visually counting fringes with the interferometer. With additional refinements now being made on the fused-quartz dilatometer, it is hoped that specimen size can be further reduced so that the effect of enamel rod and dentinal tubule orientation on the thermal expansion of tooth structure can be determined.

Investigations of the dimensional changes of extracted dentinal

collagen and X-ray diffraction studies of collagen in dentin are planned to determine whether or not melting of the collagen does occur at the temperatures at which the delayed thermal dimensional changes are observed. Shear moduli and internal friction measurements of dentin by means of a torsion pendulum are also being made for comparison with the dimensional change data.

4.4.2. Physical Properties of Soft Tissues

Sponsor: NIDR, VA, REF (ADA)

Investigations of the mechanical behavior of skin were carried out with a rocking-beam oscillator as proposed on the basis of preliminary studies mentioned in the previous report. An improved rocking-beam oscillator was designed and built. The beam of the oscillator carries a force transducer from which the specimen of skin is supported in any medium of interest. To reduce friction, mercury contacts are used to make electrical connections to the transducer. Means of accommodating various specimen lengths and for adjusting static (rest position) force on the specimen are provided. A displacement transducer (LVDT) attached to the beam support is used to measure the amplitude of vibration (changes in strain) of the specimen during oscillation. The rocking beam is driven by the variable frequency, constant amplitude sine wave output from a function generator, and a curve showing frequency versus strain amplitude is obtained for the specimen. From these data, the real and imaginary parts of the modulus, E_1 and E_2 are calculated from the following equations:

$$E_1 = \frac{4\pi^2 \ell m}{A} \left(f_r^2 + \frac{(\Delta f)^2}{2} \right) \quad E_2 = \frac{4\pi^2 \ell m}{A} (f_r \Delta f)$$

where

ℓ = specimen length

A = specimen cross sectional area

m = effective mass of beam

f_r = resonance frequency

Δf = band width (difference between frequencies for which the amplitude has $\frac{1}{\sqrt{2}}$ times its maximum value)

The energy loss or internal friction, Q^{-1} , of the specimen is determined from either the band width or the rate of decay of the

amplitude of vibration of the beam when the system is allowed to vibrate freely by means of the following equations:

$$Q^{-1} = \frac{\Delta f}{f_r} \qquad Q^{-1} = \frac{1}{n\pi} \ln \frac{A_0}{A_1}$$

where A_0 and A_1 represent amplitudes of vibration.

Measurements on several specimens of rat skin over a stress range of approximately 20,000 to 140,000 N/m² (3 to 20 psi) indicate that the real part of the modulus can be represented by an equation of the form, $E_1 = k\sigma + I$, where k and I are constants and σ is the tensile stress. Data for the specimens investigated gave values of approximately 140 for k and 41,000 N/m² (300 psi) for I . Results so far have not shown any significant differences in E_1 between back and stomach skin for male rats or between male and female rat skin.

Data for the imaginary part of the modulus have not been studied in detail, but it appears that they may be represented by an equation of the form:

$$E_2 = A\sigma^2 + B\sigma + C.$$

Although no significant difference in E_1 was observed for the different specimens of skin, the data obtained so far suggest that the value of Q^{-1} for female rat skin may be 1/3 to 1/2 higher than that for male skin. This observation is subject to future confirmation since it is based on a limited number of specimens with a rather high scatter in Q^{-1} values.

After sufficient data have been obtained at room temperature, measurements will be made at various temperatures to determine effects of temperature on mechanical behavior. Plans for development of a vibrating tuning fork apparatus for observation of shear characteristics of skin are continuing. Also, the possibility of making measurements on human skin in vivo by means of sonic wave propagation is being studied.

4.5. Dental Metallurgical Studies

Sponsor: ADA, NIDR (Grant)

Our previous work on the binary V-Pt phase diagram has confirmed the existence of an ordered intermediate phase at the composition V₅₀Pt₅₀,

but the exact origin of this compound at high temperatures was not established. The crystal structure of this compound was found to be that of an orthorhombic B19 or AuCd type and it was observed to grow as thin ribbons in the face-centered cubic platinum solid solution (our previous report erroneously reported its formation in the body-centered cubic vanadium solid solution). The formation of thin ribbons aligned along certain crystallographic planes in the face-centered cubic platinum solid solution suggests interesting possibilities of improving the strength of these alloys by fiber-reinforcement. It is important, however, to establish the maximum temperature at which the phase $V_{50}Pt_{50}$ will form and we were unable to do this by conventional quenching and microscopic or X-ray diffraction studies due to our inability to retain the phase which is stable at higher temperatures.

The phase $V_{50}Pt_{50}$ is now believed to form by an order-disorder reaction and we have obtained measurements of its thermal expansion as a function of temperature which indicate a transformation temperature of about $1500 \pm 10^\circ\text{C}$. A special high temperature dilatometer was necessary for these measurements and this was made available at the Westinghouse Research Laboratories. A volume expansion of about 0.5% was observed as the specimen was heated through the transition temperature. More work is needed to establish the optimum conditions for possible fiber-reinforcement in the V-Pt alloys.

The phase diagram for the Cr-Ir alloy system is now essentially complete and work is proceeding on the Cr-Rh alloy system. These two systems can be considered as analogues of the Cr-Co alloys since Ir and Rh are located below Co in the periodic table and may therefore be expected to exhibit similar alloying behavior. In each of these systems one observes extensive solid solutions based on the face-centered cubic and hexagonal close-packed crystal structures. The relative amounts of these two phases in an alloy has a pronounced effect on its strength and ductility. The composition range of stability for these phases is now accurately defined in each of these binary systems. We have also observed that additions of Rh to Cr substantially lower the melting temperature to the neighborhood of 1400°C . This observation is encouraging for the development of casting alloys since one would like to obtain melting

temperatures which are equal to or less than those now being used in the base-metal casting alloys ($\sim 1500^{\circ}\text{C}$). Rhodium additions may therefore be considered for imparting desirable properties to Co-Cr casting alloys since Rh is unlikely to produce undesirable corrosion or toxicity effects and may in fact yield an alloy having a lower casting temperature and a reduced reaction with the investment mold. Co is known to react chemically with investment materials during casting and, therefore, replacing Co with Rh may tend to reduce the extent of such reactions while at the same time retaining many desirable mechanical properties. Further work on this interesting alloy system is now in progress.

4.6. Dental Investment Studies

Sponsor: ADA

Two reports have been completed on the petrographic study of investments used for high-fusing cobalt-chromium base alloys. These are entitled "The Petrography of a High-Fired Phosphate-Bonded Investment" and "The Petrography of Silica-Bonded Investments". These studies provide, for the first time, information about the chemical reactions occurring in various micro-environments during the burnout and casting processes, which is basic to improving investment-casting technics.

Burnout reactions are promoted by fluxing agents present in the investment such as small amounts of chloride, sulfate sodium, zinc oxide, etc. In addition, constituents of the quartz-sand component of the investment powder, such as ilmenite, clay and various ferruginous minerals, aid in the fluxing. Calcined magnesite additions are also important fluxing agents, particularly in the later stages, and aid in the generation of investment bonds having hot strength.

Some of the more important burnout reactions in phosphate-bonded investments with spathic (ferruginous) dead-burned magnesite additions, with casting-mold temperatures up to 920 to 1000 $^{\circ}\text{C}$, are as follows:

(1) Reactions between silica grains (quartz and cristobalite) and interstitial phosphate are promoted by the various fluxing agents, and at casting-mold temperatures yield recrystallized silica bonds of tridymite, quartz and a densely dendritic vitreous silico-phosphate phase.

(2) Free lime present in the deadburned magnesite probably induces

micro-environmental liquefaction in phosphate-bonded investments at temperatures as low as 500°C.

(3) MgO is removed from encapsulating monticellite (CaMgSiO_4) in the dead-burned magnesite driving reactions toward wollastonite, thus forming compounds intermediate in composition between wollastonite (CaSiO_3) and akermanite ($\text{Ca}_2\text{MgSiO}_7$).

(4) Periclase (MgO) in the dead-burned magnesite and MgO removed by degradation of the monticellite reacts with micro-environmentally liquefied silica to form forsterite (Mg_2SiO_4) and, possibly with some alumina associated with the calcined magnesite, to form spinel (MgAl_2O_4).

(5) Magnesioferrite inclusions in the dead-burned magnesite grains aid in fluxing the periclase cores and apparently **back** oxidize in places to form hematite.

(6) Iron oxide mobilized by micro-environmental liquefaction rapidly diffuses into the investment matrix and aids in the fluxing of silica.

(7) Quartz grains commonly undergo topochemically controlled inversion, forming shallow cristobalite and/or tridymite rims.

Burnout reactions in the silica-bonded investments parallel those in the phosphate-bonded investments except that liquefaction is not as extensive. Vitreous appearing phases are less evident than in the phosphate-bonded investments. These reactions are as follows:

(1) The interstitial amorphous silica bond is converted by the action of mineralizers into cristobalite.

(2) In investments with a low content of mineralizers, and limited flux action, conversion of interstitial "bonding" silica into cristobalite is highly restricted.

(3) At higher temperatures in more extensively liquefied micro-regions, tridymite is formed.

(4) On the cooling of more extensively liquefied micro-regions, quartz is formed interstitial to the tridymite.

(5) Calcined magnesite additions (MgO) react with fluxed silica to form forsterite (Mg_2SiO_4).

(6) Ferruginous mineral constituents, e.g., ilmenite, aid in fluxing and react to form vitreous appearing micro-regions apparently containing disseminated magnetite and hematite.

Investment-mold reactions which occur during casting are of two types -- corrosive and thermal. Corrosive action is a result of vapor diffusion of alloy constituents into the investment. Oxides of these vaporized constituents, along with heat emanated from the casted alloy, cause extended liquefaction along the investment-casting interface.

Electron probe studies have shown that in the typical cobalt-chromium phase alloy, chromium diffuses most massively into the investment. Manganese, because of its high vapor pressure, is boiled out of the alloy near the interface and penetrates very deeply into the investment. Because of its lower vapor pressure, cobalt does not diffuse in nearly as much as chromium. Iron diffuses in considerably, but nickel, tungsten, tantalum and molybdenum are not present, mostly because of their low vapor pressures.

Oxides of manganese, cobalt, and iron tend to push reactions with silica toward low-melting olivine fields. These oxides thus tend to extend liquefaction along the casting investment interface. Chromium forms a refractory chromic oxide and, where sufficient fused magnesium oxide is present, will form also a refractory magnesium chromium spinel. Under low oxygen pressures, the spinel is favored over the chromic oxide. Thus, it would appear that chromium is not responsible for extended liquefaction along the interface.

Manganese, the most vaporizable alloy constituent, has been found to have diffused as deep as 60 to 80 microns into the investment mold interface. Extended liquefaction plugging pores has been found commonly up to this depth along the casting interface. Cristobalite and tridymite have formed also in the interface.

Thermal action is due to baking action of heat emanated from the casted alloy. It results in more extended liquefaction, with reactions proceeding in the same direction as in the high temperature burnout. Thermal liquefaction commonly is apparent 100 to 200 microns back of the interface and is not as laterally extended as is liquefaction in the corroded layer.

These reactions may effect:

- (1) increases in casting time with concomitant induction of shrinkage porosity by inhibiting mold gas escape due to the obstruction of casting investment interface pores by a viscous liquid;

(2) anisotropic investment-mold deformation by microdensification induced by both thermal and corrosive liquefaction during casting, giving rise to a poorly fitting casting; and

(3) production of casting roughness by the particle clumping caused by the surface tension of liquids formed both during burnout and in casting.

Based upon the petrographic insights obtained, the development of a more refractory investment will be attempted. It is thought that development of more refractory investment bonds would be the best way to do this. Under particular consideration is the use of inorganic polymer bonds generated from solutions of ammonium zirconium carbonate, zirconium acetate and chloride-complexed aluminum oxides. These will be used in conjunction with ammonia stabilized silica sols to develop from -

(1) zirconium solutions, zircon;

(2) aluminum oxide sols, mullite; and

(3) magnesium oxide, forsterite refractory bonds. Also, there is the possibility that refractory spinel bonds may be developed from aluminum oxide sols and magnesium oxide.

Also under consideration are finely milled zircon air-setting cements, calcium aluminate hydraulic cements, and zirconia air-setting cements. Weak gel bonds with zircon stoichiometry have been developed by a combination of zirconium acetate and ammonium organic silicates.

Petrographic study of dental porcelains has been launched. Attempts will be made to find methods of lowering porcelain firing shrinkage by incorporating various metallic additives (e.g., aluminum and silicon metal powders). The firing reactions of various porcelains will be studied in detail.

4.7. Grafting of Monomers to Hard and Soft Tissues

Sponsor: U.S.A.

The aim of this investigation is to graft monomers to soft and hard tissues so that after polymerization of the monomer, the proteinaceous surface is bonded chemically to the polymer chains. It is hoped that the modified collagenous surfaces will have improved physical or biological properties useful for dental (or medical) applications.

Since chemical modification of collagen powders had been successful with all monomers studied, including those that had additional functional or potential cross-linking groups, emphasis was changed during this period to the grafting of monomers to (1) collagen films of 0.0005 in. and 0.0002 in. thickness, (2) bone, and (3) dentin. Purified collagen films were used since, similar to soft tissues, they possess much smaller surface areas than collagen powders. Hence, results of these studies approximate more closely those one would encounter on grafting to soft tissues. Monomers were grafted onto the collagen films by the technique described in the previous report. Homopolymer was removed by extraction of the product for 48 hours with boiling chloroform or by 72-hour extraction with acetone. An increase in weight, as well as the presence of characteristic bands in the infrared spectra of the respective products, indicated the presence of graft side chains. Thus, the following monomers, in order of decreasing weight increase, could be grafted to 0.0002" collagen film: glycidyl methacrylate, methyl methacrylate, isobutyl methacrylate, ethyl acrylate and 1,3-butylene dimethacrylate. Yields of the graft reaction varied from 121% to 19% and were generally lower than those obtained on grafting the respective monomer to powdered collagen. Dimethylaminoethyl methacrylate was the only monomer studied for which the graft yield was poor and the presence of graft side chains could not be ascertained by infrared techniques. Exact yields for the 0.0005" films are difficult to determine. Apparently, weight increases on grafting are lower for the thin film (.0002 in.) with the exception of the monomers capable of crosslinking (1,3-butylene dimethacrylate, glycidyl methacrylate). Of practical significance is the fact that on lowering the reaction time from 3 hours to 15 minutes, a significant amount of methyl methacrylate (10%) was still grafted onto the collagen film. These results indicate that grafting of many monomers to collagen films is possible. This can be accomplished within a few minutes if only a modification of the proteinaceous surface is desired.

On grafting glycidyl methacrylate, dimethylaminoethyl methacrylate, 1,3-butylene dimethacrylate or isobutyl methacrylate to powdered bone, an increase in weight of 60%, 27%, 19% and 11%, respectively, was obtained after acetone extraction at room temperature. Infrared spectra indicate

the presence of the oxirane ring of the glycidyl group as well as the methacrylate group for the glycidyl methacrylated grafted to bone. The presence of 1,3-butylene dimethacrylate and dimethylaminoethyl methacrylate could also be detected by this technique. Grafting to bone surface is possible within one hour reaction time, as indicated by a slight increase in weight. However, a number of monomers (methyl methacrylate, ethyl acrylate) do not appear to react with bone.

To reduce the time-consuming process of obtaining dentin by pulverizing it with a dental bur, a modification of the technique described by Battistone and Burnett (J. Dent. Res. 35:255 (1956)) was adopted. The powdered dentin was then used in a series of grafting experiments. No appreciable amounts of polymer grafts or increase in weight could be detected after reacting the dentin with ethyl methacrylate, isobutyl methacrylate, glycidyl methacrylate, dimethylaminoethyl methacrylate, vinyl acetate or 1,3-butylene dimethacrylate. These results seem to indicate that the dentin surface is not as susceptible to grafting as the surface of powdered bone. Thus, the relative grafting efficiency of monomers to the solid substrate decreases in the following order: Powdered collagen > collagen film > powdered bone > powdered dentin.

To determine possible adhesion of bovine graft-treated surfaces to a commercial restorative resin, six flat tooth sections were subjected to the standard grafting procedures. They were then partially embedded in a resin and subjected to the tensile adhesion test of Lee, Swartz and Culp after placing of a Kadon restoration and storage in water for 24 hours. No significant adhesion was obtained, indicating that this particular treatment does not promote adhesion.

Considerable effort was spent on the characterization of the numerous graft polymers previously obtained by infrared techniques. By the potassium bromide sample technique, the presence of small amounts of grafted material is not likely to be detected. However, in nearly all products containing more than 10% graft polymer, new infrared bands which could be directly attributed to the grafted side chains were observed. The infrared curves of 0.0005" collagen films to which monomers were grafted were much more suitable for detecting small surface changes on grafting since the films could be analyzed without any further sample preparation. For instance, the presence of at least eight additional

absorption bands in the treated collagen indicates the presence of poly(methyl methacrylate) grafts. Collagen films of 0.0002" thickness absorb too strongly in certain regions of the infrared spectrum to be useful for definitive characterization. However, typical absorption bands such as ester or glycidyl group on the grafted chain can be detected.

The immediate effort during the coming months will be directed on exploring the usefulness of the grafting techniques to soft tissues such as skin. The previously developed procedures will be employed using calf skin or rat skin as substrate. Dehaired skin retaining the epidermal layer will be employed initially. The presence of this keratinous layer may necessitate a change in the experimental conditions.

4.8. Development of Adhesion to Enamel and Dentin Surfaces

Sponsor: U.S.A.

The objective of this study is to determine the efficiency of various enamel pretreatments to develop a rapid clinical feasible surface treatment which will result in efficient bonding between human enamel tooth surfaces and clinically available acrylic restorative materials. The commercial acrylic restorative Kadon was used in most of this experimentation. In a few experiments, the development of adhesion between enamel and the commercial dental resins, Bonfil and Sevitron, and the composite restorative, Adaptic, was examined.

Further work was conducted to correlate the acid structure-adhesion efficiency of selected polyfunctional acids. Unfortunately, many acids that may be potentially useful are only sparingly soluble in water and even a 5% aqueous solution cannot be prepared. By substitution of ethanol for water as solvent, 5% ethanolic solutions of a number of water insoluble compounds could be made. Application of these solutions invariably resulted in complete lack of adhesion. This behavior is caused by the decreased dissociation of the acid in ethanol with the lower concentration of hydrogen ions reducing the etching effect of the acid. Thus, selection of acids with the required structural differences to pinpoint structure-adhesive properties relationships was possible only on a very limited scale. For instance, no correlation was found between the number of carboxylic acid groups attached to the benzene ring and adhesive

properties. Especially puzzling is the lack of adhesion of enamel surfaces treated with benzene hexacarboxylic acid, whereas a bond strength of 56 kg/cm^2 was achieved with the pentacarboxylic acid.

Addition of 1% methacrylic acid to the monomer to obtain a more polar polymer, treatment of the enamel with a 2% solution of an acrylic copolymer in chloroform before the lactic acid etch, or treatment with a wetting agent (Aerosol OT) before the etch to possibly increase more rapid ingress of the acid into the enamel, actually decreased adhesion. Use of 50% phosphoric acid containing 7% zinc oxide etch as recommended recently by Buonocore (J. Am. Dent. Assn. 80:324, 1970) gave a significantly lower bond strength than the 20% lactic acid pretreatment studied in this investigation. Thus, this in vitro test may be indicative that 20% lactic acid is a potentially very desirable pretreatment for a clinically useful pit and fissure sealant. Application of a solution of carboxylated polyester of pyromellitic dianhydride with a hydroxyl-terminated polyester prepared from 2,2-dimethyl-1,3-propanediol did not improve adhesion to enamel surfaces despite the presence of a large number of free acid groups. Similarly, treatment of the enamel with hydrolyzed silanes did not yield beneficial results. Roughening the enamel surface by polishing with 240 carborundum paper lowered greatly the bond strength and increased markedly the coefficient of variation.

Enamel surfaces pretreated with 20% lactic acid or 5% tetrahydrofuran-tetracarboxylic acid also adhere well to other commercial dental resins (Bonfil, Sevitron) and to a composite restorative (Adaptic). Adhesion values of these resins to bovine and human enamel were of the same order of magnitude.

The pH values of the various solutions varied from 0.75 for 50% citric acid to 3.16 for 5% picolinic acid. Especially noteworthy are the pH values of 20% lactic and 5% tetrahydrofuran-tetracarboxylic acid which were 1.50 and 1.44, respectively. These solutions are much less acidic than the 50% phosphoric acid containing 7% ZnO which has a pH less than zero. The latter solution has been used clinically by Buonocore as an efficient pretreatment for pits and fissure sealants without any apparent deleterious effect on the tissues. Thus, it is likely that the less acidic lactic acid pretreatment can be tolerated by the

oral tissues and may actually be advantageous for this application. It should be realized, also, that the total amount of acid applied to the enamel is probably less than 0.1 ml and is partially neutralized within a few seconds on contact with the enamel surface.

Scanning electronmicrographs of the enamel surfaces before and after the application of the polyfunctional acids proved beyond doubt that this treatment leads to preferential dissolution of portions of the enamel surface and to exposure of the enamel rods. The largely increased surface area and greater porosity of the etched enamel facilitates the ingress of the slurry into the crevices and improves wetting by the uncured resins. This results in a better mechanical interlocking of the restorative resin with the enamel phase.

A detailed report of this investigation is being prepared for publication.

4.9. Dental Tensile Adhesion Test Methods

Sponsor: NIDR

The objective of this investigation is to evaluate two dental tensile adhesion tests - one method developed by Lee, Swartz and Culp of the Epoxylite Corp., and the other method suggested by the Subcommittee on Standard Test Methods for Direct Filling Resins of the ANSC Committee on Dental Materials and Devices. The evaluation is being conducted by employing potential dental adhesive systems and techniques approximating as closely those which could be used clinically.

The following parameters and their effects on the bond strength and reproducibility of results as obtained by the two test methods are being investigated:

- (1) Substrates (bovine enamel, bovine dentin, human enamel, human dentin);
- (2) Surface treatment of substrates (20% lactic acid (L.A.), 5% tetrahydrofuran tetracarboxylic acid (TTA), 5% AgNO_3 (for dentin only), 5% AgNO_3 & TTA (for dentin only), 5% AgNO_3 & L.A. (for dentin only));
- (3) Commercial restorative resins (Kadon, Sevriton, Bonfil, Adaptic, Durelon);
- (4) Instrumental variation

Minor changes were made in the specimen preparation for the ANSC

tests. In order to save time, a set screw is used to hold the 2-56 test screw in the penetrometer shaft. By loosening the set screw, the specimen may be removed from the penetrometer in 6 to 8 minutes, rather than the suggested 20 minutes. Modifications were also made in the specimen preparation jig. Rather than using the movable stage described in the ANSC method, split dies were made with a recess in the bottom section to hold the specimen and a recess in the top section to position the spacer. After positioning the specimen and the spacer, the two sections were held tightly together by 2 screws.

All specimens were stored in water at 37°C for 24 hours prior to testing. The bond strength of the resins was measured also on substrates which were not etched. No significant bonding was obtained with human or bovine enamel under these conditions. The only measurable bond strength for dentin was obtained with Durelon against bovine enamel with no surface treatment. Acid treatment of bovine enamel before placing the Durelon did not improve bonding. The average of five specimens was 11 kg/cm² with a coefficient of variation of 26%. All five specimens gave cohesive failures.

Representative values of the tensile adhesion to enamel surfaces are given in Table 1. It will be seen that both tests are of a semi-quantitative nature with coefficient of variations ranging between 16 and 67%. Such large variations can be expected in this type of measurement using only five specimens and discarding none of the experimental values. Despite poor reproducibility, both tests clearly indicate the absence or presence of adhesion to tooth structure. Using a large number of measurements of tensile adhesion determined by the EpoxyLite test, it was found that the standard deviation is a function of the level of the measurement. A reasonably good fit was obtained for the curve:

$$S = \bar{X}^{3/4}$$

where S is the standard deviation and \bar{X} is the average value of the tensile adhesion.

Because of the large coefficient of variation, the effect of the various experimental parameters studied is difficult to evaluate. When a rather fluid mix is used, such as for Bonfil or Sevriton, the slurry

flows out of the cylinders on placement in the Epoxylite test and tends to spread on the tooth surface. This results in poor reproducibility as indicated by the large coefficient of variation. Adhesion developed with fluid mixes is more suitably evaluated by the ANSC test. The significantly larger adhesion values of Kadon by the Epoxylite test, as compared to the ANSC test, are probably the result of the large powder-liquid ratio (high consistency) of the slurry used. The large powder-liquid ratio was especially selected because of its improved adhesion to the curved enamel surface as measured by this test.

The use of either human or bovine teeth, because of their non-homogeneous surface characteristics introduces another variable. Substitution of bovine enamel for human enamel does not appear to alter results significantly. Grinding and polishing a flat surface on the enamel surface did not give a significant difference in the results compared to teeth on which no flat had been ground. The following results were obtained using the ANSC test:

Sevriton with lactic acid on bovine enamel -

- (a) flat area - 36 kg/cm^2
- (b) no flat - 37 kg/cm^2

For the ANSC test, no clear-cut trend has been observed on varying the headspeed of the tensile testing machine from 0.02"/min. to 0.2"/min.

For many of the adhesive systems, results by the two tests appear to be within the range of the experimental error. Specimen preparation for the ANSC test is much more time consuming, which is a decided disadvantage in routine work with a large number of samples. Both methods, especially the Epoxylite test, require relatively large (preferably flat) surface areas to be bonded. This requirement is not particularly critical in adhesion testing with dentin as a substrate. However, preparing the flat human enamel surfaces necessary for these measurements without exposing dentin presents serious problems. It is likely that the effect of slight deviations from planar surfaces is less critical for the ANSC test.

A comprehensive survey describing studies of the mechanism of adhesion and reactivity of tooth surfaces, potential adhesive systems proposed for bonding to dentin and enamel and test methods used in evaluating dental adhesives has been prepared. This manuscript will be part of "The Chemistry of Biosurfaces" (Michael Hare, ed.) to be published at an early date.

TABLE 1

Summary of Representative Results[#]

<u>Etch</u>	<u>Resin</u>	<u>Powder/Liquid Ratio</u>	<u>ANSC TEST</u>		<u>EPOXYLITE TEST</u>	
			<u>bond strength*</u> kg/cm ²	<u>C.V.**</u> %	<u>bond strength*</u> kg/cm ²	<u>C.V.**</u> %
<u>Bovine Enamel:</u>						
20% L. A.	Kadon	.125g/.09 ml	29	30	64	32
	Bonfil	.11g/3 drops	23	23	33	61
	Sevriton	.12g/3 drops	40	25	22	67
	Adaptic ⁺	----	--	--	18	39
5% TTA	Kadon	.125g/.09 ml	21	37	54	28
	Bonfil	.11g/3 drops	25	44	26	51
	Sevriton	.12g/3 drops	34	42	25	52
	Adaptic ⁺	----	--	--	37	51
<u>Human Enamel:</u>						
20% L.A.	Kadon		27	29	65	19
	Bonfil	.11g/3 drops	29	26	--	--
	Sevriton	.12g/3 drops	51	35	--	--
	Adaptic ⁺		31	30	--	--
5% TTA	Adaptic ⁺		57	16	--	--

All specimens stored under water at 37°C for 24 hours prior to testing

* Average of five specimens

** Coefficient of variation

+ Equal portions of the two pastes

4.10. Adhesive Direct Filling Materials

Sponsor: ADA, NIDR (Grant)

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

(a) A glass formulation and equipment described in the previous report demonstrated the feasibility of preparing spherical particles from irregular particles, utilizing an oxygen-acetylene ceramic powder gun in conjunction with a water-cooled cyclone separator. A necessary requirement of the reinforcing filler particles is that they match the refractive index of the polymer 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. The last glass formulation investigated contained BaF_2 (8 mole percent) and had minimal but sufficient x-ray opacity; however, due to the labile nature of fluoride, the commercial glass powder, obtained by the custom preparation from a commercial source, had a refractive index that was different from that of the original experimental glass made at NBS. Consequently, during this period, five experimental glass formulations were prepared (in cooperation with the inorganic glass section), each containing 16 mole percent of 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 1.545). The variables in this approximated isofract composition line are the proportions of B_2O_3 and Al_2O_3 . All of these formulations theoretically take advantage of the "aluminoborate anomaly" that should give a further desirable property of having minimal coefficient of thermal expansion. Furthermore, these glasses should have good hydrolytic stability, a property that is most important in terms of the adhesive bonding (by way of the silane coupling agent) between the glass and the resin phases of the composite.

Scanning electron microscope studies of fractured surfaces have indicated that the "weakest link" (the region of fracture propagation) of the fractured specimens is at or very near to the interface of resin and reinforcing filler particles. In this series of glass formulations, the liquidus eutectic region will be sought.

(b) The dimethacrylate monomers studied during this period were the three condensation products of 2-hydroxyethyl methacrylate and the corresponding acid chlorides of the phthalic acid position isomers that had been synthesized originally in the Dental Research Section, but which have subsequently been obtained by custom synthesis from a commercial source. A manuscript entitled "Crystalline Dimethacrylate Monomers" is scheduled for publication in the Journal of Dental Research in its next issue (July-August 1970). There was some evidence found that one or more of these monomers might form yellow charge transfer complexes with tertiary aromatic amines. This could be a problem since such amines are used as polymerization accelerators, and this possibility is being studied further.

(c) Sterically hindered phenols are used as antioxidants and as stabilizers for monomers that polymerize by way of free radicals. The synthesis of 2-methacryloxyethyl-3,5-di-t-butyl-4-hydroxy hydrocinnamate was begun. If successful, this compound should provide an effective stabilizer that contains, in the same molecule, a methacrylate moiety capable of copolymerization in the methacrylate monomer system, which would be expected to have advantages both with respect to polymerization kinetics and also from a toxicological viewpoint, since the compound or its decomposition products would become part of the polymeric network.

(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 systematically poisonous, it is conceivable that they might contribute to the pulpal irritation that is currently being reported by various investigators. Since the composite dental materials originated in research here, it behooves the dental research section to optimize these materials and attempt to solve any problems arising in their use. Accordingly, synthesis of novel

tertiary aromatic amine accelerators continued in this period, the purpose being to determine the highest molecular weight (which would minimize tissue permeability and thus toxicity) that would be compatible with effective and useful polymerization acceleration. To this end, the polymeric reaction product of the diglycidyl ether of bisphenol A and 3,5-xylidine was prepared. This polymer (oligomer) was soluble in the monomer and gave practical hardening times when it and the stabilizer were adjusted to suitable concentrations. The product itself is a glassy, brittle solid.

A summer student is being trained in the procedures of testing adhesion between dental materials and hard tooth tissues. A surface-active coupling agent, synthesized during the last period (the reaction product of N-phenylglycine and p-chlorophenyl glycidyl ether), will be compared with NPG-GMA (the reaction product of N-phenylglycine and glycidyl methacrylate) for relative efficacy in mediating adhesive bonding between composite materials and hard tooth tissues. The purpose of this comparison will be to evaluate the relative importance of dispersion-force interactions versus copolymerization between such primers and polymeric materials.

As a prototype of adhesive varnishes or lacquers, the synthesis of a compound derived from the diglycidyl ether of bisphenol A and N-phenylglycine was commenced. This compound has two of the monovalent, tridentate chelate moieties on the same molecule (in contrast to the compounds mentioned in the previous paragraph, each of which has only one such chelate group). 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.

4.11. Three-Dimensional Panoramic Dental X-Ray Device

Sponsor: A.F., ADA

Repair and modification of the "original" panoramic dental x-ray machine has continued toward the aim of allowing simultaneous exposure of two films. The initial approach has been with the conventional camera. Variation in positioning, beam width, angulation and exposure time are being examined. The radiographs have changes in the relative positions of the objects in the pictures between consecutive films. The lack of

identity between images seen by the left and right eye is psychologically interpreted as depth in the projected radiographs. Conventional stereoscopes will initially be used to view the radiographs, but the use of a lenticular screen system permitting group viewing without use of polarizing glasses or elaborate equipment is to be explored.

4.12. Bonding Cold-Curing Acrylic to Acrylic Teeth

Sponsor: ADA

A solution, equal parts CH_2Cl_2 and cold-curing methyl methacrylate monomer, and a procedure for its use have been developed which bond cold-curing acrylic to acrylic teeth with strengths in excess of 80% of the cold-curing acrylic. The solution is applied during the processing technique, and does not increase the time or require additional equipment. Teeth subjected to this treatment pass the American Dental Association Specification No. 15 test for changes in the surface characteristics, hardness and resistance to crazing.

Simulated dentures have been made using the new procedure and the teeth are retained and the denture base strengthened. These results verify the tensile tests in the laboratory. Each manufacturer of American Dental Association certified acrylic teeth has been asked to evaluate the solution and technique. Additionally, four prosthodontists have requested information concerning this procedure and will provide information relative to its clinical effectiveness. A manuscript is in preparation.

4.13. Investigation of Dental Amalgams Utilizing Low Mercury-Alloy Ratios

Sponsor: ADA, NIDR (Grant)

The physical properties of dental amalgams, their resistance to corrosion, and mercury hygiene in dental practice are generally improved with the use of a minimum amount of mercury in the original mix. However, one is limited by the need for adequate plasticity to place the mix in the prepared tooth. Therefore, available amalgam alloys require about 46 to 50 percent mercury. Attempts are being made to reduce the amount of mercury by a judicious choice of particle sizes of spherical silver alloy. In this manner it has been possible to reduce the mercury to as low as 35 percent. However, the mix, although quite plastic, is very

grainy and appears to adapt poorly to the cavity walls. The physical properties of this amalgam are comparable to the amalgams generally in use except that the 24-hour static flow is considerably superior. This may be important clinically because of reports showing a close correlation between low flow and improved marginal integrity. Further efforts will be made to reduce the disadvantages of graininess and lack of adaptation by using smaller particle sizes.

4.14. Finishing of Composite Resins

Sponsor: ADA, NIDR (Grant)

One disadvantage of the new anterior composite restorative materials is that the dentist cannot finish them to a smooth surface. To overcome this deficiency, an instrument was constructed by bonding 1 to 5 μm diamond particles to paper discs using an epoxy adhesive. Comparisons were made of finishes obtained with this instrument with those of conventional finishing instruments by means of a scanning electron microscope. The surfaces formed by the diamond discs were superior to those obtained by conventional instruments in terms of smoothness and light reflection.

4.15. Hazard of Mercury Poisoning Using an Ultrasonic Condensing Instrument for Dental Amalgam

Sponsor: ADA, NIDR (Grant)

Mercury vapor levels in dental offices are increased during periods of manipulation of the mercury and amalgam. These manipulations include removal of existing restorations, dispensing and triturating the alloy and mercury and condensing and carving the alloy itself.

A preliminary investigation in this laboratory (designed to study the effects of ultrasonic condensation on the properties of dental amalgam) revealed that when an ultrasonic instrument was used, significant amounts of material were being emitted from the working area in the form of a vapor-like cloud. This cloud was made up of mercury droplets and alloy particles. Whether or not these materials are present in sufficient amounts to constitute a health hazard is under investigation.

4.16. Clinical Research

Sponsor: ADA, NIDR (Grant)

Clinical evaluations of composite restorative materials, the effects

of an adhesion-promoting coupling agent (NPG-GMA) and of various methods of polishing composite materials has continued.

4.17. Specifications and Related Activities

Active participation at the member, committee chairman and sub-committee chairman level in the American National Standards Committee Z156 has continued. Data on the effects of the speed of loading on the compressive and diametral tensile strength of two types of ZnO-eugenol cements were provided Working Group I, ISO/TC-106.

Continued progress toward improved specifications has been made through chairmanship of the FDI Commission on Dental Materials, Instruments, Equipment and Therapeutics.

The physical properties of a series of treated chrome-cobalt wires for use in partial denture work were determined for Brooks AFB. In response to an inquiry regarding the quality of certain hand instruments, the Knoop Hardness Numbers, % Cr and cutting edge dimensions were determined for Brooks AFB. Also provided the A.F. was a study of dimensional stability of a light-bodied polysulfide rubber base impression material of one manufacturer and a regular-bodied polysulfide rubber base impression material of another manufacturer, when the two are used in combination.

Evaluation of a hydroclone prototype unit was completed for the Army.

Site visits, review of project proposals and advisory services on dental materials were provided NIDR.

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