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REPORT ON DENTAL RESEARCH
AT THE
NATIONAL BUREAU OF STANDARDS

Progress Report
July 1 to December 31, 1969

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.

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REPORT ON DENTAL RESEARCH

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NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Dental research at the National Bureau of Standards during the half year ending December 31, 1969 included investigations of a wide range of materials used in restorative dentistry as well as studies of mineralized tissues and related compounds. 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 10061	Effects of Compositional Variations on the Atomic Ordering in A-15 Phases.
NBS Report 10127	Amine Accelerators for Methacrylate Resin Systems.
NBS Report 10128	A Refinement of the Crystal Structure of $Na_2CO_3 \cdot H_2O$.
NBS Report 10155	Preparation of Hydroxyapatite by Hydrolysis of α-Tricalcium Phosphate.
NBS Report 10177	Ultrasonic Methods for Determination of Mechanical Properties of Dental Materials.
NBS Report 10178	EBA Cements.

3. PAPERS PUBLISHED

Huget, E. F.; Brauer, G. M.; Kumpula, J. W. and Civjan, S. A Filled Cold-Curing Acrylic Resin As a Splinting Material. JADA 79:645-648, September 1969.

Ohashi, M. and Paffenbarger, G. C. Some Flow Characteristics at 37°C of Ternary Wax Mixtures That May Have Possible Dental Uses. J. Nihon University School of Dentistry Vol. 11, #3, September 1969.

Sweeney, W. T. Dental Research at the National Bureau of Standards, 1919-1969. British Dental Journal 127:289-290, #6, Sept. 16, 1969.

Dickens, B. and Brown, W. E. The Crystal Structures of $CaNa_2(CO_3)_2\cdot 5H_2O$, Synthetic Gaylussite, and $CaNa_2(CO_3)_2\cdot 2H_2O$, Synthetic Pirssonite. Inorganic Chem. 8:2093-2103, #10, October 1969.

Eick, J. D.; Caul, H. J.; Hegdahl, T. and Dickson, G. Chemical Composition of Dental Gold Casting Alloy and Dental Wrought Gold Wire Alloys. J. Dent. Res. 48:1284-1289, #6, November-December 1969.

4. WORK IN PROGRESS

4.1. Determination of Crystal Structures

Sponsor: NIDR, NIDR (Grant), ADA

Calcium carbonates and calcium phosphates account for much of the inorganic materials formed *in vivo*. Our objectives are to determine and examine germane crystal structures to increase the understanding of ionic arrangements in the solid state and to provide structural experience for postulating models for

(1) groups of ions and water molecules in aqueous solution which may be involved in reaction mechanisms.

(2) incorporation of 'defects', impurities, vacancies and/or non-stoichiometry in bone mineral in particular, and crystal structures in general. This includes investigating possible epitactical (interlayering) and syntactical (substituted domains) relationships between crystal structures and estimating the optimum molecular parameters of adherents.

(3) nucleation and crystal growth phenomena.

Automatic Diffractometer

The Picker automatic single-crystal x-ray diffractometer equipped with a highly oriented graphite crystal monochromator, was delivered in May 1969 and has been aligned and used to collect several sets of x-ray intensity data for use in the determinations of the crystal structures. Intermittent malfunctions in the equipment have caused delay; unclear, incomplete or omitted operating instructions have caused a need for some repetition. In general, the equipment is routinely producing high quality data.

$Ca_2Na_2(CO_3)_3$ (Shortite)

The structure of shortite was redetermined to provide more structural information on the coordination of Ca, Na, and CO_3 ions, and has been refined satisfactorily to R = 0.023. The Ca ion in $Ca_2Na_2(CO_3)_3$ is coordinated to 9 neighboring oxygens, including three CO_3 edges, with distances that indicate strong ionic bonding. Strong coordination to 9 oxygens is unusual for Ca and is possible because of the small 0...0 separation (∿2.2Å) in the edge of the CO_3 group. One Na ion is coordinated to 8 oxygens, including 2 CO_3 edges, in a geometry like that of Ca in $CaNa_2(CO_3)_3 \cdot 5H_2O$; the other is coordinated strongly to 6 oxygens, including one CO_3 edge, and weakly to a seventh.

$BaCa(CO_3)_2$ (Barytocalcite phase)

The structure of barytocalcite was determined and refined to R = 0.03 to learn how large cations such as Ba^{2+} and Sr^{2+} may be accommodated in structures such as calcite and aragonite, which are different forms of $CaCO_3$ and important biological minerals.

The cations in barytocalcite form a pseudohexagonal layer parallel to (101) if Ca and Ba are considered equivalent. There are similar layers of Ca ions in calcite and aragonite. The CO_3 groups lie in a buckled layer between the cation layers. The structure repeats with every fourth cation layer and is thus related more to calcite than to aragonite which repeats everty third cation layer.

The Ca ion in barytocalcite is coordinated to seven oxygens, including one CO_3 edge; this coordination is different from the Ca coordination of 6 oxygen atoms in calcite and 9 oxygen atoms in aragonite. The structure contains linear Ca-CO_3 chains along $\underline{c}$. The Ba ion is coordinated to 11 oxygens, including 5 CO_3 edges. There are non-linear Ba-CO_3 chains along c.

$BaCa(CO_3)_2$ (Alstonite phase)

We have collected 25,000 x-ray reflections from an apparently single crystal of alstonite. Alstonite is monoclinic, has a large cell a = 30.164(9), b = 17.413(5), c = 6.110(1) and β = 89.91°(1) crystallizes in space-group C2/m, Cm or C2. Work on the crystal structure is beginning. From the relationship of its cell dimensions to those of barytocalcite, alstonite may have pseudohexagonal layers of cations parallel to (001) which repeat every third layer and thus be related to aragonite.

$CaCO_3$ (Aragonite)

To our knowledge, the structure of aragonite had not been refined from the positions given by Bragg in 1924. In view of the importance of aragonite as a biological mineral and as a common phase of $CaCO_3$, we have collected new x-ray data and have refined the structure to R = 0.03. At the present stage of refinement, the CO_3 group in aragonite appears to be essentially trigonal, with C-O = 1.286(2) Å. The Ca ion is coordinated to 9 oxygens, including 3 CO_3 edges. Because of the twinning common in aragonite, the single crystal we used to collect the x-ray data was necessarily small. If we are unsuccessful in our search for a larger crystal of aragonite to improve the counting statistics and thus the precision of the x-ray data, we plan to recollect the data with the present crystal. The diffractometer has now been modified to keep the least significant digit in all counts, which it had not previously done. This will improve the precision of our results in general since we are often forced to use small crystals which do not have intense x-ray reflections.

Computer Programs

So that various experimental errors such as misalignment of the crystal, and absorption or multiple reflection of the x-ray beam by the crystal, may be checked, we routinely measure equivalent reflections with the diffractometer in gathering our sets of x-ray data for crystal structure determinations. A program to merge any equivalent reflections in a list of up to 30,000 reflections and to sort the reflections has been written for the UNIVAC 1108 computer. The program performs some value judgments on the data and is working successfully.

4.2. Physicochemical Studies of Apatite and Related Inorganic Substances

Sponsor: NIDR (Grant), ADA

Solubilities of Hydroxyapatite

The solubility of hydroxyapatite is a basic factor in tooth, bone and calculus formation, bone remodeling, and the caries process. Discordant results in the literature have created various interpretations of how hydroxyapatite crystals can equilibrate with aqueous systems. However, three sets of solubility measurements, described in previous reports, have established that the solubility principles that apply to hydroxyapatite are the same as for other calcium phosphates. Two types of anomalous behavior were observed:

1. The solubility constant appeared to be affected by sample history, particularly heating at high temperature.
2. It was difficult to attain equilibrium from supersaturation (i.e., from conditions which would prevail during crystal growth).

We have continued studies of these two effects.

Portions of a sample of hydroxyapatite (prepared as described in earlier reports by titration of a $Ca(OH)_2$ slurry with H_3PO_4 solution, followed by prolonged boiling, were heated at 1000°C in air or in water vapor. The samples heated in air became slightly colored (pink) for reasons not known, but probably related to the presence of impurities. When heated samples were placed in water, the solutions became alkaline to phenol-phthalein. The impurity responsible for the alkalinity has not been established. The only calcium phosphate that behaves in a similar manner was found to be tetracalcium phosphate, $Ca_4O(PO_4)_2$. The conditions of heating in air were such that hydroxyapatite could disproportionate into $Ca_4O(PO_4)_2$ and β-$Ca_3(PO_4)_2$, which then could produce the alkalinity. Since $Ca_4O(PO_4)_2$ cannot form in the steam-heated samples, another impurity must account for the alkalinity of these samples.

The heated samples yielded solubility products that were variable and larger than that obtained with unheated samples. Thorough washing of the heated samples with 0.02 M_3HPO_4, however, reduced their solubilities so that they gave essentially the same results as the unheated samples. The major effect of the washing was to remove the more soluble impurities so that the final measurements were made on bona fide hydroxyapatite. These results further verify the reliability of the solubility data we have obtained previously with both precipitated and steam-heated hydroxyapatite. They leave in question, however, the cause of the higher values obtained previously with the unwashed air-heated materials.

The most convincing proof that equilibrium has been achieved in a solubility measurement is to reach the same value from supersaturation and undersaturation. An earlier set of equilibrations from supersaturation gave what appeared to be a metastable isotherm that was later found to correspond to that of $\beta\text{-}Ca_3(PO_4)_2$. Our most recent experiments of this type gave variable results and the solutions were always supersaturated with respect to the values obtained when equilibrium was approached from undersaturation. The finely divided form of the hydroxyapatite used this time prevented us from using the leaching technique that had been so successful in the earlier experiments, thus accounting for part of the difference in the results.

We attach considerable significance to the fact that in neither set of supersaturation experiments did we achieve equilibrium with hydroxyapatite. The most reasonable interpretation is that other calcium phosphates (probably $\beta\text{-}Ca_3(PO_4)_2$ or $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, and possibly also materials that are vaguely characterized as the amorphous "phase") formed more rapidly than hydroxyapatite even though there was present a very large surface area which should promote precipitation of hydroxyapatite. This is consistent with numerous qualitative observations that have been made in the past. The formation of metastable precursor phases has been amply demonstrated in vitro; their occurrence in vivo (in dental calculus, carious tooth, and pathological precipitates) is being encountered in an increasing number of instances, and they have been postulated as precursors in the formation of tooth and bone mineral. All these observations are consistent with the view that metastable precursors are likely to form with the result that equilibrium will be difficult to reach from supersaturation.

Solubility of Calcium Phosphates

Our previous studies on solubilities of calcium phosphates were confined to the ternary system $Ca(OH)_2-H_3PO_4-H_2O$. These studies are being extended to include other physiologically important ions. In the current work, the effects of sodium chloride on the solubilities of $CaHPO_4 \cdot 2H_2O$ and the validity of approximations used to calculate activity coefficients at physiological concentrations are being investigated. $CaHPO_4 \cdot 2H_2O$ was selected for this work because it can be prepared in a well crystallized form easily and its solubility behavior and thermodynamic properties have been thoroughly investigated previously in the ternary system. Equilibration of $CaHPO_4 \cdot 2H_2O$ with phosphoric acid solutions containing NaCl (zero to 0.5M) is carried out at 25°C in the usual fashion. The preliminary results indicate that the amount of dissolved $CaHPO_4 \cdot 2H_2O$ is not significantly affected by the presence of NaCl, but the pH of the equilibrating solution increases with NaCl concentration ($\Delta pH = 0.3$ between solutions in which NaCl varied from zero to 0.5M and the initial H_3PO_4 concentration was 1.48×10^{-2} M). Between the zero and 0.15M NaCl solutions, the calculated solubility products do not vary greatly (3% Davies; 6% Debye-Hückel), but at higher NaCl concentrations the K_{sp} values by the two conventions for calculating activity products diverged rapidly. More experimental work is being done using different initial phosphoric acid concentrations; this should allow us to cover a pH range from 4.5 to 7.0.

Diffusion in the Ternary System, $Ca(OH)_2-H_3PO_4-H_2O$

Theory of diffusion in this sytem based on the considerations of electroneutral components, $CaHPO_4$, H_3PO_4, and H_2O and of ionic species, Ca^{2+}, HPO_4^{2-}, $H_2PO_4^-$ and H^+ were described in earlier reports.

The ionic model is used in the present report period to calculate practical (D_{ij}) and fundamental (L_{ij}) diffusion coefficients for thirteen experimental systems saturated with respect to hydroxyapatite; the compositions of these systems, pH, total calcium and phosphorous concentrations, are taken from the work previously reported by these laboratories on the solubility of hydroxyapatite. A calculation of this nature was undertaken because of the possible importance of the results in interpreting and understanding the mechanism of mineralization and demineralization of the hard tissues.

The major findings of this study are:

1. The interference of H_3PO_4 in the diffusion of $CaHPO_4$ component is significant in the pH range 4.5-7.5; the converse is true only for pH values below 6.
2. At the vanishing concentrations of $CaHPO_4$ in 4.89×10^{-5} M H_3PO_4, the practical diffusion coefficient of phosphoric acid, D_{22}, approaches a value very close to the Nernst limiting diffusion coefficient in the binary system, H_3PO_4-H_2O (1.575×10^{-5} cm^2/s); this suggests that the presence of small amounts of $CaHPO_4$ in dilute phosphoric acid solution does not affect the diffusion of H_3PO_4.
3. Dilute solutions of $CaHPO_4$ in the presence of very small amounts of H_3PO_4 do not behave as a binary system, $CaHPO_4$-H_2O, because the practical diffusion coefficient of $CaHPO_4$, D_{11}, does not approach the Nernst limiting diffusion coefficient; this indicates that the interference of H_3PO_4 persists in the diffusion of $CaHPO_4$ even at very low concentrations of both components.
4. Since large interferences can be more accurately determined than the small ones, systems shown to have high interferences (at pH about 4.5) should be selected to test experimentally the Onsager Reciprocal Relations ($L_{12}=L_{21}$).

A Generalized Least Squares Treatment of Solubility Data

In the last report it was noted that the generalized least squares procedure, devised to treat the temperature-dependent solubility data obtained for $CaHPO_4 \cdot 2H_2O$, was being extended to effect the simultaneous adjustment of the solubility data on all the calcium phosphates studied in this laboratory. The program written for this purpose has been completed, tested with selected portions of the data on β-$Ca_3(PO_4)_2$, $Ca_5OH(PO_4)_3$, and $CaHPO_4 \cdot 2H_2O$, and placed on FASTRAND. The available data on $CaHPO_4 \cdot 2H_2O$, β-$Ca_3(PO_4)_2$, $Ca_5(PO_4)_3OH$, and $CaHPO_4$ are being consolidated into one master file in preparation for production runs.

To illustrate the general utility and applicability of the multivariate least squares procedure, a program is being developed to re-evaluate the data collected by Bates and others in estimating the second dissociation constant of phosphoric acid.

The adjustment procedure as applied here is affected by a multivariate Taylor expansion; when applied to a given set of functions dependent on several error-prone variables, it may fail to reach an absolute minimum in the sum of squares. While the effect on the adjusted values of the parameters is believed to be negligible, modified procedures are being developed to insure that the true minimum is approached very closely and to afford more satisfactory insight into the geometry of the adjustment.

Electrode-Chemistry and Calorimetry

Interest in supplementing the pH data used in characterizing equilibrium conditions in various phosphate-containing solutions has led to studies of the applicability of the mercury-based "phosphate electrode", $Hg_2HPO_4/Hg(1)$ to these systems. Preliminary results, from cells with liquid junctions, have indicated that the electrode is responsive to changes in the activity of $HPO_4^{=}$ ions in neutral buffer solutions. Potentiometric solubility measurements of the dimercurous hydrogen phosphate and the use of the electrode in junction-free cells are in progress. Results from these measurements should provide independent values of the standard electrode potential, E°. Extension of the potentiometric method to classical junction-free cells incorporating hydrogen gas and silver-silver chloride electrodes is planned for studies of the quaternary system: H_3PO_4, $Ca(OH)_2$, $CO_2(g)$ and H_2O.

In addition to the use of galvanic cells, the acquisition and assembly of apparatus for the construction of a sensitive solution calorimeter is continuing.

Topical Fluoridation

The reaction of hydroxyapatite with a fluoride solution to form fluorapatite is known to proceed extremely slowly with poor yields. One possible reason for this is that this reaction takes place with virtually no change in volume of a hydroxyapatite. As a result, the crystal can become covered with a thin fluorapatite coating which is then impervious to ingress of the fluoride ions and to egress of the hydroxyl ions.

It has been shown that in both in vitro and in vivo conditions, the tooth enamel acquires larger amounts of fluoride in greater depth when pretreated with dilute phosphoric or hydrochloric acid before being exposed to the fluoride solution. This is probably because hydroxyapatite, when treated with acid is partially converted to $CaHPO_4 \cdot 2H_2O$ (or other less basic calcium phosphates). The reaction of $CaHPO_4 \cdot 2H_2O$ with a fluoride-containing solution to form fluorapatite proceeds quite rapidly because the loss of water molecules and phosphate ions inherent to the reaction results in a considerable shrinkage in the volume of the crystal. Therefore, the penetration of ions into the crystal occurs rapidly through the openings produced by the shrinkage. The reactions of hydroxyapatite with various acids to form $CaHPO_4 \cdot 2H_2O$ and other calcium phosphates are being studied. The optimum conditions for the reaction of $CaHPO_4 \cdot 2H_2O$ with calcium fluoride to form fluorapatite are being investigated; the possible reaction mechanisms are sought. The results obtained from these investigations may reduce the limitations of the methods presently in clinical use and allow a more effective topical fluoridation of tooth enamel to be developed.

4.3. Study of Dentinal and Enamel Surfaces from Sorption Isotherms

Sponsor: NIDR

The adsorption study of basic and acidic groups (characterized by NH_3 and CO_2) on components of tooth structure has progressed on schedule. The measurements have been made on dentin as well as on anorganic whole teeth at various temperatures. Isosteric heats of adsorption have been determined in each case by application of the Clausius-Clapeyron relationship. These have been compared with average heats of adsorption obtained from the C-constant of the B.E.T. equation and found to be in reasonably good agreement. For both dentin and anorganic whole teeth, the heats of adsorption were appreciably greater for NH_3 than for CO_2. Surface area available to the molecules of each gas was also computed and compared. Comparisons were also made with nitrogen adsorption results from 77°K B.E.T. data. The concentration of adsorption sites as indicated by the apparent surface areas, i.e., areas available to each adsorbate, respectively, was especially interesting. Comparable values were found for anorganic whole teeth regardless whether NH_3, CO_2 or N_2 was used. Where collagen was present, as in the case of dentin, the area available to N_2 was very small (7.5 m^2/g) as expected. The area of dentin available to NH_3 at its b.p. was virtually the same (160 m^2/g) as the area of anorganic dentin when measured by N_2 gas at the temperature of liquid N_2. The area of dentin accessible to CO_2 at its sublimation point was 50 m^2/g - considerably less than for NH_3; but more than six times as great as N_2.

There is a good possibility that gas adsorption methods can be used to suggest chemically reactive groups for possible incorporation in a dental adhesive. If amino groups behaved like NH_3 and if carboxylic groups performed like CO_2, an adhesive incorporating the amino groups in its reactive linkages would not only have stronger bonds but more of them for the same overall area of contact than would the carboxylic- containing material.

It is appreciated that this method has limitation. Probably foremost among them is the fact that many reactive chemical groups have no gaseous counterparts. The method could be expanded to include liquids with reasonable vapor pressures at room temperature, but different apparatus would have to be built.

4.4. Mechanical Properties of Oral Structures and Restorative Materials

4.4.1. Dimensional Changes in Teeth Components

Sponsor: USAF, VA, NIDR

Studies of the dimensional changes of enamel and dentin resulting from changes in temperature and water content were continued. The difference in the thermal expansion behavior of dentin below and above 40°C has been of particular interest. Between room temperature and about 40°C dentin exhibits an approximately uniform linear thermal expansion of about $7.5 \times 10^{-6}/°C$. However, when dentin is heated slowly above 40°C, the coefficient of thermal expansion decreases to near zero or may become negative. Rapid heating results in an expansion followed by a shrinkage. Although there appears to be some permanent dimensional change, the major portion of the change is reversible when the dentin is cycled a number of times over a temperature range of 20 to 60°C.

Limited data on specimens of anorganic dentin indicate that this material has a thermal expansion similar to whole dentin below 40°C, but does not exhibit the reduced coefficient above 40°C. This suggests that the reduced expansion of whole dentin is a result of a restraining effect by the organic portion of the material. Such an effect might be explained by a linear shrinkage of the collagen if it can be assumed that (1) the transition which produces a large linear shrinkage in soft tissue collagen near 60°C occurs at a lower temperature in dentinal collagen, and (2) as a result of porosity or other effects, the linear shrinkage rather than the accompanying volume expansion of the collagen is the effective force in the bulk dimensional change of whole dentin.

As an alternative explanation, the possible effect of changes in water content on the "thermal expansion" of dentin cannot be neglected. The large dimensional changes observed when the moisture content of the atmosphere surrounding whole dentin is varied are observed to only a slight extent in anorganic dentin. Attempts so far to determine whether or not "thermal" dimensional changes of whole dentin when immersed in water are related to changes in water content have been inconclusive.

4.4.2. Physical Properties of Hard Tissues

Sponsor: NIDR, AF

An improvement has been made in the proto-type torsion pendulum for the determination of the shear modulus of dental materials. The pendulum and recording system have been refined and combined. This allows for better alignment and adaptation of the test to more materials. Measurements at varying humidity and temperature are planned.

4.4.3. Physical Properties of Soft Tissues

Sponsor: NIDR

Dynamic mechanical methods and apparatus that utilize various vibrational principles and specimen geometries have been investigated for application to soft tissue or skin. Wave propagation, free vibration and forced vibration methods have been tried. Sonic methods involving a longitudinal wave propagation seem to show some promise in the determination of the dynamic mechanical behavior of skin.

Sonic velocity measurements were made with a commercial instrument, the Morgan Dynamic Modulus Tester. This instrument is designed to measure sonic wave transit times in either fibers or thin films. Velocities were determined with little difficulty on dry calf skin in sheet form giving a Young's modulus value of 180 MN/m^2. However, after the same specimen had been soaked in water or when fresh ratskin in sheet form was used, a measurable signal was not transmitted. Using rat tail tendon in fiber form, a modulus of around 2,600 MN/m^2 was determined. Measurements on a fib er or filament of the soaked calf skin gave values of about 30 MN/m^2. Attempts were also made to measure the modulus of fresh rat skin in filament form, but unrealistically high values (around 50 MN/m^2) were obtained. These are believed to result from excessive straining of the skin during preparation of the small cross-section specimen and to excessive drying-out while the measurement was being made.

The Morgan sonic apparatus in its standard form has only limited application to normally wet skin because of transducer design and lack of means for environmental control so that the water content of the skin, as well as the temperature, may be held constant during measurement. But, the results obtained indicate that the longitudinal wave propagation method could be successfully utilized to measure the dynamic properties of skin when an appropriate apparatus is custom built to meet the geometric and environment control requirements strictly prescribed by normally moist soft tissues. The method has the advantage that it can be applied to strips of soft tissue of relatively irregular cross-section and no accurate measurement of cross-section is required.

Since the wave propagation method has some limitations in complete dynamic mechanical characterization of soft tissues and to assure that the mechanical parameter values are correct and that the tissue is properly characterized, it is advisable to measure the dynamic mechanical properties of the tissue by an additional method; preferably utilizing a different vibrational principle. The second method we have applied to normally moist skin appears to be more readily adaptable to the measurement of the tissue dynamic properties. This method utilizes a rocking-beam oscillator which is driven electromagnetically at various frequencies. The apparatus can be used at resonance of the tissue sample or at off-resonance with appropriate transducers which measure the dynamic stress and strain and their phase relationship. A primitive model of the rocking-beam oscillator has been built and preliminary measurements have been made on skin; this proto-type model appears to indicate that the method can be used successfully to measure the dynamic mechanical behavior of soft tissue when the instrument is properly refined in design and equipped with appropriate force and deformation transducers. This apparatus seems to be particularly applicable in measuring internal friction in soft tissue under various conditions due to the fact that the phase relation between the stress and strain can be directly recorded. The internal friction change in a material is a sensitive indicator of phenomena such as a glass transition; thus, secondary transition phenomena, if occurring in soft tissue under various conditions, may be delineated by this method. A refinement of the prototype design is in progress in anticipation of its use in the measurement of the mechanical properties of skin.

In the past six-month period, the dynamic calorimeter was applied to rat skin samples in an attempt to detect changes in heat capacity of skin over the temperature range 15°C to 50°C. These measurements were made in an attempt to verify the second order transition reported by Mason and Rigby (Biochim. Biophys. Acta 66:448 (1963)), and by Rigby (Biochim. Biophys. Acta 79:634 (1964)). The heat capacity of the water in the skin sample is so great, however, that it appears to mask any second order change in the skin collagen, if present. Second order transitions in a temperature range not too far removed from body temperature would be expected to have a very significant effect on the mechanical properties of fibrous tissues. Efforts to detect the transition by measurement of dynamic mechanical methods will be made when the technique of such methods is satisfactorily developed.

4.5. Dental Metallurgical Studies

Sponsor: ADA, NIDR (Grant)

Our work on phase diagrams of the noble metals is continuing. One of our recent discoveries is the existence of a syntectic reaction in the Cr-Pt alloy system. A syntectic reaction is rarely encountered in the compilations of known binary phase diagrams. It may be described as a type of reaction which occurs as a liquid solution is cooled. The liquid initially separates into two immiscible liquids of differing composition as the temperature enters the region of a "miscibility gap." However, at a lower temperature (the syntectic temperature) these two liquid solutions react to form a single phase solid which, in the Cr-Pt system, is an ordered intermetallic compound having the cubic A15 (βW) crystal structure.

The paradoxical nature of this newly discovered transformation is evident when one considers that the formation of a highly ordered intermetallic compound implies a strong attractive force between unlike atoms (A-B combinations) as compared with the alternative like atom (A-A or B-B) combinations. In a region of liquid immiscibility, however, one usually assumes that the attractive forces are strongest between like atoms (A-A and B-B combinations). It is, therefore, quite intriguing as to how such widely different phenomena could occur at a given alloy composition as a result of only a small temperature change.

Thermodynamic measurements would be of great interest in providing more details of the energies involved and the source of such phenomena. It is also interesting that the syntectic reaction occurs in connection with a sharp reduction in the melting point of the Cr solid solution and may, therefore, reveal some useful information on factors responsible for improvements in the casting properties of alloys containing chromium.

We have also recently discovered that the solubility of Cr in solid platinum is extensive when the alloys are heated above their order-disorder transformation temperatures, but the solid solubility of Cr in Pt is sharply reduced below this temperature. In other words, the ordered alloys dissolve less Cr than the disordered alloys. This information was rather unexpected and may be helpful in controlling these important reactions.

In the V-Pt system, we have discovered several order-disorder transformations. In each case the crystal structures of the ordered phases can be changed by introducing cold deformation. This can be of great interest in controlling the ductility of ordered phases. In the V-Pt system, one of these phases (VPt) forms ribbons extending along certain crystallographic directions in the V-base body-centered cubic solid solution alloys. It appears possible that single crystals of such alloys can be grown having a built-in fiber reinforcement. This should certainly receive further study.

4.6. Petrography of Dental Investments

Sponsor: ADA, NIDR (Grant)

Work on investments for high-fusing chromium-cobalt base alloys has been nearly completed. A first report concerning the petrography of phosphate investments has been written. A second report on the petrograhy of silica-bonded investments is in preparation. Work is also near completion on Ticonium's gypsum-bonded investment for low-fusing chromium-cobalt alloys and on the spalling action in zirconia dental crucibles.

Major conclusions to be drawn from the work completed on dental investments are as follows:

1. The degree of liquefaction in the high-fire prior to casting is very important in determining the configuration of fine sand-sized quartz and cristobalite investment filler. On investment surfaces bounding the wax pattern, this configuration is generally coarser the higher the fire and the greater the degree of liquefaction in sinter-bond formation. Where no protective coats are used, distinct network patterns of hills and valleys are formed on the alloy cast surface which key in with those formed on the free investment surface.

2. The cold strength of investments of similar composition increases with the degree of fusion involved in the bonding.

3. Fusion is promoted by various agents in investments. Silica filler is not greatly mobilized at the low firing temperatures, 800°C, of Ticonium's gypsum-bonded investment. Sintering in this material appears to involve recrystallization bonds between calcium sulfate grains promoted by some fusion induced by both sodium and chloride ions and probably by slight disassociation of the sulfate.

4. In all investments investigated, thermal baking action of the hot cast alloy commonly results in silica mobilization to depths of 1/2 to 1 mm and sometimes up to 2 mm from the cast. These thermal effects are likely to affect particle configuration and are expected to influence the partial denture fit. It is obvious that different parts of the cast will give off differing amounts of heat and that this might affect in an anisotropic fashion particle configuration and, therefore, mold deformation.

5. The corrosive effect of the cast alloy is usually very shallow. However, at almost all investment cast interfaces, it appears that induced silica fusion is enough to fill a very high percentage of the interface pores with a viscous silica melt and melt-reaction products. The resulting texture is such that this might have a pronounced effect on gas permeability. The zircon used in protective coats along with fine-grained silica does not appear to react quickly and effectively enough to restrict this liquefaction. Certainly the incorporation of sodium, probably largely in the form of metasilicate, in these protective coats promotes fusion.

6. Investments fired from 5 to 20 minutes under Durallium-alloy

beads in dynamic atmospheres of argon and air show corrosion. Corrosion induced liquefaction appears to be more severe in the argon atmosphere than in the air. However, the air atmosphere causes the alloy to develop a highly porous structure. Chromium tends to go into the more refractory components. In these investments, a very thin blue zone is commonly developed deeper in the investment than the green chromium-rich zone. The blue color of this zone indicates that it is cobalt rich. It thus appears that cobalt oxide initially diffuses more rapidly into the investment than the chromium. Cobalt probably initiates and greatly extends silica fusion.

4.7. Reinforced EBA Cements

Sponsor: U.S.A.

Based on previous investigations in these laboratories, a number of commercial EBA luting materials have appeared on the market. Resin modified EBA restoratives show good stress-bearing characteristics and should find applications as long-term temporary or intermediate restorative materials. Recent studies by Bhaskar, Cutright, Beasley and Boyers (Oral Surg., Oral Med. and Oral Path. 28:126 [1969]) have shown that EBA cements will promote remineralization of decalcified dentins. These properties should make EBA cements the materials of choice in indirect pulp capping procedures since calcium hydroxide does not possess the excellent sealing characteristics, whereas ZOE or modified ZOE cements do not stimulate the formation of reparative dentin to any appreciable extent. A detailed review of EBA cements has been written and is appended to this report.

Pyrolysis-Gas Chromatography Techniques for Polymer Identification

The review of this subject has been brought up-to-date and is scheduled for publication at an early date in Volume II of Advances in Thermal Analysis.

4.8. Bonding of Monomers to Tooth Structure

Sponsor: U.S.A.

Improved Adhesion of Tooth Surfaces to Dental Restorative Resins

The objective of this investigation is to study various simple, clinically feasible surface treatments for enamel or dentin to obtain efficient bonding between tooth surface and commercially available acrylic restorative materials. Bovine enamel or dentin were treated with various acids or chelating agents and the bond strength was determined, generally after 24-hour water exposure, by a tensile adhesion test (J. Dent. Res. 48:211 (1969)). Round-robbin testing indicated that results of this test fairly accurately determined the magnitude of adhesion. Precision of the results between the different laboratories showed a coefficient of variation of 14%. Significant adhesion of bovine enamel to acrylic resins was obtained by application of many dilute aqueous solutions of acids and of chelating agents containing carboxylic acid groups to the tooth surface. Bond strength to polished bovine teeth increased greatly on repeated pretreatment. Increasing concentration of the acid also increases the bond strength. Thus, applying solutions of typical reagents such as 20% lactic acid, 5% 1,3,5-pentane tricarboxylic acid or 5% tetrahydrofuran-2,3,4,5-tetracarboxylic dianhydride (TTAD) for 10 seconds, rinsing with water, drying and then repeating the treatment after various time periods (3 min. to 24 hours) yielded enamel-acrylic restorative (Kadon) bond strengths of up to 73 kg/cm^2 (1040 psi).

No bonding was obtained without the pretreatment, whereas one pretreatment with TTAD gave a tensile adhesion of 21 kg/cm^2 (295 psi). For TTAD bond strength increased if the second pretreatment was delayed. Thus, repetition of the TTAD treatment after 3 min. yielded a bond strength of 28 kg/cm^2 (394 psi), whereas a second application after one hour gave a value of 54 kg/cm^2 (850 psi). Further delay in the second application does not increase tensile adhesion. Exposure of the interface to an aqueous environment for up to three months did not reduce the bond strength.

Treatment of the enamel surface with 20% lactic or 5% 1,3,5-pentanetricarboxylic acids repeated after 3 minutes gave tensile adhesion values of 61 kg/cm^2 (870 psi) and 51 kg/cm^2 (720 psi), respectively. Such pretreatments should be clinically feasible. Somewhat lower bond strength was obtained on treatment with many acids such as 50%

phosphoric-, 20% citric-, 5% quinic-, 5% 2-(hydroxyethyl)ethylenediaminetetraacetic or 5% cis, cis, cis, cis-1,2,3,4-cyclopentane tetracarboxylic acids. Adhesion was greatly lowered by pretreatment with a surfactant to improve wetting. Treatment of the tooth surface with the tetrasodium salt of ethylene-diaminetetraacetic acid in 0.001 M NaOH, a highly effective chelating agent for calcium, produced no bonding. Thus, the increased adhesion is the result of the preferential dissolution of enamel portions produced by the etching effect of the acid. This explanation was confirmed by scanning electron microscope pictures which clearly indicate that 10 or 30-second exposure to dilute acid dissolves portions of the surface enamel leading to the exposure of the enamel rods. Improved adhesion probably results from the increased surface area produced by the pretreatment. However, no bonding was obtained with freshly cut dentinal surfaces.

Future efforts will be directed to find the most effective acid treatment to be useful clinically. This study will involve the use of a wide spectra of organic acids so as to correlate chemical structure of the acid with efficiency of the enamel-restorative resin adhesive. The scanning electron microscope will be utilized to determine in more detail the etching process. Equipment more suitable for the determination of the adhesion of resin restoratives to human dentin is being constructed to evaluate the effectiveness of the various treatments in bonding human enamel to acrylic restorative resins. It is hoped that some clinical evaluation of this etching technique in combination with placement of a restorative resin can be conducted in the near future to assess its value in the treatment of precarious lesions.

4.9. Grafting of Monomers to Hard and Soft Tissues

Sponsor: U.S.A.

The initial objective of this study is to determine optimum conditions of grafting monomers to collagenous surfaces such as steer hide powder and to characterize the presence of graft polymer on the surface. A further aim is to graft by a simple experimental technique monomers to hard tissues, especially dentin and bone. Another objective is to determine what types of monomers can be grafted to a collagenous tissue to yield a product with modified surface properties.

Grafting of over 20 monomers of varying polarity was investigated with ceric ammonium nitrate as initiator. Maximum weight increases were obtained after a 3-hour reaction time. A marked increase in graft polymer yield was obtained employing 2% concentrations of a wetting agent. Use of dioctyl sodium sulfosuccinate proved most successful and resulted in grafted products having an increase in weight of up to 114%.

A standardized grafting procedure was developed to determine the amount of side chain polymer grafted onto the collagen backbone. This procedure included removal of any soluble homopolymer by extraction with a suitable solvent. Lower molecular weight acrylate and methacrylate esters can be grafted onto collagen in excellent yield. With the higher homologous acrylate or methacrylates, the weight increase due to graft polymer formed is decreased with increasing molecular weight of the monomer. This effect may be caused by steric hindrance as well as (1) the decreased solubility of the monomer in the reaction mixture, and (2) lower rate of diffusion by the monomer into collagen. Usually, smaller increases in weight were also obtained with acrylic monomers containing functional groups such as chloro-, hydroxy-, dimethylamino- or _t_-butylamino groups. With the polar methacrylic acid monomer, only a 2% increase in weight was obtained. However, a collagen-glycidyl methacrylate graft polymer with properties differing considerably from the steer hide collagen was obtained in good yield. Such a product is likely to contain a hydroxyl group which could be reacted to further modify the material.

Grafting of collagen to monomers such as vinyl acetate styrene, acrylonitrile and vinylpyrrolidone was also demonstrated. Grafting yields in aqueous solution vary widely, but probably can be improved in mixed solvents. Studies of grafting to dentin and bone were also initiated. Grafting to dentin was accomplished by presoaking dentin powder in water in the presence of a wetting agent. After extraction for 24 hours with acetone to remove homopolymer, an 8% increase in weight was obtained as compared to a 21% weight loss for dentin powder treated in the absence of methyl methacrylate monomer. Presence of grafted poly(methyl methacrylate) was clearly established by the appearance of the $COOCH_3$ absorption band around 1720 cm^{-1} in the infrared spectrum. Sections of dentin were also treated by this method. Possible bonding of these surfaces to a commercial acrylic restorative was determined by a simple tensile adhesion test after storage of the dentin-restorative resin interphase in water for 24 hours. A slight adhesion was obtained as compared to no adhesion observed for untreated dentin surfaces. However, further work is necessary to prove if these values are significant.

A simple procedure was worked out to pulverize bone. Bone marrow was cleaned and crushed in a Wiley mill in the presence of dry ice. The powder was then sieved. Use of bone marrow eliminated the tedious task of cleaning the bone of soft tissue. The powdered bone was subjected to the standard grafting procedure. A considerable amount of the material remained in solution. The presence of possible grafts is under active investigation. Thin collagen films have been procured and grafting to such films will be studied. If these efforts are successful, physical and mechanical properties of the resulting products will be determined. Possible surface changes after grafting will be viewed by scanning electron microscope techniques.

4.10. Adhesive Composite Direct Filling Materials

Sponsor: ADA, NIDR (Grant)

The development of an adhesive restorative material for anterior teeth continues. Since esthetics require that these materials have translucency comparable to that of natural teeth, the fine particulate reinforcing fillers must have refractive indexes that match, reasonably well, the refractive index of the polymeric binder material. Consequently, of the 16 glasses prepared in the previous report, one was found most suitable, and 20 pounds of it were prepared to our order in powdered form by a commercial source. Previous investigations have shown that the reinforcing filler particles should be spherical in shape, rather than irregular. Consequently, a water-cooled cyclone separator was designed and constructed. This device was equipped with a high temperature filter bag attached to the exhaust of the cyclone separator. This equipment will be used to investigate the feasibility of preparing spherical particles from the irregular particles utilizing an oxygen-acetylene ceramic powder gun in conjunction with the water-cooled cyclone separator. The glass powder to be used has a batch composition as follows:

SiO_2, 70; BaF_2, 8; B_2O_3, 4; Al_2O_3, 4; and ZnO, 14 in mole percent.

In addition to having suitable x-ray opacity, it is anticipated that its melting characteristics will be suitable for transformation into spherical particles by the aforementioned equipment.

Further investigation of the ternary eutectic dimethacrylate monomers, described in the previous report, was facilitated by cooperative efforts with a commercial organization whereby the monomer in liquid form is now commercially available. Formerly it could be obtained in crystalline form only. Utilizing this liquid, containing a minimal amount of a known phenolic stabilizer, the relationship between the concentration of the stabilizer and the hardening time of composite materials formulated with it was studied. Within the range of interest with respect to the purpose of this project, the logarithm of the hardening time had a linear relationship to the concentration of the stabilizer.

The reaction products of glycidyl methacrylate with tertiary butyl hydroquinone and with 2,5-di-t-butyl hydroquinone, respectively, were synthesized and are being investigated. This is an attempt to provide a hindered phenol-type stabilizer containing a copolymerizable methacrylate moiety, so that unreacted stabilizer or the reaction products of the stabilizer (after the induction period) will be irreversibly bound into the chains of the polymeric network.

The study of tertiary aromatic amines needed as polymerization accelerators in these composite direct filling materials was continued. The compound N,N-bis-(3-p-tolyloxy-2-hydroxypropyl)-sym-m-xylidine was synthesized and purified by fractional recrystallization. This compound's high molecular weight, purity, and effectiveness in accelerating polymerization in composite materials clearly demonstrated it to be worthy of further investigation.

A surface-active coupling agent was synthesized (the reaction product of N-phenyl glycine and p-chlorophenyl glycidyl ether). This will be compared with the previously reported coupling agents such as NPG-GMA (the reaction producty of N-phenyl glycine and glycidyl methacrylate) and the reaction producty of N-phenyl glycine and phenyl glycidyl ether, each of which significantly improved the adhesive bonding between composite materials and dentin surfaces. The purpose of this comparison will be to evaluate the relative importance of copolymerization and dispersion-force interactions between such primers and polymeric materials. Such chelating coupling agents or primers might well have extensive applications in industry where protective coatings of metal or metal-containing surfaces are of economic importance.

A presentation entitled, "Composite Restorative Material" was given at the 50th Anniversary Symposium on Dental Materials Research held at the National Bureau of Standards October 6-8, 1969, and the first draft of the manuscript, which will form a chapter of the proceedings, has been prepared.

4.11. Three-Dimensional Panoramic X-Ray

Sponsor: A.F., ADA

The inoperative "original" panoramic dental x-ray machine has been received from the Air Force (Brooks Air Base, Texas). This equipment is being renovated. A prototype 3-D camera (film carrier) is to be designed and constructed. It is anticipated that this equipment will allow two films to be exposed at the same panoramic exposure. Adaptation of the process to non-dental related portions of the body is also contemplated.

4.12. Bonding of Materials to Poly(methylmethacrylate)

Sponsor: ADA

Bonding cold-curing acrylic denture bases to acrylic teeth is needed to replace the current dependence on mechanical retention. Three methods of treating the teeth are under investigation:

1. Silica coating of the teeth followed by a silane coupling agent.
2. Swelling and softening the teeth with solvent, without or with heating.
3. Treating with a soluble polymer (PMMA) in various solvents with or without heat.

Specimens were prepared by methods similar to ADA Specification No. 15, Sec. 3.7 and 4.3.4. Controls of cold-curing base material and acrylic teeth bonded to heat-curing denture base yielded average strengths of about 500 kg/cm^2. Specimens subjected to various treatments with their respective average strengths in kg/cm^2 are:

1. No treatment, 70.
2. Silica with silane, 0.0.
3. Painting liberally with cold-curing monomer (MMA), 200.
4. CH_2Cl_2 and MMA, 260.
5. CH_2Cl and MMA for
    a. 2 min, 190
    b. 5 min, 130
    c. 7 min, 330
    d. 10 min, 100
6. Heat with a solution of CH_2Cl_2 and MMA monomer, 310.
7. PMMA dissolved in a CH_2Cl_2-MMA mixture, 380 kg/cm^2.

These preliminary results present bonding strengths exceeding the 315 kg/cm^2 required by ADA Spec. 15 in treatments 5c and 7. The decrease in strength from 5c to 5d is attributed to excessive swelling of the tooth by the solvent.

Future tests will determine the effects of successful technics on the teeth. No crazing or softening has been observed. Neither of these technics require additional equipment or time by the laboratory technician. However, a production laboratory will be asked to evaluate the technics to determine the practical merits.

4.13. Clinical Research

Sponsor: ADA, NIDR (Grant)

Clinical Evaluation of a Newly Developed Composite Restorative Material

Fifty pairs of restorations were placed clinically in October to December 1968 to evaluate a newly developed radiopaque anterior filling material. Patients were recalled in December 1969 for the first annual evaluation of these restorations. It is still too early to draw any conclusions.

Development of a Radiopaque Denture Base Material

A literature search was made to determine the extent of the need for an esthetically acceptable radiopaque denture base material. It was found in a review of 123 cases of denture foreign bodies that the greatest need was for resin based maxillary partial dentures to which are attached one or more anterior teeth.

A radiopaque glass was previously developed for use as a reinforcing filler in dental restorative materials. It was thought that this glass might be also useful as the filler in a radiopaque denture base, thus fulfilling the above need.

The radiopaque glass was used with several monomers and polymers to determine which combination appeared to exhibit the best characteristics for future development. The characteristics studied were optical translucency, radiopacity, and general handling and finishing properties. Although several of these composite materials appeared to offer possibilities for development, the one selected was based on poly(methyl methacrylate) as the resin matrix. This material was selected because of its long history of success as a denture base resin and because the composite could be handled and molded with presently used techniques and equipment.

Physical properties were determined on materials containing 30, 40, and 50% of the reinforcing glass as the filler and poly(methyl methacrylate) as the resin matrix. The results indicated that these materials would be acceptable as denture bases from a physical properties viewpoint, but several disadvantages were evident. For example, the densities and the ability to be finished to a smooth surface are less than ideal.

The materials were used in the construction of twenty technic dentures to determine certain properties under actual fabrication conditions. Although dentures could be made without difficulty, it was found that tooth breakage occurred in thick dentures containing 40 and 50% glass. The cause of the breakage appears to be the result of a silane bond produced between the porcelain teeth and the composite base material. If this is the case, then acrylic resin teeth could be used as an alternative.

The glass filler used in this study contains barium and the soluble salts of this element are extremely toxic. Therefore, before clinical studies are instituted, studies may have to be carried out to find out what, if any, hazzard exists.

Clinical Evaluation of Two Resilient Denture Liners

Twenty-three dentures, 14 lined with Silastic 616 (Dow Corning) and 9 with Coe Super Soft (Coe Dental Manufacturer) were evaluated after being in service for 21 months. The majority of both types had either deteriorated or lost their resilience to the extent that they required replacement. Consequently, the following recommendations are made for clinical use:

1. Use liners only in those cases requiring resilience to replace lost normal tissue resiliency.
2. Observe at least every 3 months.
3. Limit or confine the material to a box shaped area having 90° angle finish line.

A manuscript has been prepared describing the results of this study.

Cavity Margin Sealing by Amalgam Restorations

Dimensional changes on hardening, as prescribed in the national and international specifications, are being investigated to learn (a) how the setting change relates quantitatively to the volume of the spaces between amalgam and tooth, and (b) to establish clinically if these spaces have pertinence to recurrent caries.

The procedure in this study is to determine quantitatively, by means of air under pressure, the degree of marginal seal obtained when shrinking or expanding amalgams are placed in porcelain teeth. Additional studies will be made of delayed expansion and corrosion which may be caused by moisture condensation on the increments of zinc-containing amalgam as they are placed in the mouth. Just as moisture condenses on a mouth mirror when in the mouth, it may also condense on these increments of amalgam.

Progress to date includes:

1. Formulation and selection of 5 alloys with the following dimensional changes on hardening, +60, +20, 0, -15, and -55 μm/cm in 24 hours.

2. Preparation of amalgam and alloy samples for characterization by metallography.

3. Firing of porcelain teeth with Class I, Class V and MOD cavity preparations (these teeth have holes drilled through the root portion to the pulpal and axial walls to deliver air under pressure to the base of amalgam restorations which will be placed in the preparations).

4. Verification that the air-under-pressure test for quantitatively measuring the degree of adaptation is effective.

Future work includes:

1. Determination by using air under pressure of the effect of the various dimensional changes on hardening on the degree of marginal seal.

2. Characterizing the alloy and resultant amalgams metallographically.

3. Determining the effects on corrosion or delayed expansion caused by moisture condensation on zinc-containing amalgam during placement of the restoration.

4. Employing these variables in a clinical study.

4.14. Specifications and Advisory

Sponsor: ADA

4.14.1. Laboratory Testing for Subcommittee on Orthodontic Wire

As part of the studies to develop a specification for orthodontic wires, the modulus of elasticity of 16 austenitic stainless steel orthodontic wires was determined by a sonic method using the Dynamic Modulus Tester PPM-5. Values varied from 26.4 to 30.1 x 10^6 psi.

The 6 inch-pound Tinius Olsen stiffness tester has been calibrated, and the results indicate that it is reproducible to 0.01 in.-lb. Preliminary work with Elgiloy Resilient wire shows that the wire has a modulus of stiffness of about 17 x 10^6 psi. (The values obtained by this procedure contain both elastic and plastic components according to the Tinius Olsen Company). With the 0.016 diameter wire, a maximum moment of 0.16 in-lb was obtained for Elgiloy Resilient while a maximum of 0.12 was obtained for Elgiloy Soft. For the purpose of writing a specification, the maximum moment may be used as the measure of resilience since the modulus values are approximately the same for all wires tested.

4.14.2. Specification Committee Activities

Listed below are the Committee and Sub-committee assignments most active in this current reporting period:

Chairman, American Standards Committee PH6 dealing with nomenclature, standards and specifications for dental x-ray film and dental x-ray machines and accessories. At the present time the committee is voting on:

Draft USA Standard Exposure Time Designations for Timers of X-ray Machines, PH6.4 - 1969.

Draft of Revision of USA Standard Size Designations and Dimensions for Intraoral Dental Radiographic Film, PH6.2 - 1969.

Draft of Revision of USA Standard Speed Classifications for Intraoral Dental Radiographic Film, PH6.1 - 1969.

Proposed changes in ADA Specification No. 22 for Intraoral Dental Radiographic Film suggested by PH6 at its June 9, 1969 meeting.

All apparently are to be approved.

Leader: USA Delegation to the Plenary Session of ISO/TC 106 - Dentistry.

Vice chairman: WG 3 - Terminology and Miscellaneous.

Secretary: Subcommittee on Specification for Zinc Phosphate Cements.

Chairman: General arrangements committee for 1969 ISO/TC 106 - Dentistry meeting in Washington, D. C.

Chairman: FDI Commission on Dental Materials, Instruments, Equipment and Therapeutics.

Chairman: Joint FDI/ISO Working Groups. These and the present status of their work follow:

Joint Committee of FDI Commission on Dental Materials, Instruments, Equipment and Therapeutics; ISO/TC 106-Dentistry and ISO/TC 42-Photography on Specification for Dental Radiographic Film

The Secretariat is preparing a third memorandum establishing the rules for mail balloting, sending copies of extant or proposed specifications and a draft proposal for discussion.

Joint FDI and ISO/TC 106-Dentistry Committee on Specification For Root Canal Instruments

Rules for mail balloting have been agreed upon, a worldwide list of manufacturers was prepared, extant specifications (Japanese, Germand and USA) were collected, and several suggestions have been received. All of these have been transmitted to the joint committee along with a list of proposed definitions for root canal instruments and several motions.

An informal meeting was held by those attending the meeting of ISO/TC 106 interested in the specifications for root canal instruments. The Secretariat discussed methods of conducting the work by correspondence and mail balloting, and received comments which the Chairman will formalize as motions in the next Circular Letter.

Joint FDI and ISO/TC 106-Dentistry Committee on Specification for Zinc Silico-phosphate Cements

The Secretariat will initiate work on this project as the current work on the ISO-FDI specification on zinc oxide-eugenol cements is nearing completion.

Joint Committee of FDI, ISO/TC 106-Dentistry and IEC/TC 62-Medical X-ray Equipment for Specifications for Dental X-ray Machines

Resolutions were passed by ISO/TC 106 and this Commission at its 1968 meetings establishing such a committee. The International Electrotechnical Commission (IEC) has agreed to collaborate, but the exact mechanism of conducting the committee's work has not been established. Correspondence with IEC is proceeding to reach some agreement on the establishment of a joint committee of 24 members.

Procedure for Formulating and Revising International Specifications and Recommendations

By mail ballot the Commission voted for the establishment of a joint FDI-ISO committee of six members to draft such a procedure. The ISO/TC 106 Secretariat agreed to such joint committee. The members are:

FDI -	Dr. G. C. Paffenbarger	USA
	Mr. A. R. Docking	Australia
	Dr. F. E. Pinto	Argentina
ISO -	Prof. B. Hedegard	Sweden
	Mr. L. C. Smith	UK
	Dr. Vieillefosse	France

ISO wishes to add another member to be nominated by Germany and suggests an additional member from FDI.

Recommendations for Acceptance Programs for Dental Materials, Equipment and Instruments

By mail ballot the FDI Commission on Dental Materials, Instruments, Equipment and Therapeutics (CDMIET) voted to propose a joint FDI-ISO committee of six members to draft a procedure as was recommended at the 1968 Varna meeting. ISO/TC 106-Dentistry was invited to participate and circulated its member countries after the FDI presented a more detailed scope of the work of such a committee. The FDI suggestyd that such a committee would explore all aspects of testing and accreditation programs for dental materials, instruments and equipment, would consider who has the primary responsibility, how the responsibility should be divided, quality control, referee testing, resurveys, establishment