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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 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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U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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NBS Report 10063	Clinical Investigation of a Radiopaque Composite Restorative Material.
NBS Report 10064	Plastic Reinforced EBA Cements as Temporary Restorative Materials.
NBS Report 10065	Characterization of a Composite Resin Material Developed for Temporary Posterior Restorations.
NBS Report 10068	Determination of Shear Modulus of Dental Materials by Means of the Torsion Pendulum.
NBS Report 10072	The Solubility of CaHPO_4 at 5, 15, 25 and 37°C.

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, 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 below 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 below and are appended to this report.

2. REPORTS ISSUED

NBS Report 10059 Simple Extension of Model Making Technique of Wood, Geith, Pan Liang and Dockrill.

NBS Report 10060 Crystalline Dimethacrylate Monomers.

- NBS Report 10062 The Crystallography of Other Biologically Significant Inorganic Compounds.
- NBS Report 10063 Clinical Investigation of a Radiopaque Composite Restorative Material.
- NBS Report 10064 Plastic Reinforced EBA Cements as Temporary Restorative Materials.
- NBS Report 10065 Characterization of a Composite Resin Material Developed for Temporary Posterior Restorations.
- NBS Report 10068 Determination of Shear Modulus of Dental Materials by Means of the Torsion Pendulum.
- NBS Report 10072 The Solubility of CaHPO_4 at 5, 15, 25 and 37°C .

3. PAPERS PUBLISHED

Bowen, R. L and Cleek, G. W. X-ray Opaque Reinforcing Fillers for Composite Materials. J. Dent. Res. 48:79-82, January-February 1969.

Patel, P. R.; Moreno, E. C.; and Gregory, T. M. Calculation of Diffusion Coefficients in Ternary Systems from Diaphragm Cell Experiments. J. Res. NBS, A. (Physics and Chemistry), 73:43-49, January-February 1969.

Bowen, R. L. and Mullineaux, A. L. Adhesive Restorative Materials. Dent. Abstr. 14:80-82, February 1969.

Waterstrat, R. M. Evaluation of a Gallium-Palladium-Tin Alloy for Restorative Dentistry. JADA 78:536-541, March 1969.

Mighell, A.; Smith, J. P.; and Brown, W. E. The Crystal Structure of Phosphoric Acid Hemihydrate, $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$. Acta Cryst. 25:776, 1969.

Hein, R. A.; Cox, J. E.; Blaugher, R. D.; and Waterstrat, R. M. Superconducting Behavior of A-15 Compounds. Solid State Communications 7:381-384, 1969.

Waterstrat, R. M. Crystal Structure Transformations in VPt Produced by Plastic Deformation at Room Temperature. Transactions of the Metallurgical Society of AIME, 245: 1360-1361, June 1969.

4. WORK IN PROGRESS

4.1. Determination of Crystal Structures

Sponsor: NIDR, NIDR (Grant), ADA

Silico-carnotite: $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$

The structure of silico-carnotite was determined to

learn the extent to which it is related to the structures of hydroxyapatite and glaserite, and has been refined to $R_w = 0.05$. Thus it is well determined. The structure of $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ is intermediate to the structures of the two above compounds, with a relationship much closer to that of $\text{K}_3\text{Na}(\text{SO}_4)_2$ (glaserite) than that of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite). For simplicity, the structure of silico-carnotite is discussed in terms of the ideal formula, $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$, although the crystal used (obtained from a slag from a steel furnace) contains 3% V as VO_4^{3-} .

The crystal structure of $\text{K}_3\text{Na}(\text{SO}_4)_2$ contains K/ SO_4 columns and K/Na columns. The K/Na columns are analogous to two different Ca zigzags in $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$, and the K/ SO_4 columns are analogous to the Ca/ PO_4 columns and the SiO_4 columns. In the SiO_4 columns every cation site may be considered to be vacant. The relationship between the $\text{K}_3\text{Na}(\text{SO}_4)_2$ structure and the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ structure has been pointed out by Wondratschek. This relationship is that the (OH) column in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ has been replaced in $\text{K}_3\text{Na}(\text{SO}_4)_2$ by the movement of the anions toward the central column and the movement of the cations away from the central column. The $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ structure is related to the hydroxyapatite structure in that the central OH column in hydroxyapatite is vacant in $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$, though in the latter, one-third of the Ca ions have moved from the environment to partially occupy these columns.

$\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ is also related to $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$, the structure of which we have recently determined (June - December 1968). The $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ structure may be considered to have one cation vacancy per formula weight in its relationship to glaserite. $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$ is also related to glaserite but has three cation vacancies per formula weight. Such vacancies may be important in the incorporation of structural defects in crystal structures.

There are some unexplained anomalies in the bond distances in our determination of the $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ structure. The average P-O and Si-O distances found here are 1.595 and 1.554 Å, respectively, where the converse is expected since typical P-O and Si-O bond lengths for PO_4^{3-} and SiO_4^{4-} ions are 1.54 Å and 1.61 Å respectively. P and Si were not distinguished in our x-ray refinements, but electron microprobe analyses indicate that P:Si = 2:1. The resolution of these anomalies may not be possible without further experimental work. We plan to collect data from a crystal of $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ prepared in the laboratory known to be free from impurities to obtain independent values for the P-O and Si-O distances.

Computer Programs

(i) The latest and most convenient version of the ORTEP structure-drawing program has been made compatible with the Univac 1108 computer and other crystal structure programs in use at the National Bureau of Standards. Considerable experience in its use has recently been gained.

(ii) Programs have been adapted and new ones have been written to provide a currently available series of methods of calculating x-ray powder patterns fairly routinely. These programs have been used extensively in the dental metallurgical research of this section on VPt and $\text{Nb}_{12}\text{Al}_3\text{Ge}$.

(iii) A program to read and process the output paper tape from the recently acquired Picker single crystal x-ray diffractometer so that the quantities obtained are in a suitable stage and form for use in presently available crystallographic programs has been written and tested successfully.

(iv) The program (from ORNL) to calculate lattice energies has been tested with calculations on $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and has failed to refine the water orientation to a removable value. The problem is presumably not linear with respect

to the parameters involved in specifying the water environment. This program has now been altered so that a logical sequence of changes in the orientations or translation (or other parameters) of a group in the crystal structure can be forced on it, and the optimum parameters thus chosen by searching for the minimum energy in the range covered.

Automatic diffractometer:

The Picker automatic single-crystal x-ray diffractometer equipped with a highly oriented graphite crystal monochromator was delivered in early May 1969. Intermittent, but significant, progress in aligning the diffractometer and judging its performance has been made; interruptions by malfunctioning equipment and unclear instructions have been frequent. The diffractometer is now nearly ready for the routine collection of x-ray intensity data used in determinations of crystal structure.

4.2. Physicochemical Studies of Apatite and Related Inorganic Substances

Sponsor: NIDR (Grant), ADA

Solubility of Calcium Phosphates

The generalized least squares procedure that we use for the treatment of solubility data has been mentioned in previous reports. During the present report period, a new and very useful feature has been incorporated into this procedure; the adjustment of data is now done considering a functional dependence of the equilibrium constants (solubility or/and stability) on temperature. The new approach was used successfully with the solubility data on $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. The procedure can be used to treat simultaneously all the solubility data we have gathered on the various calcium phosphates in order to derive more reliable thermodynamic constants. As an example, solutions saturated

with respect to $\text{Ca}_5\text{OH}(\text{PO}_4)_3$ give information on the stability constant of the ion pair (CaHPO_4°), but their low concentrations and relatively high pH ranges do not permit a reliable calculation of the stability constant of the ion pair ($\text{CaH}_2\text{PO}_4^+$). However, with the new procedure, it is possible to combine the solubility data for CaHPO_4 and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ with those for more basic phosphates to obtain more reliable values for the stability constants than by the use of only one set of solubility data on a given compound.

Measurements on the solubility of $\beta\text{-Ca}_3(\text{PO}_4)_2$, Whitlockite, were completed at 5, 15, and 37°C. These data, together with the data at 25°C mentioned in the previous report, have been processed according to the above procedure. The values for the solubility product constant of Whitlockite, $K_{sp} \times 10^{29}$, are 0.97 ± 0.090 , $1.7 \pm .12$, 1.1 ± 0.08 , and 0.22 ± 0.027 at 5, 15, 25, and 37°C. It appears that the solubility product constant of Whitlockite, like that of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, has a maximum in the temperature range investigated. In the case of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ we could explain this feature on the basis of the known thermodynamic properties of the salt. Calculations are being made to ascertain whether this is also the case with Whitlockite.

A manuscript describing the results from a study on the solubility of CaHPO_4 at 5, 15, 25, and 37°C was completed and was submitted to the Journal of Physical Chemistry for publication.

Hydroxyapatite Studies

Previous studies made by workers in our laboratory and also data presented by other investigators have shown the solubility product constant for hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, to vary depending on the history of the sample. We are presently making solubility measurements on

particularly dentin. Changes in the relative humidity of the air surrounding dentin are rapidly reflected in dimensional changes of the dentin.

One question to be answered by future work is whether or not structural changes in the collagen component, such as the linear shrinkage observed in soft tissue collagen above 60°C, are responsible for some of the dimensional changes of dentin. In this regard, it is recognized that the magnitude of the dimensional changes in collagen are far larger than those in dentin.

Future studies will involve measurement on anorganic materials as well as whole tooth materials. Compacted specimens made from ground tooth substance may offer some advantages for this work since the organic material can be readily removed from dentin in small particle form. Attention will also be given to the effect of changes in water content with change in temperature of tooth structure immersed in water.

4.4.2. Mechanical Behavior of Soft Tissues

Sponsor: NIDR

Employing rat skin as a model system in the study of the mechanical behavior of the mucous membrane of the oral cavity, physical properties and their variations, such as specific volume, density, change in density with temperature, enthalpy changes, stress-relaxation, stress-strain and creep, have been previously measured in this laboratory. A complicating factor has been the demonstration of non-linear elastic behavior. The question arises as to what structural change in the structure of the skin accompanies the non-linear elastic behavior.

From a physical point of view, it would be highly desirable to construct a physical analog model relating the mechanical components of skin and their physical

interaction in various phases of the elongation of the skin. This is one of the ultimate objectives of the project.

From a chemical point of view, the mechanical behavior of skin must be relatable to its structural components. This can be approached by varying the quantities of the respective structural components, e.g., water, or by introducing specific structural changes in specific components, e.g., changing the cross-linking status of the collagen component. A preliminary investigation of both methods of modifying the mechanical system has been initiated. In the former procedure, the role of the water component is being examined, while in the latter, treatment of skin specimens with highly specific enzymes or reagents has been initiated. The enzymes used were collagenase (bacterial), elastase (pancreatic) and hyaluronidase (bovine testes). D-penicillamine, reputed to induce solubilization of collagen fibrils, was the reagent employed. Wet skin specimens (130-200 mg) were suspended for 48 hours at 37°C in 50 ml of saline solution containing approximately 5 mg of enzyme or 0.8 g of D-penicillamine. Controls were run by exposure of specimens to the saline solution only.

Exposure of the skin to collagenase greatly reduced the tangent modulus (stress-strain measurement), but also induced an unstretched length twice that of the control specimens. This latter effect was not observed in specimens treated with the other enzymes or with D-penicillamine. The tensile strength of the collagenase treated specimens was reduced by a factor of 20. This loss in tensile strength and modulus on reaction with collagenase supports the conclusion that collagen is a major contributing component to the mechanical properties of skin.

Hyaluronidase treatment caused a moderate reduction

in the stress-strain modulus of the skin, indicating much less dependence of the mechanical properties of the skin on its polysaccharide components. Hyaluronidase (bovine testes) is believed primarily to attack the polysaccharide hyaluronate yielding a tetrasaccharide.

Elastase treatment induced no change in the stress-strain behavior of the skin.

Saline solution containing approximately a 0.1 molar concentration of D-penicillamine affected the stress-strain behavior of the skin to approximately the same degree as hyaluronidase treatment. The D-penicillamine is presumed to cleave intermolecular cross-linkages of collagen by formation of hemimercaptals with the aldehydic-like linkages.

The results reported here have been derived from very preliminary experiments and are only of an exploratory nature. It is anticipated that dynamic testing (equipment is being procured for this purpose) will play a dominant role in the next phase of this research.

4.5. Dental Metallurgical Studies

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

During the past six months the accumulation of data leading to the construction of phase diagrams for binary alloys containing noble metals has continued. The work on the systems Cr-Pt, V-Pt, and Cr-Ir has progressed to the point where final examinations of alloys that have already been prepared are under way. These alloys will be subjected to thermal analysis, high-temperature x-ray diffractometry and dilatometry. The experiments are essential if the diagrams are to be completely usable.

In all three systems, one observes order-disorder reactions through which certain types of atoms occupy preferred positions within the atomic lattice structure.

These order-disorder reactions are known to play an important role in determining the mechanical properties in certain alloys such as the Au-Cu dental alloys. It is, therefore, of considerable value to learn more about the various factors which determine the rate of such reactions or the ordering mechanism itself.

We have completed a study of the effects of alloy composition on the degree of ordering in noble metal phases having the Al₅ type structure. This structure is a simple one which is unusually amenable to such studies. Composition changes which can be related to the position of the constituent elements in the periodic table were observed.

Also, it was observed that elements such as osmium tend to be less highly ordered than elements such as platinum or gold. This information may lead to means for controlling the ordering reactions to obtain the optimum properties for dental applications. This work will be published shortly in the proceedings of an international conference on ordered alloys to be held in September 1969 at Lake George, New York.

4.6. A Petrographic Study of Dental Investments

Sponsor: ADA, NIDR (Grant)

During this period, work has centered on the petrographic study of dental investments used in the preparation of partial dentures. Gypsum, ethyl silicate and phosphate-bonded investments were examined after casting in both polished and thin sections. In all examined investments, cast alloy was found to have reacted with the investment or its refractory coat. Magnetic concentrates were prepared of these reaction products and were examined in transmitted light as crushed fragments and in reflected light as polished sections.

Examinations reveal that the sand-sized quartz filler in gypsum-bonded investment is not greatly mobilized in the high fire prior to casting. However, it appears that a weak sinter bond between calcium sulfate particles is the main bonding mechanism in these investments. In high-fired silicate-bonded investments, sand-sized quartz is commonly greatly mobilized and the bond appears to be primarily a sinter bond. Phosphate-bonded investments exhibit extensive sinter bonding and the sand-sized quartz filler has been highly mobilized. The exact determination of investment bonding reactions is now being undertaken.

The gypsum and phosphate-bonded investments and silt-sized zircon-and-quartz filler refractory coats applied to silicate investments have been vitrified at the cast surface. Chromium spinels and other chromium-rich phases appear to be the major cast-reaction products in all investments. Detailed study of these reactions under different oxygen pressures is now being undertaken.

Preliminary examinations reveal that cast surface roughness and investment gas permeability are influenced by the degree of cast-investment reaction and the extent of liquefaction in the formation of sinter bonds. The character of the sinter bonding affects investment-particle configuration. Extended liquefaction in sinter bonding may promote coarseness of investment-particle configuration which, in turn, promotes cast roughness. Liquefaction or vitrification in the cast-investment reactions probably inhibits gas permeability by the filling of interface pores.

Crucibles used for high fusing and low fusing alloys exhibit vitrefaction and corrosion. In Ticonium crucibles, the formation of a chromium-rich reaction layer promotes thermal-shock spalling.

4.7. Reinforced EBA Cements

Sponsor: U.S.A.

Previous investigations have resulted in improved zinc oxide-eugenol-o-ethoxybenzoic acid (EBA) cements useful as luting media and as insulating bases. Because of their brittleness, these cements are not contraindicated for temporary restoration of multiple surface carious lesions in areas subject to heavy masticatory forces. In the study completed during this period, incorporation of powdered polymers of relatively low elastic moduli properties lead to products with improved stress-bearing properties. Special emphasis was placed in determining the physical, mechanical and solubility characteristics of selected formulations. Among the polymeric reinforcing agents investigated, acrylic and vinyl copolymers appeared to be the most suitable additives. The resultant products exhibited significant increases in tensile strength (maximum tensile strength 1700 psi as compared to 700 psi for unreinforced EBA cements and 170 psi for ZOE cements). Tissue tolerance studies conducted by Walter Reed Army Institute of Research indicate that these materials are tolerated as well as zinc oxide-eugenol formulations.

These materials present good manipulative qualities. Limited clinical evaluation indicates that certain polymer-reinforced materials, on the basis of demonstrated mechanical and palliative properties, may be highly useful as long-duration temporary restoratives.

Details of this study, including the physical properties and solubility characteristics of the cements investigated, are described in the report which is appended (NBS Report 10064).

4.8. Improved Restoration Adhesion by Specific Tooth Surface Treatments

Sponsor: U.S.A.

One of the unsolved problems in restorative dentistry is the lack of adhesion between tooth tissues and permanent restorations under conditions existing in the oral cavity. Microleakage between cavity and restoration can result in the formation of secondary caries.

Development of materials that adhere to the tooth structure by interfacial forces and thus prevent fluid flow at the tooth-filling interface would greatly prolong the effective service life of the restoration.

During this report period, the effect of specific surface treatment of dentin and enamel with respect to improvement of bonding to acrylic restorative materials was studied.

The tensile adhesion test of Lee, Swartz and Culp was used to determine bond strength. This procedure is rapid and, therefore, quite suitable as a screening test. To decrease the number of teeth needed, all polished enamel or dentin surfaces were reused in subsequent experiments. Later, experiments actually showed that much higher tensile adhesion was obtained with reused teeth. Thus, the actual values should be considered as relative as compared to the respective control. However, the relative order of adhesion obtained on varying the surface treatment should not be altered appreciably by using this protocol.

Tooth treatment was conducted approximating conditions that would be clinically feasible. The surface was cleaned with a chelating agent such as tetrahydrofurane tetracarboxylic acid and primed with a solution of sodium hydroxide. A dilute aqueous solution of a heavy metal or transition metal was then applied. A steel cylinder with

a cavity filled with dental resin was pressed on the tooth surface and the samples were stored either at 100% relative humidity or in water for 20 to 24 hours. Treatment of enamel surfaces with certain halides (FeCl_3 , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, PbCl_2 , HgCl_2 , SnF_2 , etc.) gave a marked adhesion after 24-hour storage in water. It is not certain if the adhesion resulted from an exchange of Ca^{+2} ion for metal ions. Compounds like FeCl_3 , SnF_2 , PbCl_2 or AgNO_3 , probably formed a thin layer of a coherent precipitate after addition of the base which may have improved adhesion to the filling resin. Pretreatment with the chelate cleansing solution is necessary for effective bonding. It is likely that the cleanser removed Ca^{+2} ions from the surface layer which were replaced by Al^{+3} ions. Priming with sodium hydroxide is essential when FeCl_3 or AlCl_3 solutions are used. For enamel surfaces, treatment with silver nitrate, ceric ammonium nitrate or sodium molybdate is effective even without the NaOH primer. Only the silver nitrate was effective to dentinal surfaces, but because of the poor tissue tolerance of this material, its application in clinical dentistry appears to be limited. On the other hand, ceric ammonium nitrate has been used as a catalyst for graft polymerization to collagen and further studies of its usefulness and that of other transition metal salts appear in order.

A more complete study of the bond strength on extended exposure to water showed that the adhesion is lowered rapidly on prolonged storage in water, so that the tensile strength after 30 days is insignificant. Storage in an acidic environment also lowers the tensile strength.

Based on the results of this study, it is hoped that the use of potential adhesives in combination with treatment of the surfaces with salts, especially those of

transition metals, may lead to improved bonding at the tooth surface-acrylic interface.

4.9. Grafting to Hard and Soft Tissues

Sponsor: U.S.A.

In the last few years, significant progress has been made in the chemical modification of proteinaceous materials with the aim of improving the physicochemical properties of the resulting products. Grafting of monomers polymerizable to high molecular weight polymers on natural products offers an attractive technique of changing the overall properties and especially the surface behavior of proteinaceous fibers such as wool, corium collagen, dentin or bone. In such a modified product, a second polymer is attached at intervals along the chain of the original backbone polymer. By judicious choice of the type of monomer unit to be "grafted" on to the original base polymer, tailor-made products with new and desirable properties may be obtained. The initial aim of this investigation is to delineate the optimum conditions (such as kind and concentration of initiators, pH, rate of diffusion of solvent and monomer into the "backbone") of grafting monomers to collagenous surfaces. Similar experimental parameters should give satisfactory results for other soft tissues.

Whenever possible, conditions and reagents were used that may be employed clinically. In the grafting experiments, purified collagen or powdered dentin was reacted with methyl methacrylate or acrylonitrile monomer in water or in 50% aqueous dimethylformamide solutions in the presence of ceric ammonium nitrate. Under carefully controlled conditions, treatment with monomer resulted in an increase in weight of collagen ranging from 6% to 114%. This increase in weight, which is caused by formation of

homopolymer or graft polymer, was obtained if the collagen was soaked for one hour in water prior to the addition of monomer and catalyst. This soaking period appears to be necessary to swell the collagen fibers and thus increase the number of active sites accessible for grafting. Swelling also will increase the rate of diffusion of monomer into the collagen.

In a typical experiment, 1 gm of purified collagen was stirred in 30 ml of water for one hour and 1 ml of 0.05 M ceric ammonium nitrate in 1 N nitric acid was added. The mixture was deaerated with nitrogen for 15 min. Then 2.25 ml of freshly distilled methyl methacrylate was added and the mixture stirred for 3 hours at approximately 37°C. During this time the mixture became viscous and frothy. The product was filtered, dried and weighed. The appearance of the product differed considerably from the original collagen. Infrared transmission spectra using the potassium bromide pellet technique clearly indicated the presence of collagen and poly(methyl methacrylate). Twenty-four hour extraction of the product with ethylene dichloride, which should remove any homopolymer, did not indicate the presence of any soluble material (homopolymer) and produced only a negligible decrease in weight. Thus, the product appears to be collagen onto which methyl methacrylate side chains have been grafted.

Reducing the reaction period to one hour or omitting the removal of oxygen from the solution lowered the amount of polymer grafted into the collagen. Largest weight increases were obtained on addition of 0.2 percent of a wetting agent to the reaction mixture. Preliminary investigations have been made to graft methyl methacrylate monomer onto the dentin surfaces. No appreciable increase in weight was obtained on adaptation of the procedure used successfully to graft monomer onto collagen. However, on

employing an anionic wetting agent, products showing a 10% increase in weight were obtained indicating possible grafting to the dentin. Definite characterization of this modified dentin is being conducted.

To ascertain that grafting between collagen and the vinyl monomer has taken place at the collagen surface (as opposed to an intimate mixture where no chemical bonding between collagen and the vinyl homopolymer has occurred), a study was initiated to utilize the infrared spectra obtained by multiple internal reflection or ATR (attenuated total reflection) spectroscopy techniques for the possible elucidation of chemical modifications of collagen, enamel or dentin surfaces. A single 25 reflection ATR module with KRS-5 prism and a variable beam attenuator for balancing the reference beam was procured. No sharp spectra were obtained for purified collagen strands or collagen-poly(methyl methacrylate) mixtures. Dentinal powders yielded reasonably distinctive spectra. However, further experimentation will be necessary to use routinely this rapid non-destructive technique for the accurate study of the chemical composition of odontic powders within a few microns of their surface.

4.10. Composite Direct Filling Materials

Sponsor: ADA, NIDR (Grant)

The development of an adhesive restorative material for anterior teeth continues. A manuscript, "Crystalline Dimethacrylate Monomers", has been prepared which describes the syntheses and properties of three crystalline dimethacrylate monomers that appear to have advantages over the monomers previously used in composite materials.

Methacrylate monomers require various additives such as stabilizers and polymerization accelerators. Compounds were synthesized having characteristics especially suited

for use with these monomers. Special emphasis was placed on the synthesis of tertiary aromatic amines having unusually high molecular weights so as to minimize their solubility in tissue fluids and thus their freedom to diffuse into the pulp or other tissues. Knowledge previously gained regarding the requirements for color stability was utilized, resulting in experimental composite formulations having greater color stability than previously obtainable. A manuscript describing these compounds is nearly ready for publication.

A close match between the x-ray opacity of the tooth and the restorative material greatly facilitates the detection of secondary caries. Our previous work on this subject is described in a paper, "X-ray Opaque Reinforcing Fillers for Composite Materials", that was published during the report period. Sixteen additional glass formulations have been prepared, most of which contain reduced concentrations of barium oxide or barium fluoride. The objectives are to obtain a reinforcing filler glass that (1) can be spheroidized without adversely affecting the refractive index, (2) has a low coefficient of thermal expansion, and (3) obviates the necessity of mixing two parts of fused silica with the barium glass powder in the formulation of the reinforcing filler. This would simplify the manufacture of such materials; dental companies have shown considerable interest in x-ray opaque reinforcing fillers.

A review article entitled "Adhesive Restorative Materials" was prepared and was published. As a continuation of work in this area, adhesion tests were made to evaluate various synthetic coupling agents that differed slightly from the coupling agent NPG-GMA (the reaction product of N-phenylglycine and glycidyl methacrylate, described in our previous reports) which we have found to be

most effective. Four such compounds were prepared and each significantly improved bonding between a composite material and dentin surfaces relative to the application of the same solvent containing no coupling agent. However, none gave greater bond improvement than did NPG-GMA. Means were discovered for prolonging the storage stability of NPG-GMA solutions.

4.11. Composite Resin Material for Temporary Posterior Restorations

Sponsor: U.S.A.

Laboratory evaluation of certain experimental composite materials as potential temporary restoratives in posterior teeth has continued. These composites are based on formulations previously developed for use in restorations for anterior teeth. These formulations originated in the course of research at NBS sponsored jointly by the American Dental Association and the National Institute of Dental Research. The materials are based on a monomer formulation of a ternary eutectic system (isomeric phthalate esters of 2-hydroxyethyl methacrylates) and a resin filler consisting of vitreous silica and x-ray opaque glass. The latter component is included to enable the dentist to distinguish between the restoration and caries.

The previous report delineated physical properties of a restorative material prepared by employing a ratio of 1.35 g of powder per 0.4 ml of liquid. In the current report period, two additional mixing consistencies have been laboratory evaluated. These additional ratios, 1.10 g and 1.45 g of powder per 0.4 ml liquid, were included to give a range of mixing consistencies within which one might optimize certain desirable physical properties and handling characteristics. The following properties were evaluated: setting time, temperature rise on setting, setting shrinkage,

compressive strength, tensile strength, elastic moduli (Young's and Shear), thermal expansion, indentation resistance, hardness, water sorption, solubility, color stability and optical opacity. From the point of view of ease of manipulation for the tests involved, the 1.35 g to 0.4 ml ratio has exhibited optimum working consistency of those tested.

A setting time of 5 min., which includes a mixing period of 1 min, and 15 sec., indicates these formulations allow sufficient working time for clinical use irrespective of powder-liquid ratio. An increase in temperature above room temperature of 5°-7° C was measured 4 - 5.5 min. after beginning the mix. It is during this period that a large part of the polymerization shrinkage will have occurred, although such shrinkage is observed to continue on a much reduced scale for up to one week. Considering that the size of the mix used for the measurement was much larger than would be placed in a cavity preparation, this temperature rise would not be sufficient to cause injury to the pulp.

Compressive strength data (measured at 1.5 hr., 6 hr., 24 hr., 1 week and 4 weeks) show that the powder-liquid ratio did not significantly affect this property. One-day strengths were on the order of 26,000 psi and increased to about 28,000 psi after one week. These data indicate strengths which are one-half that of amalgam, comparable with silicates, and two times that of unfilled resins.

Tensile strengths were determined at the same time intervals as indicated above for compressive strengths. After 6 hrs., tensile strength of the 1.10 g per 0.4 ml ratio measured 3700 psi as compared with 4400 psi for each of the other mixes. Tensile strengths of about 5900 psi were attained with each ratio in one week.

Varying the powder-liquid ratio did not have a significant effect on modulus data. Shear modulus was determined by two dynamic methods giving about $0.7 - 0.8 \times 10^6$ psi (torsion pendulum) and 1.0×10^6 psi (ultrasonic). A Young's modulus of 2.5×10^6 psi was determined ultrasonically. The Shear and Young's modulus values for the composites are much lower than for amalgam.

Interferometer measurements of thermal expansion over the temperature range $24-58^\circ\text{C}$ indicated a value approximately one-half that for unfilled acrylic resins and about 10 ppm greater than that of amalgam. Values of this extremely important physical property were 39, 30 and 34 ppm per $^\circ\text{C}$ for the 1.10 g, 1.35 g, and 1.45 g to 0.4 ml ratios, respectively.

Water sorption values were measured after 24 hr. and 1 week at 37°C to be $0.2 - 0.3 \text{ mg/cm}^2$ and 0.4 mg/cm^2 , respectively. These data indicate considerably less sorption than the maximum American Dental Association Specification limit for denture base resin. Water solubility, 0.15%, was low compared to silicate cements.

From this data, it may be concluded that precise proportioning does not appear to be a critical factor for producing optimum properties of these composite cements.

A new silica powder has been made. This contains the same proportions of silica glass and BaF_2 glass as used previously. The materials are also from the same batch as those of the previous work. The difference is that the silica was "spheroidized" by being put through a plasma gun. The same percentages of silane and peroxides were used as before. This powder is now ready for testing.

4.12. Clinical Research

Sponsor: ADA, NIDR (Grant)

Activities in the clinical testing of dental materials

were increased, with particular emphasis placed on materials recently developed in these laboratories.

A. Development of criteria and guides for clinical evaluation of operative restorative materials: This project is preliminary to the evaluation of newly developed restorative materials. A series of guides or references was developed, including a shade guide for estimating lightness or darkness, a step block for estimating flushness at the margins, a gauge for estimating the crevice size at the margins, and a series of glass blocks of varying roughness to estimate the surface condition of the restorations. Other criteria were developed, but without reference guides.

B. Clinical evaluation of a newly developed composite restorative material: Fifty pairs of restorations were placed clinically. A newly developed radiopaque composite filling material for anterior teeth was placed in one of each pair; in the other was placed a commercially available radiolucent material. The pairs of restorations will be compared over an extended period using the reference guides in (A) above.

C. Clinical evaluation of an adhesion-promoting agent for resin restorations: Fifty-five pairs of restorations were placed in 26 patients using the newly developed radiopaque material. In one of each pair, an adhesion-promoting substance (NPG-GMA) was applied to the preparation surface. The other preparation in each pair was restored without the use of the NPG-GMA and will serve as a control. These restorations will be observed for an extended period.

D. Evaluation of radiolucencies found at the tooth restoration interface during placement of the restorations in (B) and (C) above: During the placement of the above restorations, it was noted in post-operative radiographs

that there was an unexpected incidence of radiolucent areas. An attempt was made to determine the causes of these radiolucencies by serial grinding of extracted teeth containing similar restorations. It was concluded that the radiolucencies were caused by the operator's inability to introduce the first increments of the filling material into restricted areas due to lack of access and/or air entrapment.

E. Development of a radiopaque denture base resin: The feasibility of making a resin-glass composite material for denture bases is being investigated. The glass would make the material radiopaque so that it could be located by present medical radiographic technics if aspirated or swallowed. Specimens for screening purposes indicate that such a material can be developed. However, physical properties and handling characteristics have not yet been determined.

F. Resilient liners: In a continuation of the study of resilient liners for dentures, 13 lined with Silastic 616 and nine with Coe's Super Soft were re-examined after being in service for 22 months. Three of the cold-curing silicone (Silastic 616) and one of the Coe Super Soft resilient liners have retained their original resiliency, adhesion and surface integrity. The others had varying degrees of deterioration sufficient to warrant replacement. These observations indicate that resilient liners, particularly those designed for chair-side curing, should be inspected routinely and replaced as needed.

G. Other programs: Two new programs have been initiated. One concerns cavity-margin sealing by dental amalgams to determine the relevance of national and international specifications on dimensional changes that occur during hardening. The other concerns a method for the bonding of self-curing denture base acrylic to acrylic teeth. On

both of these projects, work has been limited to laboratory investigations preliminary to clinical trials.

4.13. Specifications and Advisory

Sponsor: ADA, NIDR, NIDR (Grant), VA

Active participation in the specification work of the Dental Materials Group, IADR, continues. This includes guidance and aid in organization of the new USASI Standards Committee for Dental Materials and Devices. Dr. Paffenbarger, as chairman of USASI Sectional Committee PH6 for Dental X-ray Machines, Radiographic Films and Accessories, has made major contributions to progress in establishing standards for designation of timer dials for x-ray machines, specifications for dental radiographic films, specifications for dental x-ray machines, and revision of standards for dental radiographic film-speed classification and size.

A notable development was the revision and approval by the IADR subcommittee of the first specification on dental materials -- American Dental Association Specification No. 1 for Alloys for Dental Amalgam. The specification has been updated by using mechanical amalgamation for setting changes at 5 minutes instead of 15, and by adding an early tensile strength requirement.

The evaluation of stainless steel orthodontic wires by developing necessary physical test methods has been initiated.

The tensile adhesion test developed under NIDR contract (Lee, Swartz and Culp, J. Dent. Res. 48:211 (1969)) was critically evaluated for the Biomaterials Research Advisory Committee, NIDR. Only when the test conditions were rigidly controlled could fairly reproducible results be obtained. Length of application of cleansing and primer liquids must be specified. Changes in the viscosity (or

consistency) of the adhesive resin when applied to the surface affect the bond strength. Bond strength depends largely on the length of storage as well as the environmental conditions employed (atmospheric, 100% relative humidity or water). Potential adhesives for a round-robin evaluation test were screened under conditions considered to be clinically feasible and approximating those encountered in the oral cavity. After storage in water for 24 hours none of the systems investigated gave a high enough adhesive tensile strength (bond strength of more than 300 psi) to highly polished enamel surface to be useful for an interlaboratory evaluation test. Considerably higher values were obtained with previously used or roughened enamel surfaces. It is hoped that a test evaluation protocol can be developed in the near future using carefully prepared enamel or dentin surfaces. The availability of a scanning electron microscope (scheduled for delivery to NBS during fiscal 1970) should greatly facilitate the standardization of the surfaces of enamel and dentin to be used in these evaluation tests.

To determine solely which operating parameters affect the results of the test procedure, flat, polished aluminum or stainless steel disks were substituted for the usually curved enamel specimens. The recess of the cleaned cylinder was filled with a commercial resin. The bond strength was determined after 24 hours of storage under atmospheric conditions. This procedure appears promising for interlaboratory comparison of the reproducibility of the test method since manipulative variables used by the adhesive are kept at a minimum.

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