NATIONAL BUREAU OF STANDARDS REPORT

9492

Report on Dental Research
at the
National Bureau of Standards

PROGRESS REPORT

July 1 to December 31, 1966

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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NBS PROJECT **NBS REPORT**

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The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Army Dental Corps; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Introduction

The cooperative dental research program at the National Bureau of Standards has as its objectives the betterment of dental treatment to the public. The long record of dental materials research and standardization by the cooperative support of the American Dental Association and the Federal Dental Services has demonstrated the feasibility of enlisting the support and cooperation of physical science competence to advance the cause of better health services.

The modern concept of systems or group research has been shown to be effective and will be more effective as we get in position to use the full range of our new facilities at NBS. The relatively small amount of money that is assigned to dental research at NBS buys much more than the scientific workers which it directly supports. It brings to the biophysical problem the effective knowledge of a staff of several hundred senior scientists covering the fields of physics, chemistry, mathematics, and engineering.

It has always been the policy at NBS for all staff members to be helpful to any other scientist on the staff, through consultation, loaning of equipment and teaching the skills necessary to get maximum results. The members of the Dental Research Section have made use of this high degree of competence for assistance in a large number of problems in dental research. Some recent examples are: (1) electron probe for metal analysis; (2) X-ray fluorescence

for amalgams; (3) computer assistance in programming rheological and other studies; (4) X-ray protection for dental scientists; (5) development of ultrasonic equipment; (6) study of ionization constants; (7) crystallographic studies; (8) solubility studies; (9) measurement of particle size, porosity relative amounts of phases in a microstructure by photoelectric scanning of a photomicrograph; and (10) general assistance from library and shop services. Details of some of these examples are given below.

Crystallography:

(a) Cooperation with personnel of the crystal-structure section resulted in determination of structure of $H_3PO_u \cdot 1/2\ H_2O$ without expenditure of funds for salaries on our part. This is the result of an interest in the determination of this structure generated by our personal contacts.

(b) The crystal structure section is completing the installation of automated single-crystal X-ray intensity equipment. This equipment is complex, expensive, and requires skill in maintenance. Very few laboratories can afford to maintain this facility. We have made arrangements to use this equipment for collection of data on crystals of importance to dental science. This equipment will result in considerable saving in time in our structure studies.

(c) The crystal structure section has developed competence in computing which is equalled by few laboratories. We have received full cooperation from this group in our own calculations

(to the extent that they even provide desk space for our specific use).

Solubility:

(a) One of the most important and difficult measurements in our solubility studies is that of pH. Work done at NBS has made it possible to increase the precision of pH measurement by an order of magnitude. We have consulted frequently with Dr. Bates and members of his group and have been helped particularly in the standardization of our equipment.

(b) Considerable assistance has been received from the NBS data processing personnel in relation to computing programs used in solubility studies. In particular, the adaptation of available subroutines to our specific problems has been a great help in our calculations.

X-Ray Protection:

The use of radioisotopes in our investigations on the surface chemistry of hydroxyapatite has been facilitated by the monitoring of laboratories and equipment done by the NBS health physics personnel. Their services also include the disposal of radioactive waste.

The above are representative examples of the routine operations of the Dental Research Section - to document our many contacts with the staff of other sections of the NBS. It must be stated that we make a real effort to help others by giving help on materials and tests in which our staff has special competence. One area is the measurement of properties of small specimens

and precious alloys. It is not our purpose to over-emphasize these features, but to place in true perspective the great benefit which the dental research program at NBS receives from the cooperative assistance of NBS scientists engaged in research in other areas.

1. TOOTH STRUCTURE

1.1 Crystallography

Crystal-structure analysis yields detailed geometric information in the form of interatomic distances and angles about the arrangement of atoms in crystals. In general, the interatomic distances are inversely related to the attractive forces between atoms, and thus the nature of the forces holding the crystals together can be elucidated. Further, the structural information can be used to develop reasonable chemical models, involving geometries compatible with experience, for chemical reactions involving those crystals. For example, epitaxial relationships, crystal-growth mechanisms, crystal-hydrolysis processes, the variable stoichiometry in materials such as the apatites, and the nature of defects have all received great impetus from the use of structural information, and can be visualized when the structures of the respective crystals are known. In the period covered by this report, we have studied crystallographically three salts of potential importance to tooth and bone mineralization.

$\underline{CaCO_3.6H_2O}$: The hydrated calcium carbonates are of interest to dental chemistry because of the parallels between calcium carbonate and calcium phosphate mineralization and because of

an apparent correlation between caries and the carbonate content of enamel. It is known that carbonate interferes with calcium phosphate crystal growth but the mechanism of this interference is not known. The possible importance of the hydrated calcium carbonates in crystal nucleation (because of their lower surface energy) was stressed in an earlier report (NBS Report 9079).

A single-crystal X-ray study of $CaCO_3 \cdot 6H_2O$ yielded the following parameters:

a = 8.84 A
b = 8.36
c = 11.1
β = 110°25'

z = 4
d(calc.) = 1.80 g/cc
d(lit.) = 1.81_7 g/cc
space group = Cc or C2/c

On the basis of crystal morphology it is concluded that C2/c is the more probable of the two possible space groups. In this space group, the calcium and carbonate ions must lie in special positions; this fact should facilitate determination of this structure. It is possible to predict that all the carbonate ions are parallel to a given crystallographic plane, and the approximate orientation of this plane can be deduced from the optical properties. It is expected that the structure, once it is known, will yield valuable information concerning the coordination of calcium ions by water molecules and carbonate ions, and may be of value in understanding the transition of $CaCO_3 \cdot 6H_2O$ to the more stable anhydrous species found in vivo. An interesting and important sidelight of this work is the discovery that the transition $CaCO_3$(calcite) + H_2O (liquid) → $CaCO_3 \cdot 6H_2O$ (solid)

is accompanied by a 20 percent decrease in volume. This may have great significance relative to mineralization and calcium carbonate phase transitions in the ocean deeps.

Work on the determination of the structure of $CaCO_3 \cdot 6H_2O$ has been started, and a paper covering this phase of the work is in preparation.

$\underline{Ca_4Mg_5(PO_4)_6}$: Whitlockite, ($\beta$-$Ca_3(PO_4)_2$, is of interest to dental science because it is found in calculus, particularly in individuals from areas in which there is considerable magnesium in the drinking water. Experiments, *in vitro*, have shown that magnesium ions, for reasons as yet unknown, promote the crystallization of β-$Ca_3(PO_4)_2$. It is an unusual property for a crystal to be stabilized by impurities; an explanation for this will probably come from an understanding of the crystal structure of β-$Ca_3(PO_4)_2$. We have undertaken an investigation of the crystallographic parameters of $Ca_4Mg_5(PO_4)_6$ which is analogous in composition to β-$Ca_3(PO_4)_2$ and contains the stabilizing cation, magnesium. It was thought that a knowledge of the unit-cell parameters of $Ca_4Mg_5(PO_4)_6$ would give insight into the properties of β-$Ca_3(PO_4)_2$ (or α-$Ca_3(PO_4)_2$) without requiring a lengthy structural investigation.

A single-crystal X-ray study of $Ca_4Mg_5(PO_4)_6$ yielded the following parameters:

$\underline{a}$ = 22.9 A	$\underline{z}$ = 8
$\underline{b}$ = 9.9	d(calc.) = 2.83 g/cc
c = 17.4	
β = 99°55'	space group = Cc or C2/c

The data do not reveal an obvious relationship with the cell of β-$Ca_3(PO_4)_2$ [or of α-$Ca_3(PO_4)_2$]. The unit cell is so large (it contains 39 unique atoms) that a determination of the structure would probably be as difficult as that of β-$Ca_3(PO_4)_2$ and, thus, does not warrant priority over the structures of immediate interest such as the tricalcium phosphates, tetracalcium phosphate, and the calcium carbonates. The presence of a pronounced pseudo-hexangonal projection on the <u>b</u> face is indicated by the hol X-ray reflections. The pseudohexagonal character and the 9.99A spacing which is similar to a prominent spacing in α-$Ca_3(PO_4)_2$ suggest that there is a crystallographic relationship between the two and that eventually $Ca_4Mg_5(PO_4)_6$ may provide important clues to understanding the properties of tricalcium phosphates.

<u>$CaMgP_2O_7$:</u> When mixtures containing Ca, Mg and PO_4 are heated, the products may contain β-$Ca_3(PO_4)_2$ and $Ca_4Mg_5(PO_4)_6$ along with apatite. Such products are frequently encountered in the study of mineralized tissues and marine organisms. During our study of $Ca_4Mg_5(PO_4)_6$ it was found that when the $(Ca+Mg)/PO_4$ ratio is less than 3/2, another product is formed. Chemical analysis proved the new salt to be $MgCaP_2O_7$. A single-crystal X-ray study of this salt revealed that it resembles closely the salt β-$Mg_2P_2O_7$ as seen by the comparison of their unit-cell parameters in the tabulation.

	$CaMgP_2O_7$	$\beta\text{-}Mg_2P_2O_7$
a	6.46	6.49A
b	8.23	8.28
c	4.46	4.51
β	104°10'	104°5'
z	2	2
d(calc.)	3.44	2.98
d(lit.)	---	3.06
space group	Cm, C2 or C2/m probably Cm or C_2	Cm, C2 or C2/m* probably either Cm or C_2

* C2/m assigned in literature

The indexes of refraction ($n_\alpha = 1.61_6$, $n_\beta = 1.63_1$, and $n_\gamma = 1.63_5$) are, as expected, slightly higher than those of $\beta\text{-}Mg_2P_2O_7$, and the two sets of indexes have about the same spread. The salt $MgCaP_2O_7$ shows a pronounced cleavage, as does $\beta\text{-}Mg_2P_2O_7$.

The pyrophosphate ion plays an important but, as yet, poorly understood role in biological mineralization. Recent work has shown that pyrophosphate interferes with calcification and certain calcium pyrophosphates have been identified in arthritic joints. Saliva and some calcified tissues are believed to contain as much as 10 percent of the total phosphate as pyrophosphate. We know of no study of the possible presence of magnesium pryophosphates in hard tissues, and at this time the lack of information on the chemical properties of $CaMgP_2O_7$ prevents us from knowing if it can be involved in such tissues. There is still some uncertainty as to the configuration of the

$P_2O_7^{4-}$ ion in its various salts. The report on the structure of β-$Mg_2P_2O_7$ is of questionable accuracy; in the report it was stated that the $P_2O_7^{4-}$ ion is linear; in other structures it has been shown to be bent and in general is expected to be bent since a linear configuration implies double bonds from the phosphorus atoms to the bridging oxygen atoms. It has been suggested that the $P_2O_7^{4-}$ ion in β-$Mg_2P_2O_7$ undergoes a transition from bent to linear form at 68°C. If this is true, this is certainly an important consideration in the crystallography of pyrophosphates, and has implications relative to biologically important compounds such as adenosine diphosphate. Also, if $CaMgP_2O_7$ and β-$Mg_2P_2O_7$ are iso-structural, as is indicated by our results, it is probable that they will form solid solutions. For these reasons, we believe that the salt, $CaMgP_2O_7$, may prove to be an important compound in furthering our understanding of calcium phosphates in tooth and bone mineral and that determination of its structure and further study of its chemical properties are warranted.

1.2 Solubilities of Calcium Phosphates

Solubility of $CaHPO_4 \cdot 2H_2O$: The solubility of a calcium phosphate gives a direct indication of its thermodynamic properties and its stability relative to other calcium phosphates. The relative stability depends on variables such as temperature and composition of the solution (i.e., pH, concentrations of Ca, PO_4, and other electrolytes). From a knowledge of the relative stabilities one can predict which chemical reactions, involving the calcium phosphates, can occur under a given set of conditions;

for this reason, an extensive program on the solubilities of the calcium phosphates is being carried out. Also, provided the measurements are sufficiently precise, one can estimate the degree of association (complexing or ion-pair formation) between calcium and phosphate ions in solution. Studies on the solubility of $CaHPO_2 \cdot 2H_2O$ at 25° and 37.5°C were completed in previous report periods. During the present period, measurements at 15°C were completed and those at 5°C were initiated. We now have values for the solubility constant, defined by

$$CaHPO_4 \cdot 2H_2O(\text{solid}) = Ca^{++} + HPO_4^{--}$$

and the two dissociation constants

$$CaHPO_4(\text{solution}) = Ca^{++} + HPO_4^{--}$$

and $$CaH_2PO_4^{+}(\text{solution}) = Ca^{++} + H_2PO_4^{-}$$

at three temperatures, 15°, 25°, and 37.5°C. In the range 15° to 37.5°C, the solubility constant and dissociation constants for the ion pairs, $[CaHPO_4]^{\circ}$ and $[CaH_2PO_4]^{+}$, go through maxima. Work at 5°C was initiated so as to define these constants as functions of temperature more accurately. A new computer program has been written to give the best values for the solubility and dissociation constants, taking into account the various restrictions imposed on the system, yet allowing deviations from these restrictions commensurate with the experimental errors. The new program corrects the difficulty encountered earlier when we tried to use the conditions of electro-neutrality and mass balance without allowing for possible error. Sometimes the calculations would tend to "blow up" in attempting

to apply these conditions too strictly.

Solubility of $CaHPO_4$: Measurements on the solubility of $CaHPO_4$ at 37° and 25°C, initiated in the previous report period, were completed and those at 15°C were carried to completion. Work at 5°C and conductivity measurements of saturated solutions at 25°C were initiated. The data are being evaluated with the new computer program. Comparisons of the results for $CaHPO_4$ with those for $CaHPO_4 \cdot 2H_2O$ will be of particular value because they provide an independent check of the dissociation constants for the ion pairs.

When applied to physiological situations, the results clearly show that at 15°, 25° and 37.5°C, the salt $CaHPO_4$ is more stable than $CaHPO_4 \cdot 2H_2O$. The finding of $CaHPO_4 \cdot 2H_2O$ and not $CaHPO_4$, in calculus and pathological deposits is clearly an indication of the play of kinetic factors. The presence of the uncharged ion pair, $[CaHPO_4]$, in significant concentrations in saliva, serum, and other biological fluids is indicated by our results. This may have considerable significance relative to transport of calcium and phosphate through capillaries, membranes, and dental enamel because, in all these instances, surface charges may have great effects on rates of transport of charged ions. The effects and concentrations of these ion pairs must also be taken into account in physiochemical studies involving nucleation, crystal growth and rates of crystal dissolution.

1.3 Surface Properties of Hydroxyapatite

It is well known that tooth and bone crystallites present large surface areas to biological fluids, and that the amounts of calcium and phosphate ions on these surfaces are several orders of magnitude greater than the amounts present in the surrounding solutions. There is, however, considerable uncertainty as to the structural kinetic and thermodynamic picture of how these ions are held to and released from the surfaces. We have undertaken a program to elucidate some of these factors employing the simplest possible system to facilitate interpretation of the results. For this reason we are using a synthetic hydroxyapatite of relatively high surface area in solutions which contain, as far as possible, only calcium, phosphate, and water ions. To eliminate reactions involving the crystal lattice, it is an important prerequisite that we deal only with saturated systems.

A new procedure for equilibrating hydroxyapatite with dilute phosphoric acid was developed. This involves continuous recirculation of the solution through a column of the solid. This method gave solubilities with a finely divided crystalline material (specific surface area = 25 m^2/g) which agreed well with those obtained earlier on a coarser crystalline material in batch equilibrations. From the apparent nonstoichiometry of the dissolution reaction, it was possible to calculate quantities of adsorbed calcium or phosphate per unit area of the crystallites.

A second procedure for the study of surface calcium and

phosphate employed isotopic exchange techniques. The amounts of exchangeable phosphorus and calcium on the surface in a saturated solution of pH = 5.7 to 6.5 were found to be in the order of magnitude 10^{-6} moles/m^2. The amounts of each vary as a function of the solution composition. This dependence is presently under investigation.

Calcium electrodes: Recently, two electrodes for measuring calcium-ion activity in aqueous solutions became commercially available. These electrodes have tremendous potential for the study of many biological phenomena but their application to solutions saturated with calcium phosphates is in doubt. Tests on the suitability of these electrodes for measuring calcium-ion activities in solutions saturated with calcium phosphate were initiated, also, to give an independent means of estimating calcium-ion activities in our solubility measurements. Both electrodes have been tested and calibrated in solution free of phosphate. Thus far the electrodes have performed well in the solutions saturated with calcium phosphates, but evaluation of the data is incomplete.

1.4 Diffusion Studies

Diffusion processes in dilute solutions of the ternary system $Ca(OH)_2$-H_3PO_4-H_2O have biological and theoretical importance. Several mechanisms for calcification, based on diffusion of calcium and phosphate species present in serum have been advanced. Models involving diffusion as the crucial factor in the formation of caries in teeth have also been proposed.

Ternary systems are the simplest systems in which the validity of Onsager's reciprocal relations can be tested for a diffusion process. The theoretical and experimental treatments of the present system have, besides the difficulties inherent to any multicomponent system, the complications originating from the presence of a weak electrolyte (phosphoric acid) and the impossibility of using optical methods to monitor the diffusion process such as has been done at higher concentrations.

A theoretical treatment of diffusion in the system $Ca(OH)_2-H_3PO_4-H_2O$ was described in the previous report. This treatment was substantially refined to take into account a Debye-Huckel treatment in the calculation of ionic activities. The results of our initial experiments, with 8 different concentrations, indicate that the treatment is valid and that Onsager's reciprocal relations are obeyed quite well. An important result is that the cross terms in the diffusion matrix were found to be of the same order of magnitude as the diagonal terms. This means that a simple Fick's law diffusion model of the system, which is frequently employed, is inappropriate, that a model of the type used in the derivation is mandatory, and that the conclusions of investigators who have used Fick's law in dissolution and diffusion studies must be critically re-examined. Experimental testing of the equations is being continued.

In terms of one of our ultimate goals--understanding the diffusion of calcium and phosphate through enamel--the present theoretical development will make it possible to understand

why various factors influence the relative rates of diffusion of these two species, and will allow us to study how these factors effect the cross terms. We believe that herein lies an important approach to the discovery of a method for the prevention or control of caries.

1.5 Adsorption Studies

Another approach to the study of the surfaces of tooth and bone mineral is through low-temperature gas-adsorption techniques. This is the most reliable way of measuring specific surface areas. It is not generally recognized that porosity and pore-size distribution have very important influences on the apparent chemical properties attributable to these surfaces. The gas-adsorption technique is the only approach that is applicable to pores in the size range encountered in tooth and bone tissue. We are making surface area and pore-size distribution determinations on tooth, bone and synthetic apatites. Some of the measurements relate to the materials being used in the radioactive exchange studies and the heats of immersion study described elsewhere in this report, and others to materials that will be used in studies of adsorption from aqueous solutions. One of the difficulties encountered in this research is that the computations, when done by hand, are extremely tedious. Considerable effort was spent during this report period in developing a program for automatic data processing. It accomplishes the following tasks:

(a) converts raw data to adsorption points to determine the adsorption isotherm;

(b) determines and plots the B.E.T. least-squares fit to obtain the surface area, together with an estimate of the precision; (c) calculates the "dead space" in the sample container from which the absolute density of the solid can be determined; (d) provides a curvelinear interpolation over the entire length of the adsorption isotherm for input to pore-size computation; (e) determines the pore-size distribution and plots the pore-volume profile.

This program was tested successfully using adsorption data that had previously been processed by manual methods. This program will greatly enhance output of gas-adsorption results.

Adsorption on solids from solution is an area with many applications in dental research and which we plan to give more attention to in the future. A physiochemical model describing the kinetics of the adsorption process which has considerable promise was reported by us (J. Res., NBS 66:503 (1962). Its complexity (being nonlinear) has limited its use because of difficulty in handling the computations necessary

to determine its two parameters. Accordingly, a computer program has been worked out which tested successfully when used with published data. This work is being continued in the hope of applying the computer technology successfully to an even more complicated three-parameter equation for predicting desorption in solution, particularly in connection with the radiocalcium and phosphorus research described in this report.

1.6 Heat of Reaction of Components of Tooth Structure

It has been generally agreed that a major advance in filling materials would be the development of a restorative material that would adhere to the tooth by cross boundary forces between the tooth and the restorative material.

Studies of reactions taking place at the solid-liquid interface are much needed to gain basic knowledge necessary to obtain chemical bonding to tooth surface. Measurements of the heat of the surface reaction of powdered dentin, enamel, anorganic tooth tissue and synthetic fluorapatite with compounds containing different functional groups or ions should facilitate the development of procedures for modifying tooth structure necessary to achieve a chemical bond and the determination of those groups that will bond effectively to the components of tooth structure in an aqueous environment.

In previous work the specific surface of ground dentin has been determined by the BET method and the apparent heats of wetting of dentin powder of different particle size has been determined.

The measurements of the apparent heats of wetting and heats of reaction of the mineral components of tooth structure and synthetic fluorapatite have been continued. The water content of selected sample powders was decreased to study the effect of residual water upon the apparent heats of wetting. An increase in the heat of wetting was observed with decrease in the water content of the sample. Water vapor saturation of powdered tooth structure prior to its immersion was utilized to determine the surface area of the mineral components of tooth structure by the Harkins method.

The apparent heats of wetting of powdered tooth structure in various aqueous solutions were determined to measure quantitatively the reactivity of powdered tooth structure with various ionic species and functional groups. The values of the apparent heats of wetting in pure water and in aqueous solutions are markedly affected by the presence of collagenous matter. Dry powdered dentin reacts with 0.006 to 0.6 M aqueous ammonium citrate, malonic, ascorbic, citric,

and methacrylic acid to yield H_w values ranging from 26 to 67 cal./g. The H_w values obtained for enamel, anorganic whole tooth tissue, and synthetic fluorapatite ranged from 0.50 to 21 cal./g.

The reactivity of powdered tooth structure with cola beverages was also investigated. The comparison of the reactivities of anorganic tooth tissue (17.8 cal./g.) and enamel (17.7 cal./g.) with dentin (7.8 cal./g.) in dilute cola solutions indicates that the reactivities of these substances are dependent upon the relative amounts of calcium present.

The extraction of collagen from powdered dentin with o.1 M ammonium citrate and the subsequent recovery of the collagen by dialysis against tap water has been accomplished. The reactivity of the recovered collagen will be further studied.

The effect of dilute solutions of stannous fluoride upon tooth structure is also being investigated.

2. MECHANICAL PROPERTIES OF MATERIALS AND ORAL STRUCTURES

2.1. Introduction

The importance of understanding the nature and effects of mechanical forces associated with the oral structures is evident since these structures exist primarily for the purpose of applying forces to materials. When teeth are lost through biochemical or mechanical action, the primary function of the restorative material is again the application of forces. Thus, although other properties may be of concern, for example, for esthetic reasons or for chemical stability, the essential function of restorative materials as well as natural tooth structure depends upon their mechanical properties. Forces exerted by natural teeth and restorative materials must be borne by the supporting bone and soft tissues. Information on the effects of these forces on the biological tissues is meager. An adequate understanding of the effects of mechanical forces on dental structures requires:

(1) measurement of the magnitude of the forces involved;

(2) analysis of the stress distribution in natural and artificial teeth and supporting structures;

(3) determination of the effects of stresses on teeth, restorative materials and supporting structures. At the National Bureau of Standards work is in progress on the second and third of these areas.

Measurement of the magnitude of forces on oral structures, such as biting or swallowing forces, have been reported by a number of investigators. With the new small measuring devices now available, determination of such forces is greatly facilitated. Work is not now being conducted in this area at NBS since it is thought that more can be accomplished by concentrating on the analysis of stresses and determination of the effect of these stresses.

Analysis of stress distribution in teeth, restorations and supporting tissues is a difficult problem. Theoretical stress distribution studies are generally concerned with materials with well defined properties and specimens having simple shapes. The inhomogeneity of properties and irregular shapes of natural or even artificial oral structures present a very complicated problem

in stress analysis. At NBS both theoretical and experimental methods are being developed for an attack on this problem.

The determination of the effects of forces on restorative materials have been studied by well-known methods by many workers. However, application of more modern methods is needed to provide basic knowledge in this area. The problem of the effects of mechanical forces on the oral structures, which has received relatively little attention, is an obvious example of the need for cooperation between the physical and biological sciences. At NBS modern procedures are being applied to determine the effects of mechanical forces to both restorative materials and natural structures.

2.2. Stress Analysis

In determining the mechanical properties of materials, forces are applied to specimens in standardized simple shapes so that stresses in terms of force per unit area can be calculated and the failure or dimensional change observed can be related to a known stress. Structures

made from materials also fail or change dimensionally in response to specific stresses, but in an irregularly shaped structure of varying composition the stresses resulting from applied force are seldom, if ever, uniform. Maximum strain and failure occur in areas of maximum stress. If the reactions that occur in oral structures are to be realistically related to the properties of materials and the applied forces, analyses must be made of the stresses in the structures involved.

Initial efforts on this project have included a review of the literature on previous work in the area and study of the feasibility of various possible methods of attacking the problem. Both theoretical and experimental approaches will be used. In both approaches it will be necessary to begin work on simplified models and work toward the actual dental structures as the methods are developed.

For the theoretical method of analyzing stresses in teeth, it appears that it may be possible to utilize extensive programs that have been developed for analysis of

stresses in rockets. If corresponding elements in the rocket analysis program can be made to represent an outer shell of enamel, an inner shell of dentin and a pulp chamber in a simplified model of a natural tooth, the procedure will greatly expedite the initial progress on the problem.

For experimental work in this area, photoelastic methods seem to offer promise. Suitable equipment is being selected and experimental work will be started as soon as the equipment can be obtained. Other methods, such as those using minute resistance strain gages or brittle coatings, will also be employed for determining strain patterns. The combination of experimental data and theoretical analysis will provide a much better understanding of the actual stresses and strains in oral structures than is now possible.

2.3 Properties of Materials

Many investigators have reported on the mechanical properties of dental materials and many are now working on these properties. The conventional methods which have been used have contributed significantly to the improve-

ment and standardization of dental materials. However, in the future, major developments in this field are most likely to come from the employment of newer methods of investigation which provide different types and often more basic information.

One of the difficulties with the conventional methods is that the results obtained often depend upon the method of measurement as much as upon the properties of the material. For example, the usual stress-strain curve for dental amalgam can be compared only with another curve obtained by an identical procedure. If, however, the basic elastic and viscous properties of the amalgam are determined, these are independent of the method and, in fact, can be used to predict the shape of a stress-strain curve run under any known stress-time relationship.

At NBS the emphasis in work on the physical properties of dental materials is directed toward developing new or improved methods for measuring properties and to obtaining data on properties not previously investigated.

2.3.1 Study of Elastic Properties by Ultrasonic Methods

When stresses are applied to dental amalgam both elastic and viscous responses are produced. The high viscous and retarded elastic responses of amalgam have resulted in reports in the literature of chord or secant moduli of elasticity varying from about 1 to 4 x 10^6 psi. In reality these moduli depend upon both the elastic properties of the material and the time required to make the determination. One method of reducing the time of stress application and time-dependent strain to a negligible value is by the use of ultrasonic vibrations. If a pulse of ultrasonic vibrations is introduced into a specimen, the velocity of the ultrasonic wave depends upon the elastic characteristics and the density of the material. Thus, by measuring the density of a material and the velocity of an ultrasonic wave passing through it, the elastic characteristics can be determined. This method is being applied to dental amalgam.

Using a pulsed oscillator operating at a frequency of about 5 MHz and quartz transducers, either transverse or

longitudinal ultrasonic vibrations are introduced into an amalgam specimen. Using the same transducer or a second transducer at the opposite end of the specimen as a detector, the ultrasonic vibration is detected after one or more passages through the specimen. The transit times of a few microseconds are measured with an oscilloscope and the velocities are calculated. These measurements have given a value of about 9×10^6 psi for Young's modulus of elasticity in amalgam and a value of about 0.33 for Poisson's ratio. The modulus of elasticity decreases with increased mercury content. Reducing the Hg content from 50 to 35 per cent resulted in an increase of about 1×10^6 psi in Young's modulus. The method is rapid and nondestructive and should prove to be effective in evaluating the relationship of elastic constants to factors such as composition, particle size or age of the amalgam.

2.3.2 Tensile Strength of Dental Amalgam

To evaluate the effects of variations in such factors as composition, particle size, method of preparation or age on dental amalgam, it has been customary to measure

compressive strength. Compressive strength has been used because it is an easily measured property. However, failure of amalgam is usually by shear or tensile fracture. One of the difficulties in measuring tensile strength has been the problem of gripping the ends of the specimen. This problem is eliminated in two methods now in use at NBS. In one method the tensile stress is applied by centrifugal force, in the other by diametral compressive loading. The diametral loading method is being used to study the change of tensile strength with age of the amalgam.

Tensile strength of a large number of amalgam alloys has been studied at various time intervals from five minutes to 24 hours after completion of trituration. The strength of 30 alloys at 15 minutes ranges from 225 to 900 psi. These same materials at 3 hours have a strength of 1,600 to 5,600 psi. All specimens were made using a three to two mercury-to-alloy ratio, 40 seconds trituration time and a mechanical packing method with 2,000 psi

packing pressure. Tensile strength was determined by the diametral compression test. Clinical data on two of these alloys show good correlation between the rate of increase of early strength and what practicing dentists consider to be slow- or fast-setting alloys. It is hoped that additional clinical data on the other alloys will give the same correlation so that we will have a method of differentiating fast- and slow-setting alloys.

2.3.3 Dimensional Changes of Dental Amalgam

Although amalgams are the major restorative material used in dental practice, much still remains to be known about how the physical and mechanical properties relate to the way amalgam is mixed and packed. A group of 50 alloys, with which considerable experience has been obtained using hand-mixing methods, was used in a study employing a standardized all-mechanical trituration and packing procedure. The property that received our major attention during the report period was the "24-hour setting change." This measures the expansion or contraction of the set amalgam after the first 24 hours during which time the major changes in dimension occur. Since the largest

changes occur during the first 15 minutes, and this corresponds to the approximate manipulation time for the dentist, fiducial readings were taken at 5, 10, and 15 minutes for comparison with the final reading at 24 hours. The average values for the 50 alloys are given in the tabulation which also lists the value previously obtained by manual procedures.

Procedure	Time of Fiducial Readings	24-hour Setting Change Average of 50 alloys
	min.	μ/cm
Standard-mechanical	5	0.0
" "	10	+1.9
" "	15	+2.9
Manual	15	+5.9

The mechanical procedure allows us, for the first time, to obtain fiducial readings as early as 5 minutes. The results verify that there is a rapid contraction during the early period of setting. Less expansion occurred with the mechanical procedure. The main advantage of the mechanical procedure is that it eliminates the variability associated with the operator and thus permits a more systematic study

of the properties of dental amalgam. Further work planned with mechanically mixed amalgams includes study of their early flow properties and of the effect of prior thermal treatment of the alloy on the 24-hour setting change.

2.3.4 Mechanical Properties of Skin

The oral cavity is lined with a mucous membrane, the outside layer of which is epithelium. Beneath this is the lamina propria, the supportive connective tissue of the epithelium. The lamina propria contains flat collagen and elastic fibers which penetrate into and through the fatty elastic submucosa. The degree of attachment of the submucosa to the deeper tissue layers determines the mobility of the mucous membrane. The mucous membrane covering the gingiva (surrounding each tooth) and that covering the hard palate are those portions of the oral mucosa most like skin. These two areas of the oral mucosa are the ones most often subjected to mechanical stress which can cause inflammation. If too much stress is applied too long to one area of the mucous membrane, an inflamma-

tion occurs in the lamina propria. Then the mechanical behavior of the membrane changes in the inflamed area since the mechanical properties of the mucous membrane are largely controlled by the lamina propria. Thus, a study of the mechanical properties of the mucous membrane should give some insight into its behavior when subjected to the stress applied by a denture. Also, some knowledge would be obtained on how inflammation and other metabolic processes govern the mechanical behavior of the mucous membrane.

Since the progression of periodontal disease is governed by the inflammation of the connective tissue of the gingiva, a measure of the progress of the inflammation in terms of metabolic variables and mechanical parameters may lead to a better understanding of the disease and how to control its progression.

The model system now being used is rat skin which is obtainable in reasonably large sizes and in sufficient amounts to study the mechanical properties of connective tissue.

An examination of the viscoelastic and thermodynamic phenomena associated with the mechanical behavior of rat skin is being carried on. Instruments are being designed specifically for this purpose. This work is being done in cooperation with Dr. John C. Houck, Department of Biochemistry, Division of Medical and Dental Sciences, Georgetown University Graduate School.

Since specimens obtained from the skin of animals are difficult to cut in such a manner as to give a perfectly uniform cross-sectional area, previous determinations of the cross-sectional area of skin have been somewhat inaccurate. However, an average cross-sectional area can be obtained by using the density of the specimen. Then, too, changes of density as a function of temperature are indicative of certain types of thermodynamic changes in the connective tissue. Therefore, the density of rat skin specimens was determined over the temperature range from 0°C to 40°C and the measurements will probably be made up to 90°C. The density of rat skin was found to be 1.085 gm/cc at 30°C. The coefficient of volumetric

expansion of skin over the physiologic temperature range was found to be 3.3 x 10^{-4}°C^{-1}. The coefficient of volumetric expansion is to be used in calculating internal energy changes and entropy changes occurring in skin under load. These thermodynamic changes can be related to molecular changes occurring in skin as a function of mechanical stress and temperature.

Phase transformation studies have been made on skin over the temperature range from 0°C to 100°C to evaluate their contribution to the mechanical behavior of skin. Further studies are being conducted on these thermodynamic-governed phenomena and evaluated in relation to the normal and abnormal physiological functions of connective tissue.

Also, preliminary studies, conducted on the mechanical stress behavior of rat skin, have indicated that viscoelastic-governed phenomena play a dominant role in the mechanical function of skin at physiological temperatures while at higher temperatures thermodynamic control behavior becomes dominant.

3. DENTAL METALLURGY

One of our major objectives in dental metallurgy is to encourage technical innovations useful in dental applications and devices. This means developing alloys to the stage where private industry will be encouraged to market and sell the product to the dental profession. In accomplishing this objective we must be aware of the needs of the dental profession but equally important is an awareness of current technology. For example, when a new process was developed by industry to produce spherical metal powders a knowledge of this enabled us to use it to improve dental amalgams.

The successful development of this new dental alloy marks only the beginning of a new program of research; it has stimulated our research toward understanding how the microstructure of this alloy is related to physical characteristics such as strength, carvability, corrosion resistance, setting expansion, rate of hardening and adaptability. This renewal of interest in microstructures stems from the unique ability to identify the location

and relative quantity of each constituent in the spherical alloy amalgam. This is due to the uniform size and shape of the alloy particles which are clearly recognizable under a microscope.

Accurate measurement of the relative amount of each phase in the microstructure, however, requires sophisticated equipment which has only recently become available as the result of a technique developed in the Metallurgy Division of the National Bureau of Standards. This technique incorporates a photo-electric cell and a rapid scanning device to measure the relative areas of light or dark regions on a photomicrograph and feeds the results directly to a computer. The computer then calculates average particle size, distance between particles, circumference of the particles, percentage of each size, and other relevant quantities.

We have applied this technique to study microstructures of spherical-alloy amalgams prepared at various packing pressures (and thus containing different amounts of mercury)

and employing different sizes of alloy particles. The amalgams were sectioned, polished and etched. Scanning and computer processing of the resulting photomicrographs is essentially complete, and evaluation of the results has begun. Our first, and still tentative, conclusion from this work is that the volume percentage of the matrix phases (i.e., silver-mercury and tin-mercury reaction products) is directly proportional to the mercury content. Although one might anticipate this result, this research will be the first time that it has been tested experimentally.

Work on the microstructures of amalgam is continuing. We believe that the scanning technique will now enable us to test percentage of matrix phase and other quantitative characteristics of the microstructure, as independent variables, in their relationship to strength and rheological properties of spherical-alloy amalgams. It is believed that the strengths of the matrix phases govern the achievable strength of amalgam. Recent research has shown that amalgams with very low mercury contents seem practicable. We plan to study the properties of such amalgams using the scanning

technique, ultrasonic determinations of mechanical properties and clinical trials.

We are also working to improve alloys for inlays, partial dentures, porcelain to metal bonds and other applications. Many of these alloys are, unfortunately, of little use to industry simply because their cost is prohibitive in the majority of industrial applications. Consequently, very little basic research has been done on alloys containing precious or noble metals. If their potential is to be utilized in improving dental alloys, where cost is not a severe restriction, we must first develop the rudiments of alloy theory as it applies to these systems. The minimum information needed to develop an alloy is a pertinent phase diagram; we are therefore beginning phase-diagram studies of noble metals. The thermal properties of these alloys require the use of a special, high-temperature, vacuum furnace. Work on this project has progressed to the point where the furnace has been put into operation and the special materials used to accurately calibrate the temperature scale for the furnace have been prepared.

No metallurgical work was done on the gallium alloys during this report period; the alloys we have developed have satisfactory physical characteristics and further work on them is contingent on their biological compatibility. The formulation we developed is undergoing clinical testing at the National Institute of Dental Research and at the University of Buffalo. We will initiate further clinical trials once the formulation is approved for extended testing on humans.

4. DEVELOPMENT OF AN ADHESIVE DENTAL RESTORATIVE MATERIAL

One of the most pressing needs in dental practice is a restorative material that adheres permanently to the hard tooth tissues. Some of the desired properties of such a material are described in the book Adhesive Restorative Dental Materials - II, Proceedings from the Second Workshop sponsored by the Biomaterials Research Advisory Committee, NIDR, U. S. Department of Health, Education, and Welfare, Public Health Service Publication No. 1494, 1966 (pages 225-231). The material we have developed is a composite material made up of a high percentage of inorganic reinforcing filler and a smaller amount of a cross-linked organic polymeric binder. The reinforcing filler consists of microscopic spheres of fused silica (giving low coefficient of thermal expansion to the composite), a barium-containing glass (giving x-ray opacity to the composite material), and an amber glass (as needed to obtain the proper color of the filling material so as to match the patient's teeth). Chemical adhesion

is obtained between the particles of filler and the organic binder by means of a silane coupling agent.

Dimethacrylate monomers were developed in our laboratories to serve as the organic binder for such composites. The first of these ("Bis-GMA") was based on the reaction product of an epoxy resin and methacrylic acid; it is the basic monomer for the commercial composite materials now being sold to the dental profession. Unfortunately, this monomer is too viscous for use without being thinned with methylmethacrylate or some other volatile monomer and, furthermore, the compound and its polymer are not completely color stable. More recent research has suggested means of obtaining other dimethacrylate monomers with improved color stability and with sufficiently low viscosity for use without the addition of volatile monomers.

Accordingly, dimethacrylate monomers were synthesized, utilizing condensation reactions of isophthaloyl chloride (I) or terephthaloyl chloride (II) with hydroxypropyl methacrylate (III) or 2-hydroxyethyl methacrylate (IV). The product from the reaction of (I) with (III) was a nearly colorless liquid

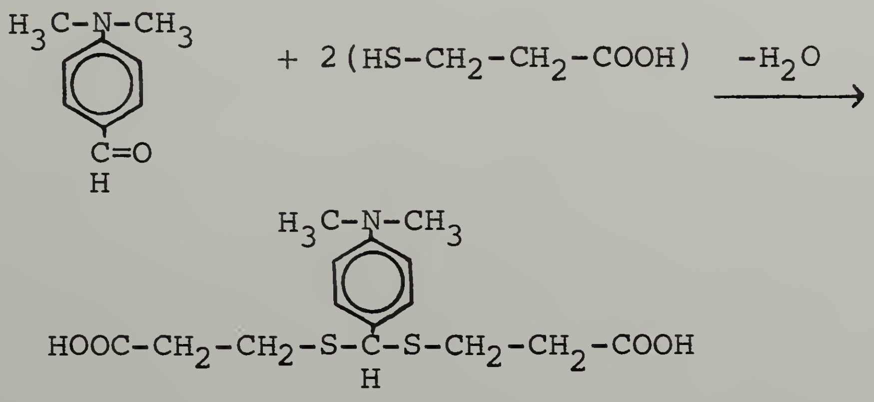
with a viscosity low enough for use without being thinned. Its formula weight was approximately 400, and it is not miscible with water. Composites prepared with it appeared to have better color stability than did those prepared with Bis-GMA. The products from the reaction of (I) with (IV) and of (II) with (IV) were each liquids that crystallized at room temperature. By recrystallization of these, two colorless monomers were obtained. When these were melted and mixed together, a colorless liquid of suitable viscosity resulted, this mixture did not crystallize on standing at room temperature.

Other current work and future research involve the synthesis of improved stabilizers, accelerators, and initiators for the polymerization of one of these monomers to give improved composite filling materials.

Such composite materials are not inherently adhesive to hard tooth tissues. To mediate bonding between such materials and the tooth surface, an adhesive primer has been devised, and shown to be effective. The essential ingredient in the adhesive primer is a coupling agent consisting of a compound containing both a group (or groups)

capable of forming stable chelate bonds to calcium and also a methacrylate group (or groups) capable of copolymerizing with the dimethacrylate resin in the composite material. Current work pertains to the synthesis and evaluation of a series of such coupling agents, and with other compounds to be used in conjunction with them. These compounds include a stabilizer and a surface-active acclerator.

One such surface-active accelerator for use in the adhesive primer formulation is a condensation product of p-dimethylamino benzaldehyde with 3-mercaptopropionic acid. Based upon the general established reaction between mercaptans and carbonyl groups, the reaction is (pending confirmation):



The condensation was carried out in refluxing benzene, the water being removed as the benzene-water azeotrope. The observed melting point, after recrystallizing from acetone-water, was 125-127°C. This product 3,3 -[[*p*-(dimethylamino)benzylidene]dithio]dipropionic acid, accelerated the polymerization of methylmethacrylate in the presence of N,N-dimethyl-*p*-toluidene. It showed qualitative evidence of being surface-active.

The adhesive restorative material under development thus contains three major subdivisions: an adhesive primer formulation which would be applied as a thin liquid film to the tooth surface, a powder and a liquid, which would be mixed to a thick consistency and placed upon the primed tooth surface. For the purpose of minimizing pulpal irritation, as far as possible, all ingredients are to be insoluble in water, have high molecular weights (within the limits imposed by viscosity), and be capable of copolymerizing to form integral parts of a highly cross-linked, glassy solid. We believe that these materials offer considerable promise as components of adhesive restorative materials.

5. BONDING OF ACRYLIC RESIN TO PORCELAIN TEETH

Direct bonding of acrylic resin denture bases to porcelain teeth has proved inadequate in dental use. It is, therefore, necessary to place metal pins or retention holes and canals in porcelain teeth to hold them in the denture base. These locking mechanisms are costly, weaken the tooth unnecessarily, and do not prevent the entrance of fluids along the tooth-resin interface which is sensitive to temperature changes. These changes cause widening of the crevice at the tooth-resin interface because the coefficients of thermal expansion of the currently used denture bases (70 to 100 parts per million per degree C) are from 9 to 12 times that of the porcelain tooth (8 parts per million per degree C). Therefore, when a denture at room temperature (20°C) is inserted into the mouth (37°C), the acrylic resin base may expand as much as 0.17% linearly while the porcelain tooth expands only 0.013%.

Furthermore, the lack of adequate or stable bonding between porcelain teeth and acrylic resin establishes surfaces

of fracture, especially in the anterior sections of dentures which are both thin in cross-section and are subjected to high stress. In nearly every broken denture, the surface of fracture appears to be at the tooth-resin interface (Fig. 1). If porcelain teeth could be bonded stably to the denture base, they could be made without pins or diatoric retention and should be stronger than they are now.

Significant improvements in bonding were accomplished by the use of a silane coupling agent between the porcelain teeth and the acrylic resin base.

The porcelain teeth were cleaned, to remove wax and other contaminants, by washing three times in a boiling water solution ofa household detergent and were then rinsed in clean hot water.

The cleaned porcelain teeth were placed into a 0.5% solution of the silane(acidified with acetic acid to a pH between 3 and 4) for 30 minutes. Acidification catalyzes hydrolysis at the methoxy groups (A to B in Fig.(2) and prepares the silane for bonding to the surface of the porcelain tooth (C in Fig.(2). The hydrolysis reaction was

allowed to continue for one hour. The teeth were then dried for 10 minutes in an oven at 110°C.

The bonding was demonstrated by (1) tensile tests on specimens made by polymerizing resin on single teeth and (2) by fabricating dentures of clear acrylic resin using silane-treated and untreated teeth, and then testing for penetration of a dye around the teeth. The tensile tests were patterned after those described in Section 3.7 of American Dental Association Specification No. 15 for Acrylic Resin Teeth.[7] The tests consisted of applying tensile forces to the acrylic resin rods until rupture occurred. In no case did a rod or the bonding area rupture.

Bonding test results are summaried in Table 1. Some specimens were immersed in distilled water at 37 ± 2°C. Others were cycled seven or eight times through a temperature range of 10 to 65 ±3°C in distilled water. (See column headed "Comments" in Table 1.)

The untreated teeth showed no measurable bonding to the resin. All thirty control specimens were too weak to withstand deflasking. The porcelain surfaces of the untreated teeth retained their gloss and the opposing rods of acrylic

resin showed smooth, glossy surfaces, indicating that very little, if any, bonding had taken place (A in Fig. (3).

The silane-treated teeth bonded with both the self-curing and the heat-curing denture base resins; considerable force was required to rupture the specimens (Table 1), and in every instance either the tooth fractured or pieces of the tooth adhered to the acrylic resin (B and C in Fig.(3).

Lines 5 and 6 in Table 1 give strengths of specimens which were silane-treated prior to waxing as previously described. This appeared to make little, if any, difference, in view of the large standard deviation.

Also, as shown in Table 1, temperature cycling in water did not seriously affect the bonding, nor did prolonged soaking in water.

To demonstrate, in another way, the sealing of the porcelain tooth-acrylic resin interface by the silane treatment, seven upper dentures were constructed. In three cases, the silane solution was poured over the teeth in the flask; in another case, the teeth were treated prior to the wax-up, and in three other cases, the teeth were not treated. Except

for the foregoing, the processing of all seven dentures was identical. All dentures were temperature-cycled six times in distilled water from 8 to 65 ± 3°C.

All seven dentures were immersed in a saturated aqueous solution of methyl blue (1 gm/25 ml) for fifteen minutes in a desiccator evacuated with a mechanical pump. The vacuum assisted penetration of the dye into fissures around the teeth. The dentures were then scrubbed with soap and water. The relative amount of acrylic resin-porcelain tooth interface closure affected by the silane treatment is shown in Figure (4). There was little penetration of the dye around the silane-treated teeth. In fact, the silane-treated teeth were so well bonded to the denture base that fracture occurred in some of the molars and bicuspids (Fig. (5). These teeth, because of the diatoric design, are susceptible to fracture and would be greatly strengthened if they were made solid.

We conclude, therefore, that porcelain teeth can be bonded to acrylic resin denture base by an appropriate silane treatment. The bonding strengthens the denture, prevents seepage of material around the necks and ridge lap portions

of the teeth, and hence aids in maintaining good denture hygiene. The bonding places strain in the porcelain teeth which may fracture during or after processing. The suggested silane treatment points the way to the re-designing of porcelain teeth with the probable elimination of the metal pins and the diatoric design as retaining features. Thus a stronger, more serviceable and esthetic porcelain tooth can be produced.

Brand of Porcelain Tooth	Brand of Acrylic Resin	Mode of Cure	No. of Treated Specimens	Comments	Tensile Strength† (psi)	Standard Deviation* σ (psi)	Coefficient of Variation, %
1 Trubyte New Hue®	Hygienic Acrylic	74°C for 1½ hr 100°C for ½ hr	8	7 days in H_2O at 37°C	1610	390	24
2 Polychrome®	"	"	3	"	1610	410	25
3 Myerson®	"	"	5	Taken through 7 temp. cycles**	1530	300	20
4 Polychrome®	"	"	6	Taken through 8 temp. cycles**	1570	570	36
5 Trubyte New Hue®	"	"	6	7 days in H_2O at 37°C***	1430	100	7
6 Trubyte New Hue®	"	"	7	"***	1200	470	40
7 Trubyte New Hue®	Densene 33	"	4	"	2050	1150	56
8 Trubyte New Hue®	Acralite Fastcure	Self-curing	5	29 days in H_2O at 37°C	1750	320	18
9 Trubyte New Hue®	Densene 33	"	5	7 days in H_3O at 37°C	1840	330	18
10 Trubyte Bioblend®	Acralite 88	"	5	"	1530	410	27
11 Trubyte Bioblend®	" "	" "	6	32 days in H_2O at 37°C	2280	400	17
Totals and Averages			60		1670	440	26

† Force required to rupture tooth divided by cross-section area of contact surface

* $$\sigma = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n - 1}}$$

** 65°C ± 3°C to 10°C ± 3°C during the cycling. These specimens were in water for two to three days.

*** Data of lines 5 and 6 were not combined, as it was desired to illustrate the variability of results in a test of this nature with averages of 6 or 7 specimens.

Fig. (1) Fractures of dentures which follow the porcelain tooth-denture base interface because of lack of bonding between the tooth and the plastic. (A) An upper acrylic resin denture which fractured when the patient chewed a piece of hard caramel candy. A slightly malpositioned natural molar occluded with the porcelain tooth shown in between the pieces of the broken denture. (B) An upper polystyrene denture that fractured in use. This is a typical midline fracture involving the notch for the frenum, the tooth-resin junction and the central anterior area of a denture. (C) A lower acrylic resin denture that was broken by pressing it in the hand. Notice the impression of the proximal surface of the incisor in the right hand piece of the broken denture.

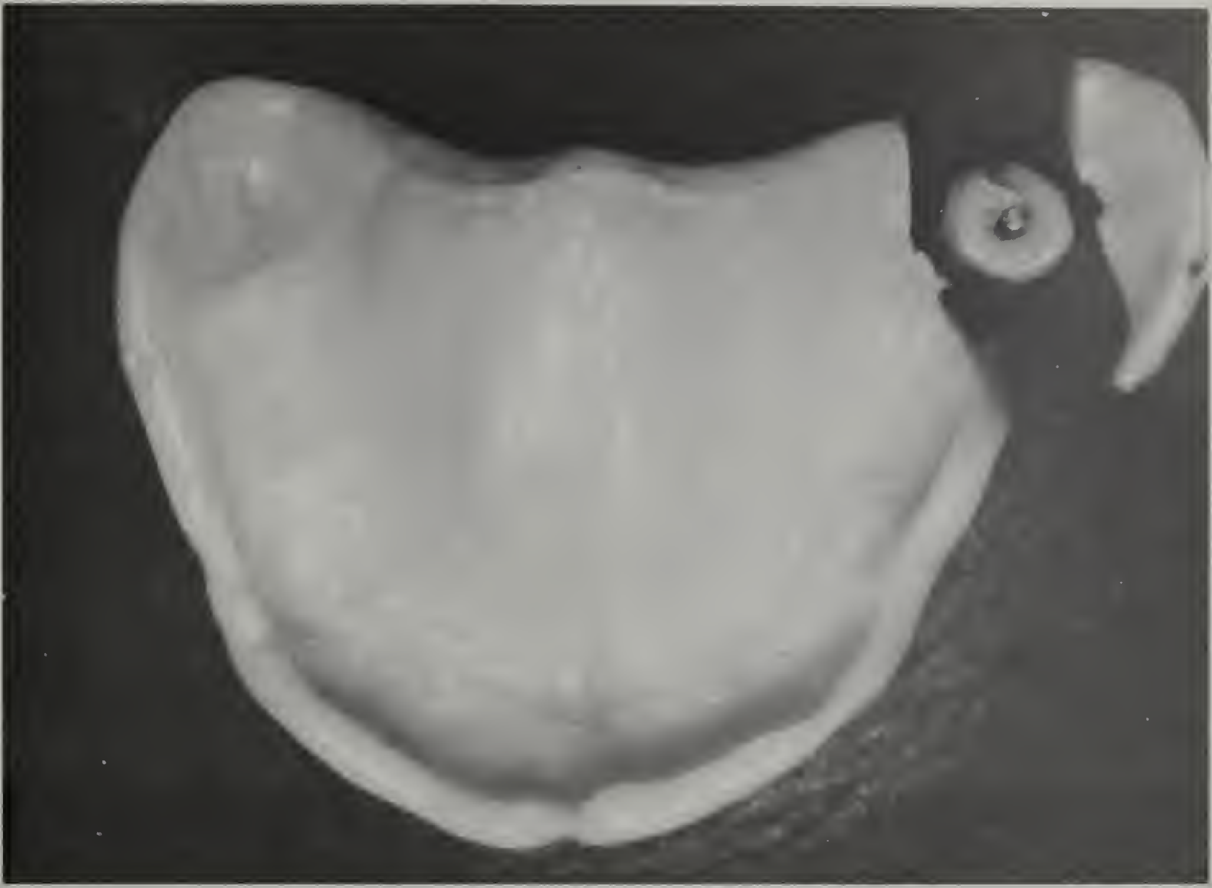


Fig. 1(A)

Fig. 1(B)

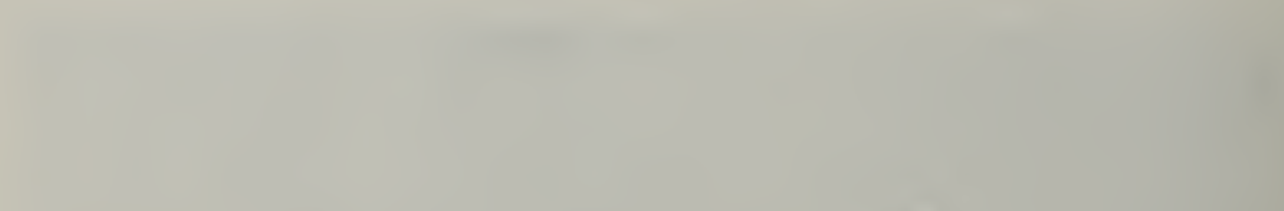


Fig. 1(C)

Fig. (2) Hypothetical schematic diagram of chemical reactions occurring in the treatment of the silica-containing surface of the porcelain teeth with the silane coupling agent.

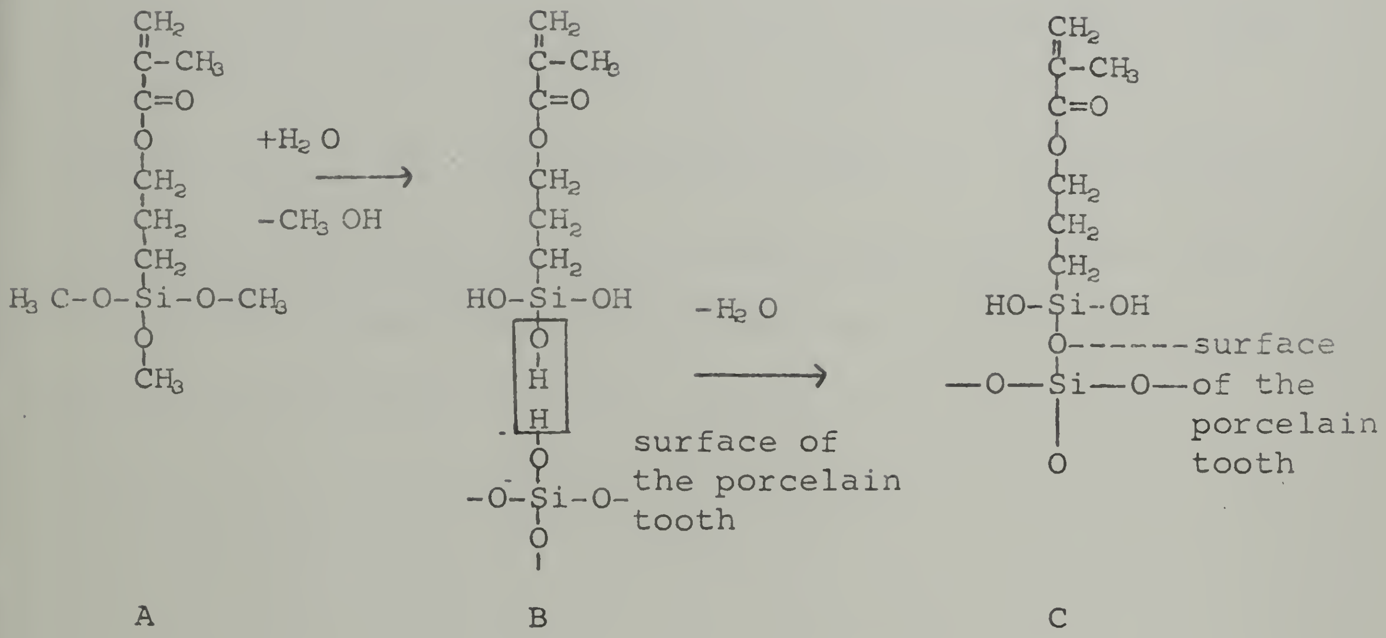

CH2
C-CH3
C=O
O
CH2
CH2
CH2
H3 C-O-Si-O-CH3
O
CH3
+H2 O
-CH3 OH
HO-Si-OH
O
H
H
O
-O-Si-O-
O
surface of the porcelain tooth
-H2 O
HO-Si--OH
O------surface
—O—Si—O—of the porcelain tooth
O
A
B
C

Fig. 2

Fig. (3) Fractured tensile specimens showing labial surfaces of incisors and ends of acrylic resin rods polymerized against the labial surfaces. In (A) there was no adhesion as the surface of the untreated tooth is undisturbed. None of the resin rods adhered to any untreated tooth. In (B) the surface of the silane-treated tooth has a saucer shaped concavity where the porcelain stuck to the end of the rod. In (C) the silane-treated teeth fractured leaving a large part of each tooth on the end of each rod.

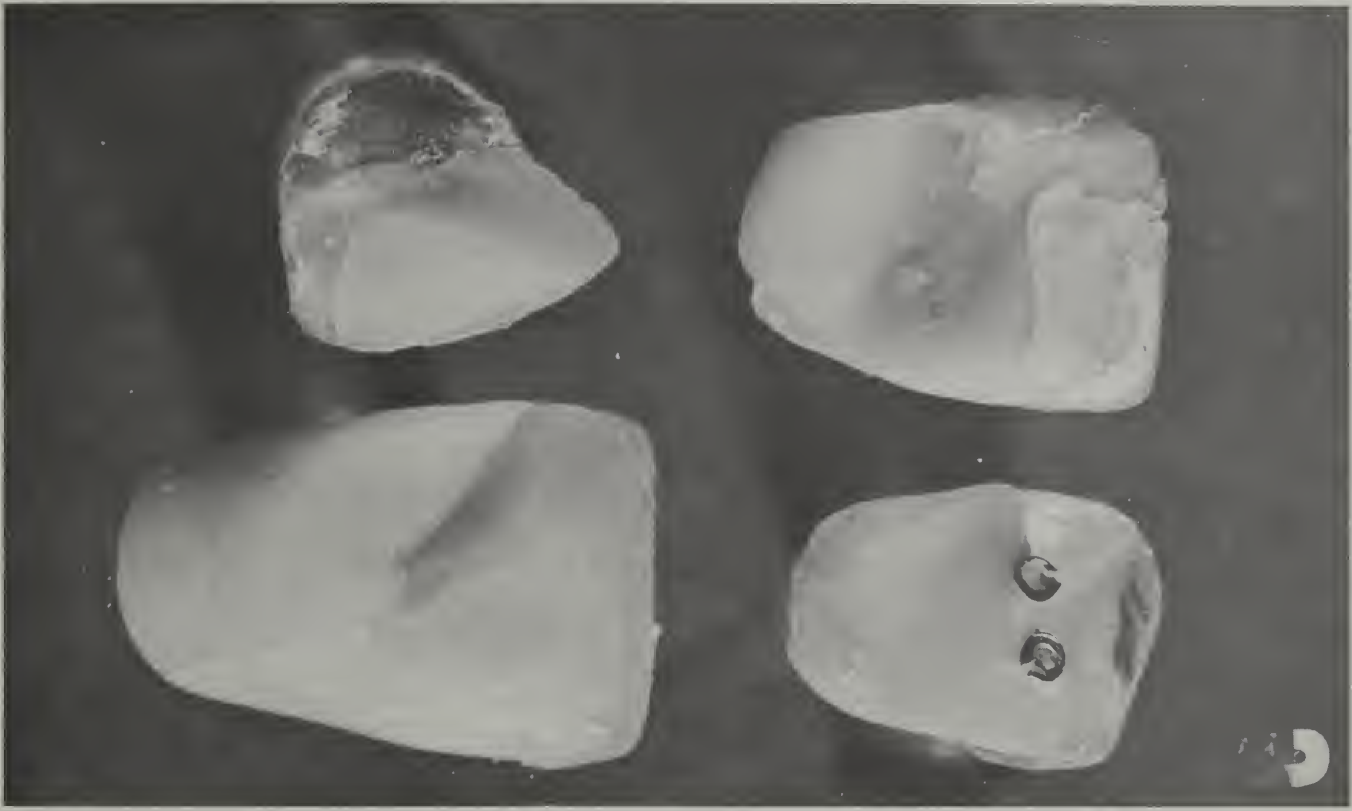


Fig. 3

Fig. (4) Dye penetration of the porcelain tooth-denture base interface. The methyl blue penetrated between the teeth and the acrylic resin base in (A) where the teeth were not treated with the silane. An angular view of the left side of (A) shows the dye penetration on the ridge lap surfaces (C). In (B) the teeth were treated with the silane and little or no penetration occurred. The upper right second bicuspid was fractured in (B) so the dye leaked into the diatoric space but did not penetrate on the ridge lap surface. The dark area in (B) is a photographic artifact, a shadow cast by the porcelain teeth on the left side of the denture.

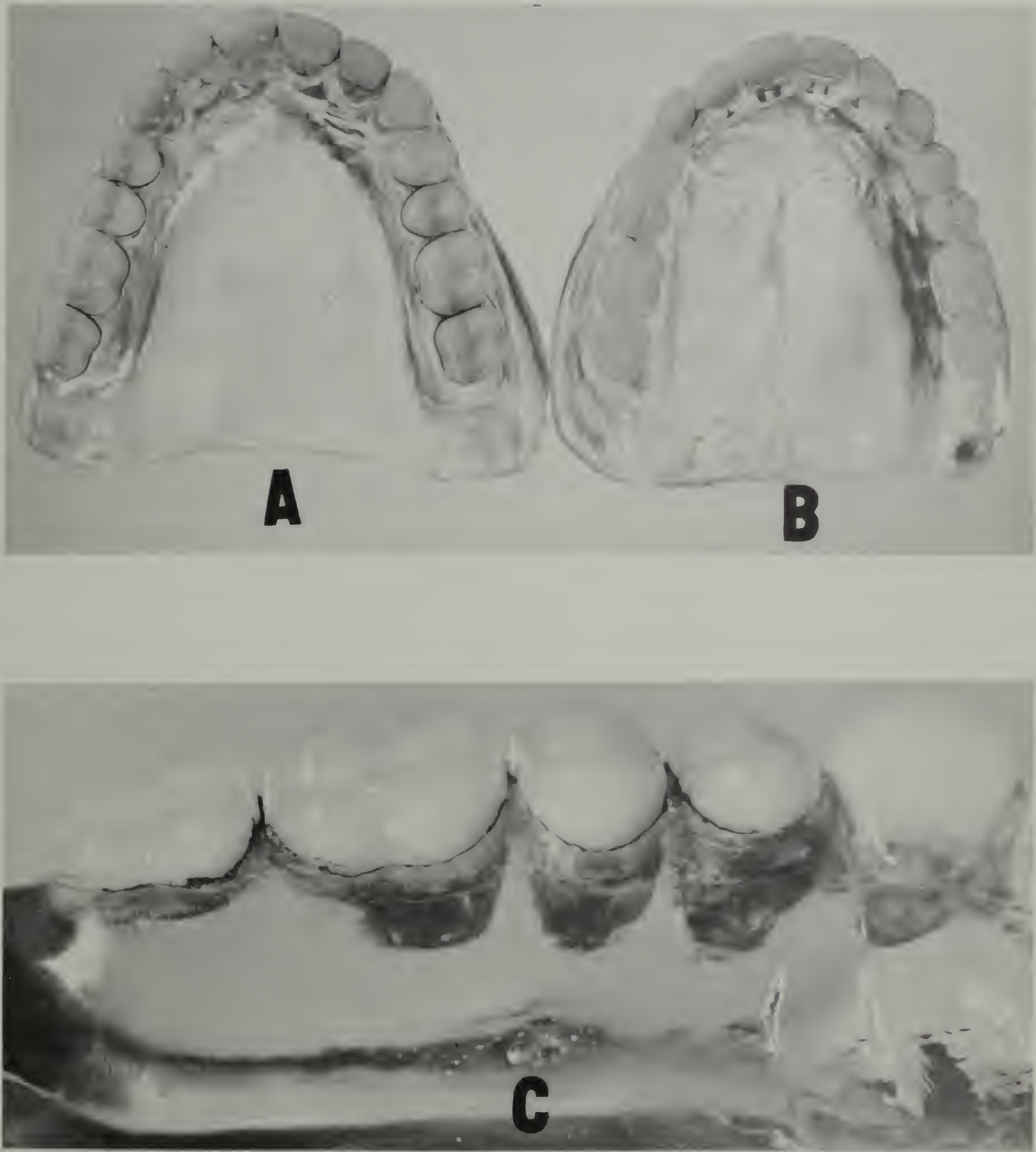


Fig. 4

Fig. (5) Fractured teeth caused by the bonding of the silane-treated teeth to the acrylic resin denture base. These fractures are difficult to see unless the angle of incidence of the lighting is adjusted to cause one-half of the broken tooth to appear darker than the other half.

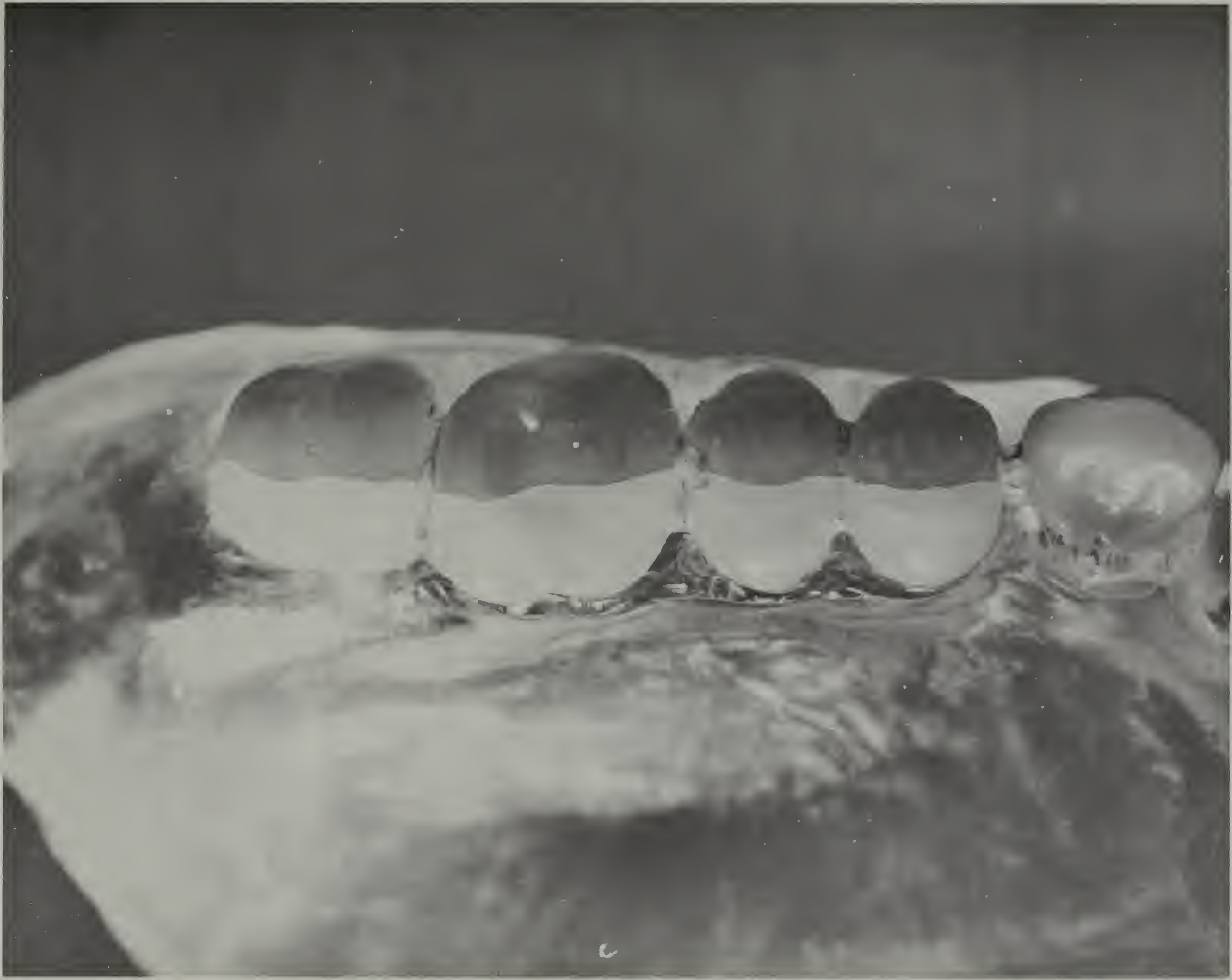


Fig. 5

6. ZINC OXIDE-EUGENOL CEMENTS

Zinc oxide-eugenol cements possess much better compatibility than most dental materials with both the hard and soft tissues of the mouth. Their biggest disadvantages are their lack of strength and lack of resistance to wear.

Previous work in this laboratory showed that a zinc eugenolate chelate is formed during the setting reaction which acts as matrix for the excess zinc oxide. Based on these findings other chelating agents have been studied and a cement was developed that has greatly improved physical properties. This crown and bridge cement is commercially available from at least three manufacturers.

Further improvement of these cements is desirable so that they will be superior to the commonly used zinc phosphate cements. Furthermore, much fundamental knowledge is needed to develop a longer lasting ZOE type filling material. This problem is complicated since correlation between laboratory tests for solubility and disintegration and clinical wear have been unsatisfactory.

Recently replacement of fused quartz by aluminum oxide in the formulation of the fortified zinc oxide- o-ethoxybenzoic acid (EBA)-eugenol cements has led to products showing physical properties similar to those of zinc phosphate cements.

The cements have improved mixing properties, improved film thickness (25 microns) and low in vitro solubility and disintegration. However, use of Al_2O_3 whiskers with particle diameter as low as 1μ did not result in any increase in physical properties. A tensile adhesion apparatus was constructed and it was found that the EBA containing cements showed slightly higher tensile adhesion than three commercially available zinc phosphate cements. As expected these formulations gave much superior adhesion compared to zinc oxide-eugenol cements.

Temporary non-hardening crown and bridge cements, which may be useful for a variety of dental applications, were developed. These cements consist of aluminum oxide powder and eugenol or glycerin liquid. These compositions confer

excellent adhesion to glass plates stored under water for prolonged periods of time. Their clinical usefulness is now being studied at Walter Reed Army Medical Center.

A paper on the ionization constants of substituted benzoic acids in ethanol-water was written up for final publication. The pk values previously reported were corrected for junction potential and the medium effect which measures the difference in free energy of the proton in water and aqueous ethanol. Assuming that the Hammett equation is valid, results of these basic studies will allow the estimation of chelate stability constants, and may allow the prediction of the solubility behavior of these cements.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