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Dental and Medical Materials
Polymer Science and Standards Division
Center for Materials Science
National Measurement Laboratory
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Washington, DC 20234

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Interagency Agreement
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Prepared for
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**U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, *Secretary***
**Luther H. Hodges, Jr., *Under Secretary***
**Jordan J. Baruch, *Assistant Secretary for Science and Technology***
**NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director***

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# ABSTRACT

Promising new dental resins that have been synthesized include surface energy reducing polymethacrylates (ave. M.W. = 10,320; each repeating unit of 1032 M.W.), a diurea dimethacrylate to lower polymerization shrinkage and methacryloxyethyl-1-adamantylcarboxylate. The latter is a tri-cyclic saturated monofunctional monomer that should also aid in reducing polymerization shrinkage and residual vinyl unsaturation. Initial attempts to improve durability used a rubber toughening approach with BIS-GMA and indicate a less brittle but tougher matrix can be achieved. Acetylthiourea and ascorbic acid have been shown to be promising non-amine type of accelerators for the BIS-GMA system. New amine accelerators such as N,N-dialkylaminophenethanol and N,N-dimethylaminophenylacetic acid are highly reactive and yield composites with high compressive strengths and good initial color. The amine, N,N-dimethyl-p-t-butylamiline, originally synthesized in this laboratory but now commercially available, gives cured denture base materials with excellent color stability and offers potential for solving some current problems in achieving matching shades in such materials. Urethane methacrylates containing residual isocyanate groups confer much lower bond strengths than are achievable with the 2-cyanoacrylate esters reported on last year. Wear data indicate that sintered hydroxyapatite is a suitable model for human tooth enamel. Fatigue as a mechanism contributing to wear is being examined by measuring wear resistance on pre-fatiguing materials.

Dimensional changes induced thermally in commercial dental porcelains are indicative of differences such as the crystalline forms that

are present. Be appears to reduce corrosion resistance of crown and bridge Ni-Cr alloys subjected to anodic polarization measurement following casting or casting and fire-cycling to simulate procelain bake on. Calculation of secondary radiation effects imparted to oral tissues from neutron irradiated gold crowns indicates the desirability for developing more information in this area.

# SUMMARY

The research on dental materials that is described in this report is a part of a larger total effort that is carried out in collaboration with the American Dental Association Health Foundation. The U.S. Army and Navy Medical R&D Command are also part of this collaborative effort through support funding and/or assignment of research personnel.

While the bulk of the research progress in this report represents only the efforts of NBS staff supported under the Interagency Agreement with NIDR, there will of necessity be a degree of contribution that originates through the intentionally strong interaction among all persons participating in this collaborative dental program.

The objective is to effect improved dental health through development of new knowledge and better understanding of the mechanical, chemical, and physical properties of restorative and caries-preventive materials and the mechanisms by which clinical performance is governed.

A wide variety of techniques has been brought to bear to generate approaches by which new and improved adhesive restorative dental materials might be developed. These include syntheses to improve today's composite restorative materials and pit and fissure sealants, investigation of new approaches to bonding restorations to tooth surfaces and exploration of rubber toughening of the composite's resin matrix as a means of generating increased durability in these systems. The precision of an automatic wear-generating and recording system is being improved to permit valid laboratory assessment of the wear resistance of dental materials. Thermal expansion and contraction data are

determined on base metal alloys and dental porcelains in order to assess the influence of this factor in the bonding of porcelain fused to metal.

The need for more durable dental composite resin systems has suggested that the use of elastomeric prepolymer monomers be considered as a means for reducing the brittleness in the glassy resin matrix while at the same time toughening the composite to allow better finishing by the dentists as well as greater durability in service. Preliminary formulations using 44% BIS-GMA, 49% triethyleneglycoldimethacrylate and 7% of a resin that is basically butadiene acrylonitrile copolymer modified with about 3% of acrylate groups produced polymers by the usual cold-curing (benzoyl peroxide-amine) and photocuring (benzoin methyl ether + UV) techniques that were less brittle than the control material. Dynamic mechanical testing of these and other similar materials is being delayed until adequate temperature control is achieved with the servo-hydraulic mechanical test machine.

Several promising new dental resins have been synthesized. These include: Polyfluorinated methacrylates (average M.W. = 10,320; each repeating unit of 1032 M.W. and having two methacrylate groups as side chains and 24 fluorines substituted in isopropylidine units of the prepolymer chain to lower the surface energy and gain greater resistance to hydrolytic degradative processes); a diurea dimethacrylate which should be useful in gaining reduced polymerization shrinkage; and methacryloxyethyl-1-adamantylcarboxylate (a tri-cyclic saturated monofunctional monomer which because of its bulk and relative paucity of reactive double bonds should also aid in reducing polymerization shrinkage and residual unsaturation.

Efforts to improve the catalyst system employed with dental resins has continued with particular emphasis on development of more efficient, less toxic accelerators. Particularly promising are two non-amine type accelerators, acetylthiourea and ascorbic acid (or its palmitic acid ester) while newly synthesized amines such as N,N-dialkylaminophenethanol and N,N-dimethylaminophenylacetic acid appear to be very efficient and capable of yielding composites with high compressive strengths, good initial color and color stability and low water adsorption characteristics. Blending glass filler particles with a solid peroxide initiator with glass filler coated with ascorbic acid or ascorbyl palmitate seems to produce a storage-stable mixed glass filler. By employing these blended fillers in powder/liquid formulations with the liquid consisting only of dental resin or dental resin plus very small amounts of a redox metal or an amine accelerator, we have obtained composites with excellent esthetics, superior to comparable composites prepared using amine accelerators.

One amine synthesized several years earlier by Research Associates of the American Dental Association for application in composite restorative systems, has now been shown to have particular merit for denture base application. This amine, N,N-dimethyl-p-t-butylaniline or DMBA (now commercially available) was shown to produce denture base specimens with no evidence of discoloration as compared to the usually very evident discoloration observed with the commonly employed N,N-dimethyl-p-toluidine. Subsequent exposures to UV light showed specimens with 0.5 and 0.25% UV absorber to be virtually free of discoloration. DMBA appears to have much promise for achieving matching shades with denture base systems.

Development of an adhesive restorative dental material has been a long sought goal of researchers in numerous laboratories. A truly adhesive technique would conceivably eliminate the marginal leakage that induces secondary caries and attacks restorations but it would also allow modified tooth cavity preparations that minimize removal of sound tooth structure. One of the more promising approaches to such adhesion has been demonstrated with 2-cyanoacrylates which, when a proper acidic cleansing of the tooth surface is utilized,yield the highest bond strengths to dentin heretofore determined. A detailed summary of this research-including quantitative data on the discouragingly rapid rates of debonding that occur in such systems in the presence of water and under thermal cycling conditions - has been prepared and published as a part of an ACS symposium on the durability of macromolecular materials.

Based on knowledge that organic isocyanates react readily with active hydrogen compounds such as the amino acid hydroxy and amino-containing side chains, methacrylate monomers with pendant isocyanate groups have been synthesized and examined for adhesiveness to bone and dentin surfaces. Optimum one-day bond strengths, obtained after an alkaline rinse of the substrate surface,were relatively low, indicating that these compounds as we have used them to date do not appear to have as much promise as the cyanoacrylate adhesives.

The synthesis of a multifunctional surface-active amine accelerator Poly SAM-1 capable of complexing $Ca^{++}$ was reported earlier. Currently the efficacy of this and other surface active amines as polymerization accelerators and as coupling agents for mediating bonding to hard tooth tissues is being evaluated. Measurements of diametral tensile strengths of hydroxyapatite powder-filled composites with and without surface-active amine accelerators adsorbed to the hydroxyapatite indicate that this is promising route to be continued.

Improvements in both the wear-generating and data acquisition components of equipment being developed to measure the wear resistance of dental materials have significantly increased the reliability of this test method. To negate the inhomogeneity and inconvenience of preparation experienced with human tooth enamel pins and to investigate the influence of different opposing materials on the wear process, measurements have been made on one composite and one amalgam with a sintered hydroxyapatite (durapatite), a mild steel and a stainless steel. The greater wear resistance of amalgam in the initial stages of wear generation relative to that observed as the wear process continues is tentatively attributed to the presence of an oxide layer, typical of what would be present continually in the clinical situation. The usefulness of softer pin materials to simulate opposing body effects generated by food particles is being considered.

As a part of the program to determine mechanisms of wear, work has been initiated to investigate the relationship between wear resistance of composite materials, their fatigue behavior, their fracture toughness and their crack propagation characteristics.

In a porcelain-fused to base metal alloy study, the dimensional change resulting from thermal cycling has been completed for nearly all ceramic specimens. The considerable variation in the expansion/contraction characteristics noted among different ceramic products appears related directly to the thermal history of the specimens, i.e., the number of firing cycles to which the material has been exposed during fabrication. Qualitative and/or quantitative changes in crystallinity of the ceramic materials appear to develop as a function of thermal history. Raman spectroscopy and x-ray analysis are being applied in structural determinations.

Specific combinations of alloys and bonding porcelains have been fused together and analyzed for void (no contact) formation at the interface (i.e. for completeness of "wetting"). Variations in porcelain alloy combinations as well as techniques of porcelain application appear to influence the area of contact. The physical and mathematical design for a porcelain-dental alloy composite structure to be used for evaluating the net effects of the factors studied on residual interfacial and tensile stresses (primary contributions to porcelain-metal failure) has been completed. An initial stress analysis has indicated the desirability of developing appropriate theory for the change in gap of a multi-layered split metal ring to allow for stress analysis within and between layers.

Anodic polarization studies of three Ni-Cr alloys indicates that fire cycling and/or conditioning and the presence of Be may influence corrosion resistance.

Calculation of secondary radiation effects from neutron irradiated gold crowns indicates the need for further efforts in this area.

# INTRODUCTION

The National Bureau of Standards is primarily a measurement organization. Paths from measurement to improved dental service lead from measurement and characterization to development of new techniques for using materials, to laboratory prototypes of improved materials and devices, to clinical evaluation, and finally, to commercial production by industry.

The dental research program at NBS is a cooperative effort both in personnel and funding, involving the American Dental Association and the U. S. Army and Navy Medical R&D Commands. With the exception of the research on porcelain fused to base metal alloy - research also participated in and partially funded by the U. S. Navy Medical R&D - the research described herein is only that portion of the dental program supported by interagency agreement with the National Institute of Dental Research.

The objective of the research effort discussed briefly in the following pages is to effect improved dental health through development of new knowledge and better understanding of the mechanical, chemical and physical properties of materials used or potentially of use in restorative and preventive dental practices. The four major areas of research as approved in the interagency agreement are given below:

I. Dental Composite, Resin and Sealant Chemistry and Development
II. Development of Adhesive Bonding Techniques
III. Wear Resistance and Mechanical Properties of Dental Materials
IV. Dental Alloy, Ceramic and Implant Research

# TECHNICAL REPORT

## I. Dental Composite, Resin, and Sealant Chemistry and Development

Dental composite restorations have essentially replaced silicate cements as the preferred technique for an aesthetic restoration procedure. With the development of filled and unfilled resins , means for fractured incisal repair, pit and fissure sealant, anticaries treatments and orthodontic bracket attachment are being realized. Despite improved dental health as a result of the use of composite restorations, their color stability, storage stability, durability and finishability are still in need of improvement.

The objective of this part of the research is to provide direction for improved composite restoratives and sealants with enhanced durability, color and storage stability and lower toxicity levels.

### A. Prepolymer Monomers for Dental Resins

Prepolymer monomers are oligomers or low MW polymers which have reactive functional groups (e.g. acrylate, methacrylate, isocyanate, etc.) capable of further polymerization.

#### 1. Polyfluorinated Prepolymer Monomers

##### a. Synthesis of Polyfluorinated Oligo (Ether Acrylates)

Direct esterification of the polyfluorinated oligo (ether-ol), as shown below, with methacryloyl chloride (Method A) or acrylic anhydride (Method B) gives the corresponding polyfluorinated prepolymer monomers in excellent yield. A paper entitled "Synthesis of Polyfluorinated Polymethacrylates for Dental Applications," presented at the (March 1979) IADR meeting, gives details of this work (1). That study demonstrated the feasibility of using prepolymer monomers as the major constituent of dental resin systems. The polyfluorinated polymethacrylate, PFMA, can be formulated to give low surface energy resin binders or sealants that have excellent mechanical strength. The use of low surface energy dental resins,such as those derived from polyfluorinated monomers, should lead to polymeric matrices that are highly resistant to degradative processes (e.g.,hydrolysis, oxidation, etc.) that occur in the oral environment. Not only should these dental polymers resist chemical or biochemical modification, such as may be evidenced by discoloration and material loss through chemical degradation, but they should also resist physical modifications such as staining or excessive mechanical wear. Moreover, as demonstrated by Craig et al., (2-4), dental composites utilizing fluorinated resin binders exhibit extremely low water sorption properties and marginal leakage. These new fluorinated monomer systems, which have much higher fluorine contents than those of Craig et al., would be expected to exhibit similar hydrophobic characteristics.

### b. Synthesis of Polyfluorinated Dimethacrylates

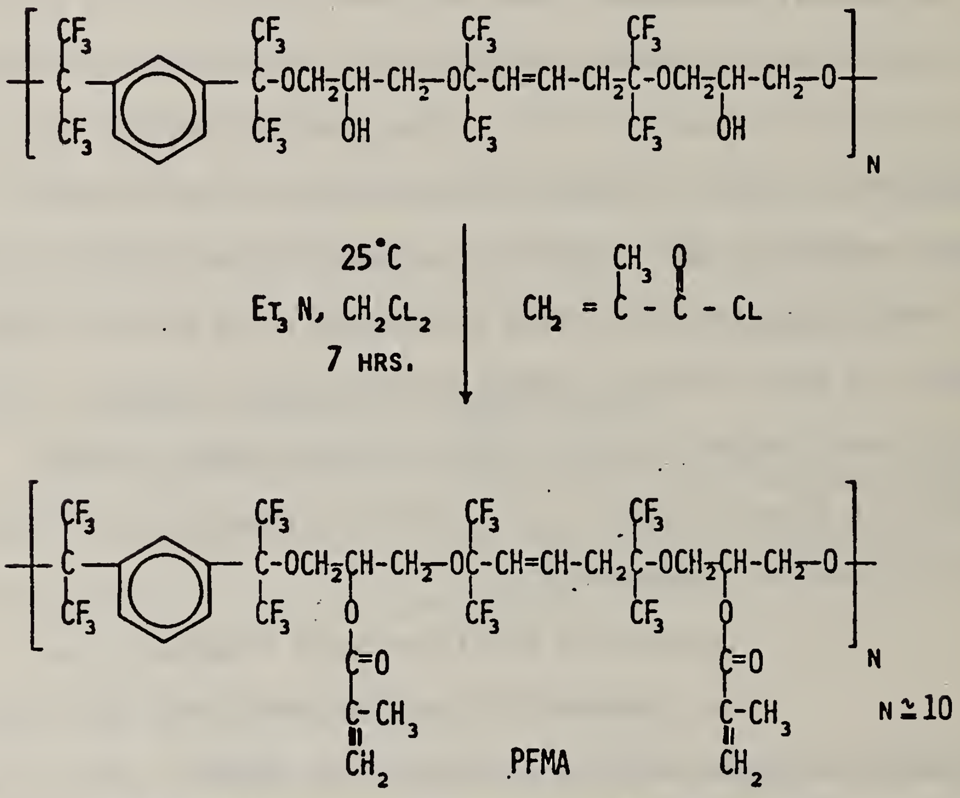
The synthesis of dimethacrylates from the corresponding polyfluorinated diols as outlined below (Method C and D) represents another approach to forming dental polymeric matrices of low surface energies and good mechnaical properties (1). These monomers will be formulated into dental resin systems and their properties evaluated.

## 2. Rubber Toughened Dental Composites and Sealants

We have expanded our studies on the use of prepolymer monomers to include <u>elastomeric</u> prepolymer monomers. It is hoped that

METHOD A

## SYNTHESIS OF FLUORINATED POLYMETHACRYLATE (PFMA)

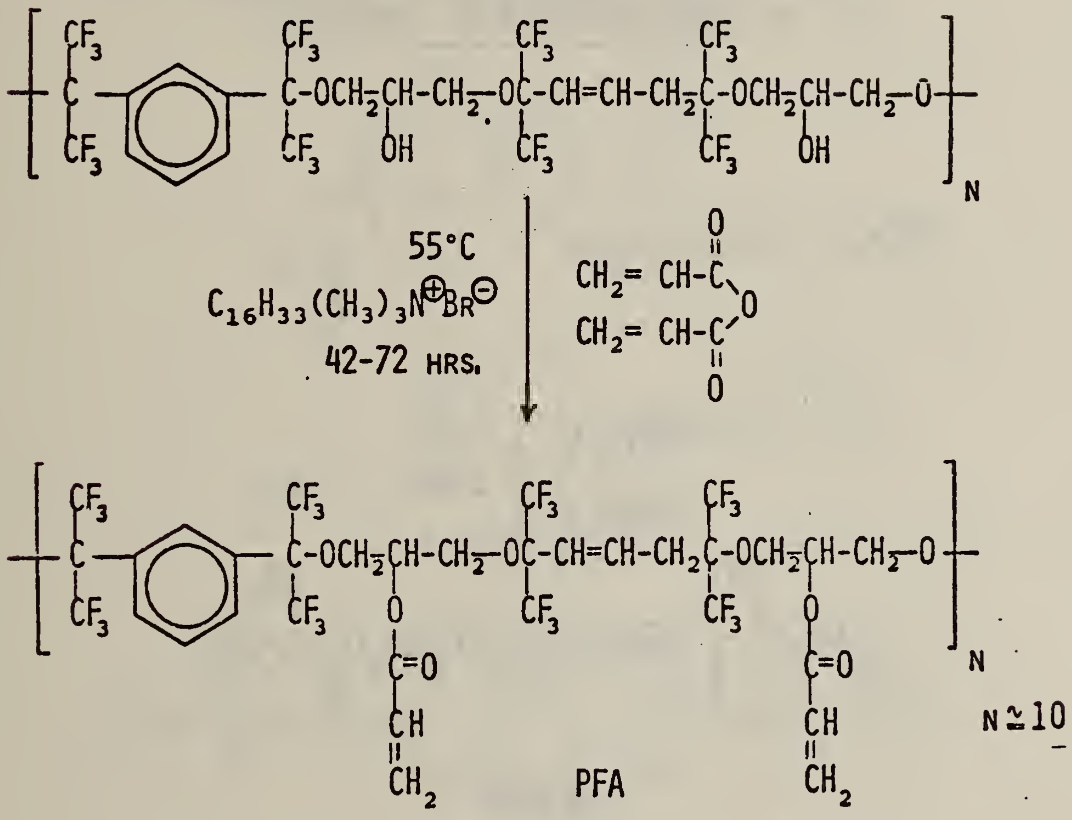


MW OF REPEATING UNIT = 1032 AVG MW = 10,320

VISCOUS LIQUID ≈ BIS-GMA

METHOD B

## SYNTHESIS OF FLUORINATED POLYACRYLATE (PFA)

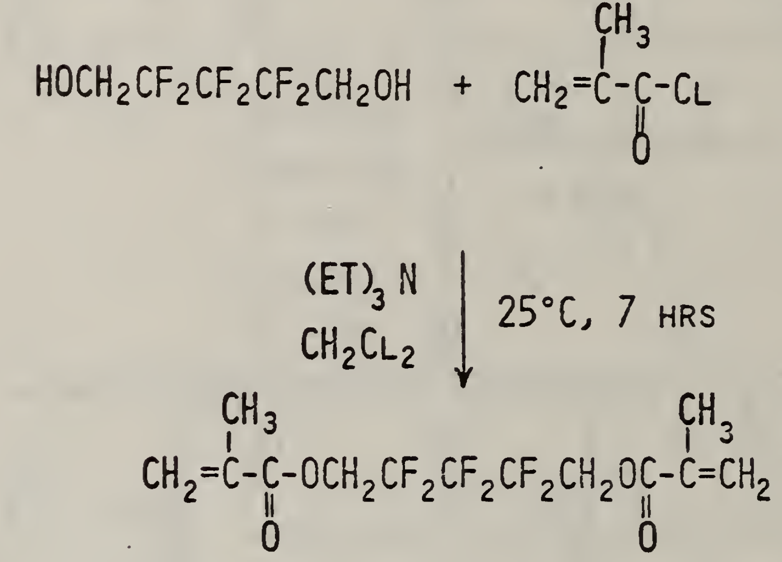


MW OF REPEATING UNIT = 1004; AVG MW = 10,040

VISCOUS LIQUID ≳ BIS-GMA

METHOD C

## SYNTHESIS OF HEXAFLUORO-1,5-PENTANEDIOL DIMETHACRYLATE (HFPDMA)



$$HOCH_2CF_2CF_2CF_2CH_2OH + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CL$$

$$\xrightarrow[CH_2CL_2]{(ET)_3N}\quad 25°C,\ 7\ HRS$$

$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OCH_2CF_2CF_2CF_2CH_2O\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

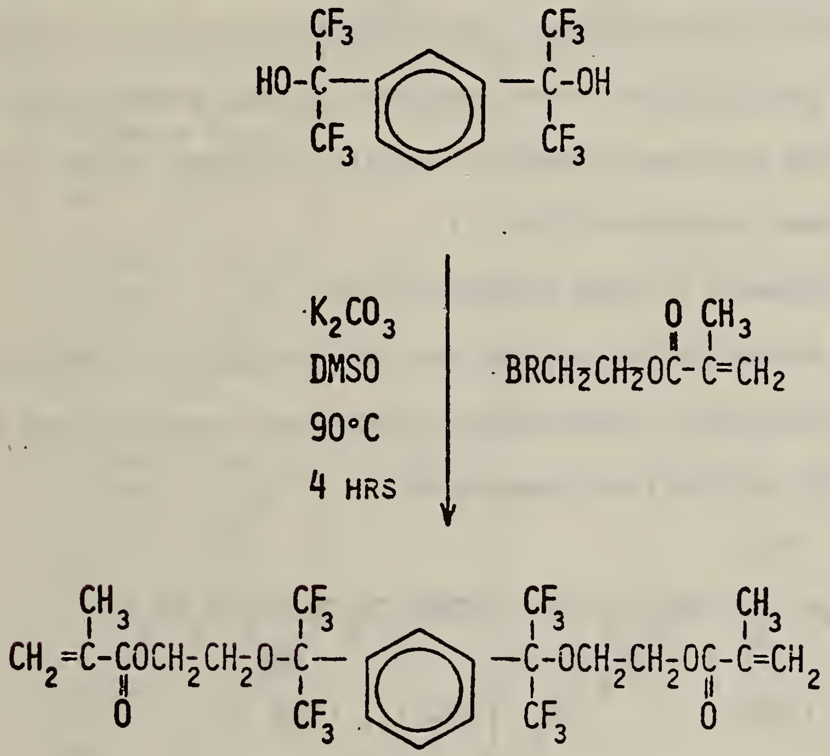
HFPDMA

MW = 348

VISCOSITY = MOBILE LIQUID ~ MMA

METHOD D

## SYNTHESIS OF BIS-(2-METHACRYLOXYETHOXYHEXAFLUORO-2-PROPYL)BENZENE [BIS(MEHFP)0]



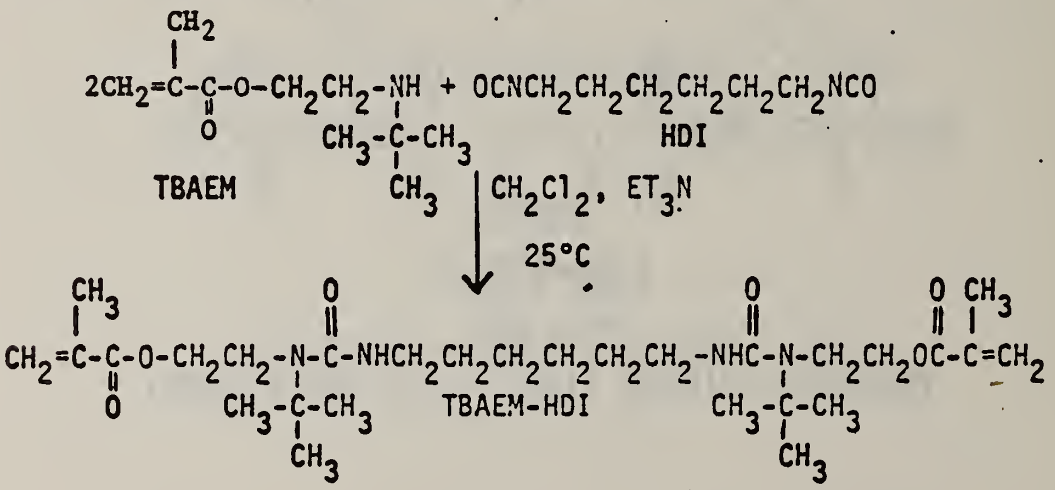
BIS(mMEHFP)0

MW = 634

MODERATELY VISCOUS LIQUID (LESS THAN BIS-GMA) their use in relatively minor amounts with conventional dental resins will result in dental composites and sealants of enhanced wear resistance without adversely affecting the other properties of these materials. Preliminary experiments have been with a commercial viscous liquid copolymer of butadiene and acrylonitrile that has been modified with a few percent terminal acrylate groups (Hycar Resins, B. F. Goodrich Co.). Formulations of conventional dental resins with Hycar resins were easily cured at ambient temperatures. The resulting copolymers containing between 2.4 and 10% Hycar resin appear to be less brittle than the normal BIS-GMA resin and diametral tensile strengths of the corresponding composites were acceptable (Table 1).

B. Synthesis of Urea Dimethacrylates

A diurea dimethacrylate was synthesized in excellent yield from N-t-butyl-2-aminoethyl methacrylate (TBAEM) and hexamethylene diisocyanate (HDI) by the reaction shown below:



$$\underset{\text{TBAEM}}{2CH_2{=}\overset{\overset{CH_2}{|}}{C}-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2-\underset{\underset{CH_3-\underset{\underset{CH_3}{|}}{C}-CH_3}{|}}{NH}} + \underset{\text{HDI}}{OCNCH_2CH_2CH_2CH_2CH_2CH_2NCO}$$

$$\Big\downarrow\ CH_2Cl_2,\ ET_3N,\ 25°C$$

$$CH_2{=}\overset{\overset{CH_3}{|}}{C}-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2-\underset{\underset{CH_3-\underset{\underset{CH_3}{|}}{C}-CH_3}{|}}{N}-\overset{\overset{O}{\|}}{C}-\underset{\text{TBAEM-HDI}}{NHCH_2CH_2CH_2CH_2CH_2CH_2-NH}\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3-\underset{\underset{CH_3}{|}}{C}-CH_3}{|}}{N}-CH_2CH_2O\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

Preliminary structural confirmation of this new monomer was obtained by infrared spectral analysis. The diurea dimethacrylate (TBAEM-HDI) is a white, waxy low melting solid, (m.p.50°C). This monomer which

Table 1. Setting Times and Diametral Tensile Strength of BIS-GMA/TEGDMA Composites* Toughened with HYCAR

| Formulation | Monomer System | Setting Time (min) | Diametral Tensile Strength MPa ± std. dev. (No. of specimens) |
|---|---|---|---|
| 1 | BIS-GMA = 44.4%<br>TEGDMA = 48.4%<br>HYCAR = 7.0%<br>PMSX = 0.2% | 2.0 | 41.1 ± 3.8 (3) |
| 2 | BIS-GMA = 44.9%<br>TEGDMA = 44.9%<br>HYCAR = 9.9%<br>DMSX = .025%<br>BHT = .08% | 2.0 | 40.1 ± 1.9 (3) |
| 3 | BIS-GMA = 66.4%<br>TEGDMA = 28.4%<br>HYCAR = 4.8%<br>DHPPT = 0.32%<br>BHT = 0.10% | 1.45 | 57.3 ± 2.8 (5) |
| 4 | BIS-GMA = 68.1%<br>TEGDMA = 29.2%<br>HYCAR = 2.4%<br>DMSX = .18%<br>BHT = .1% | 1.0 | 49.4 ± 3.0 (6) |

[*] Composites were prepared using usual powder/liquid formulation technique; powder-liquid ratio = 3

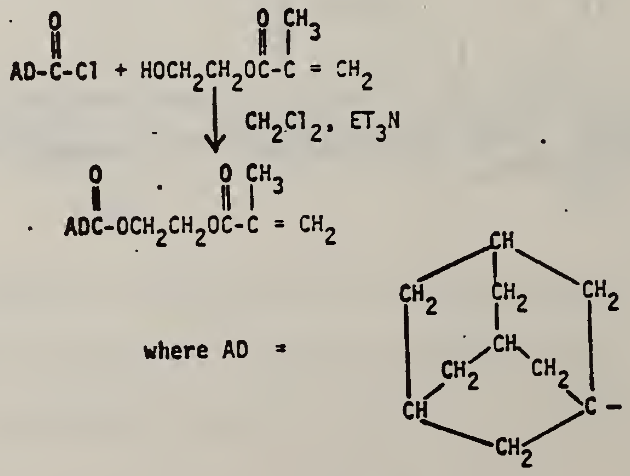
can be expected to exhibit low polymerization shrinkage, will be evaluated as an organic resin for dental composites.

### C. Bulky Monofunctional Monomers for Dental Resins

We have synthesized several types of relatively high molecular weight (bulky) monomethacrylates for use as comonomers with the usual dimethacrylate dental monomers (e.g. BIS-GMA). The usual diluent comonomers are relatively low molecular weight monomethacrylates (e.g. methyl methacrylate) or higher molecular weight dimethacrylates of relatively low viscosity (e.g. TEGDMA). Infrared analytical techniques have shown that cured dental composites have a considerable quantity of unreacted methacrylate groups (5-7). Dental resins containing methyl methacrylate had the highest degree of polymerization; i.e. least residual methacrylate groups (5). Unfortunately, the use of MMA as a diluent monomer leads to increased polymerization shrinkage of dental resin systems. The relatively bulky monofunctional methacrylates described below are designed to reduce both polymerization shrinkage and residual unsaturation.

#### 1. Synthesis of Methacryloxyethyl-1-Adamantanecarboxylate (MAC)

The synthesis of this tri-cyclic saturated bulky monofunctional monomer is shown below:

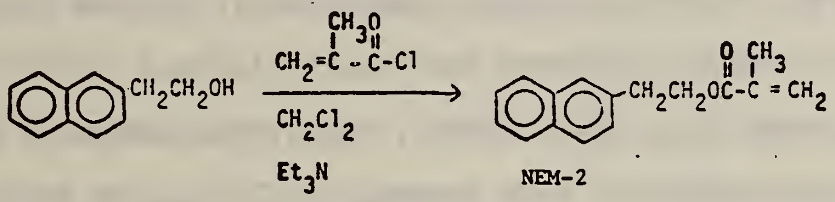


$$\mathrm{AD{-}\overset{\overset{O}{\|}}{C}{-}Cl + HOCH_2CH_2O\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C} = CH_2 \xrightarrow{CH_2Cl_2,\ ET_3N} AD\overset{\overset{O}{\|}}{C}{-}OCH_2CH_2O\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C} = CH_2}$$

This monomer, a colorless liquid, is currently undergoing characterization and will be examined in dental resin formulations for its potential in reducing polymerization shrinkage. Infrared spectral analysis confirms the assigned structure.

2. 2-Naphthylethyl Methacrylate (NEM-2)

The monomethacrylate, 2-naphthylethyl methacrylate (NEM-2), was synthesized from 2-naphthylethanol and methacryloyl chloride as shown



NEM-2 is a low melting solid, m.p. 35-6°C, which gives a liquid of moderate viscosity on melting. The assigned structure was confirmed by IR analysis. This liquid polymerizes quite readily by the usual cold-curing methods (BP/amine, UV + photoinitiator).

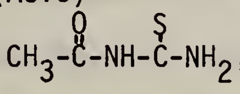
D. New Initiator/Accelerator Systems

1. Non-amine Accelerators

a. Thiourea Accelerators

Certain thiocarbonyl compounds such as thiourea, allylthiourea and acetylthiourea have been used to accelerate the free radical decomposition of hydroperoxide initiators (8,9).

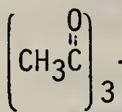
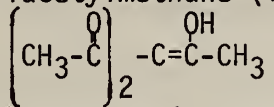
(1) Acetylthiourea (ACTU)

Acetylthiourea,  $CH_3-\overset{O}{\overset{\|}{C}}-NH-\overset{S}{\overset{\|}{C}}-NH_2$, was dissolved in a typical dental monomer system, e.g. BIS-GMA (7)/TEGDMA (3). Solutions of ACTU ranging in concentration from 0.25% to 1% by weight were evaluated for their ability to activate the decomposition of 1 and

2 percent solutions in BIS-GMA (7)/TEGDMA (3) of the following initiators: Benzoyl peroxide, t-butyl perbenzoate, t-butyl hydroperoxide and cumene hydroperoxide. Rotational hardening times (e.g. crossed slide technique) indicated that ACTU did not accelerate the decomposition of benzoyl peroxide at ambient temperatures; with t-butyl perbenzoate, the rate of cure was too slow (> 1 hour) for dental applications. With the hydroperoxide (CHP), the rotational hardening times were considerably less. However, in contrast to most amine/benzoyl peroxide initiator systems which require relatively small quantities (0.2 - 0.3%) of the amine accelerator (e.g. DMSX, DMAPAA), the hydroperoxide/ACTU initiator system requires relatively large amounts of ACTU (e.g. 2% CHP requires 1% ACTU for rotational hardening time of 6½ min., or a setting time (Gilmore test) of 6 min). One percent solutions of allylthiourea (ALTU) also gave a rotational hardening time of 6½ min. with the 2% CHP solution. Other thiocarbonyls such as 2-thiohydantoin and 2-thiobarbituric acid resulted in much longer rotational hardening times (> 1 hour) and soft sets.

Composites prepared with a paste (P/L = 3) containing 1% ACTU and a similar paste containing 2% CHP exhibited no coloration (similar to those obtained with ascorbic acid) and had excellent diametral tensile strengths (47.4 MPa ± 2.4 MPa, 4 specimens). Color stability of these composites also was excellent, showing little change after 24 hours exposure to UV. In addition, the storage stability of the peroxide component (e.g. CHP) in BIS-GMA/TEGDMA is superior to that of a 2% bonzoyl peroxide solution in the same monomer system at ambient temperatures. However, the biocompatibility of ACTU needs to be evaluated before it can be recommended for clinical application.

b. Triacetylmethane

Triacetylmethane (TAM),  $\left[CH_3\overset{\overset{O}{\|}}{C}\right]_3\text{-}CH$ which exists largely as the enol,  $\left[CH_3\text{-}\overset{\overset{O}{\|}}{C}\right]_2\text{-}C{=}\overset{\overset{OH}{|}}{C}\text{-}CH_3$ did not prove effective as an accelerator for hydroperoxides, (e.g. CHP), peresters (e.g. TBPB) or benzoyl peroxide (BP). BP solutions in BIS-GMA (7)/TEGDMA (3) cured the fastest with TAM but the setting times are excessive for dental applications. In fact, under aerobic conditions, TAM is an effective stabilizer for BP solutions. Only 0.1% TAM stabilized a 1% BP solution in BIS-GMA (7)/TEGDMA (3) without loss of its cold-curing effectiveness after 6 months storage at room temperature in a polyethylene container.

c. Ascorbic Acid Systems - Blended Glass Filler Formulations

We have shown previously (10) that it is possible to blend a glass filler coated with a solid peroxide (e.g. t-butyl peroxymaleic acid, benzoyl peroxide, etc.) with glass filler coated with ascorbic acid (AA) or ascorbyl palmitate (AP) and obtain storage (thermally) stable mixed glass filler. These blended fillers are then employed in powder/liquid formulations with the liquid consisting of only dental resin or dental resin plus small amounts of redox metal or amine accelerator, depending on the nature of the blended glass employed. Some results obtained using a blended filler of BP glass and AA or AP glass are shown in Table 2. All of these composites exhibit excellent esthetics, superior to comparable composites prepared using only amine accelerators. A synergistic mechanism of acceleration may be operative here, as indicated in our earlier reports (compare Formulations 1-3).

## Table 2

**Setting Times and 24 Hour Diametral Tensile Strength of Experimental Composites Based on Blended Glass* Formulations**

| Formulation | Monomer System | 1:1 Blend Glass Initiator/ACC | Setting Time (Min.) | Diametral Tensile Strength in MPa | (No. of Specimen) |
|---|---|---|---|---|---|
| 1 | BIS-GMA[1] 70%<br>TEGDMA[2] 30%<br>DMAPE[3] 0.028%<br>BHT[4] 0.02% | 1% BP/0.3% AP | 4 | 42.9 ± 2.8 | (5) |
| 2 | Same as above but no DMAPE | Same as above | 4 1/2 | 38.4 ± 2.3 | (4) |
| 3 | Same as above but DMAPE=0.08% | Same as above | 2 1/2 | 44.8 ± 2.5 | (3) |
| 4 | THUDMA[5] 67%<br>BIS-GMA 23%<br>TEGDMA 10%<br>DMSX[6] 0.077%<br>BHT = 0.05% | Same as above | 2 | 46.6 ± 3.4 | (3) |
| 5 | Same as above | 1% BP/0.3% AA | 2 | 50.1 ± 1.1 | (3) |
| 6 | THUDMA 83%<br>BIS-GMA 12%<br>TEGDMA 5%<br>DMSX 0.039%<br>BHT 0.02% | Same as above | 2 1/2 | 42.7 ± 2.3 | (4) |
| 7 | Same as above | 1% BP/0.3% AP | 2 | 46.8 ± 3.3 | (3) |
| 8 | THUDMA 50%<br>BIS-GMA 35%<br>TEGDMA 15%<br>DMSX 0.115%<br>BHT 0.07% | Same as above | 1 | 44.7 ± 1.8 | (3) |
| 9 | Same as above | 1% BP/0.3% AA | 1 | 46.7 ± 3.0 | (6) |
| 10 | Ternary Ether Eutectic[7]<br>DMSX 0.125%<br>BHT 0.1% | 1% BP/0.3% AP | 4 | 43.2 ± 0.3 | (2) |

---

*Powder/liquid ratio = 3; Powder = silanized 325 mesh glass beads.

[1] BIS-GMA = Bis-[p-(3-methacryloxy-2-hydroxypropoxyphenyl)] isopropylidene.

[2] TEGDMA = triethyleneglycol dimethacrylate.

[3] DMAPE = p-N,N-dimethylaminophenethanol.

[4] BHT = 2,6-di-t-butyl-p-cresol.

[5] THUDMA = trimethylhexamethylene diurethane dimethacrylate (Vivadent).

[6] DMSX = N,N-dimethyl-sym-xylidine.

[7] Ternary Ether Eutectic

## 2. Amine Accelerators

Amines are crucially important to the hardening of dental resins since _in situ_ polymerization requires chemical means rather than thermal to generate free radicals from the peroxide initiator. Since amines can be a source of discoloration, of toxic response and can through the manner in which they influence the rate of free radical formation affect the molecular weight and molecular weight distribution of the polymeric matrix, it is very important to develop information that can yield efficient, biocompatible and non-color inducing amines.

### a. Structure-Property Studies Employing Slower Acting Amine Types Including Surface Active or Adhesive-Generating Amines

The critical properties (e.g. reactivity, color stability, biocompatibility, etc.) of tertiary aromatic amine polymerization accelerators are governed by aromatic ring substituents as well as substituents on the amine nitrogen. We have studied the effects of such substituents by examining setting times (Gilmore needle test) and diametral tensile strengths (DTS) of composites prepared from an experimental P/L formulation consisting of silanized glass filler coated with 1% BP and the resin system BIS-GMA (7)/TEGDMA (3). The resin component, in some cases, had in addition to the amine accelerator, 0.09% by weight of BHT (butylated hydroxytoluene) as an inhibitor.

The amines selected for this study with their abbreviations are listed in Table 3. Composites were prepared in all cases by using a 3:1 powder-liquid ratio.

Some indication of how chemical structural variations

## Table 3

## Amine Accelerators

| Name | Abbreviation | Source |
|---|---|---|
| N,N-Dimethyl-3,5-Xylidine | DMSX | Commercial |
| N,N-Dimethyl-p-t-butylaniline | DMBA | Commercial |
| N,N-Disopropyl-p-toluidine | DIPPT | Commercial |
| 4-Dimethylaminobenzoic Acid | 4-DMAB | Commercial |
| N,N -Di-(2-hydroxypropyl)-p-toluidine | DHPPT | Commercial |
| 3-Dimethylaminobenzoic Acid | 3-DMAB | Commercial |
| Ethyl 4-dimethylaminobenzoate | 4-EDMAB | Commercial |
| 4-Dimethylaminosalicylic Acid | 4-DMAS | Commercial |
| Acetyl 4-dimethylaminosalicylic Acid | ADMAS | Synthesized |
| 4-Dimethylaminocinnamic Acid | 4-DMAC | Synthesized |
| 4-Dimethylaminocinnamic Acid | 4-DEAC | Synthesized |
| Polyfunctional Surface-Active Amine Polymerization Accelerator | Poly SAM-1 | Synthesized |

in the amine accelerator can effect such properties as setting time and diametral tensile strength of a composite material are shown in Table 4. The monomer system used in this study was formulated without added BHT but contained inhibitors added by the manufacturer.

Because of the extremely short working times (< 1 min) of composite materials containing DMSX and DMBA, it was necessary to employ paste/paste formulations rather than the usual powder/liquid technique. Even then it was difficult to prepare specimens for DTS measurements. Of the two amines, DMBA appeared to be the more reactive accelerator as measured by the setting time of equimolar mixtures. For practical applications these extremely reactive accelerators require the addition of more inhibitor or a slower polymerizing monomer system. For example, better composites were prepared from DMBA when 0.09% BHT was added to the monomer system (Table 5). On the other hand, longer setting times and somewhat lower DTS values result from adding BHT to monomer containing DHPPT or DMAB. The setting time of the composite formulated with the sterically hindered amine, DIPPT, increases from 2 3/4 min to > 8 min on adding 0.09% BHT. A clinically acceptable setting material now requires higher concentration of DIPPT (0.25% vs 0.41%.)

DHPPT, a moderately fast-acting accelerator, gave composites with the highest DTS values in the absence of added BHT (Table 4). The para and meta forms of DMAB at 0.25% gave almost identical DTS values but the setting time with the meta isomer was significantly shorter. At higher concentrations (0.50%), 3-DMAB appears to give composites with higher DTS values. The study of the newly synthesized DMAC and DEAC was limited because of the relatively low solubility of

Table 4

Setting Time and Diametral Tensile Strength of an Experimental Composite Material* Using Various Types of Amine Accelerators

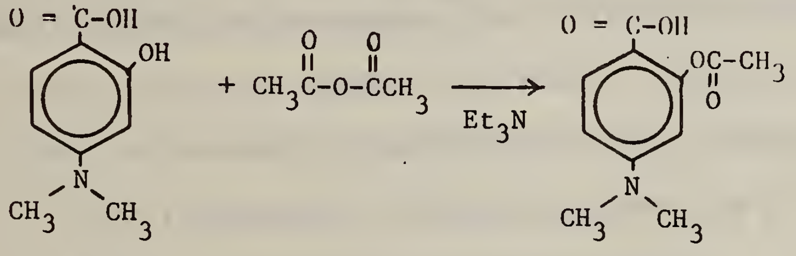
| Amine | Concentration wt. % | Concentration mMolal | Setting Time (min) | Diametral Tensile Strength (No. of specimens) MPa ± Std. Dev. |
|---|---|---|---|---|
| DMSX** | 0.20 | 13.4 | 2/3 | 41.9 ± 1.8 (2) |
| DMBA** | 0.23 | 13.0 | 1/2 | 43.9 ± 2.2 (3) |
| DIPPT | 0.25 | 13.1 | 2 3/4 | 46.9 ± 3.6 (6) |
| DHPPT | 0.28 | 12.6 | 1 1/2 | 58.4 ± 2.4 (5) |
| 4-DMAB | 0.25 | 15.2 | 6 1/2 | 51.5 ± 2.2 (4) |
| 3-DMAB | 0.25 | 15.2 | 2 1/2 | 51.5 ± 3.8 (6) |
| 4-DMAB | 0.50 | 30.3 | 4 | 51.4 ± 3.7 (5) |
| 3-DMAB | 0.50 | 30.3 | 2 | 56.8 ± 4.9 (4) |
| DEAC | 0.22 | 10.0 | 2 1/2 | 47.6 ± 3.3 (5) |
| DMAS | 0.36 | 21.0 | 3 | 53.3 ± 2.5 (4) |
| ADMAS | 0.50 | 23.5 | 4 | 49.6 ± 4.1 (5) |
| Poly SAM-1 | 0.50 | 2.5 | 1 1/2 | 49.7 ± 2.3 (4) |

* Powder/Liquid formulations employed powder/liquid ratio = 3
Powder is glass filler (325 mesh) silanized with γ-methacryloxypropyltrimethoxysilane and coated with 1% benxoyl peroxide. Liquids are monomer mixtures consisting of 7 parts of BIS-GMA and 3 parts of TEGDMA containing the various concentrations of amine but no added BHT.

**Paste/paste rather than powder/liquid formulations. Powder/liquid ratio remains 3:1.

these amines in the monomer system. These amines, which are bright yellow solids, give solutions of similar hue. In the presence of sunlight, polymerization occurs with the fading of color to yield colorless polymers and composites. However, with BP initiated polymerizations the color is only partially diminished which is probably indicative of the lack of participation by the vinyl groups of these amines in the polymerizations involving BP.

The fact that DMAS, a derivative of salicylic acid, accelerates the polymerization of BIS-GMA/TEGDMA as well as it does is surprising in view of its chemical structure which contains not only the electron withdrawing carboxyl group para to the amine function but also a built-in inhibitor in the phenolic-OH group. Composites prepared with this amine had high DTS but were pinkish. The acetyl derivative, ADMASA, a white solid, m.p. 117-18°C, was synthesized as shown below:



DMAS

ADMAS

The acetyl derivative, ADMAS, also gave glass particle reinforced composites with excellent strength (50 MPa) but with only slightly less coloration than observed with the parent amine, DMAS.

In spite of its bulky nature (M.W.> 2000), the polyfunctional surface active amine polymerization accelerator, Poly SAM-1, previously prepared (11) proved to be an effective activator even at low concentrations as shown in Table 4.

Most of the composites had good to excellent initial colors except those prepared with DMAC, DEAC, DMAS, and ADMAS. However, during storage at 37°C in a 100% relative humidity chamber overnight the initially white composites prepared with 4-DMAB and 3-DMAB darken to a light tan hue, with the para isomer giving the darker shade. DMAC and DEAC composites which are already colored appear to behave similarly. The origin of this post coloration reaction is not known. The other light composites darken only slightly on 24 hour storage in this chamber.

Color stability tests indicate that all composites prepared with BP-amine accelerator undergo a color change on exposure to UV. Color changes are difficult to quantify, but subjectively it appears that the following amines gave the least color change for the same equimolar concentrations, DMSX, DMBA, DHPPT, and 4-EDMAB. With 4-EDMAB at moderate concentrations composites with the best initial color (white) were obtained. In addition, 4-EDMAB, by analogy with its parent, the local anesthetic, ethyl-p-aminobenzoate (Benzocaine), has a high probability of exhibiting excellent biocompatibility.

From theoretical considerations, 4-EDMAB would be expected to be a relatively slow-acting promotor for the decomposition of BP. With a slow-polymerizing monomer such as methyl methacrylate, for example, polymerization proceeds much slower by many hours than with a fast-acting accelerator such as DMBA or DMSX. However, with fast-polymerizing monomers, such as BIS-GMA, TEDGMA, ETC., clinically acceptable hardening times (< 8 min.) are possible using the usual powder/liquid formulation technique (see Table 4 and 5). The mechanical

Table 5

Setting Time and Diametral Tensile Strength of an Experimental Composite Material* With Added BHT Using Various Amine Accelerators.

| Amine | Concentration wt. % | Concentration mMolal | Setting Time (min.) | Diametral Tensile Strength MPa ± Std. Dev. (No. of specimens) |
|---|---|---|---|---|
| DMBA | 0.23 | 13.0 | 1.0 | 50.1 ± 2.6 (5) |
| DIPPT | 0.41 | 21.5 | 8.0 | 50.1 ± 2.0 (5) |
| DHPPT | 0.28 | 12.6 | 5.5 | 51.0 ± 2.2 (4) |
| DHPPT | 0.32 | 14.4 | 4.0 | 51.3 ± 1.8 (5) |
| DHPPT | 0.42 | 18.8 | 3.5 | 52.0 ± 2.7 (5) |
| 4-DMAB | 0.28 | 17.0 | 6.5 | 40.9 ± 6.4 (5) |
| 4-DMAB | 0.33 | 20.0 | 5.0 | 44.0 ± 2.0 (5) |
| DMAC | 0.20 | 10.3 | 5.0 | 41.1 ± 3.0 (5) |

* Same as in Table 4; P/L = 3, Monomer system contains 0.09 BHT in addition to the amine accelerator

properties of composites prepared with this amine can be quite acceptable (Table 6 and 7). Compressive strengths for 0.5% and 0.7% EDMAB were 285.6±13.1 (4) and 301.4±11.2 (3) MPa. Higher DTS values and shorter setting times are obtained when the monomer system is free of added BHT (Table 6). Significant reductions in DTS values and somewhat longer setting times often result from the addition of 0.09% BHT. Slow-acting promotors, such as 4-EDMAB and 4-DMAB, are more susceptible to the inhibitory effects of BHT than are fast-acting accelerators such as DMSX and DMBA (see Table 4 and 5 as well as Tables 6 and 7).

In Table 8 are shown some composites prepared by using ascorbyl palmitate-BP blended powder/liquid formulations with 4-EDMABA as a synergistic promotor. The initial colors of these composites are the best we obtain when using amines as part of the initiator system. In addition, color stability is also greatly improved while the setting times are shortened considerably. Mechanical properties are quite acceptable (see Table 8).

Another advantage of the use of a relatively slow promotor as 4-EDMAB is that it permits a wider amine concentration range to be studied with fast polymerizing monomers than is possible with the fast acting amines such as DMSX, DMBA, DMAPAA and DMAPE. This should prove helpful in not only leading to a better understanding of the amine/peroxide initiator system but also in determining the extent of polymerization of monomer systems by techniques such as differential scanning calorimetry.

Table 6

Effect of EDMAB Concentration on the Setting Time and Diametral Tensile Strength of an Experimental Composite Material* _With No Added BHT_

| EDMAB Concentration wt.% | mMolar | Setting Time (min.) | Diametral Tensile Strength MPa ± Std. Dev. (no. of specimens) |
|---|---|---|---|
| 0.20 | 10.4 | 11.0 | 44.3 ± 1.6 (5) |
| 0.26 | 13.5 | 8.0 | 50.6 ± 1.0 (3) |
| 0.30 | 15.6 | 8.0 | 51.2 ± 2.2 (5) |
| 0.40 | 20.7 | 7.5 | 47.7 ± 2.6 (7) |
| 0.50 | 25.9 | 6.0 | 54.2 ± 1.1 (3) |
| 0.60 | 31.1 | 5.5 | 50.9 ± 1.4 (4) |
| 0.70 | 36.3 | 6.0 | 54.9 ± 1.5 (4) |
| 0.80 | 41.4 | 5.5 | 51.7 ± 1.9 (5) |
| 0.90 | 46.6 | 5.0 | 52.0 ± 1.5 (4) |
| 1.30 | 67.4 | 4.5 | 53.8 ± 2.3 (7) |

*Same as in Table 4 except for amine

Table 7

Effect of EDMAB Concentration on the Setting Time and Diametral Tensile Strength of an Experimental Composite Material* <u>With Added BHT</u>

| EDMAB Concentration wt. % | mMolar | Setting Time (min.) | Diametral Tensile Strength MPa ± Std. Dev. (no. of specimens) |
|---|---|---|---|
| 0.20** | 10.4 | 17.5 | 35.6 ± 1.7 (7) |
| 0.30** | 15.6 | 13.5 | 42.1 ± 1.2 (8) |
| 0.40*** | 20.7 | 12.0 | 45.1 ± 1.4 (4) |
| 0.50 | 25.9 | 7.0 | 45.4 ± 1.1 (4) |
| 0.58 | 30.0 | 8.5 | 42.8 ± 2.4 (5) |
| 0.69 | 35.8 | 7.0 | 44.6 ± 2.7 (5) |
| 0.80 | 41.4 | 6.5 | 48.0 ± 1.8 (5) |
| 0.90 | 46.6 | 6.5 | 47.4 ± 3.5 (5) |
| 1.00 | 51.8 | 7.5 | 47.6 ± 3.3 (5) |
| 1.50 | 77.7 | 6.0 | 48.2 ± 2.5 (8) |
| 2.00 | 103.6 | 4.5 | 47.0 ± 2.3 (4) |

* Same as in Table 4 except monomer system contains 0.09% BHT in addition to EDMAB

** Cured in mold for 30 minutes instead of customary 15 minutes

*** Cured in mold for 20 minutes

Table 8

Effect of EDMAB Concentration on the Setting Time and Diametral Tensile Strength of An Experimental Blended Powder*/Liquid‡Composite Material

| EDMAB Concentration wt. % | mMolar | Setting Time (min) | Diametral Tensile Strength MPa ± Std. Dev. (no. of specimen) |
|---|---|---|---|
| 0.05 | 2.6 | 5.5 | 45.8 ± 2.1 (5) |
| 0.10 | 5.2 | 5.5 | 43.0 ± 1.5 (4) |
| 0.20 | 10.4 | 3.5 | 43.4 ± 2.4 (4) |
| 0.30 | 15.6 | 3.5 | 51.2 ± 1.8 (4) |
| 0.40 | 20.7 | 4.0 | 51.4 ± 0.5 (3) |
| 0.50 | 25.9 | 3.5 | 51.7 ± 1.7 (3) |
| 0.60 | 31.1 | 3.5 | 51.9 ± 2.0 (3) |
| 0.70 | 36.3 | 3.0 | 49.6 ± 0.9 (5) |
| 0.80 | 41.4 | 3.0 | 48.0 ± 2.1 (4) |
| 0.90 | 46.6 | 4.0 | 51.2 ± 3.4 (7) |

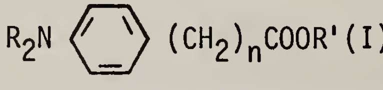
* Blended powder consists of equal parts of silanized glass coated with 1% benzoyl peroxide and 0.3% ascorbyl palmitate, respectively, P/L ratio = 3

‡ Liquid = same monomer system as in Table 7

### b. Fast Acting Amine Homologues of N,N-Dimethylaminophenylacetic Acid and N,N-Dimethylaminophenethanol

We have previously reported (12) dimethyl aminophenylacetic acid (DMAPAA) to be a very reactive accelerator for the diacyl peroxide initiated polymerization of composite resins. The overall characteristics of composites derived with this amine or its methyl ester compared favorably with composites cured with commonly used commercially available tertiary amines. An important additional characteristic of DMAPAA is that it has been shown to be non-mutagenic and non-cytotoxic (13). A preliminary evaluation of a related amine p-methylaminophenethanol (DMAPE), also synthesized in this laboratory, indicated very high reactivity and excellent properties in derived composites

We have therefore continued to synthesize homologues of these amines (both of which are highly reactive but likely to be non-toxic.) We have prepared the following series of new amines.


(I) where $R = CH_3, C_2H_5$

$R' = H, CH_3, C_2H_5$

$n = 1$ or $2$


(II)

Most of the compounds were synthesized from primary amines. Their structures were confirmed by IR and NMR. Products were purified carefully since secondary amine by-products act as inhibitors in the curing of composites. Purity was established by gas chromatographic analysis to be ≥99%. Physical properties are given in Table 9. A brief description of those amines synthesized during this year follows:

Table 9

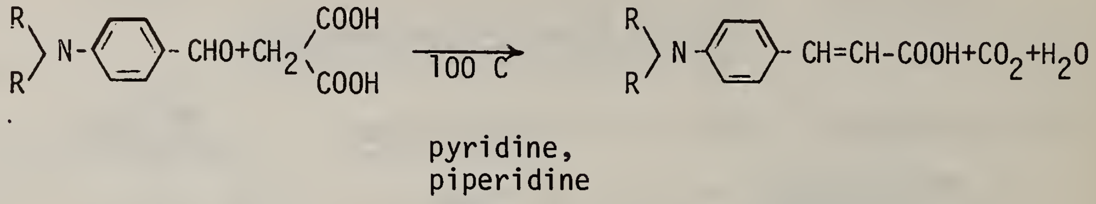
Tertiary Aromatic Amines Synthesized

| Amine | Abbreviation | Melting or Boiling Point, °C |
|---|---|---|
| 1. Aminophenethanol | | |
| N,N-dimethyl[a] | DMAPE | MP = 52-53 |
| N,N-diethyl[b] | DEAPE | BP = 153-154/4 mm |
| 2. Aminophenylacetic Acid | | |
| N,N-dimethyl[c] | DMAPAA | MP = 108-112 |
| N,N-diethyl[d] | DEAPAA | MP = 148 |
| 3. Aminophenylacetic Acid | | |
| N,N-dimethyl-methyl ester[e] | DMAPAA-ME | BP = 107/1 mm |
| N,N-diethyl-ethyl ester[f] | DEAPAA-EE | BP = 135-137/2 mm |
| 4. Aminophenylpropionic Acid | | |
| N,N-dimethyl[g] | DMAPPA | MP = 103-106 |

Method of synthesis: primary amine and [a]$CH_3I$ through quaternary ammonium salt, [b]$C_2H_5I$ in aq. MeOH, [c]$CH_3I$, [d]$C_2H_5I$, [e]$CH_3I$ in DMSO, [f]$C_2H_5Br$ in DMSO [g]dimethylaminobenzaldehyde + malonic acid. The resulting cinnannic acid was reduced with zinc amalgam.

### p-N,N-Dimethyl and Diethylaminocinnamic Acids

These compounds were first synthesized as intermediates using a modification of the Shoppe procedure (14) for the diethyl homologue. The general reaction is as follows:



Yields of 44% and 22% were obtained respectively for the methyl and ethyl derivatives.

Both the p-N,N-dimethyl and -diethyl derivatives act as photo-initiators for composite resins in sunlight. The photocuring process occurs with the disappearance of the yellow coloration of the initiator in the cured resin.

### p-N,N-Dimethylaminophenylpropionic Acid

This compound, mp = 104-106° C, was prepared by reduction of the corresponding cinnamic acid (see above) using a zinc amalgam prepared from mossy zinc, mercuric chloride, water and concentrated HCl. Although the procedure we followed (based on the Clemmensen reduction reaction) is rather easy, the yield proved to be poor (approx. 7%). This however, was sufficient to evaluate the usefulness of this compound as a polymerization accelerator for composite resins.

### p-N,N-Diethylaminophenylacetic Acid

Preparation of this compound was accomplished as follows: 39.3 g (0.40 mol) of potassium acetate and 150 ml of ethanol were added, with stirring, to 15.1 g (0.10 mol) of p-aminophenylacetic acid. Then, dropwise, 18.4 ml (0.23 mol) iodoethanane were added, the reaction mixture was gradually heated to 78 C and refluxed 6 hours. The insoluble material was filtered off. Most of the ethanol was evaporated and the solution was made strongly acidic with concentrated HCl. The resulting precipitate was filtered. The filtrate was diluted and brought to pH 4.5 with aq. NaOH. A precipitate formed which was filtered. The brown solid (9 g.) on recrystallization yielded nearly colorless crystals. MP = 148.5-149° C. It is probably the quanternary ammonium salt. Its structure is being established from IR and NMR spectra.

### p-N,N-Diethylaminophenethanol

This compound was prepared by the following procedure: 12.0 g (0.087 mol) potassium carbonate and 100 ml 25% aq. methanol were added, with stirring to 9.0 g (0.057 mol) p-aminophenethanol. Then 10.8 ml (0.135 mol) ethyl iodide was added dropwise. The mixture was gradually heated and refluxed for 24 hours. The impure product formed a brown top layer which was separated. It distilled at 123-125 C/2mm. yield: 9 g; 79%.

The product was purified by refluxing 8.8 g. (0.046 mol) for 6 hours with 5 ml (0.063 mol) iodoethane and 8 g. $K_2CO_3$ in 40 ml 25% ethanol. The two layers were extracted with dichloromethane. The extract was combined, the solvent evaporated and the impure product distilled. BP: 127-129 C/2mm . Yield: 6.4 g; 52%.

Further purification through the amine hydrochloride neutralization and subsequent extraction with dichloromethane yielded a product BP: 153-154 C/4mm, $n_D^{24} = 1.5503$.

### p-N,N-Diethylaminophenylacetic acid-ethyl ester

The reaction of p-aminophenylacetic acid (22.7 g), anhydrous $K_2CO_3$ (80 g), dimethyl sulfoxide (75 ml), bromoethane (25 ml) and KI (75 mg) was carried out for 2 hours with stirring in a flask equipped with reflux condenser, thermometer and dropping funnel. An equivalent second portion of bromoethane was added and stirring continued for an hour . The mixture was heated overnight at 55 - 60°C, cooled and extracted with dichloromethane. After evaporation of the solid the product was obtained by vacuum distillation. Further purification was achieved by refluxing the ester 10 min. with acetic anhydride before pouring the reaction mixture into 50 ml of water. After 30 min. the pH of the solution was adjusted to 8 with 10% NaOH and the oil layer was separated. Vacuum distillation yielded a product with a boiling point of 135-137° C/2mm and $n_D^{24} = 1.5262$.

### N,N-Trimethylammoniumphenyl butyric acid halide

Reaction of p-aminophenylbutyric acid (16.6 g), aqueous 25% (by vol.) methanol (300 ml) and $K_2CO_3$ (28 g) was carried out in an appropriate flask. Iodemethane (21.8 ml) was added dropwise with stirring and the reaction mixture refluxed for 8 hours. On evaporation of the solvent KI separated and was filtered off. The filtrate was neutralized with 20% HCl and the resulting precipitate recovered by filtration.

NMR analysis shows that refluxing this compound with ethanolamine or refluxing it with silver oxide in aq. methanol and heating the resulting solid at 140° C in an inert atmosphere did not decompose the quanternary salt. The quanternary ammonium salt, purified from n-amyl alcohol had a MP = 165 to 166° C.

### (1) Evaluation of DMAPAA and DMAPE Homologues

To determine the reactivity of the amines and the properties of the resulting materials, composites were prepared using a 3 to 1 powder/liquid ratio. The powder was Corning glass 7724 treated with gamma-methacryloxypropyltrimethoxysilane and coated with 1% benzoyl peroxide. The liquid contained 72.4% BIS-GMA, 27.6% 1,6-hexamethylene glycol dimethacrylate (diluent) and 0.2% butylated hydroxytoluene inhibitor. This diluent was substituted for the triethyleneglycol dimethacrylate (TEGDMA) since there is some evidence (15) that diluents having only $\leftarrow CH_2 \rightarrow_n$ may be preferable to those having $(CH_2\text{-}CH_2O)_n$ groups in the chain. The properties of the composites are given in Table 10. They were determined by procedures described in ADA Specification No. 27 (16). All amines studied gave adequate setting times with dimethylaminophenylacetic acid (DMAPAA) yielding the shortest and the higher homologue dimethylaminophenylpropionic acid (DMAPPA) the longest setting time. For unfilled resins the rate of curing proceeds most rapidly for molar peroxide to amine ratios between 1.1 to 1.5. For composites containing initially undissolved peroxide a much larger excess of peroxide is required to obtain a minimum setting time. This should be expected since only a small portion of the peroxide is accessible to the amine before the composite is cured. The mechanical properties are not as dependent on the amine concentration as was observed previously with TEGDMA. Optimum properties (tensile strength: 53 MPa, compressive strength: 302 MPa, water sorption: 0.55 gm/cm$^2$) were obtained in the 15-19 millimolal concentration range. The propionic acid or esters of N,N-diethyl derivatives did not yield composites with better mechanical properties than those containing the corresponding acetic acid or dimethyl derivatives. For all formulations tensile strength is much above the minimum specification requirement of 34 MPa (16). The initial shades of many composites are very light. Color stability, even without incorporation of an ultraviolet stabilizer into the material, and water sorption are very satisfactory. Best overall physical properties were observed for the dialkylaminophenethanols and DMAPAA. The low volatility and reduced diffusion rates of the higher molecular weight amines, especially those containing alcohol or ester groups, should confer good biocompatibility.

### c. A New Amine Accelerator for Denture Base Resins

Denture base resin systems that are currently on the market employ N,N-dimethyl-p-toluidine (DMPT) as the amine for accelerating the polymerization of the methacrylate monomer. The amount needed varies from zero in heat cured systems to 1/2 - 1% for low temperature autopolymerizing materials such as pour resins and the reline and repair materials. Due to the differing amounts of amines used, and subsequent discoloration from the presence of amine, it is currently not possible to match all shades of heat cured denture bases with pour or reline and repair materials; however, it is desirable to be able to accomplish this for economic and esthetic reasons.

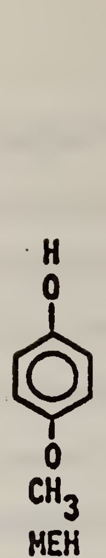
In cooperation with the American Dental Association Research Institute at the National Bureau of Standards, a newly commercially available amine (N,N-dimethyl-p-t-butylaniline, of DMBA) was evaluated for color effects in denture materials.

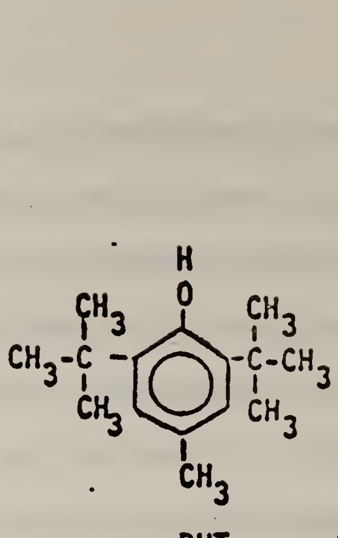
Specimens of cured denture base were prepared using commercial poly(methyl methacrylate) powder and methyl methacrylate monomer with DMPT as were specimens prepared from the same powder and a solution of 0.5 DMBA in methacrylate monomer; various weight percentages of UV absorber were added to monomer portions. Curing times were approximately equal to room temperature. The specimens prepared using DMBA displayed no evidence of discoloration upon curing whereas those prepared with DMPT displayed the usual high degree of discoloration. Subsequent exposures to UV light showed specimens with 0.5 and 0.25% of UV absorber and DMBA to be virtually free of discoloration due to UV light.

From the standpoint of color it is concluded that DMBA is more suitable for use in denture base systems than is DMPT. If the application of DMBA for this purpose results in the use of sufficient quantities to reduce its price, some of the current problems in achieving and matching shades within denture base systems could be eliminated.

### E. New Stabilizers for Dental Monomers

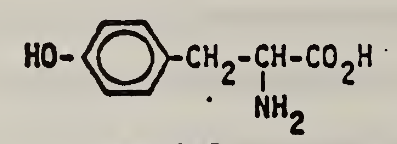
One of the requirements of a dental composite restorative or sealant materials is a reasonable shelf-life, preferably at ambient temperatures or at least under simple refrigeration. The paste or liquid component which contains the initiator (e.g. "catalyst"), usually benzoyl peroxide (BP), exhibits the poorest shelf life. The use of stabilizers which are antioxidants and polymerization inhibitors stabilizes the monomer system against autoxidation and premature polymerization. Common stabilizers for dental monomers are the methyl ether of hydroquinone (MEH) and 2,6-di-tert-butyl-p-cresol (BHT) shown below

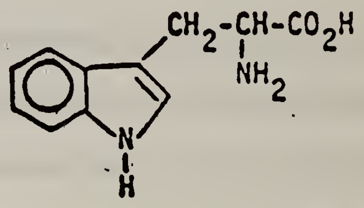

MEH


BHT

An ideal stabilizer for dental monomers should be biocompatible, highly effective as an inhibitor, but without adverse affects on the "cold-curing" process.

We have investigated the feasibility of using two naturally occurring amino acids, tyrosine and tryptophan, as potential stabilizers for dental monomers. The structures of these α-amino acids are shown below:


TYROSINE


TRYPTOPHANE

We prepared solutions of these amino acids in BIS-GMA (7)/ TEGDMA (3) in the concentration range of 0.05 to less than 0.1%. To these solutions were added various amounts of BP to give several concentrations of the initiator (0.25%, 0.5%, 1% and 2.1%). These solutions were stored in air permeable polyethylene bottles and have remained unpolymerized after 7 months. In addition, several solutions stored in partly filled glass vials have also not gelled. The tryptophane solutions have taken on more color (yellow) than those containing tyrosine or a 0.1% BHT control solution. All the solutions have retained their "cold curing" effectiveness as measured against a standard monomer solution containing 0.2% p-dimethylaminophenylacetic acid.

Composites prepared from the tyrosine/BP solutions utilized in paste/paste formulation have shown excellent diametral tensile strength, comparable to those obtained with BHT/BP systems.

### F. Reaction of Silane Coupling Agent with Quartz

To improve dental composite restoratives attention must be directed not only to the resin but also to the filler and its bonding to the matrix. The interface between fused quartz or glass particles and the polymeric matrix plays a profound role in the behavior of composite dental materials. The basic load transfer mechanisms between the substrate and matrix is dependent on a strong interfacial bond, either chemical or mechanical. The interface furthermore plays an important role in the fracture behavior of composites. An understanding of the reactions at the interface and the ability to control them would yield mechanically improved, more homogeneous materials.

Coupling agents applied on the surface of $SiO_2$ substrates greatly improve the interfacial and water susceptible properties of the composite. The mechanical strength of glass reinforced composites is significantly increased by pretreatment of the glass particles with silanes. Glass, or fused quartz particles employed as reinforcing agents in BIS-GMA based composites are usually pretreated with a dilute solution of $\gamma$-methacryloxypropyltrimethoxysilane (MPTS) coupling agent

Table 10

Properties of Composites with Various Amine Accelerators

| Amine Type | Amine mMolal Conc. in Liquid | Setting Time Min. | Tensile Strength MPa | Compressive Strength MPa | Color Stability[b] | $H_2O$ Sorption mg/cm$^2$ |
|---|---|---|---|---|---|---|
| DMPT | 15 | 4.5 | 45.9 | 276 | 3.5 | - |
| " | 17 | 3 | 43.0 | 246 | 3.5 | .58 |
| " | 19 | 4.5 | 47.6 | 246 | 3.5 | .56 |
| DMAPE | 15 | 3.5 | 46.1 | 262 | 3.5 | .53 |
| " | 17 | 3 | 47.7 | 271 | 3 | .55 |
| " | 19 | 3 | 50.1 | 302 | 3 | - |
| " | 21 | 2.5 | 39.6 | 286 | 3 | - |
| DEAPE | 15 | 6 | 45.6 | 277 | - | - |
| " [a] | 17 | 3 | 53.4 | 302 | - | - |
| " | 17 | 4 | 49.1 | 294 | 3 | - |
| " | 19 | 4.5 | 48.0 | 279 | 3 | - |
| DMAPAA | 13 | 2 | 49.8 | 288 | - | - |
| " | 15 | 2 | 52.2 | 276 | 3 | .56 |
| " | 17 | 2.5 | 51.6 | 279 | 3 | - |
| " | 19 | 2 | 50.2 | 296 | 3 | .61 |
| DMAPPA | 15 | 6 | 41.4 | 241 | 3 | .55 |
| " | 17 | 4 | 43.1 | 263 | 4 | .55 |
| " | 19 | 5 | 45.8 | 258 | 3 | .58 |
| DMAPAA-ME | 17 | 3.5 | 49.8 | 273 | - | - |
| DEAPAA-EE | 13 | 4.5 | 51.2 | 278 | - | - |
| " | 15 | 4 | 48.0 | 276 | - | - |
| " | 17 | 4 | 46.5 | 276 | 3 | - |
| " | 19 | 5 | 47.0 | 283 | 2.5 | - |

[a] prepared with 0.1% BHT.

[b] rating scale by visual observation: 1 very large change to 4 no change.

which appears to be the most compatible silane for the acrylic monomers used as the dental matrix resin. In a recently started study we are seeking the most effective treatment to obtain a permanent bond to glass or fused quartz. We are investigating the affects of different applications of the silane to the glass or fused quartz surface on the permanency of the bond and on the mechanical properties of the cured composite. Initially, the presence and permanency of the bond is being studied by infrared spectra of the treated powders. Changes in the application of the silane will include the following parameters: (1) type, volatility, and polarity of solvent to be used, (2) silane concentration, (3) reaction time, (4) drying procedure (rate of drying, maximum temperature employed), (5) pH of solvent media, and (6) effect of impurities such as water in the solvent and effect of substrate particle size and distribution on the effectiveness to obtain a permanent bond.

Wafers were molded from Cabosil colloidal silica and subjected to various silanizing treatments for 2 hours. Formation of chemical bonding between the silica and the silane was established from the disappearance of the free hydroxyl band of silica at 3740 $cm^{-1}$. The siloxane peak of the bulk silica at 1850 $cm^{-1}$ was used as internal standard. Only incomplete bonding takes place when the wafers are treated with MPTS dissolved in acetone, n-pentane or cyclohexane (Table 11). Furthermore, the MPTS solution in acetone decomposes rapidly in the presence of light. With 2% n-propylamine catalyst added to the silanizing solution the free hydroxyl band disappears indicating that the silane has reacted with the silica. This bond is not destroyed for the treated wafer stored for 280 hours in water at 68 C if the silane treatment was conducted with cyclohexane as solvent using n-propyl amine as catalyst (Table 12). Other treatments - even those employing the catalyst - result in a partial hydrolysis of the bond and a reappearance of free hydroxyl groups in the silica. This hydrolysis of silanized silica will be studied further.

Table 11

EFFECT OF N-PROPYL AMINE ON CHEMICAL BONDING OF SILANES TO SILICA SURFACES

Reaction Time: 2 hr at room temperature

| | Bonding, %[a] | |
|---|---|---|
| Silica Treatment | With no catalyst | 2% n-propylamine |
| 2% A-174 in acetone<br>(solution decomposes in light | 0 | 100 |
| 2% A-174 in 90% acetone - 10% $H_2O$ | 23.0 | 100 |
| 2% A-174 in _n_-pentane | 33.5 | 100 |
| 2% A-174 in cyclohexane | 26.5 | 100 |

[a] Calculated from relative intensity ratio of infrared absorption peak at 3740 $cm^{-1}$ (free OH band) and around 1850 $cm^{-1}$ (siloxane linkage in the bulk of the silica). Samples were washed with acetone for 15 minutes and air-dried prior to infrared measurements.

Table 12

STABILITY OF SILICA - SILANE BOND

Wafer stored in water at 68°C for 280 hrs.

| | Bonding, %[a] | |
|---|---|---|
| Silane Treatment (2 hr) of Silica Wafer | Before Storage | After Storage |
| 2% A-174, 2% n-propyl amine in cyclohexane | 100 | 100 |
| " " " " " in pentane | 100 | 71.5 |
| " " " " " 90% acetone-<br>10% $H_2O$ | 100 | 41.1 |
| " " " " " 100% acetone | 100 | 26.5 |
| " " " in cyclohexane | 26.5 | 0 |
| " " " in pentane | 33.5 | 33.5 |
| " " " in 90% acetone - 10% $H_2O$ | 23 | 20 |

[a] Calculated from relative intensities ratio of IR peaks at 3740 $cm^{-1}$ and 1850 $cm^{-1}$.

## G. Autocurable Blends as Route to Improving Chemical and Mechanical Properties of Denture Base Materials (and Other Dental Materials)

Denture base materials as well as direct filling resins and bone cements are based on use of a monomer/polymer system such as methyl methacrylate (MMA) in poly(methyl methacrylate )(PMMA). There are limitations to the improvement in properties that can be gained by this route and alternative approaches are needed. The use of an elastomeric polymer or copolymer in place of or to supplement PMMA with MMA or similar monomer systems can produce polymer blends or alloys with greater toughness and ductibility and less brittleness. The polymer blend approach to achieving new or improved properties in polymeric-based systems is one being given forefront consideration today. In such polymer blends component polymers are bound together by forces which are relatively weak when compared with covalent bonding in copolymers. Because of compatibility properties, a major generic problem is to control phase separation which unless on a micro scale can be very deleterious.

Purely physical polymer blends are commonly prepared by mechanical mixing of polymer components in the melt or by dissolution in a common solvent followed by casting and solvent removal. Our route will be to form polymer blends by autocuring bulk polymerization techniques.

### 1. Solubility Studies

Various copolymers of polyvinylidiene fluoride, $PVF_2$, will dissolve in methyl methacrylate (MMA) to varying degrees depending on such factors as the molecular weight of the copolymer, degree of crystallinity, etc. A copolymer of tetrafluoroethylene and vinylidene fluoride is quite soluble in MMA ( 30%). Similarly Kel-F elastomer consisting of 70% $PVF_2$ and 30% $\{CF_2\text{-}CFCl\}$ is also soluble in MMA. Viton A, an elastomeric copolymer vinylidene fluoride and perfluoropropylene is also soluble in MMA. However, the homopolymer $PVF_2$ is only swelled by MMA at room temperature.

Heating $PVF_2$ in MMA in a sealed tube (25-140 C) resulted first in solution, followed by polymerization. The concentration of $PVF_2$ was of the order of 10% and the acrylic rod appears to have a tougher character than that of pure PMMA. At this point it is not known whether a blend of PMMA and $PVF_2$ or a graft or copolymer of the two was formed. The polymer is soluble in MMA so crosslinking apparently did not occur. We plan to study the autocuring behavior of the MMA-$PVF_2$ copolymer solutions and evaluate the properties of these polymers.

## II. Development of Adhesive Bonding Techniques

A clinically applicable technique which establishes and maintains adhesive bonding to the dentin tooth surface would offer an important means of reducing the recurrent caries that is encouraged by the microleakage of saliva and bacteria between restoration and tooth. Perhaps even more important is the potential for significant modification of cavity preparation and technique of placing restorations that would allow for greater preservation of sound tooth structure than is now possible.

### A. Cyanoacrylates

A summary of research in which we have been investigating the potential of various cyanoacrylate monomers as a means for generating adhesive bonding between the tooth surface (dentin) and a composite restorative material was prepared for review by the NBS editorial process and has now been published as a part of the ACS Symposium Series, No. 95 - 1979 Durability of Macromolecular Materials (17).

We showed in the previous Annual Report (10) that the pretreatment of dentin with dilute acids such as 0.1 or 1% aq. alc. (1:2) citric acid prior to application of isobutyl cyanoacrylate yields strong bonding between acrylic rods and dentin even after thermocycling the assembly for 24 hours. Stanley et al. (18) and others have shown that etching of dentin with rather concentrated solutions, such as 37% phosphoric acid, can produce an undesirable pulp response. The proposed dilute acid pretreatment may be applicable clinically where a strong, short-term attachment to dentin is desired provided that the very dilute (0.1 to 1%) citric acid solution can be tolerated by the tissues. To evaluate the possible clinical use of dilute citric acid solutions, the effect of citric acid on the surfaces of dental cavity preparation and the underlying pulpal tissues has been initiated by Dr. P. M. McInnes and Dr. Clayton Jones of the Dental Research Institute of the University of the Witwaterstrand, South Africa.

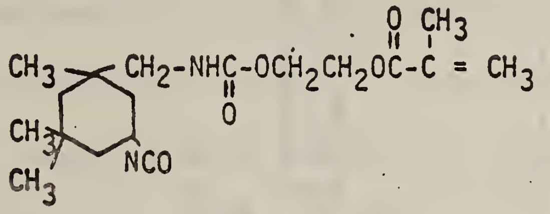
In this study 48 vervet monkeys (cercopithecus aethiops pygerthrus) are being used as the experimental model. Restorations have been placed after the following pretreatments: no etching and filling with negative and positive control material (ZOE and silica cement) and etching with 0.1% and 1% aqueous and 30% alcoholic citric acid and subsequent placement of an amalgam filling. The animals are being sacrificed after 2 days, 28 days and 56 days. The teeth and tissues will be examined histologically and histopathologically using the criteria suggested by Stanley (19) following details outlined by the present investigators. Results of the 2-day interval study will reveal the initial response to the acids and to the trauma of the operative procedure. The 4-week interval observations will be more severe than those of the 2-day interval and should show the full-blown inflammatory response to the pulp. After 8 weeks it is expected that the pulpal lesions will have undergone resolution.

### B. Urethane (Isocyanate) Adhesives

The well-known reactions involving organic isocyanates and active hydrogen compounds and the potential availability of a significant number of such active sites in the collagenous component of dentin suggested the synthesis of methacrylate monomers with pendant isocyanate groups. This synthesis was reported in an earlier report (10) and the galley proofs of an accepted manuscript have been returned to the Journal of Dental Research. Laboratory investigation of some of these urethane derivatives is described in what follows.

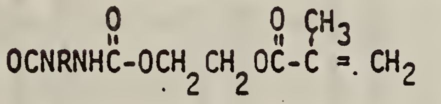
Bone specimens were cemented together with formulations containing the urethane-methacrylate, a polymerizable diluent (such as methyl methacrylate or triethylene glycol dimethacrylate), and suitable redox initiating systems (benzoyl peroxide initiator and dimethyl-p-toluidine accelerator).

The urethane derivatives used were:



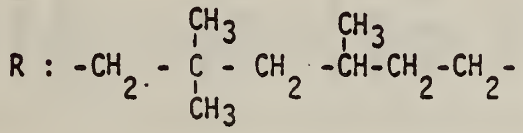
IPDI-HEMA

and



$\mathrm{OCNRNH}\overset{O}{\overset{\|}{C}}\mathrm{-OCH_2CH_2O}\overset{O}{\overset{\|}{C}}\mathrm{-}\overset{CH_3}{\overset{|}{C}}\mathrm{=CH_2}$

where



$\mathrm{R:\ -CH_2-}\overset{CH_3}{\underset{CH_3}{C}}\mathrm{-CH_2-}\overset{CH_3}{CH}\mathrm{-CH_2-CH_2-}$

TMDI-HEMA

and R: $C_{36}$ hydrocarbon DDI-HEMA

In the initial studies, little or no adhesion was indicated with formulations containing TMDI-HEMA or DDI-HEMA after thermocycling the bone specimens for one day at 5° and 55°C (540 thermocycles per day). Some results for bonding an IDPI-HEMA based adhesive to bone are given in Table 13. Significant adhesion was obtained only on pretreatment of the bone with 1% NaOH to expedite urethane or urea formation, followed by storage of the bonded specimens in air from 5 to 30 min. before 24 hr. storage in water. Optimum one-day adhesion of 2.6 MPa was found on keeping

# TABLE 13

## BONDING OF EXPERIMENTAL URETHANE-METHACRYLATE CONTAINING ADHESIVES TO BONE

Adhesive: 67% IDPI-HEMA - 33% triethylene glycol dimethacrylate + 0.5% benzoyl peroxide + 0.25% dimethyl-p-toluidine.
Tensile strength is mean of 5 determinations after thermocycling specimens for 1 day between 5° and 55°C.

| Pretreatment of Bone | Storage | Tensile Strength, MPa |
|---|---|---|
| None | $H_2O$ at 37°C, 1 day | 0.25 (0.24)[a] |
| 1% NaOH | " " " " " | 0.58 (0.56) |
| " " | Air at 37°C, " " | 0.02 (0.04) |
| " " | Air for 5 min, $H_2O$ at 37°C, 1 day | 1.20 (0.71) |
| " " | Air dried with blower for 5 min, $H_2O$ at 37°C for 1 day | 1.52 (0.85) |
| " " | " " " " " " " " thermocycled 7 days | 1.87 (0.66) |
| " " | Air for 15 min, $H_2O$ at 37°C, 1 day | 0.94 (0.61) |
| " " | Air for 30 min, $H_2O$ at 37°C for 23.5 hr. | 2.62 (0.89) |
| " " + 0.5% T-9[1] | " " " " " " " " " " | 1.45 (0.62) |
| " " + 0.5% T-12[2] | " " " " " " " " " " | 1.15 (0.70) |
| " " + 3% $H_2O_2$ | No adhesion after 3 min. | - - |
| 10% $NaHCO_3$ | Air for 5 min, $H_2O$ at 37°C, 1 day | 0.50 (0.20) |
| 0.1% N $CaCO_3$ | " " " " " " " " " | 0.22 (0.13) |
| 1% $Na_4EDTA$ | $H_2O$ at 37°C, 1 day | 0.44 (0.44) |
| " " | Air at 37°C, 1 day | 0.01 (0.02) |
| " " , 0.2% T-12 catalyst | $H_2O$ at 37°C, 1 day | 0.18 (0.17) |
| " " , 0.5% T-9 catalyst | " " " " " | 0.67 (0.39) |
| " " , 0.2% DABCO[3] | " " " " " | 0.49 (0.30) |
| " " | " " " " " | 0.25 (0.26) |
| 1% citric acid | " " " " " | 0.07 (0.09) |

---

[a] Standard deviation.

[1,2] Organometallic catalysts.

[3] DABCO = triethylenediamine.

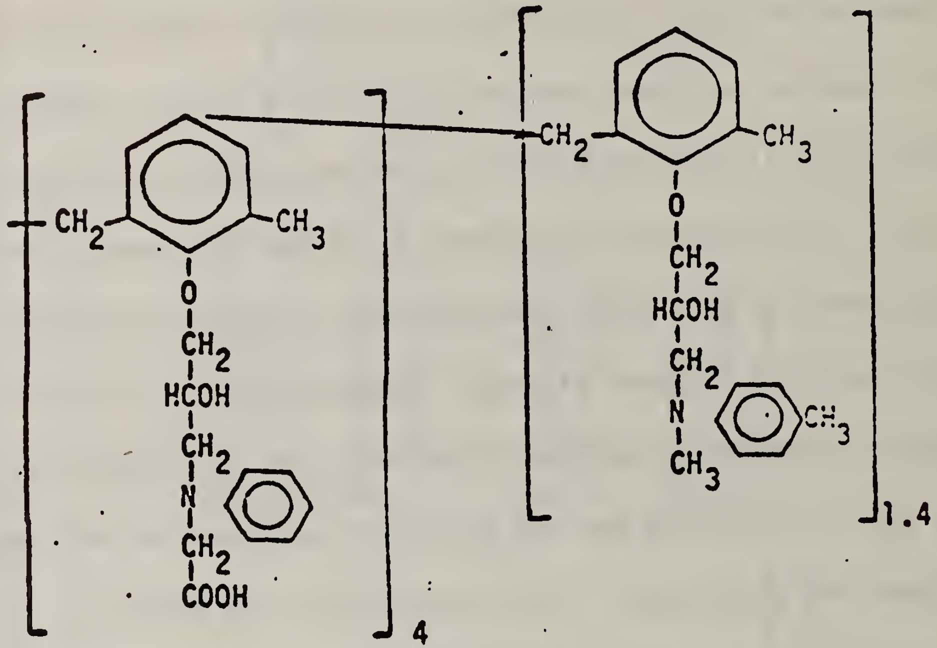
the sample at room temperature for 30 min. before immersion in water. Specimens treated in the same manner and thermocycled for 7 days had bond strength of 1.9 ± 0.7 MPa, but the specimens fell apart on thermocycling for 30 days. Storage of the bone in air, or pretreatment of the substrate with 1% $NaHCO_3$, 1% $Na_4EDTA$, 1% citric acid, 0.1 N $CaCO_3$ or 1% $H_2O_2$ did not improve adhesion. Application of several commercial urethane curing agents containing organometallic compounds which should speed up urethane formation to the bone did not improve joint strength even if the substrate had previously been treated with 1% EDTA. Bond strength of specimens of 1% NaOH pretreated bone varying from 0.1 to 1.0 MPa were obtained on curing of compositions containing 48.6% trimethylolpropane trimethacrylate, 38.1% of a trimethylhexamethylene urethane dimethacrylate and 14.3% of either IPDI, DDI, or IPDI-HEMA and the previously employed concentrations of initiator and accelerator. On decreasing the concentration of polymerizable dimethacrylate diluent so that the HEMA-IPDI concentration increased to 60%, a bond strength of 1.5 MPa was obtained.

Although statistically significant adhesion was obtained with these isocyanate urethane methacrylate-containing adhesives, the values for the strength of the bonded joints was considerably lower than for those cemented with 2-cyanoacrylate esters.

## C. Multifunctional Adhesion Promoting Surface-Active Amine Accelerators

### 1. POLYSAM-1 and Other Amine Accelerators

We have previously (20) reported the synthesis of a polyfunctional surface active amine accelerator designated POLYSAM-1, the structure of which is illustrated as follows:



POLYSAM-1

The proposed mechanism for adhesion involves a bifunctional action: 1) attachment to the apatite surface via chelation bonding between the multiple N-phenyl glycine groups and surface calcium or calcium-substituted atoms (e.g., Fe, Cu), and 2) formation of a radical cation on the N-methyl-p-toluidine portion of the structure which then forms a free radical that may participate by covalent bonding in the polymerization process.

In spite of its MW (> 2000), POLYSAM-1 can be an effective amine accelerator for the cold-curing of BIS-GMA monomer systems containing benzoyl peroxide (BP). For example, one part of a 0.5% solution of POLYSAM-1 in BIS-GMA(7)/TEGDMA(3) was mixed with three parts of silanized glass coated with 1% BP to give composites having excellent diametral tensile strengths [49.7 ± 2.3 MPa (4); setting time - 1 1/2 min.]. Earlier we had shown that POLYSAM-1 can be irreversibly adsorbed onto powdered synthetic hydroxyapatite (HA). In this adsorbed state, POLYSAM-1 is also an effective polymerization accelerator for BIS-GMA monomer systems, thereby making it feasible to prepare HA filled composites from HA having various quantities of chemically adsorbed POLYSAM-1. The maximum amount of chemisorbed POLYSAM-1 is 4.2%.

We had previously shown that HA with 4.2% adsorbed POLYSAM-1 accelerated the polymerization of methyl methacrylate containing 1% BP if the bulk polymerization was conducted under aneorobic conditions (e.g., vacuum). The polymer obtained from this polymerization was not completely soluble in good solvents ($CHCl_3$, $CH_2Cl_2$) for poly(methyl methacrylate). About 15-20% of the polymer resisted dissolution. Infrared analysis revealed the presence of $PO_4^{-3}$, and therefore, HA. Treatment of this polymer fraction with aqueous HCl, followed by extraction with $CHCl_3$, resulted in the solubilization of most of this fraction in that solvent. The IR spectra of the $CHCl_3$ soluble material no longer had adsorption bands for HA (e.g., $PO_4^{-3}$) but was essentially that of poly(methyl methacrylate) with some adsorption bands indicative of the presence of POLYSAM-1 moieties.

A similar experiment was performed with a new monomethacrylate, 2-naphthylethyl methacrylate (NEM-2). (Synthesis described in Section I.)

NEM-2 is a low melting solid, m.p. 35-36°C, which gives a liquid of moderate viscosity on melting. This liquid polymerizes quite readily by the usual cold-curing methods (BP/amine, UV + photosensitizer) and the polymer of NEM-2, PNEM, is soluble in $CHCl_3$. A thin composite disc was prepared using liquefied NEM-2 containing 1% BP and HA coated with POLYSAM-1. Only 50% of the PNEM appeared to be susceptible to dissolution. A control experiment with uncoated HA gave only soluble polymer.

These preliminary results suggest that POLYSAM-1 has potential as an adhesion promoting agent for dental composites and sealant materials.

Several additional surface-active amines have been examined for adhesion promoting ability. Dr. Misra of this laboratory has demonstrated that p-N,N-dimethylaminophenylacetic acid (DMAPAA) is irreversibly adsorbed on synthetic HA from methylene chloride solutions. However, unlike the irreversible adsorption of POLYSAM-1 onto HA from both protic solvents (e.g., $C_2H_5OH$) and aprotic solvents (e.g., $CH_2Cl_2$), the adsorption of DMAPAA is reversible from protoic solvents (e.g., washing with excess solvent will eventually remove the amine in the case of protic solvents). Using powder liquid formulations with an HA to which DMAPAA was adsorbed and BIS-GMA(7)/TEGDMA(3) containing various concentrations of BP, extremely fast cures were observed (< 1 min.). This amine appears to be more reactive in the adsorbed state than when dissolved. Preliminary experiments with a dilute solution of dimethylaminobenzoic acid (DMABA) in methylene chloride and hydroxyapatite indicate a certain amount of solute is adsorbed irreversibly. However, protic solvents will remove the DMABA from hydroxyapatite. The amine p-N,N-dimethylaminosalicyclic acid (DMASA) is also adsorbed irreversibly to HA from aprotic solvents but reversibly from protic solvent. HA-filled composites with the adsorbed DMASA were readily prepared also.

The diametral tensile strength determination (DTS) has been shown to be a valid and useful method for assessing the relative effectiveness of different silane coupling agents used in glass-filled composite resin systems (21). Table 14 compares the DTS obtained with specimens prepared with unsilanized and silanized glass filler, respectively. The results are clearly indicative of the existence of some coupling action between the glass filler and dental resin via the agency of the silane. It seemed reasonable to expect that DTS measurements of HA-filled composite specimens could reveal the presence or absence of coupling between resin and HA via POLYSAM-1 and other surface active amines and therefore serve as an indicator of adhesive potential.

Table 15 summarizes the setting times and DTS values obtained using HA with various amounts of adsorbed POLYSAM-1. Table 16 lists similar data for HA containing adsorbed p-N,N-dimethylaminosalicyclic acid (DMASA). The highest DTS for a composite prepared from HA containing an adsorbed surface-active amine accelerator was that of Formulation 2, Table 15.

The results summarized in Table 17 are for uncoated HA-filled composites with the various surface-active amine accelerators initially dissolved in the accelerator paste. Again the highest DTS value is for a POLYSAM-1 formulation (B). Significant DTS values were observed for a DMAPAA formulation (D) and for formulation (F) which utilized the acetyl derivative of DMASA, ADMASA, as the accelerator. The latter DTS value was for 72 hours rather than 24 hours.

Table 18 represents an attempt to devise a control for the preceding experiments. The accelerator, DMSX, is an effective but non-surface-active amine accelerator. The DTS values of HA-filled composites using DMSX were significantly lower than those for some surface active amine formulations (e.g., Formulations 2, Table 5 and B, Table 17).

Since the diametral tensile strength of a composite is affected not only by the coupling agent, but also by the degree of polymerization of the dental resin, which in turn is dependent on the nature and concentration of the amine accelerator (22), it is not surprising that the results of Tables 15-18 are difficult to interpret compared to the results shown in Table 14 on the unsilanized versus silanized glass composites. The surface-active agents used in HA-filled composites have a dual function, acting as polymerization accelerators as well as potential coupling agents. The nature of the amine-peroxide reaction is still not well understood and may not be the same in every respect with all tertiary aromatic amine accelerators. However, the results of this study seem to indicate that at least a modest coupling action may accrue from the proper use of POLYSAM-1 and other surface-active amine accelerators.

## TABLE 14

## DIAMETRAL TENSILE STRENGTHS OF EXPERIMENTAL COMPOSITES[*] FORMULATED WITH UNSILANIZED [U] AND SILANIZED[†] [S] GLASS FILLER (325 mesh)

| Formulation | Peroxide Paste | Acc. Paste | P/L | Setting Time (min.) | Diametral Tensile Strength in MPa (no of spec) |
|---|---|---|---|---|---|
| U | BIS-GMA (7)<br>TEGDMA (3)<br>BP = 1%<br>TYR[1] = 0.1% | BIS-GMA (7)<br>TEGDMA (3)<br>DMAPAA[2] = 0.18%<br>TYR = 0.05% | 3 | 3½ | 28.3 ± 1.5<br>(5) |
| S | Same as above | Same as above | 3 | 3 | 49.8 ± 1.9<br>(4) |

[*] Composites were prepared from equal parts of peroxide and accelerator paste

[1] TYR = Tyrosine

[2] DMAPAA = p-N,N-dimethylaminophenylacetic acid

[†] Silane agent = gamma methacryloxypropyltrimethoxy silane

## Table 15

### Setting Times and Diametral Tensile Strengths (24 hr.) of HA-Filled Composites* Using Adsorbed POLYSAM-1

| Formulation | Monomer System | HA† | P/L | Setting Time (min.) | DTS in MPa (no of spec) |
|---|---|---|---|---|---|
| 1 | BIS-GMA (7)<br>TEGDMA (3)<br>BP = 1%<br>TYR = 0.2% | 4.1%<br>POLYSAM-1 | 5/6 | 2½ | 23.4 ± 1.9<br>(7) |
| 2 | Same as above | 4.2%<br>POLYSAM -1 | 2/3 | 2 | 29.9 ± 2.6<br>(4) |
| 3 | Same as above | 2.2%<br>POLYSAM-1 | 5/6 | 4 | 18.8 ± 2.5<br>(5) |
| 4 | Same as above | Same as above | 2/3 | 2 | 25.5 ± 1.3<br>(7) |
| 5 | Same as above | Same as above | 5/6 | 6 | 22.4 ± 6.0<br>(7) |
| 6 | Same as above | Same as above | 2/3 | 6 | 21.2 ± 0.9<br>(4) |
| 7 | Same as above but BP = 0.5% | 4.2%<br>POLYSAM-1 | 2/3 | 3½ | 23.2 ± 2.2 |

* Composites prepared using powder/liquid technique

† POLYSAM-1 adsorbed on HA from methylene chloride solution

## Table 16

### Setting Times and Diametral Tensile Strengths of HA-Filled Composites* Using Adsorbed Surface-Active Amines

| Formulation | Monomer System | HA | P/L | Setting Time (min.) | Diametral Tensile Strength in MPa (no of spec) |
|---|---|---|---|---|---|
| I | BIS-GMA (7)<br>TEGDMA (3)<br>BP = 1%<br>TYR = 0.1% | 1.9% DMAPAA | 5/6 | very fast | 19.9 ± 4.9<br>(4) |
| II | Same as above | same as above | 2/3 | 1¼ | 24.5 ± 6.6<br>(4) |
| III | Same as above but BP = 1% and TYR = 0.1% | 2.4% DMASA† | 2/3 | 5 | 24.1 ± 5.4<br>(5) |
| IV | Same as above but BP = 2.1% and TYR = 0.1% | 2.4% DMASA | 2/3 | 3 | 23.2 ± 2.9<br>(4) |

* Composites prepared by powder/liquid technique

† DMASA = p-N,N-dimethylaminosalicylic acid

## Table 17

### Setting Times and Diametral Tensile Strengths of HA-Filled Composites* Using Dissolved Surface-Active Amine Accelerators

| Formulation | Peroxide-Paste | Acc. Paste | P/L | Setting Time (min.) | Diametral Tensile Strength in MPa (no of spec) |
|---|---|---|---|---|---|
| A | BIS-GMA (7)<br>TEGDMA (3)<br>BP = 1%<br>TYR = 0.1% | BIS-GMA (7)<br>TEGDMA (3)<br>POLYSAM-1 1% | 5/6 | ~ 1 min<br>very fast | 20.9 ± 1.5<br>(4) |
| B | Same as above | Same as above<br>POLYSAM-1 = 0.5% | 2/3 | ~ 10 | 36.5 ± 4.4<br>(4) |
| C | Same as above | Same as above<br>DMAPAA = 0.18% | 2/3 | 3 | 22.3 ± 5.2<br>(5) |
| D | Same as above<br>BP = 0.25%<br>TYR = 0.05% | Same as above<br>DMAPAA = 0.18% | 2/3 | 8 | 31.9 ± 3.7<br>(4) |
| E | Same as above<br>BP = 1%<br>TYR = 0.1% | Same as above<br>4-DMASA = 0.36% | 2/3 | 15 | 16.9 ± 2.7<br>(5) |
| F | Same as above<br>BP = 1%<br>TYR = 0.1% | 4-ADMASA[2]<br>0.5% | 2/3 | 17 | 34.0 ± 8.4<br>(5) |

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* Composites were prepared from equal parts of peroxide and accelerator paste

[1] Formulation F was stored for 72 hours in 100% humidity bath at 37°C

[2] ADMASA = Acetyl derivative of DMASA

## Table 18

### Setting times and Diametral Tensile Strengths of HA-Filled Composites* Using DMSX (Control)

| Formulation | Peroxide Paste | Acc. Paste | P/L | Setting Time (min) | Diametral Tensile Strength (MPa) (no of spec) |
|---|---|---|---|---|---|
| 1 | BIS-GMA (7)<br>TEGDMA (3)<br>BP = 1%<br>TYR = o.1 | BIS-GMA (7)<br>TEGDMA (3)<br>DMSX† = 0.23% | 5/6 | 4 | 23.7 ± 1.7<br>(5) |
| 2 | Same as above but BP = 0.5%<br>TYR = 0.05% | Same as above but<br>DMSX = 0.23% | 2/3 | 2 | 23.2 ± 2.6<br>(5) |

* Composites were prepared using equal parts of peroxide and accelerator paste

† DMSX = N,N-dimethyl-sym-xylidine, a non-surface-active accelerator.

## III. Wear Resistance and Mechanical Properties of Dental Materials

The principal objective is to develop, or make use of, appropriate techniques to measure wear resistance and mechanical properties of dental materials and to use the forthcoming data as performance indicators to predict *in vivo* durability of these materials. The completion of the development of these methods to a satisfactory state is particularly important because of the long times and efforts required for clinical evaluations. In order to accomplish this task, some fundamental research on wear and related mechanical properties is being done to obtain a better understanding of the relevant degradation processes. This information will be of use in determining the principal variables of influence from which appropriate modifications may be incorporated in the wear apparatus to obtain meaningful results. In addition, the improved understanding of the ways in which specific mechanical properties of the composite systems correlate with wear behavior is expected to be instrumental in developing improved systems. The following paragraphs describe the work performed during this fiscal year on wear and mechanical properties of dental materials.

### A. Wear Instrumentation and Data

The wear apparatus consists of three identical rotating platforms containing specimens of the material to be investigated. A stationary slider of about 2 mm diameter containing human enamel, or appropriate substitute, makes contact with each of the rotating specimens producing a wear track of about 12 mm in diameter. The slider is loaded to obtain a normal stress of 10 MPa on the wearing surface of the specimen. The depth of each track is measured automatically at arbitrarily selected intervals (depending on the wear rate) at 10 equally spaced positions along the track circumference using linear variable differential transformers with suitable probes. Distilled water at 37°C flows over the platforms to control temperature, lubricate, and wash away debris. Figure 1 is a photograph of the entire wear apparatus. The mechanical part of the apparatus is shown in Fig. 2 depicting the three wear stations. A closeup of one of these is given by Fig. 3 revealing its specimen cup, wear pin and mounting collet, and track depth measurement assembly.

The assembly of the data acquisition equipment has now been completed and the apparatus made operational. As mentioned in the previous annual report (10), the data acquisition equipment used previously was owned by the USAF and was repossessed by them last fiscal year. Although replacement imposed considerable inconvenience upon us and delayed our research effort, we were able to incorporate substantial improvements and a much higher degree of reliability in the new system. The apparatus is now controlled by a computer, which actually simplifies the measurement procedure and makes it more flexible. The computer also has sufficient memory (36k bytes) to carry out the wear statistical calculations using a program written in the programming language BASIC.

The measurement system has been modified to determine the wear track length by counting cycles rather than from the product of the assumed angular velocity and time interval. Counting cycles is a more direct approach and also removes a small uncertainty in the track length resulting from fluctuations in angular velocity.

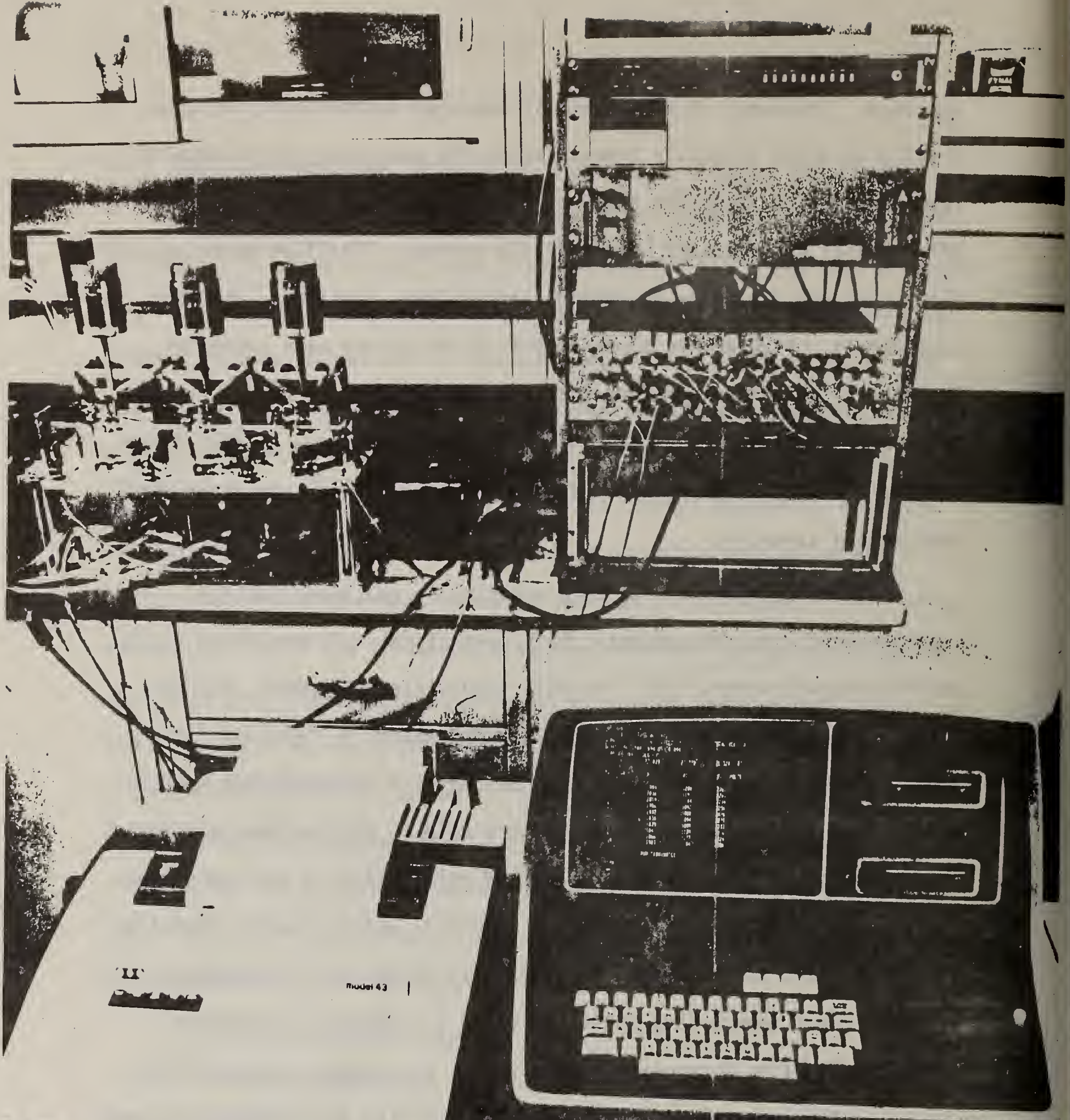

Fig. 1. General view of the wear apparatus.

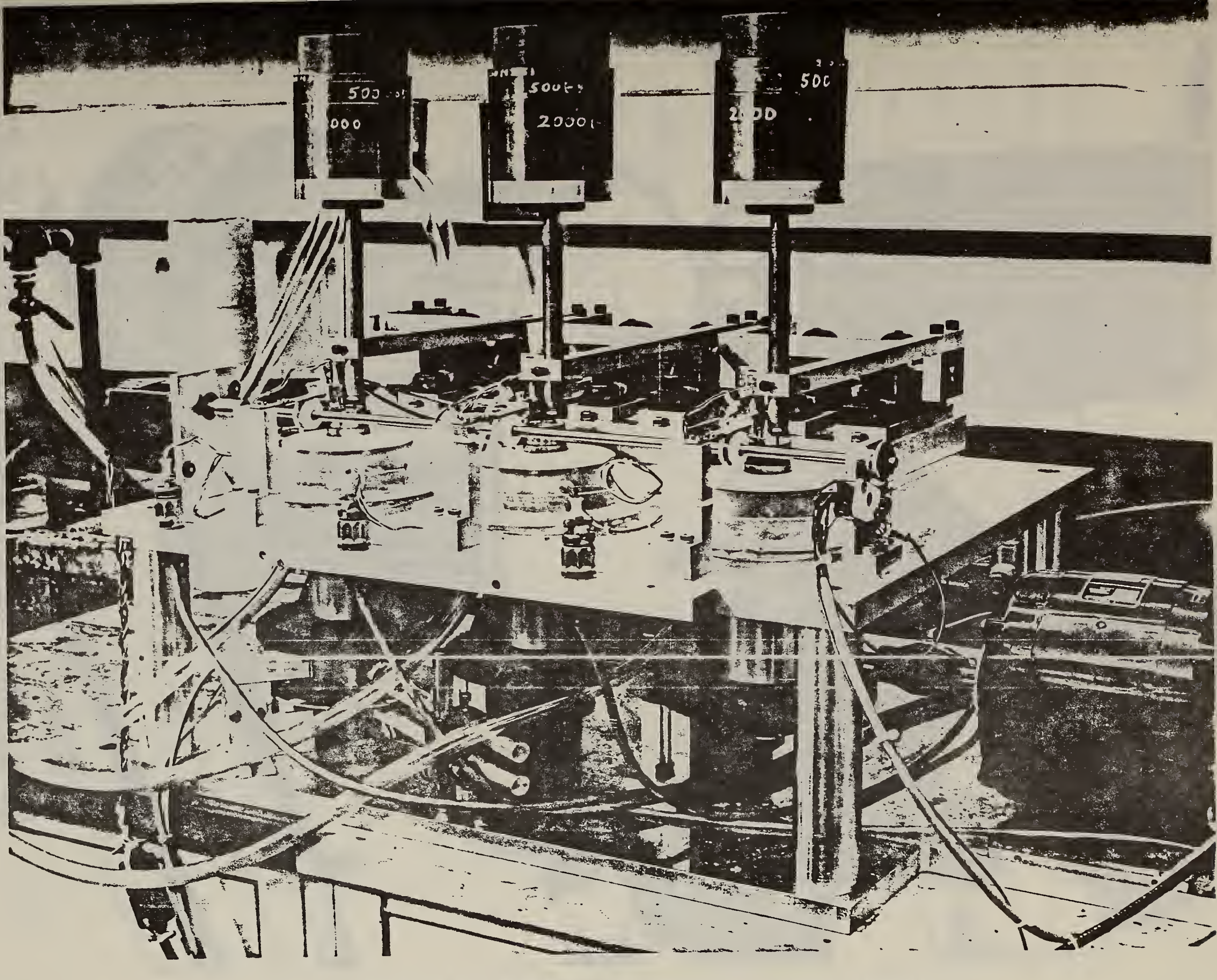

Fig. 2. View of the mechanical portion of the wear apparatus.

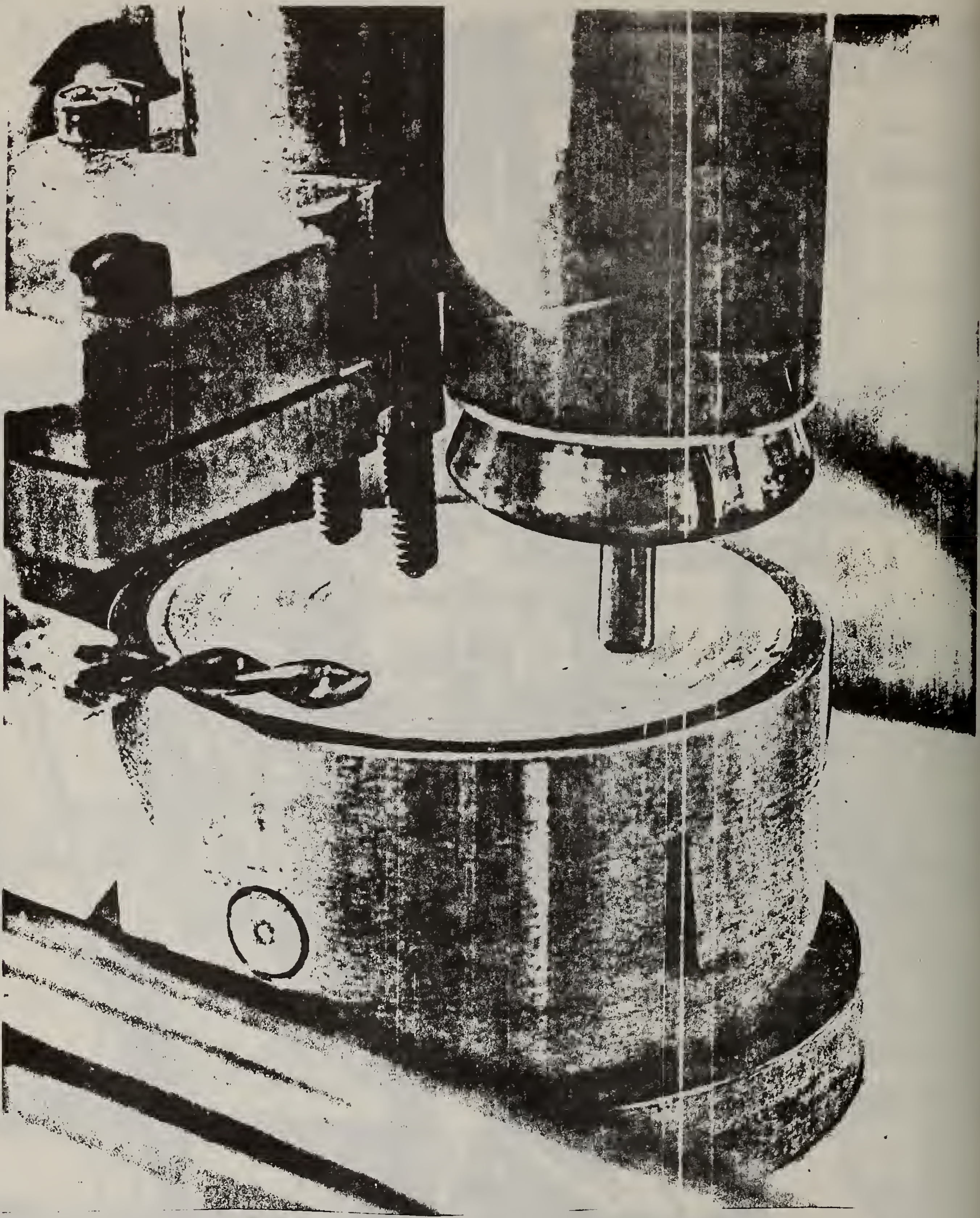

Fig. 3. Close-up view of single wear station showing specimen cup, wear pin and mounting collet, and track depth measurement assembly. The thermocouple junction shown in contact with the specimen is immersed in the lubricating fluid (distilled water).

In our preliminary measurements the wear pins (approximating 2 mm diam.) were secured in their cup-like holders using a poly(methyl methacrylate) denture base resin. After completing long wear runs we occasionally observed a slight tilt of the pins with respect to their holders which resulted from a small amount of creep in the resin. In order to correct this problem the pin mounting assemblies were modified to accommodate jewelers' lathe collets and draw bars as depicted in Fig. 3. The pins are secured by applying appropriate manual torque to the weight support table in a manner similar to securing a drill in a jeweler's lathe. This technique is particularly suitable for the accommodation of the durapatite wear pins, which we are evaluating as an alternative to enamel.

The definition of the wear rate used in this work is

$$G = \frac{V}{LW} \tag{1}$$

where V is the volume loss from wear, L is the total sliding distance, and W is the normal force. The units are expressed in terms of compliance (reciprocal modulus) or, alternatively, volume/energy. Although the wear rate as defined above may appear to be a material property, it is not because wear always involves at least a wear couple, and the results depend considerably on the properties of the opposing material. The influence of different pin materials will be shown later in this report.

In terms of the experimental variables, r and s, where r is the number of revolutions and s is the track depth, Eq. (1) takes the form

$$G = \frac{4}{\pi a \sigma} \frac{ds}{dr} \tag{2}$$

where a is the pin diameter (assumed to be equal to the track width) and $\sigma$ is the normal stress. An advantage of using Eq. (2) over other possible forms is that the track diameter does not appear (as it does implicity in Eq. (1)), thus eliminating a small source of systematic error. This redundancy is removed in a cancellation of V and L in Eq. (1). Both of these quantities are linearly dependent on track diameter.

Two dental materials, an amalgam Velvalloy and composite Adaptic, have been selected to evaluate the performance of this technique. The particular materials were chosen because they represent two different classes of dental materials and were used by Phillips and coworkers (27) in their clinical tests for durability taken over three years.

In the previous annual report (10) we described our measurements on these materials using wear pins made from human enamel. Although enamel is taken to be a component of the oral wear process, there are several serious objections to its use in our wear tests. First, enamel is anisotropic and inhomogeneous. The effect on the wear on the opposing material may depend upon the orientations of the crystal structure with respect to the pin axis and the location in the tooth from which the pin is made. Second, there is considerable variation in properties between specimens from different subjects and even from the same subject. In evaluating restorative materials which are nearly alike, we do not wish to test them against a reference material whose properties may vary considerably. Third, there is no acceptable way of knowing when the enamel layer is depleted during the tests and the underlying dentine becomes effective in the wear couple. Fourth, enamel is chemically unstable. It is very difficult to store the enamel pins for long periods of time and to be sure that significant degradation has not occurred. Finally, fabrication of enamel pins is extremely difficult and time consuming.

In view of the objections to human enamel in this application, we have been evaluating other materials to determine a satisfactory substitute. The forthcoming results are expected to be useful in evaluating the influence of different opposing materials on the wear process. To date, in addition to human enamel, we have made wear measurements on Velvalloy and Adaptic using durapatite, mild steel, and stainless steel.

Table 19 includes a summary of what we take to be our best values of G for the wear couples measured to date. The first three were measured by the old acquisition system, where the values of G are taken from averages of those at number 1 and 6 positions (180° apart) on each rotor. The statistical quantities for these measurements have not yet been completed because the old system was taken from us before we could change the tape format to evaluate the data on the new system. We are planning to do this at a later time in order to evaluate all of the data consistently. The remaining couples were measured with the new acquisition system where the values of G are averaged over 10 positions on each of the three rotors.

Two different standard deviations for the last four couples are included in the table. The first, Average Standard Deviation, is the usual one where the standard deviations of the wear rates are calculated from the residuals about a linear regression on the track depth/ number of revolutions data at each position and then averaged over the ten positions. The second, Position Standard Deviation, is that obtained from the 10 wear residuals (over position) about their average.

The difference between the two standard deviations is illustrated in Fig. 4, where the values of $m = ds/dt$ (proportional to the wear rate G) are plotted against the track position number (1 thru 10). These values pertain to Velvalloy using stainless steel pins for which the corresponding wear rate and deviations are included in Table 19. The average value (over position) of m is shown on the right hand side. The standard deviation of each slope is indicated by the vertical

## TABLE 19

## WEAR DATA SUMMARY

| Couple | Wear Rate G $TPa^{-1}$ | Average Std. Dev. G $TPa^{-1}$ | Position Std. Dev. G $TPa^{-1}$ | Pin Wear Rate nm/rev |
|---|---|---|---|---|
| PMMA-En | 0.141 | - | - | - |
| Vel-En | 0.0632 | - | - | 1.4 |
| Ad-En | 0.0106 | - | - | 4.2 |
| Vel-Dur | 0.0533 | 0.00049 | 0.0058 | - |
| Ad-Dur | 0.0084 | 0.00012 | 0.0032 | - |
| Vel-SS | 0.0488 | 0.00036 | 0.0055 | 0.16 |
| Ad-SS | 0.0615 | 0.00070 | 0.0036 | 4.7 |

PMMA = poly(methyl methacrylate)

Vel = Velvalloy

Ad = Adaptic

En = enamel

Dur = durapatite

SS = stainless steel, type 18-8, 303

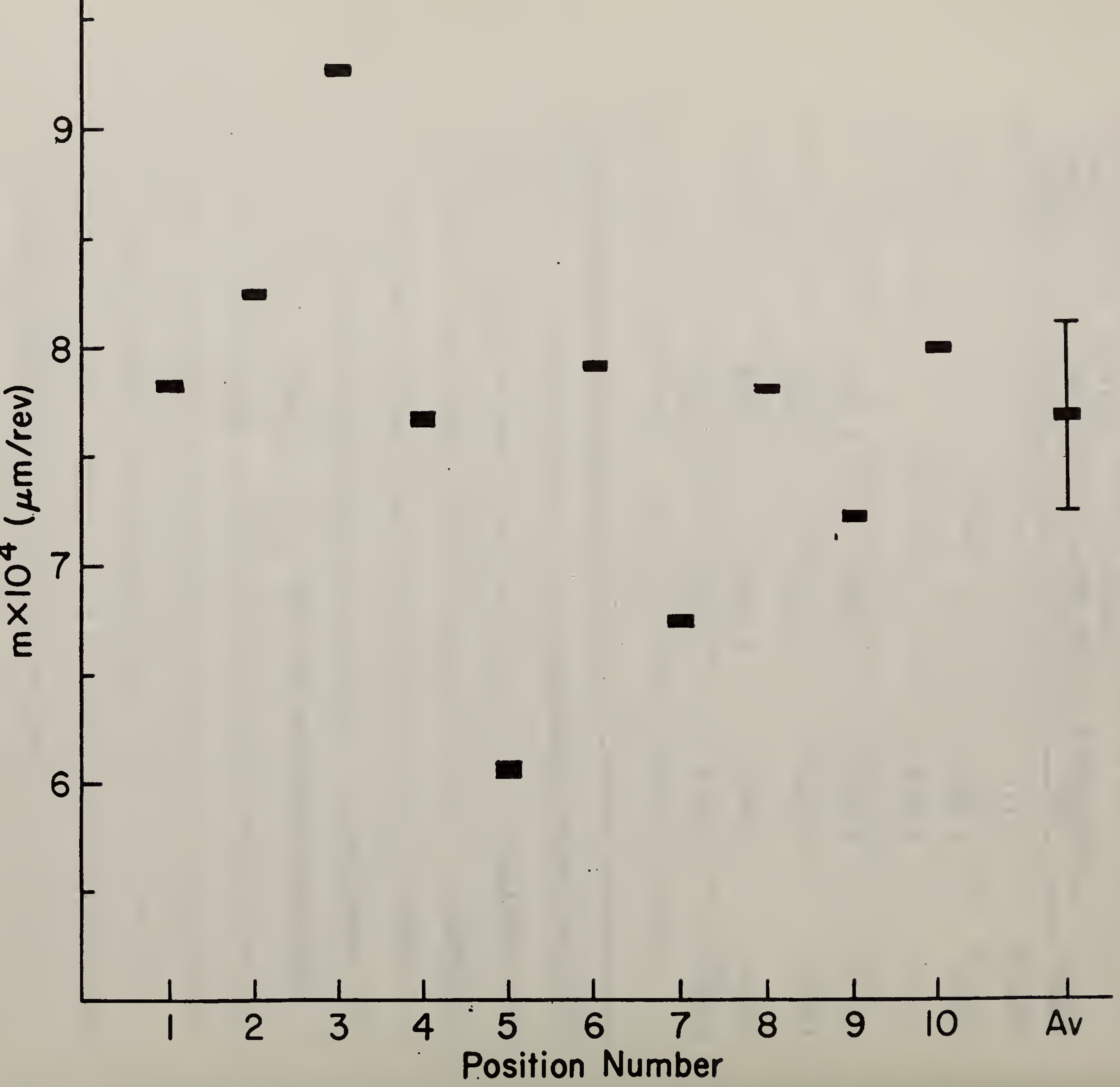

Fig. 4. Dependence of the amount of wear on rotor position for Velvalloy and illustration of the two types of standard deviations used to evaluate the data.

thickness of each solid rectangle, and the average of these deviations is designated by the thickness of the rectangle on the right. The large bracket on the right gives the standard deviation of the residuals (over position) of m about their average.

The average standard deviation, which is the average (over position) of the standard deviations of the slopes m, is a measure of experimental imprecision and irregular wear behavior of each position. The position standard deviation, which is the standard deviation of the residuals of m about their average, is a measure of the variation of the wear rate with position and is assumed to be related to inhomogeneity. With the dental materials examined, the position standard deviation is much larger than the average standard deviation as indicated by Table 19.

Filling materials are expected to be inhomogeneous because of the manner in which they are prepared. Since our specimens are large (in comparison to the amount of material used in a restoration) they are prepared in several stages. With the short condensation, or cure times, it is essentially impossible to pack these specimens with no voids, discontinuities, or density gradients. Accordingly, it is necessary to obtain many measurements along the track circumference (as is done with our apparatus) to obtain a reliable average value of the wear rate.

Wear rate data on the pins are included in Table 19 for the few cases where they are available. These were obtained from two point micrometer readings before and after each run. They are not considered to be particularly reliable, since each value in the table is based on only two points, and the precision of the micrometer is about ± 10 μm. However, they are an indication of how these dental materials degrade when opposed by enamel (or other dental materials which may oppose them). Adaptic wears enamel three times as fast as Velvalloy and wears stainless steel 30 times as fast as Velvalloy. The high wear rate with Adaptic against stainless steel indicates that Adaptic may inflict serious damage when contacting, for example, a gold or base metal restoration. On the other hand the same result would apply to enamel since the wear of enamel and stainless steel are about the same against Adaptic. We hope to obtain more extensive and reliable data on pin wear and may wish to incorporate this facility in the apparatus. This additional information could be of considerable value to assess the relative damage inflicted on proximate opposing Class 2 restorations of the same or different materials.

Dr. W. Bailey of the University of Connecticut has also made wear measurements (unpublished data) on the Adaptic-durapatite couple using a pin and disc machine similar to ours. The principal differences are that his machine has seven rotors instead of three and makes two measurements along the circumference of each track instead of ten. Under similar conditions he obtained an average value of $m = 0.81 \times 10^{-4}$ μm/rev which compares with our value of $1.32 \times 10^{-4}$ on the same couple. Considering that our minimum value at position 2 is $0.51 \times 10^{-4}$ and our position standard deviation is $0.42 \times 10^{-4}$, we and Dr. Bailey consider these results to be in reasonable agreement in that the difference may be essentially attributed to sample variation and inhomogeneity. His corresponding value of G for the Adaptic-durapatite couple is 0.0051 $TPa^{-1}$ which compares with our value of 0.0084 given in Table 19.

The following is a more detailed account of our wear activity during FY 1979.

Immediately after the new acquisition system was completed in January, we made wear measurements on Velvalloy and Adaptic using durapatite wear pins. Durapatite is a form of sintered hydroxyl apatite, supplied by Sterling-Winthrop Institute. The name durapatite is used to distinguish this form from other forms of hydroxyl apatite. Machining wear pins from durapatite is very tedious and time consuming. It is harder and much more brittle than enamel.

The results using these couples are shown in Fig. 5, where the wear track depths are plotted against the number of revolutions. The track depths shown are the average values taken over the ten positions along the track circumference. The separations of adjacent data points along the abscissa correspond to approximately one hour. These measurements were taken after the wear track profile was assumed to have been established (in this case 20 hours at full load). As usual Velvalloy reveals a more irregular response than Adaptic.

For both materials there are initial responses which are distinct from the apparent steady state. Discontinuities in rates are commonly observed in wear measurements and are often attributed to wearing through a surface layer which has different properties from the bulk. This behavior is typical of metals, which usually form oxide surfaces. It is

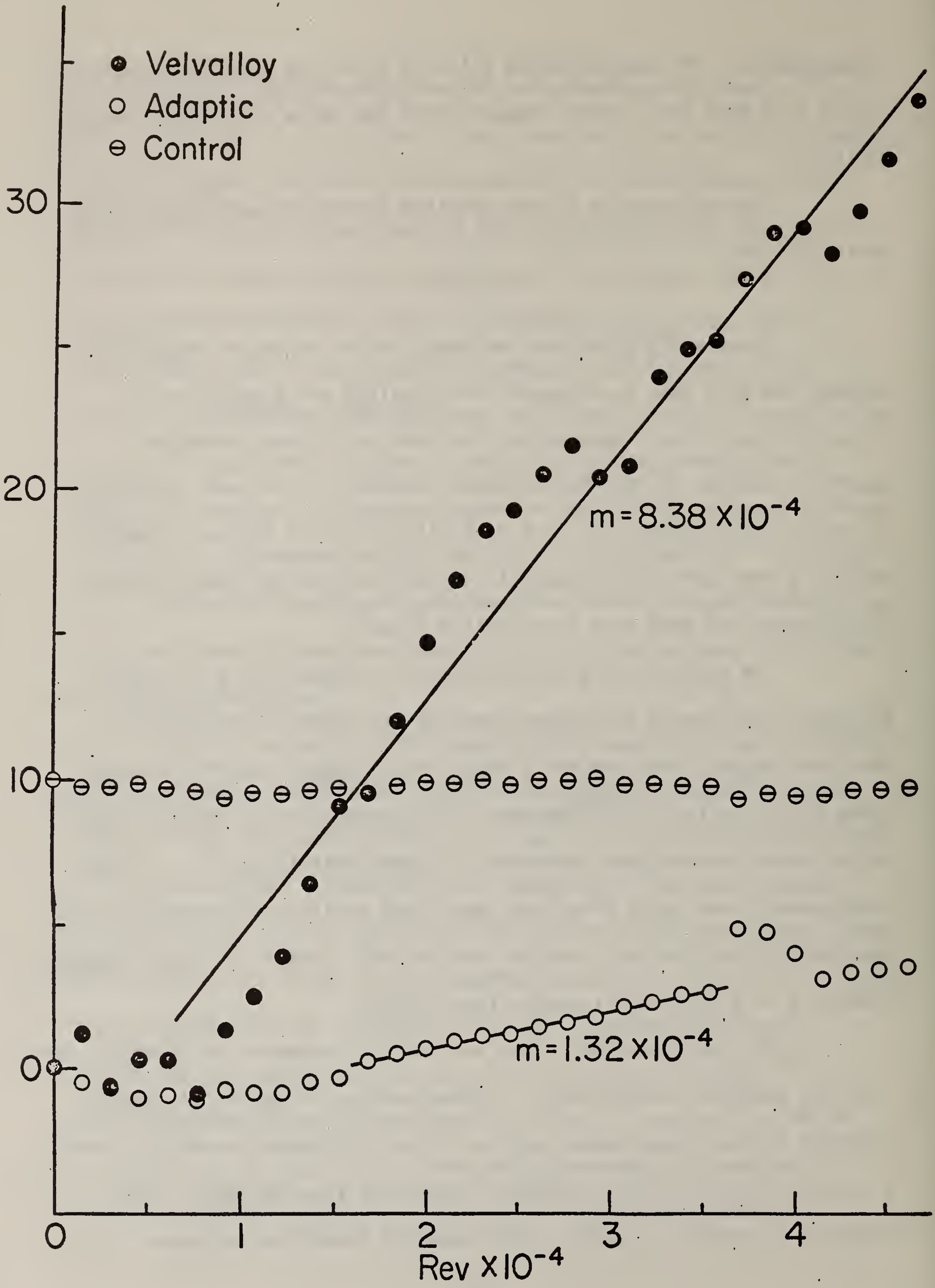

Fig. 5. Track depth(s)/revolution response for Velvalloy and Adaptic using durapatite wear pins.

not clear why such a low initial rate, including an apparent negative one, should exist for a composite unless the wear track profile was not completely established.

The control values shown on Fig. 5 were obtained using a brass disc (in lieu of a dental material specimen) which was not subjected to wear. These values are obtained to determine the imprecision and possible drifts which could bias the results. Since these measurements were taken, improvements which result in higher precision have been made to further stabilize the measurements.

The values of m are obtained from linear regressions over the regions included by the calculated straight lines. Using Eq. (2) for which m = ds/dt, the wear rates and deviations given in Table 19 for these couples are obtained.

At about 37,000 revolutions Adaptic reveals an anomaly which apparently arose from a spurious electronic instability in the signal conditioner for the linear variable differential transformers. This kind of a result is not apparent in either Velvalloy or the control. As indicated on Fig. 5, the points including and above the spurious region are excluded from the linear regression analysis.

Values given in Table 19 for the durapatite couples may be compared with our earlier values (10), 0.0632 and 0.0106, on the same materials using enamel wear pins. The durapatite values are slightly smaller, but considering the amount of variance mentioned earlier they are considered to be in good agreement and consistent in that the ratios of the former values to the latter approximate 0.82.

In the previous annual report (10) we stated that our values on Velvalloy and Adaptic are not in agreement with those obtained by different workers, Powell and Dickson (23), on a prototype apparatus for which the values 0.013 and 0.022 $TPa^{-1}$, respectively, were obtained. Their values would reverse the order of wear resistance ranking. These results are based on unpublished data and, apparently, on a very limited amount which has not been repeated. The same ranking was obtained by Powell, et al. (24), using a pin and disc device; however, the authors noted with Velvalloy that amalgam debris deposited on the enamel pins during wear. This could result in some effective lubrication reducing the amount of wear. We did not find such deposits in our work, which could account for this discrepancy.

A motor control failure on our jeweler's lathe has temporarily prevented us from making the durapatite pins necessary to continue measurements on dental materials using durapatite pins. Our shops are to supply some additional durapatite pins. To obtain some insight on the influence of a vastly different material on the wear process, we made some wear pins from drill rod (mild steel), which is available in 2 mm diameter. The mild steel turned out to be a bad choice because of the rapid accumulation of rust from the continuous supply of 37°C distilled water. To circumvent this problem we obtained from our shops some pins of type 18-8, 303 stainless steel which revealed no significant amount of rust during the measurements.

The results on Velvalloy and Adaptic using stainless steel pins are depicted in Fig. 6, where the average values of the track depth are plotted against the number of revolutions. This is one of our longer

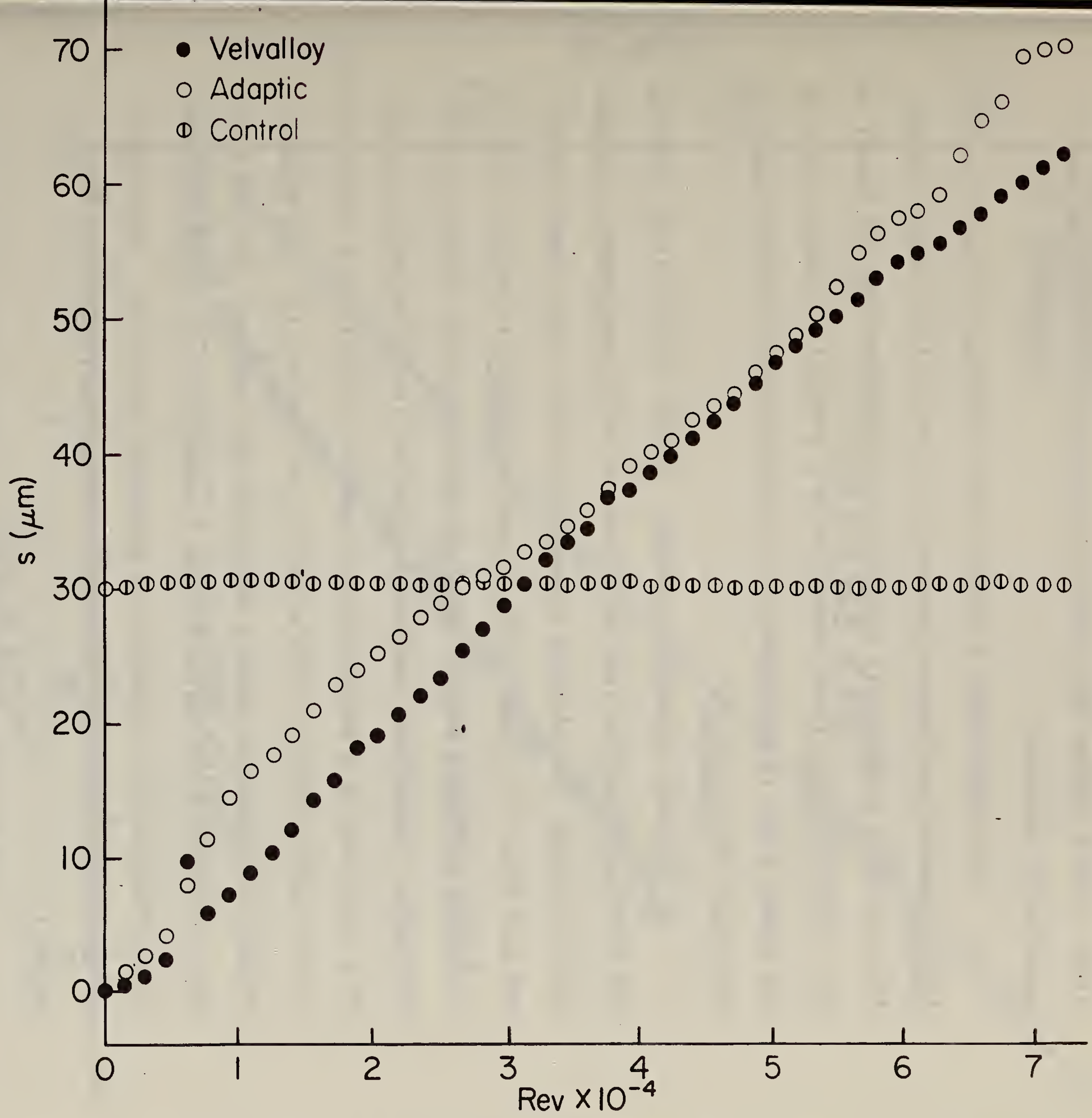

Fig. 6. Track depth/revolution response for Velvalloy and Adaptic using stainless steel wear pins.

runs, taken over 48 hours. With stainless steel pins, the wear on Adaptic is more irregular and increases by a factor of six over that obtained using durapatite pins. On the other hand, wear on Velvalloy using stainless steel is more regular than that with durapatite, but the rates are essentially identical.

With these data, distinct initial responses are again observed. Adaptic reveals accelerated wear nearly in the initial region; however, this may be an irregularity similar to that observed near the end of the run. With Velvalloy there appears to be a gradually increasing rate as the steady state is approached. This kind of initial response seems to be typical of Velvalloy.

In order to determine whether or not these initial responses are artifacts resulting from track break-in only, measurements on these couples through and slightly beyond the initial region were repeated one week later. As shown in Fig. 7, wear on Adaptic is regular but the gradually increasing wear on Velvalloy persists as the steady state is approached. Composites sometimes display air inhibition during curing. This could lead to a surface effect revealed initially by a faster rate such as that seen in Fig. 6. This effect is not seen in Fig. 7, presumably because the undercured surface would have been removed. With the amalgam our tentative conclusion is that a protective layer reforms (assumed to be oxidation) during periods of mechanical inactivity. According to our data, the reformed surface has higher wear resistance than the bulk material.

The values of m shown on Fig. 7 for the steady state regions are used to obtain the corresponding values of G in Table 19. The initial

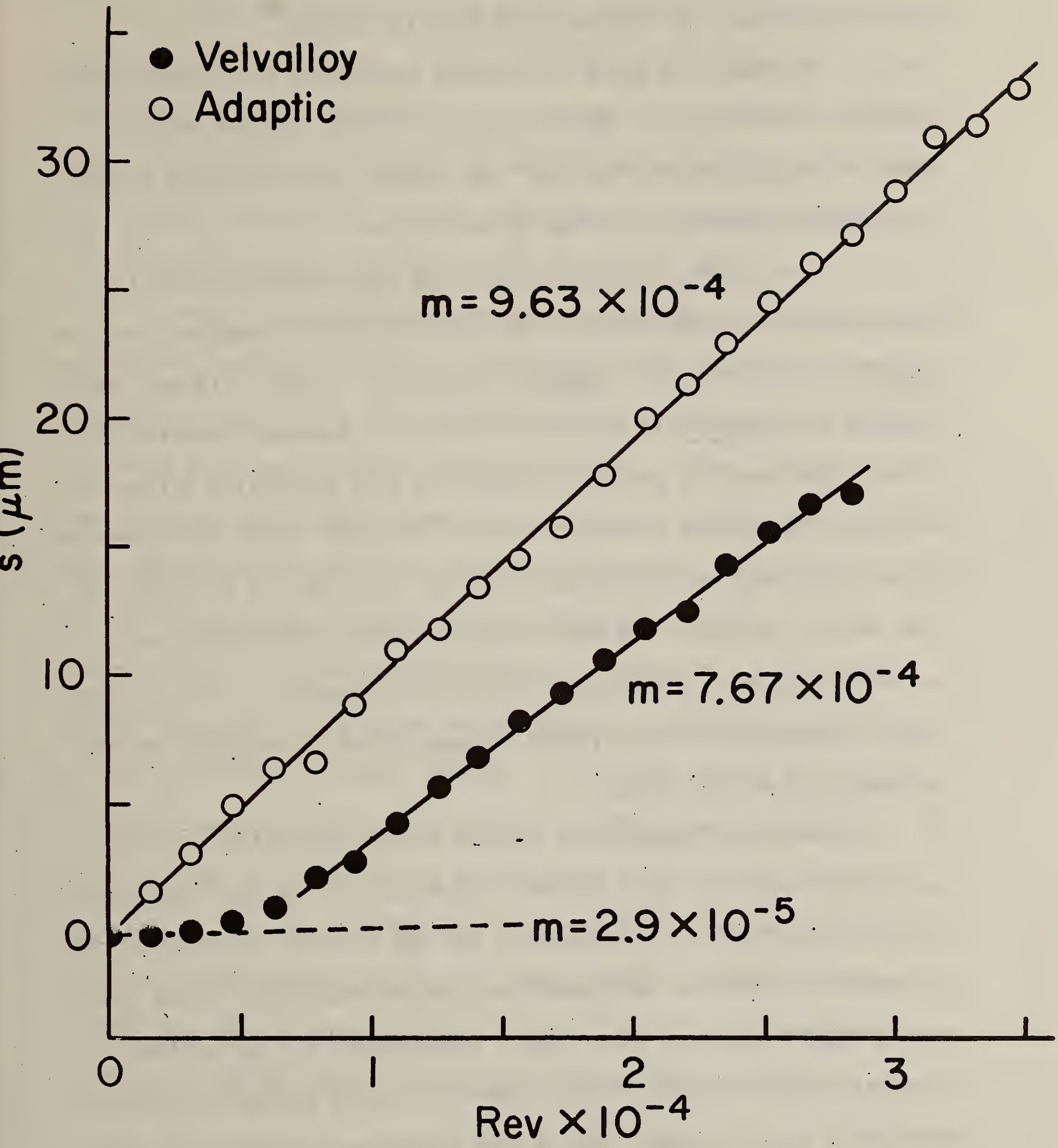

Fig. 7. Repeat of initial regions of Fig. 6 used to assess the meaning of these regions.

value 2.9 x $10^{-5}$ for Velvalloy is taken from a linear regression on the first three points. The corresponding value of G is 0.0018 $TPa^{-1}$, which is far below that for the Adaptic-durapatite couple.

Although the above results are considered to be somewhat preliminary in our research effort, they do indicate certain factors which may be relative to the oral wear process and indicative of the direction of research to follow in the future.

The clinical results of Phillips and coworkers (25-27) on these materials indicate very slight deterioration in anatomic form of Velvalloy compared with Adaptic, whereas our steady state wear data indicate that Adaptic is superior, which is in apparent contradiction. On the other hand the oral wear process is only physically active for a very small portion of time (say 1 to 4%) relative to the total, whereas in our tests wear is continuous. Thus at least for the amalgams and base metals, we should not rely entirely on the steady state wear, but should pay more attention to the initial response. It is the wear region immediately after physical dormancy which is probably the most relevant to the oral process.

The other possibility is that we are conducting our tests on an opposing material which may not be dominant in the oral wear process. As pointed out by Dr. R. L. Bowen of the ADA Research Institute at NBS, the enamel-restorative wear couple may not be appropriate since enamel rarely comes in contact with Class 2 restorations during mastication. Alternatively, different kinds of food of varying degrees of hardness, much below that of enamel, may be more effective in the *in vivo* wear process. Our results, using wear pins made from several different materials, demonstrate considerable differences on the amount of wear, and in one case the ranking on the wear is reversed. Although stainless steel is softer than enamel, it is still much harder than the average constituent of food. Accordingly, it appears to be appropriate that we should investigate the influence of much softer materials used as wear pins, such as a plastic or rubber, for which the physical properties, in particular hardness, are much closer to that of food.

Another argument relevant to the apparent contradiction in the wear ranking between clinical and laboratory tests mentioned above is the following. Phillips and coworkers (25) also made *in vitro* abrasion tests with a mechanical tooth brushing machine. Using a slurry of calcium carbonate the abrasive wear on Velvalloy and Adaptic was about the same. However, when pumice, a much harder material, was used the weight loss of the Velvalloy exceeded that of Adaptic by a factor of ten. As pointed out earlier, their observations on changes in anatomic form indicate Velvalloy to be superior to Adaptic. A possible explanation for the differences in these rankings is that both enamel and pumice are hard materials which appear to wear Velvalloy more than Adaptic. On the other hand softer materials as indicated from our work, and from the clinical tests of Phillips and coworkers (assuming that food is effectively the opposing material in mastication), produce more wear on Adaptic. Our planned tests using the softer materials mentioned above should reveal whether or not this supposition is valid.

## B. Mechanical Properties Measurements

In the course of initiating work on mechanical properties, we have adopted two approaches which we feel will provide information which is essential to an understanding of the wear processes which lead to the degradation of dental composites. Part of this work also focuses on the development of new types of resin systems for use in dental composites and will be discussed under the section on Materials.

In the first instance, we have decided to study the relationship between wear resistance and the fatigue behavior of the composite systems. The approach is based upon the concept of damage accumulation* which has been elucidated by work performed in the NBS Polymer Science and Standards Division (28,29) and elsewhere (30). The basic premise in this approach is that clinical wear processes occur over time and are superimposed on a composite system which is undergoing continual thermal and mechanical cycling. Thus, the wear observed clinically occurs on a restoration which undergoes progressive thermal and mechanical fatigue damage with time.

Experimentally, we take samples of material and determine the fatigue lifetime. By cycling the material to various fractions of that lifetime (various states of accumulated damage) and then conducting wear studies on the fatigued sample, we determine how the wear rate is affected by the state of damage.

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*In general, time and cyclic failure can be modeled as a process in which the damage in a material accumulates as a function of time and/or cycles. Although the material has not failed it has accumulated a certain amount of damage which has changed the residual durability of the material. This could affect observed wear data which are generally obtained on virgin or undamaged material.

A preliminary attempt to begin this sort of experiment was unseccessful. We wanted to perform compressive fatigue tests on samples which could be sectioned and placed directly into the wear apparatus. As it turned out, the sample size required was a cylinder approximately 15 mm in diameter by 50 mm in length. This size is too large to test in a reasonable time on our MTS testing machine, which has a 10 kN capacity. Thus, the maximum stresses attainable on the machine are below the endurance limits reported by Draughn (31) for composite restorative systems. In order to avoid extensive modification of the wear apparatus to accept smaller specimen sizes, we are currently planning on performing fatigue tests on thin sheets which have been cut into dumbbell shaped specimens and then conducting the wear tests on the face of the specimens. These specimens should be adequate to assess the effects of fatigue and damage resistance on wear performance.

The second approach which we are taking to correlate the mechanical properties of dental composites with wear behavior is the study of the resistance of these materials to crack propagation. By studying fracture toughness and fatigue crack propagation in dental composites and correlating them with the fatigue/wear study discussed above, we plan to determine the contribution of these parameters to the wear of dental composites.

The fracture toughness of a material is essentially its resistance to unstable propagation of a crack. Strictly speaking, the fracture mechanics analyses are valid only for linearly elastic materials and not for viscoelastic materials. However, even with this limitation, fracture mechanics does serve as a useful empirical tool for the study of the resistance of materials to crack propagation.

For our studies we have chosen to use the compact tension specimen (32) depicted in Fig. 8. For this specimen geometry the stress intensity factor $K_1$ is determined from the following equation (see ref. (32)):

$$K_I = \frac{Y P\sqrt{a}}{BW} \qquad (3)$$

where

P = load

a = crack length

B = specimen thickness

W = effective width of specimen

Y = geometry factor

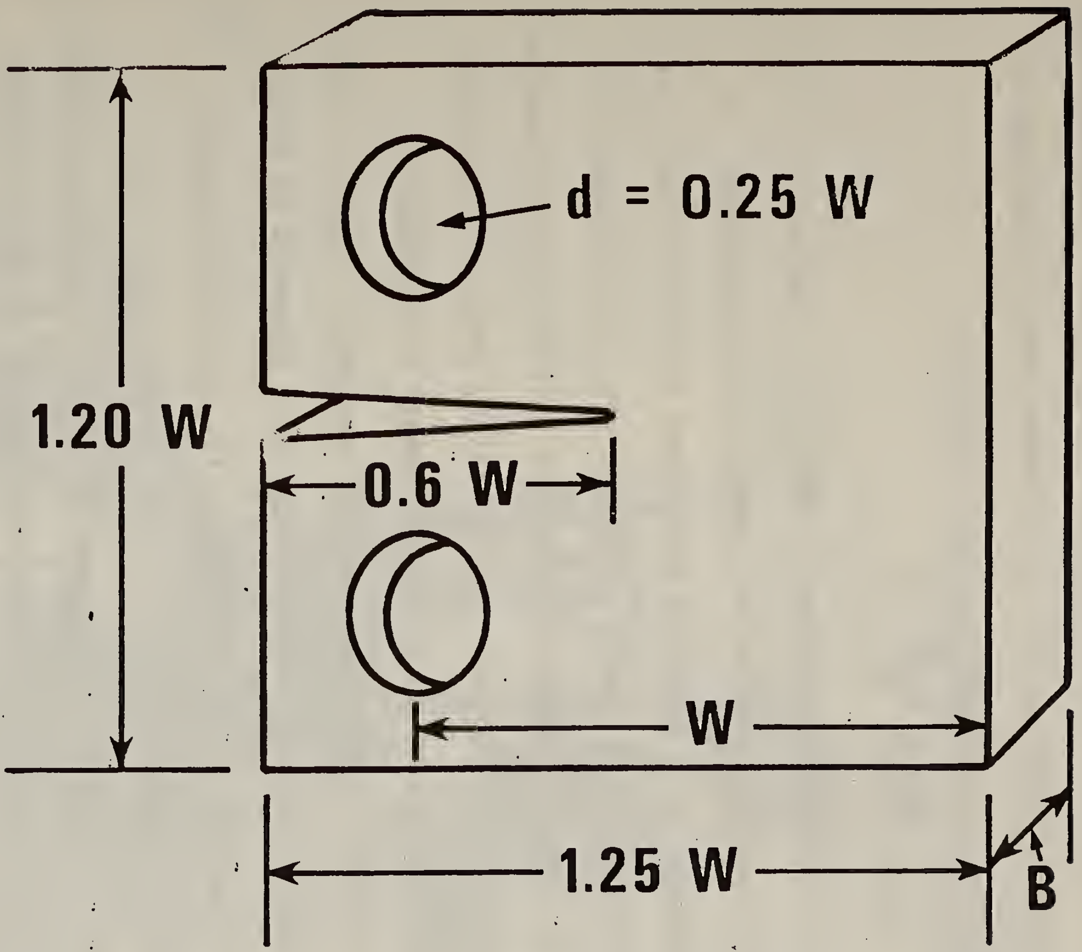
The geometry factor Y in units of $in^2$ is given by ASTM E399-74 (32)

$$Y = 29.6 - 185.5 \frac{a}{w} + 655.7 \left(\frac{a}{w}\right)^2 - 1017 \left(\frac{a}{w}\right)^3 + 638.9\left(\frac{a}{w}\right)^4 \qquad (4)$$

and the conversion of $K_I$ from psi $\sqrt{in}$ given by equation (3) to MPA $\sqrt{m}$ is:

$$K_I(\text{psi } \sqrt{in}) \times 1.099 \times 10^{-3} = K_I(\text{MPA } \sqrt{m}) \qquad (5)$$

Thus, if one has a known crack geometry, it is possible to obtain one of two pieces of information. The fracture toughness, $K_{IC}$ (critical stress intensity factor), can be determined by increasing the load on the specimen until unstable propagation occurs. $K_{IC}$ is determined from the maximum load and the initial crack length. The other piece of information which can be obtained is the rate of stable crack



W = 1.00 inches = 25.4 mm
B = 0.25 inches = 6.35 mm

COMPACT TENSION SPECIMEN

Fig. 8. Compact tension specimen used for fracture and fatigue crack propagation experiments.

propagation under an oscillating load. It is conventional to obtain the incremental growth per cycle, da/dN, and correlate it with the range of the stress intensity factor $\Delta K$. It is often found (33-35) that a power law relationship describes the data quite well:

$$da/dN = A\Delta K^m \qquad (6)$$

In our experimental program we have built adapters for the MTS universal testing machine to hold the compact tension specimen. In addition, we have set up a traveling microscope to follow crack propagation. Figure 9 shows the general setup and Fig. 10 a closeup of a specimen and the adapter. To gain experience with this type of specimen and the problems with initiating a stable fatigue crack, we have conducted some preliminary work on commercial sheets of poly(methyl methacrylate) machined into compact tension specimens. Figure 11 shows the results obtained using a sinusoidal load at a frequency of 0.50 Hz. The data fit an equation of the form of Eq. (6) and agree reasonably well with data from the literature.

Because varying the temperature of polymer and composite specimens can significantly influence mechanical response of such materials and provide clues to the understanding of the mechanical properties per se, we have ordered a temperature controlling unit for the MTS universal testing equipment.

## C. Materials

Part of this program is involved with tests and measurements on commercial composite restorative materials. However, in order to gain the experience needed in the molding techniques required for

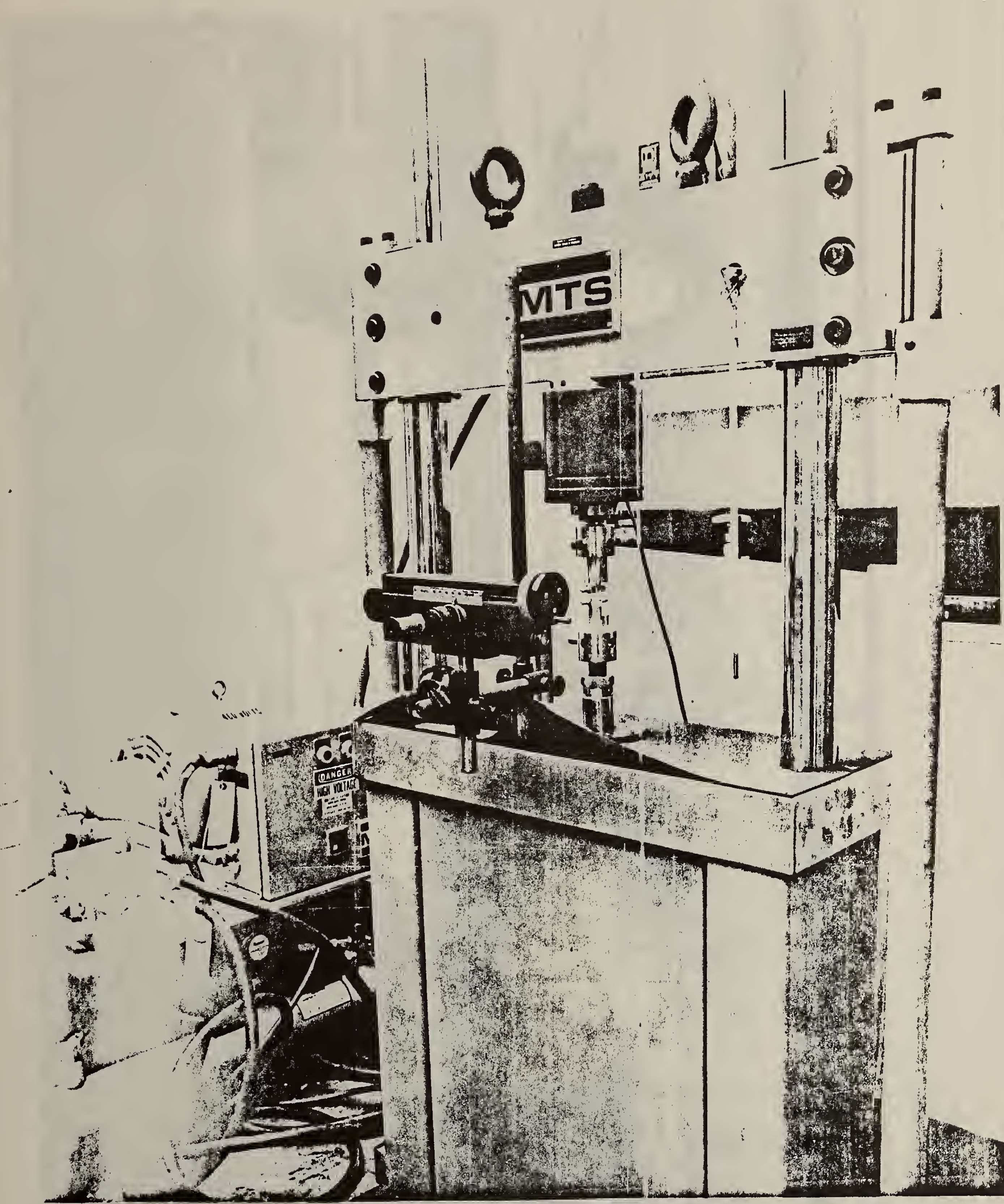


Fig. 9. General view of MTS servo-hydraulic equipment showing fracture specimen and travelling microscope for measuring crack length.

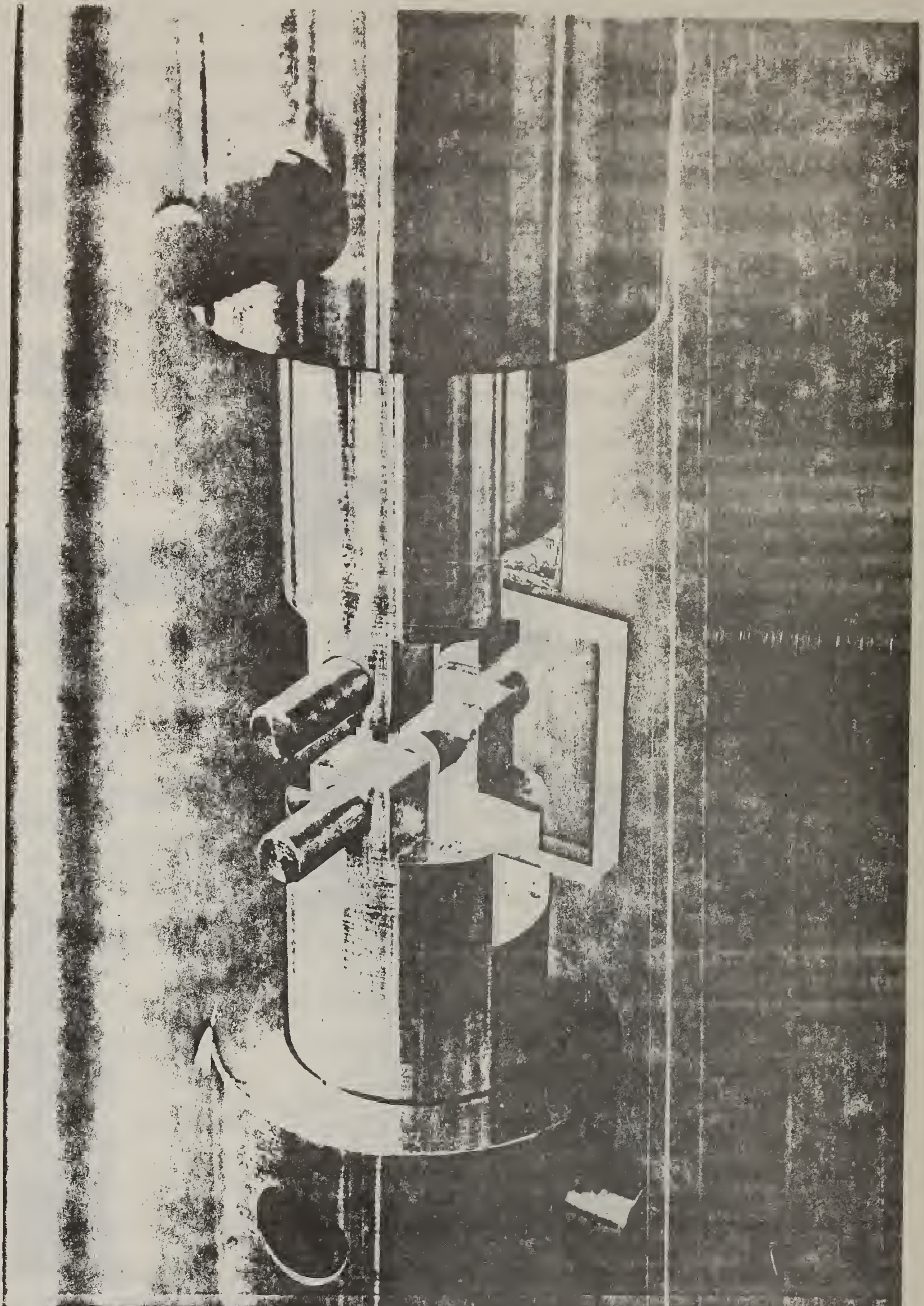


Fig. 10. Close-up view of grips used to mount compact tension specimen in servo-hydraulic machine.

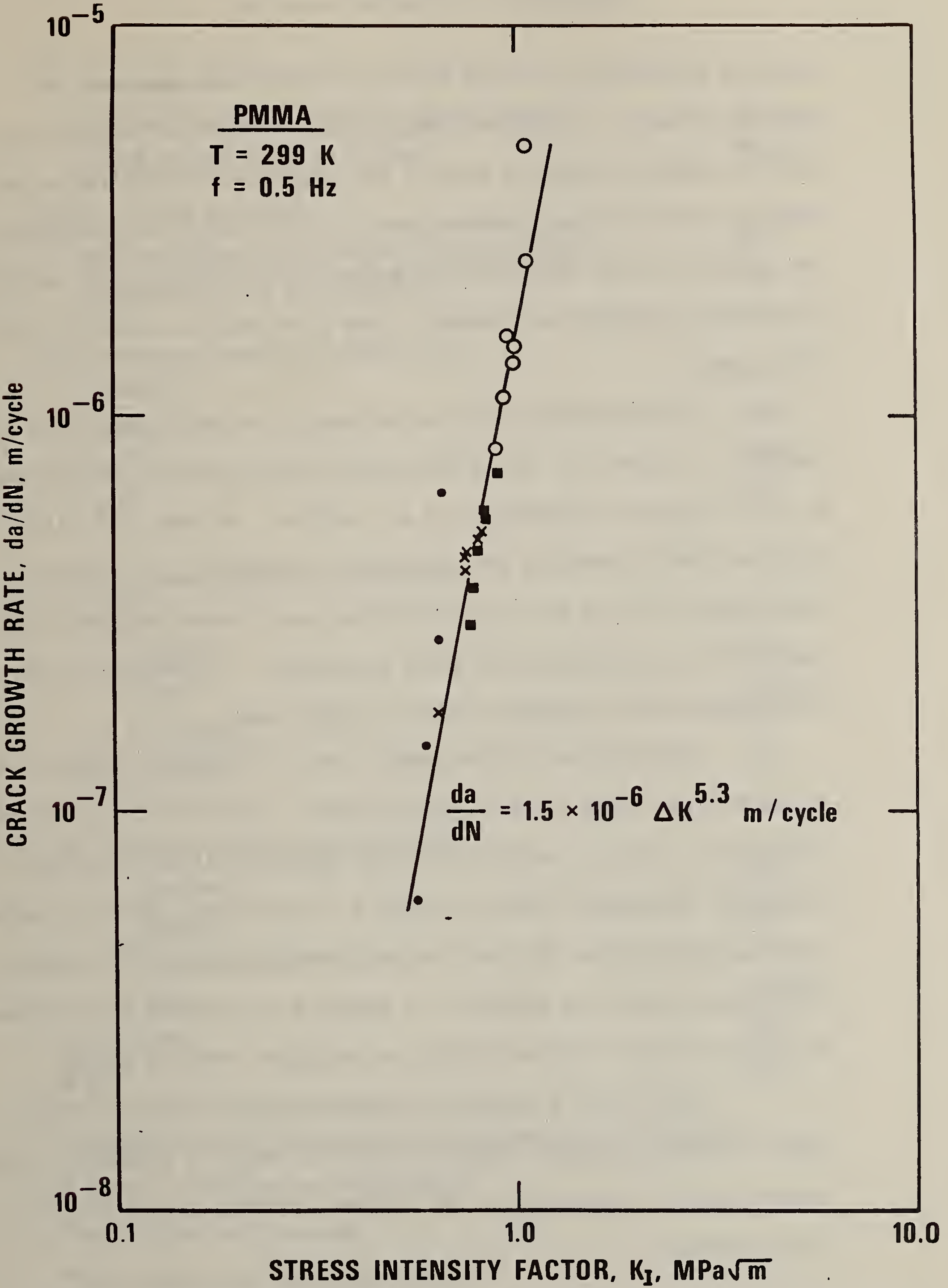


Fig. 11. Fatigue crack growth rate versus maximum stress intensity factor, $K_I$ for poly(methyl methacrylate). Tests were run as half-sines in load control at 0.5 Hz.

specimen preparation, we have begun working with bone cement and BIS-GMA systems. In addition, because of our observation that the BIS-GMA system so commonly used in the composite restoratives is extremely brittle we have started working with a method for toughening the system which we think has the potential for improving the performance of composite restorative systems. (See also Section I, part A, 2 of this report.)

The formulations for our successful attempts in molding are included in Table 20. One of the more serious problems we encountered is the inclusion or generation of air bubbles. In some cases these may be alleviated by reducing the viscosity, or extending the cure time. In formulations 1 and 2 for bone cement the cure time was extended over several hours by deleting the amine accelerator. Suitable cylinders were obtained for compression tests in both cases.

The remainder of the samples involve BIS-GMA. Formulation 3 is photo-cured using ultraviolet radiation. The difficulty with this technique is that air bubbles are often generated after the curing is initiated, apparently from air formerly in solution. Since the radiation was applied from the top, the top surface cured first, trapping the bubbles after they appeared. A possible solution to this problem is to use a glass plate and apply the radiation from the bottom.

Formulation 4 produced a good sample which will be tested later. Although we would prefer a 70 to 30% ratio of polymer to diluent, the viscosity is too high for air bubbles to diffuse out during the curing process.

TABLE 20

Formulations for Mechanical Test Specimens

| | | | |
|---|---|---|---|
| #1 | Bone Cement (Heat Cure) | | |
| | Poly(methyl methacrylate)with 1%* benzoyl peroxide | | 62% |
| | methyl methacrylate (no accelerator) | | 38% |
| #2 | Bone Cement (Heat Cure) | | |
| | poly(methyl methacrylate) with 1%* benzoyl peroxide | | 50% |
| | methyl methacrylate (no accelerator) | | 50% |
| #3 | Experimental Dental Resin (Photo Cure) | | |
| | BIS-GMA[1] | | 68% |
| | TEGDMA[2] | | 29.2% |
| | BHT[3] | | 0.9% |
| | BEE[4] | | 1.9% |
| #4 | Experimental Dental Resin (Cold Cure) | | |
| | M= | BIS-GMA | 50% |
| | | TEGDMA | 50% |
| | | BHT | 0.09% |
| | M + 0.23% DMSX[5] | | 50% |
| | M + 0.7% BP[6] | | 50% |
| #5 | Experimental Dental Resin (Cold Cure) | | |
| | M= | BIS-GMA | 45% |
| | | TEGDMA | 48% |
| | | Hycar (Prepolymer Acrylate) | 7% |
| | | BHT | 0.05% |
| | M + 0.2% DMSX | | 50% |
| | M + BP | | 50% |

---

[1] BIS-GMA = Bis-[p-(3-methacryloxy-2-hydroxypropoxyphenyl)] isopropylidene

[2] TEGDMA = triethyleneglycol dimethacrylate

[3] BHT = 2,6-di-t-butyl-p-cresol

[4] BEE = benzoin ethyl ether (auto initiator)

[5] DMSX = N,N-dimethyl-sym-xylidine

[6] BP = benzoyl peroxide

Finally, a sample using a prepolymer according to formulation 5 was molded in an attempt to obtain a specimen with higher impact strength but with little or no decrease in tensile strength. Although no testing has been performed on this material, the initial observation that the material machines in a less brittle fashion than does formulation 4 and has a rougher fracture surface when broken are encouraging. Further work with other rubber contents, etc., will help to determine how much potential this approach has for improving the performance of the composite restorative materials.

## IV. Dental Alloy, Ceramic and Implant Research

Chromium-cobalt-nickel based alloys developed for removable partial denture prostheses have demonstrated properties and clinical serviceability surpassing those of the previously used gold alloys. The increased casting precision required in crown and bridge application has been a prime factor in efforts to expand the use of such alloys to fixed appliances. A previous annual report (10) has addressed this concern. An additional concern for such application has been with the excessive stresses developed interfacially in fusing porcelain to such substrates; such stresses can result ultimately in failure of the prostheses.

In the area of dental ceramics the fabrication of dental porcelain from feldspar is of increasing concern as a result of diminished availability of inexpensive high quality feldspar with low iron content and high potash concentration. New methods of production and sources for new materials are needed. In a related field it has become desirable to develop nonradioactive fluorescing agents for dental porcelain to avoid unnecessary radiation exposure to technicians or patients. An additional concern with radiation effects involves the neutron activation of dental materials following their exposure to sublethal doses of neutron radiation.

Much of the interest in dental implants centers around theoretical analysis to provide a clearer understanding of the effects of stress on alveolar bone with anticipation that implants may be more effectively designed than has been possible up to now. There is need for purely theoretical studies to help point the direction for combined theoretical-clinical and purely clinical efforts.

## A. Porcelain-Alloy Characterization

The characterization of ceramic materials available for bonding to dental casting alloys has progressed well. The measurements of dimensional change resulting from thermal cycling has been completed for nearly all ceramic specimens. The degree of expansion/contraction of the ceramic materials relative to the same properties in the substrate alloys during recommended firing schedules must be compatible since interfacial stress can be increased markedly through a "mismatch" of these properties. The data collected thus far identify considerable variation in the expansion/contraction characteristics among different manufacturers' ceramic products. Further, these changes appear to be linked directly to the thermal history of the specimen, i.e., the number of firing cycles to which the material is exposed during fabrication processes. Generally, it would appear on early examination of the data that the expansion coefficient ($\alpha$) increases with repeated thermal cycling. However, this phenomenon does not manifest in the same way for all materials. Further observations suggest that qualitative and/or quantitative changes in crystallinity of the ceramic materials may develop as a function of thermal history. Preliminary results from x-ray diffraction analyses indicate that, indeed, diffraction patterns are different for these specimens. Another technique well suited for a study of crystallinity is Raman spectroscopy. Analysis of discrete regions with a lateral spatial resolution of 6 μm is possible with the Raman microprobe. This technique was applied to porcelains subjected to a variety of defined firing schedules. Raman spectra were obtained from 10-4000 $cm^{-1}$ using the 514.5 nm line of an argon-krypton laser at 60 mW. Sequential analyses were made at 20 μm intervals on the surface of discs cut from 4 mm rods. The spectra obtained from the various specimens differed significantly. Specimen A exhibited a glassy silicate spectrum with a very broad band at 810 $cm^{-1}$ and shoulders at 1600 and 2350 $cm^{-1}$. Specimen B presented a typically crystalline spectrum with sharp bands at 615, 450 and 250 $cm^{-1}$, and weak bands at 925, 875, and 335 $cm^{-1}$. Variations in spectra occurred from microregion to microregion, but identical spectra repeated every ∿ 60 μm. This indicates that regions of heterogeneity repeat spatially. Work is in progress to examine larger areas of numerous specimens to determine the overall internal structure. An abstract has been prepared on this work for submission for the 1980 meeting of the AADR. Further work is underway to correlate these differences with changes in the refractory nature of the materials. These observations may have major operational significance inasmuch as some ceramic materials can, apparently, withstand more (repeated) exposure to high temperatures during laboratory fabrication processes without showing appreciable changes in either coefficient of expansion or phase structure.

The ability of ceramic powders to "wet" substructure alloy surfaces during the fusion process is a critical element in promoting chemical and mechanical interaction at the interface which is necessary for accomplishing optimum bonding of the materials. Factors which may influence this "wetting" phenomena include: 1) chemical composition of the materials, 2) particle size (and configuration) of the ceramic powder, 3) nature of oxides formed on the metal surface, 4) substrate alloy surface preparation, and 5) techniques employed in applying the (opaque layer) porcelain. Analyses of particle size distributions among

the various manufacturers' products have been completed and the data is being examined at this time. Some differences in this regard have been found to exist among the products examined. Specific combinations of alloys and bonding porcelains have been fused together and are presently being analyzed via void (no contact) formation at the interface for completeness of "wetting." Variations in alloy surface preparation, preconditioning of the substrate (oxidation) and (opaque) porcelain application techniques are being evaluated to ascertain the effects of these variables on the wetting process. Preliminary analysis of the data collected in this phase of the investigation suggest that:
1) variations in porcelain alloy combinations influence the area of contact between the materials after fusion, and 2) different techniques used for applying (opaque) porcelain powders to the alloy substrate may alter the completeness of the "wetting" process. Knowledge gained from the foregoing experiments should assist greatly in more appropriate selection or matching of compatible alloy/porcelain combinations as well as fabrication techniques.

Correlation of the above scientific data with the recognized clinical problem being studied is essential. The physical and mathematical design for a porcelain-dental casting alloy composite structure to be used for evaluating the net effects of the factors studied on residual interfacial and tensile stresses (primary contributors to porcelain-metal failure) has been completed. Although the specimen has been designed, further investigation into optimization of experimental procedures and methods of measurement for the specimen is required.

A porcelain veneered split metal ring is the specimen of choice. The gap or opening of the split provides a self-referencing measurement of residual stress within porcelain and metal. Timoshenio (36) developed the following expression relating the curvature, $\rho$, of a bimaterial strip to its original curvature R, the coefficients of expansion $\alpha_\beta$, $\alpha_A$, the thickness, t, of the strip and the temperature range through which it is heated:

$$\left(\frac{1}{\rho} - \frac{1}{R}\right) = \frac{+K(\alpha_\beta - \alpha_A)\Delta T}{t} \tag{1}$$

where K is a function of layer thicknesses and their elastic moduli. For a split metal ring, and for small changes in $\rho$, we can write

$$\frac{1}{\rho} - \frac{1}{R} = \frac{1}{R+\Delta R} - \frac{1}{R}\,, \quad \text{where } \rho = R+\Delta R \tag{2}$$

$$\cong \frac{1}{R} - \frac{\Delta R}{R^2} - \frac{1}{R} = \frac{-\Delta R}{R^2} \tag{2a}$$

Since the change in gap is very nearly equal to the change in circumference for a narrow split, if $\Delta d$ = change in gap, then

$$\Delta d \cong 2\pi\Delta R \quad \text{and} \quad \Delta R = -R^2\left(\frac{1}{\rho} - \frac{1}{R}\right) \tag{3}$$

so that

$$\Delta d \cong -\,2\pi R^2\left(\frac{1}{\rho} - \frac{1}{R}\right) \tag{4}$$

and

$$\Delta d = \frac{-\,6.28\ K(\alpha_\beta - \alpha_A)\Delta T}{t}\,. \tag{5}$$

A more refined analysis yields

$$\Delta d = -\,6.22\ K\,\frac{(\alpha_\beta - \alpha_A)\Delta T}{t}\,.$$

Equation 6 differs from Eq. 5 by ∿ 1%.

Experimentally, the change in gap of one porcelain veneered metal ring was measured to be - 0.538 mm, the calculated value based on Eq. 5 predicted a change of - 1.09 mm, in good agreement considering the following factors: 1) Timoshenio's work considers only a one-dimensional stress analysis and does not allow for stress gradients, and 2) the analysis does not provide for multiple layers of material with differing coefficients of expansion.

As a consequence of the preceding, it has been decided to develop, with cooperation from the U. of Ill., Chicago, the appropriate theory for change in gap of a multi-layered split metal ring to allow for stress analysis within and between each layer. It has also been decided to pursue the use of finite element analysis to check the analytic approach. Abstracts have been prepared for submission of 1) theoretical, and 2) experimental results at the 1980 meeting of the AADR, as well as submission of implications of measured differences of porcelain expansion curves at the 1980 meeting of the IADR. Specimen fabrication methods are undergoing development at this time.

### B. Alloy Corrosion Study

The extent to which pitting corrosion might be predicted in a clinical situation for a given alloy of a given composition and microstructure is of importance for at least two reasons: 1) the greater the degree of pit formation, the more the tendency for plaque formation with its accompanying undesired organic acid release, and 2) the pit formation process must of itself release ions to the surrounding medium that may be deleterious in one way or another. Availability at NBS of extensive expertise and instrumentation in the area of corrosion and alloy microstructure determination and the presence on the staff of a guest worker from the University of Düsseldorf for a year with a strong interest in this area allowed an immediate attack on this phase of our base metal alloy effort.

Anodic polarization curves of as cast and fire-cycled samples were generated and breakdown potentials determined. Essentially the procedure of Meyer and Nally (37) was employed. The electrolyte used was the artificial saliva solution of Fusayama but modified through an adjustment in pH to 3.2 by addition of hydrochloric acid. The solution pH was lowered to reproduce plaque conditions and/or crevice environments which occur in the mouth. The pH adjustment assured that each polarization curve was measured under constant conditions since we have noted some variation in the pH of the Fusayama solution with time.

Three Ni-Cr alloys being used currently for porcelain veneering and representing typical materials of this kind have been investigated: NP2 (no Be but 8% Ga) Ultratec (Be), Wiron 77 (no Be). These materials not only consist of different chemical compositions but their microstructures which were observed by light micrographs and SEM exhibit major differences. NP2 appears to be almost single phase with only a few precipitates within the grain whereas Ultratec and Wiron 77 show a eutectic constituent in the microstructure.

Samples were either cast or cast and fire-cycled to simulate porcelain bake-on procedures. Judged by these test procedures NP2 appears to be the most corrosion resistant alloy (highest breakdown potential) followed in turn by Wiron 77 and Ultratec. This sequence remained the same in the as-cast as well as the fire-cycled condition.

The values for pitting potential were lowered by fire-cycling. Ultratec was the only alloy to show an active peak under the chosen test conditions.

SEM pictures of samples after anodic polarization runs revealed differences in surface film and pit formation. On NP2 samples (Figs. 12 and 13) pittings occurred within the grain. Pits were not as numerous as the precipitates or irregularities mentioned earlier. This alloy was not covered by a continuous oxide layer. Such a layer was only generated in a small area around the pits. Wiron 77 exhibited a thick continuous oxide film showing considerable evidence of cracks. This film appeared to be thicker on the eutectic microstructure and could not be penetrated by back scattered electrons (Figs. 14 and 15). Ultratec was covered by a thin oxide film which could be penetrated by back-scattered electrons (Figs. 16 and 17). The preferential attack of the eutectic microstructure was quite evident since one phase of these areas had been completely removed from the surface. According to the literature (38), these parts possess a high percentage of the total beryllium content.

The following conclusions can be drawn to this point: 1) in the as-cast and fire-cycled forms NP2 evidence greater corrosion resistance by the tests applied followed in turn by Wiron 77 and Ultratec, 2) fire-cycling and/or conditioning lowers the corrosion resistance of each casting alloy examined, 3) Ultratec undergoes active corrosion under the test conditions, has a low breakdown potential and appears to be subject to crevice or other corrosion attack, and 4) the eutectic component of Ultratec microstructure appears to be preferentially attacked while that of Wiron 77 is not.

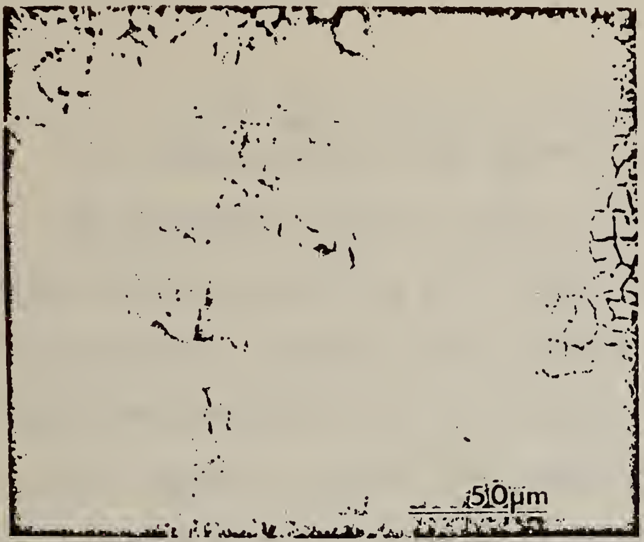


Fig. 12 NP2, SEM Micrograph

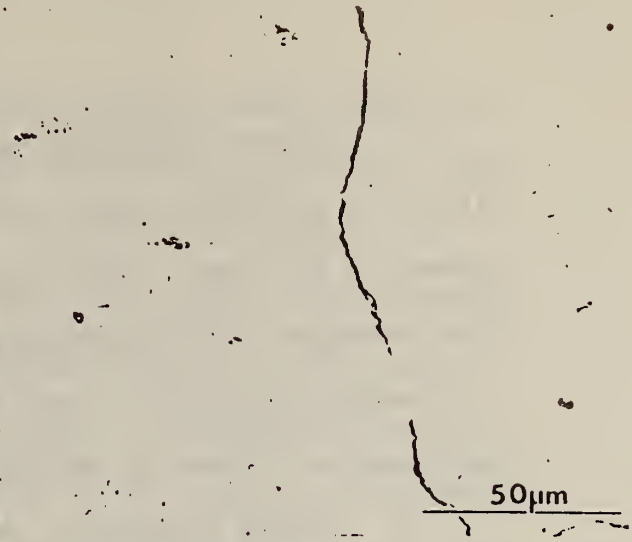


Fig. 13 NP2, Light Micrograph

Fig. 14 Wiron 77, SEM Micrograph

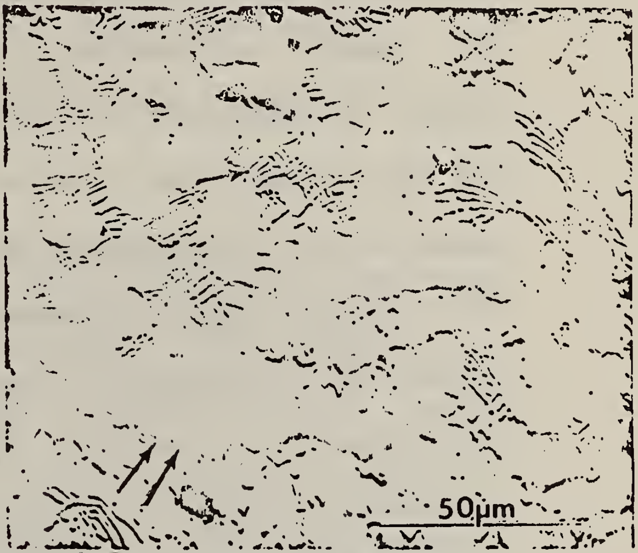


Fig. 15 Wiron 77, SEM Micrograph

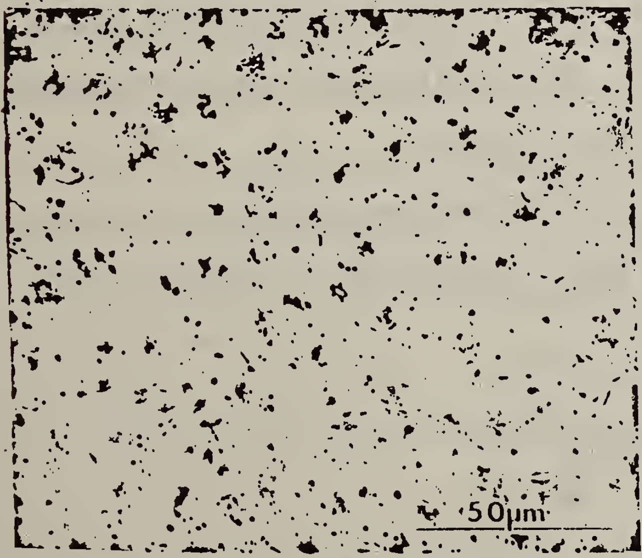


Fig. 16 Ultratec, SEM Micrograph

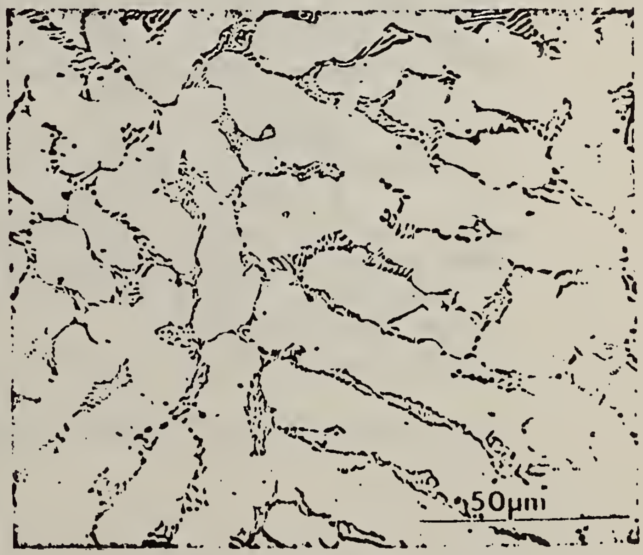


Fig. 17 Ultratec, SEM Micrograph

Further investigation is needed with other Be-containing alloys to ascertain whether their *in vitro* corrosion resistance may generally be lower. The sites on Wiron 77 as well as on Ultratec causing the breakdown of the protective surface film in terms of pitting should be chemically analyzed. Results obtained to date have been summarized and reported in part at the 37th Annual ESMA meeting in August 1979.

### C. Dental Porcelain: Processing Methods and Raw Materials

Porcelain Manufacturing Processes: The American Dental Association Health Foundation Research Unit at the NBS has been involved in research on production of dental porcelain utilizing a gel technique. In cooperation with this effort, a modification of this approach has been suggested and is being explored. Experimental batches of porcelain are being prepared for evaluation against commercially available porcelain regarding properties and esthetic consideration, new avenues for introduction of fluorescence into porcelain without the use of uranium will be explored. Potential fluorescing agents have been identified and generally involve the use of rare earth elements; these are also being considered by others. The methods of introducing the fluorescing agents into porcelain will utilize some approaches which have not been followed by others. Fluorescing agents have been procured.

### D. Castability and Fabrication Research

A review of casting, finishing and production processes for fabrication of metal crowns has been initiated but is currently only in the early stages.

## E. Irradiation Effects from Neutron Activated Dental Materials

As a result of the very limited information available in the literature, calculations have been made to estimate the effects of secondary radiation from gold crowns. Gold is the only element examined to date and was chosen because of its high neutron activation cross section, relatively short half life (2.7 days), its extensive use as a dental restorative material, and the fact that information in reference 39 provided some concept of the maximum neutron energies which could be expected to be encountered. The latter is important due to the energy dependence of the activation cross section. Gold crowns were approximated by 2.3 grams equivalent, 0.5 cm radius discs located at buccal proximal positions.

Estimates on $\gamma$ radiation doses delivered to soft tissue were made for single crowns and a mouth full of crowns using activation cross sections for neutrons of the following energies: thermal neutrons, 1 ev neutrons and 4.91 ev neutrons; (4.9 ev corresponds to a neutron resonance energy for gold (40)). An approximate expected epithermal neutron distribution was calculated and used for determining the fraction of neutrons which might exist near the resonance activation energy and thereby estimate the additional secondary radiation. A 50 REM neutron exposure was assumed as this is clearly a sublethal exposure (41), higher exposures cause proportionally higher activation and secondary radiation. Activated crowns consist of gold$^{197}$ and radioactive gold$^{198}$ which has a $\Gamma$ constant of 2.3 R-cm$^2$/hr-millicurie (42). The results are that a single gold crown is likely to provide an additional 2 REM $\gamma$ dose to local tissue and six or more adjacent crowns provide an additional dose between 3 and 5 REM.

The second type of radiation emitted from $\text{gold}^{198}$ is $\beta$ radiation which consists of electrons having a distribution of energy. Exact calculation of the dose delivered to tissue is complex due to the energy distribution and the energy dependent absorption and shielding within the crown itself. Beta rays have a relatively short range relative to the diameter of the disc and therefore the estimate of dose to local tissue may be well approximated by considering the radiation as emanating from a semi-infinite slab. Several approximate formulations are available for estimating the dose (43,44). These consider $\beta$ rays emanating from an infinite area of variable source strength per unit area. Some calculations were also made using modifications which rendered approximate corrections for the attenuation of energy and absorption of particles within an emitter of finite thickness. A range-energy relation $R = .407\ E^{1.38}$ (45) and an exponential absorption law, $N = No\ e^{-ux}$ (46) were combined to estimate the dose in basal cells at 10 $\mu$m and 56 $\mu$m (36) from the surface of epidermal tissue. Stopping power in tissue tabulations by Berger and Seltzer (47) was also employed. The results show that local tissue can receive a $\beta$ dose of $\sim$ 100 REM following a 50 REM neutron dose.

Combined effects of $\beta$ plus $\gamma$ radiation can be at least $\sim$ 100 REM or higher, which is 200% of the initial dose. Further, if an individual were to receive a neutron dose of 200 REM, which allows for a high level of survival (41), local tissues would receive an additional dose of $\sim$ 400 REM, which certainly provides increased concern over long term complications from the additional exposure, especially as the effects of partial irradiation of an organ are not known and $\beta$ damage may be irreversible.

It has been calculated that temporary shielding of local tissues from maximum energy $\beta$ radiation from gold is possible by using .40 cm of ordinary mouth guard material. The use of higher density materials decreases the thickness of shielding required according to the relationship $t\rho = .40\ \text{g/cm}^2$, where t is the thickness and $\rho$ the density. However, for subgingival restorations, shielding is virtually impossible. The results of these calculations have been prepared for submission as an abstract for the 1980 meeting of the IADR.

F. Implant Research

A feasibility study for the development of finite element models of teeth and tooth shaped implants, with inclusion of directional, non-uniform response to the periodontal ligament has been initiated. Use of such properties has not been included in previous studies by researchers in this field. Finite element analysis studies have progressed to the state that it is important to know how results may be affected by this refinement. The feasibility study is being conducted in cooperation with the University of Illinois, Chicago, where the Materials Engineering Department has been involved with bioengineering studies for several years using finite element techniques (48-53).

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11. Adsorption of a Polyfunctional Surface-Active Amine Accelerator on Hydroxyapatite, 178th ACS National Meeting, Washington, DC, Sept. 1979; Colloid and Surface Chemistry, Abstract No. 33; D. N. Misra, R. L. Bowen, J. M. Antonucci and W. F. Cuthrell. (Submitted for publication in Journal of Colloid and Interface Science.)

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15. Fit of Porcelain Fused to Metal Crown and Bridge Castings, G. Eden, O. Franklin, J. Powell, Y. Ohta, and G. Dickson. (Publication now promised by J. Dent. Res., Nov. 1979.)

16. Casting Roughness of Dental Alloys, R. Bauer*. (Invited paper at Third International Precious Metal Conference, Chicago, IL, May 1979; based on work done in NBS alloy program.)

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*Research Associate, Nat. Assoc. Dental Labs., 1976-77.

17. Solders and Fluxes, J. A. Tesk. (A chapter accepted for publication in the to be published Dentists Desk Reference by the American Dental Association.)

18. Conceptualization and Development of New Dental Biomaterials--A Marketing-Manufacturing-R&D Perspective, J. A. Tesk; Johns Hopkins University, Baltimore, MD (February 6, 1979).

19. Fit of Non-precious Alloys for Ceramic Restorations and Surface Roughness of Dental Castings, R. Bauer*; Mid American Dental Laboratory Conference, Chicago, IL, September 13-15, 1979; based on work done in NBS alloy program.

20. SEM Studies of Dental Casting Alloy Corrosion Behavior, H. Weber** and A. Fraker***; Thirty-Seventh Annual Electron Microscopy of America Meeting, San Antonio, TX, August 13-18, 1979; (to be published in proceedings).

21. The Casting of Non-precious Porcelain Fused-to-Metal Alloys, R. P. Whitlock; Tri Services Dental Laboratory Symposium, San Antonio, TX, September 24-26, 1979.

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Abstracts Prepared for Presentation in FY1980

1. Theoretical Stress Analysis of Porcelain Veneered Split Metal Ring for Evaluation of Compatibility of Porcelain-Alloy Systems, G. E. O. Widera, J. A. Tesk, and R. P. Whitlock; AADR Meeting, Los Angeles, March 1980.
2. Biocompatible Amine Polymerization Accelerators: Para-Dimethylaminobenzoic Acid and its Ethyl Ester, J. M. Antonucci, R. J. Peckoo, C. Schruhl, and E. Toth; AADR Meeting, Los Angeles, March 1980.
3. A Porcelain Veneered Split Metal Ring for Evaluation of Compatibility of Dental Porcelain-Alloy Systems, R. P. Whitlock, J. A. Tesk, E. E. Parry, and G. E. O. Widera; AADR Meeting, Los Angeles, March 1980.
4. Intraoral Secondary Radiation Dose from Neutron Activated Dental Materials, J. A. Tesk and R. P. Whitlock; IADR Meeting, Japan, June 1980.
5. The Accelerative and Adhesive Bonding Capabilities of Surface-Active Accelerators, J. M. Antonucci, D. N. Misra, and R. J. Peckoo; IADR Meeting, Japan, June 1980.
6. Observations of Significant Differences in Thermal Expansion Characteristics of Dental Porcelains, R. P. Whitlock, J. A. Tesk, E. Parry, and G. Dickson; IADR Meeting, Japan, June 1980.
7. *In Vitro* Wear Measurements on Dental Materials, J. E. McKinney; IADR Meeting, Japan, June 1980.
8. Derivatives of p-N,N-Dialkylaminophenylalkanoic Acid: New Accelerators for Dental Composites, G. M. Brauer and J. W. Stansbury; IADR Meeting, Japan, June 1980.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Promising new polymerization shrinkage-reducing dental resins that have been synthesized include prepolymer fluorinated polymethacrylate monomer (ave. MW = 10,320); diurea dimethacrylate; and methacryloxyethyl-1-adamantylcarboxylate, a tri-cyclic saturated monofunctional monomer. Initial experiments to gain greater durability using a rubber toughening approach with BIS-GMA indicates a less brittle but tougher matrix can be achieved. Acetylthiourea and ascorbic acid have been shown to be promising non-amine type of accelerators for the BIS-GMA system while new highly reactive amine types such as N,N-dimethyl-p-t-butylaniline, gave cured denture base materials with excellent color stability and may solve current problems in achieving and matching shades in such materials. Research to develop adhesive restorative materials indicates that urethane methacrylates with residual isocyanate groups yield less adhesion than is achievable with 2-cyanoacrylate esters. Pin-on-disc wear data indicated sintered hydroxyapatite pins may be useful substitutes for tooth enamel. A plan to evaluate fatigue as a contributing wear mechanism calls for pre-fatiguing materials before determining the laboratory wear resistance.

Dimentional change data that results from thermal cycling of different porcelains indicate considerable variation, some of which appears relatable to the crystalline forms that are present. Be appears to lower corrosion resistance in crown and bridge Ni-Cr alloys subjected to anodic polarization measurement following casting, or casting and fire-cycling, to simulate porcelain bake on.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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