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Properties and Interactions of Oral Structures and Restorative Materials

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Dental and Medical Materials Section
Polymers Division
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

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ABSTRACT

Previous encouraging results with titanium and silicone based coating agents for coupling dental resins to tooth surfaces have been reinforced with accelerated aging data. Accelerated aging data for bone bonded to bone specimens indicates that a viscous isoamyl cement may be worthy of clinical evaluation. Procedures for synthesis and purification of crystallizable materials offer promise as adhesion promoters through reaction with collagen and may have utility as diluent comonomers with Bis-GMA in composites or sealants. The feasibility of generating free radical induced polymerization of dental resins by using more thermally stable organic peresters or hydroperoxides and an ascorbic acid ester has been demonstrated. Design, assembly and debugging of a new multispecimen wear instrument has been completed. Judging by their thermal expansion characteristics, high copper type amalgams show little or no evidence of phase changes at temperatures less than 9 °C. The technique sensitivity of the higher melting non-precious bonding alloys has been demonstrated by examining quantitatively the goodness of fit attained by manufacturers of such alloys who made castings to a standard die and wax pattern that we supplied. A technique to fabricate oversize Ni-Cr crown castings is described.

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. Also part of this collaborative effort through support funding and/or assignment of research personnel are the Armed Services Dental Corps. In addition, the National Association of Dental Laboratories, representing some 3,000 prosthetic laboratories, is a participant via the research associate program of the National Bureau of Standards.

While the bulk of the research progress in this report represents the efforts of persons 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 mechanical, chemical, and physical properties of restorative and caries-preventive materials and their interaction or relationship with the natural components of the oral structure.

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 surface characterization, methods for evaluating coupling agents, synthesis to improve todays composite restorative materials and pit and fissure sealants, investiga-

tion of new approaches to bonding restorations to tooth surfaces and measurements of critical dimensional changes in newer type amalgams. A wear-generating and recording system, redesigned and built to allow multiple specimen examination has been debugged and is in initial stages of evaluation. Procedures for quantitative assessment of the goodness of fit of dental alloy castings, gold or non-precious types, have been developed.

From analysis of water adsorption data including calculation of heats of adsorption, we conclude that these types of data do not aid in predicting the potential of a coating agent as a coupling agent between the resin matrix of a composite and the hydroxyapatite of a tooth surface. Previous encouraging results with two coating agents assessed as promising coupling agents by an indirect mode of tensile adhesion testing, have been reinforced with accelerated aging data.

We have made several advances in our efforts to develop highly purifiable, less viscous methacrylate monomer systems as substitutes for the currently used Bis-GMA resin which is excessively viscous and inherently difficult to purify. Using a fast amine accelerator we have shown that both the hardening rate and diametral tensile strength of composites prepared from resin systems Bis-GMA/Triethyleneglycol dimethacrylate and a highly purifiable ether-linked aromatic dimethacrylate system requiring no diluent are comparable. We have synthesized but have not purified a "star" methacrylate monomer that appears to be less viscous than Bis-GMA despite an expected two-fold increase in molecular weight and should undergo less volume change on polymerization. We have demonstrated procedures for synthesis and purification of an isomeric system of aromatic aldehyde dimethacrylates. The system is considered primarily as promising for evaluation as adhesion-promoting agents but since the component isomers are soluble in Bis-GMA, they offer utility as diluent comonomers for composites or fissure sealants. Five methacrylate monomers with isocyanate functional groups capable of reaction with the collagen of dentin have been synthesized and isolated in varying degrees of purity. These monomers, miscible and copolymerizable with Bis-GMA will be examined as adhesion promoters and as components of composite resin systems.

To improve the thermal stability of composite systems, we are examining potential substitute peroxides for benzoyl peroxide. Using ascorbyl palmitate as the means of generating the free radicals from more stable organic peresters or hydroperoxides, we have shown cure times comparable to those normally observed with the conventionally cured Bis-GMA system that employs benzoyl peroxide and dimethyl-p-toluidine.

Based on amine structure-property relations that we have established, we were encouraged to synthesize several new amines as potential polymerization accelerators in the anticipation that they would be more efficient and less toxic than those currently employed with dental resins. Dimethylaminophenyl acetic acid, based on results achieved to date, appears particularly to be of promise. Effect of amine concentration on physical properties of composites has been determined for both currently used and experimental amines. Tensile strength is a more sensitive measurement to the type and concentration of amine than is compressive strength with the maximum in tensile strength of the composite being achieved only over a narrow concentration range of amine accelerator.

A study of methods for evaluation of pit and fissure sealants has been concluded. A series of relatively simple test methods has been proposed.

An investigation of the potential application of cyanoacrylates as adhesion promoters for dental application has been extended to include long term body temperature as well as accelerated aging. After 6 months storage in water at 37°C, n-amyl, isoamyl and a viscous isoamyl cyanoacrylate bonding to bone was reduced 30-35%, a reduction much less than that shown with the ethyl derivative. Accelerated aging for one month at temperatures cycled between 5° and 55°C gave comparable results. The viscous isoamyl cyanoacrylate with the highest initial bond strength to bone appears to be the least degradable in water and hence may be worthy of clinical evaluation, provided its toxicity is acceptable. However, the results to date indicate that the presently available non-filled 2-cyanoacrylates are of limited use for dental application as adhesives due to their degradability and their inability to serve as a gap filling adhesive.

As a part of a general investigation of the physical and clinical properties of amalgams made from some of the recently introduced alloys with high copper content, the thermal expansion characteristics of the amalgams have been determined. Information on the stability of the amalgams at elevated temperatures was sought rather than coefficient of expansion data. In addition to a "normal" reversible thermal expansion of about 25 ppm per ^{o}C, "conventional" amalgams exhibit large dimensional changes that are time dependent as well as temperature dependent. The high copper alloy amalgams show little or no evidence of phase changes within the range investigated. It appears that the general features of the three types of thermal expansion curves are related to the peritectic transformation γ_1 (Ag-Hg) $\rightleftarrows$ β (Ag-Hg) + Hg and the diffusion reaction γ (Ag-Sn) + Hg $\longrightarrow$ β (Ag-Hg)

Design and assembly of a new multispecimen wear instrument and data collection system has been accomplished. Debugging of the equipment has not been excessively difficult and wear data on dental materials is anticipated to show an even more significant difference between classes of direct restorative materials and at a higher confidence level than was shown with the prototype single specimen device.

A significant problem with non-precious alloy crown and bridge fabrication as identified by a survey undertaken of prosthetic dental laboratories is the difficulty in attaining the required goodness of fit in such castings. The degree of problems with fitting was shown to be in inverse order to the noble metal content of the alloy employed. In like manner the problems with porcelain fused to metal restorations were seen to be major with non-precious alloys and minimal with high noble metal alloys.

We have verified the technique sensitivity of the higher melting non-precious, e.g. Ni-Cr, porcelain bonding alloys exhibited in our early laboratory experimentation, by examining quantitatively the goodness of fit attained by manufacturers of such alloys who made castings to the standard die and wax pattern which we supplied. A gold based alloy as well as a non-precious alloy offered by the manufacturer were cast at the same time. In every case, the high nobel metal alloys were cast oversize whereas all non-precious alloys were cast undersize. This consistent difference in casting size between the two alloy types under a wide variety of laboratory techniques could discourage use of Ni-Cr alloys for operators unwilling to use shims or die coats (of questionable accuracy) or to machine out the interior of undersized castings to permit seating and cementation.

We have reported herein a technique modification involving hand spatulation, dry asbestos, and hygroscopic expansion that provides sufficient expansion for one phosphate bonded investment at least, to permit fabrication of oversize Ni-Cr castings.

We have shown that casting size is dependent on melting point of the alloy with casting diameter decreasing linearly with increasing melting point under fixed mold conditions.

Cooperatively with the Armed Forces Defense Personnel Support Center and the U. S. Navy, we have developed a castability test applicable to either Ni-Cr or gold alloys.

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, commercial production by industry.

The dental research program at NBS is a cooperative effort both in personnel and funding, involving the American Dental Association, the Armed Forces Dental Corps, and the National Association of Dental Laboratories. The research reported in the following pages is only that portion of the dental program which is supported by interagency agreement with NIDR.

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. An outline of the research as approved in the interagency agreement is given below:

I. Adhesion of Restorative and Caries-Preventive Materials to Tooth Surfaces

    A. Surface Characterization of Dental Materials by Water Adsorption*

    B. Technique for Assessing Coupling Agents*

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*Areas of work supported by interagency agreement only for first half of year.

    C. Research for Improved Composite Restorations and Sealant Materials

    D. Techniques for Bonding to Mineralized Collagen Surfaces

II. Physical Properties of Hard Tissue and Dental Materials

    A. Dimensional Change Measurements

    B. Wear Resistance of Restorative Materials

    C. Base Metal Alloy Research

TECHNICAL REPORT

I. Adhesion of Restorative and Caries-Preventive Materials to Tooth Surfaces

A. Surface Characterization of Dental Materials by Water Adsorption

For several years we have used adsorption measurements from vapor phase as an analytical tool for characterizing dental materials, both natural and synthetic [1,2,3]. Relative to the development of improved coupling agents between restoration and tooth surface, we have shown that the surface area available to water molecules on a "coupling"agent - coated hydroxyapatite (HA) surface is reduced by the coating, irrespective of whether the coating agent could be shown by any other means to represent a poor or good coupling agent. Therefore surface area, as determined by adsorption measurements, is not a viable means of distinguishing between coupling agents.

Since the heat of adsorption defines the intensity of interaction on the surface, this aspect of vapor adsorption has now been examined. Employing BET equation [4], isosteric heats of adsorption (ΔE) were obtained from the c-parameter for uncoated and silane* coated HA (Table 1). ΔE represents the difference between the average heat of adsorption for the first monolayer of water vapor and the heat of liquification of water at 23°C.

Coating with the silane coupling agent shown by other means to be a potential coupling agent (IB of this report), is seen to nearly double the value for ΔE. Since the lower concentration of silane

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* 3-methacryloxypropyltrimethoxy silane

was more than sufficient to form a monolayer, the four-fold concentration increase, corresponding to the high concentration of Table 1, did not further increase the heat of adsorption. These observations also suggest that the water vapor did not penetrate the silane coating.

TABLE 1

Comparison of Heats of Adsorption (water) of Uncoated and Silane-Coated Hydroxyapatite.

	ΔE Cal/mol	
	Sample 1	Sample 2
Uncoated Hydroxyapatite	850	890
Silane-Coated Hydroxyapatite (low concentration)	1600	1560
Silane-Coated Hydroxyapatite (high concentration)	1620	---

B. Technique for Assessing Coupling Agents

We have described in several Annual Reports [5,6] a novel indirect testing procedure designed to minimize some of the disadvantages that are inherent in routine butt-joint adhesion testing to enamel surfaces. We have utilized this test procedure to evaluate the capabilities of coupling agents for adhering resin restorative systems to tooth surfaces. The test employs tensile strength measurements on composite specimens that are prepared by dispersing varying amounts of hydroxyapatite powder that has been coated with a coupling agent of interest in a resin matrix

(Bis GMA)* and then polymerizing. Specimen tensile strength is plotted as a function of the particulate weight fraction for each series of tests involving the same coupling agent. The more negative the slope of such plots, the poorer is the coupling agent. The choice of synthetic amorphous HA (as opposed to a fibrous state) precluded any structural reinforcement which would have interfered with the interpretation of the effect of the coupling agent being evaluated. A description of the test procedure and some results obtained with it is scheduled for publication in a current issue of the Journal of Dental Research [7].

In the previous Annual Report [6] we have described results obtained by the indirect testing procedure that indicated good coupling between HA and Bis-GMA was achieved by using either of two coating agents, isopropyltrimethacryl titanate (TI) or 3-methacryloxypropyltrimethoxy silane (SI).

During the current reporting period, a means of accelerated aging was adopted to assess the stability of the coupling effect achieved with the two promising coating agents. The composite specimens were directly exposed in a water bath for one month to temperatures that cycled between 7°C and 60°C with a two hour duration at each temperature. This rather severe aging procedure produced a weakening of the adhesion developed with either of the promising coating agents TI or SI. For example, when tensile strength of the non-aged composite specimens containing varying amounts of coated HA powder suspended in Bis-GMA was plotted against the

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* Abbreviation used to describe addition product of biophenol A and glycidyl methacrylate.

2/3 power of the particulate weight fraction, the tensile strength fell off from about 30 MPa at zero weight fraction (i.e., resin only) in a reasonably linear fashion giving slopes of -18 MPa and -19 MPa respectively for the SI and TI specimens as opposed to -94 for uncoated HA specimens (Table 2). Upon accelerated aging for one month a decrease in strength of the coated specimens was observed as indicated by increased slope values for both TI and SI specimens of -69 MPa.

Table 2

Slopes of Tensile Strength vs. $(\text{Particulate Concentration})^{2/3}$

	Non-Aged (MPa)	After Accelerated Aging (MPa)
SI	-18	-69
TI	-19	-69
NPG-GMA*	-66	---
Uncoated	-94	---

* N-phenylglycine glycidyl methacrylate, a coupling agent developed by R. Bowen previously in this laboratory [8].

That the silane and titanate coupling agents do have potential is shown by the fact that the slope values of the severely aged specimens were not essentially different from that found with non-aged NPG-GMA coated specimens. NPG-GMA has been considered the best coupling agent for its purpose developed to date although it has found only limited applications.

These results are being prepared for publication as an annotation in the Journal of Dental Research.

C. Research for Improved Composite Restorations and Sealants

In spite of the many merits of dental composite restorative and sealant materials, there is still need for further improvements, especially in the two critical areas of adhesion to dental tissues and overall stability.

An important constituent of these materials is the dental resin system. The current most widely used resin systems are based on the monomer, Bis-GMA, developed by Dr. R. L. Bowen [9] of this laboratory. This work represented a major breakthrough in the area of dental composite and sealant materials. However, in spite of its many excellent properties, it does suffer from several deficiencies, e.g. a color problem which may be inherent in its chemical structure or due to impurities, and a highly viscous nature which necessitates the use of a diluent monomer. The use of the usual thinner comonomers (e.g. triethyleneglycol dimethacrylate, methyl methacrylate, etc.) increases the polymerization shrinkage of the system and may make it less biocompatible (e.g. due to volatility, tissue penetration).

1. New Resin Systems

In this laboratory we have pursued several possible solutions to these problems. A major emphasis has been placed on the evolvement of a resin system capable of being highly purified and not requiring a diluent to achieve the workable viscosity necessary for clinical application.

To achieve high purity in the resin component we have developed systems of crystallizable isomeric dimethacrylate monomers. We have shown that when mixed in proper proportion, eutectics with melting point less than room temperature are obtained and the viscosity of the resulting liquids is low enough that dilution is not required.

The first of such isomeric monomer systems was that developed by Bowen [10] in this laboratory on an NIDR supported grant. This system consisted of three aromatic diester dimethacrylates derived from the condensation reaction of the appropriate acid chlorides of the phthalic acid isomers with 2-hydroxyethyl methacrylate. The phthalic acid derived monomer system unfortunately developed a color instability when polymerization was induced by the usual benzoyl peroxide-tertiary amine initiator system. The source of the color instability was traced to the formation of colored charge transfer complexes involving the pi electron deficient aromatic diester dimethacrylates and the pi electron rich tertiary aromatic amine accelerator [11].

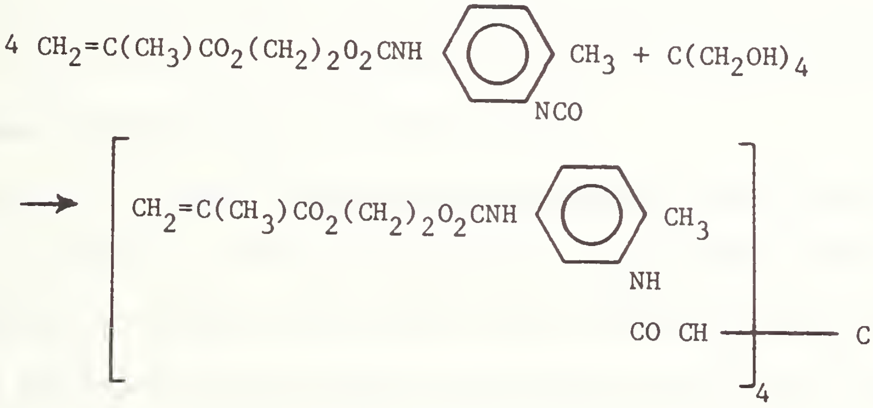
To circumvent the formation of a colored charge transfer complex, we synthesized two analagous crystalline dimethacrylate monomer systems with greater pi electron densities [12,13]. One system is based on the dimethacrylate derivatives of the isomeric dihydroxybenzenes (e.g. hydroquinane, resorcinol and catechol), the other on dimethacrylate derivatives of the three corresponding hydroxybenxoic acids. These systems, the one a diether, the other an ether-ester, proved to be color free in the presence of tertiary aromatic amines, and were readily purified by recrystallization. On proper admixture they formed ternary liquid eutectics of moderate viscosities at room temperature.

a. Some Property Data on the Diether Methacrylate System

In this report period we have examined some of the properties of composite systems prepared from these monomer systems. With a slow amine accelerator such as N,N-bis(2-hydroxyethyl)p-toluidine, the hardening time of a system comprised of the eutectic diether monomer system and glass powder coated with benzoyl peroxide was more than twice that observed with 70% Bis-GMA/30% TEGDMA*. With DMSX**, which is a faster amine accelerator, hardening rates were comparable as were the diametral tensile strengths, i.e. 37 and 43 MPa respectively. This result is similar to that reported earlier for the eutectic diester monomer system [14].

b. "Star" Monomer Synthesis

Even though the Bis-GMA based composite restorative systems significantly reduce the volume change that occurs on in situ hardening relative to that which occured with direct filling resin systems, it has been recognized that further reduction may be required if adhesion to the cavity wall is to be possible. To this end we have prepared a tetra star monomer from pentarythritol and an isocyanato urethane methacrylate as shown below:



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* Triethyleneglycol dimethacrylate

** Dimethyl symmetrical xylidine

While we have improved the color of the reaction product through use of decoloring charcoal, we have not, as yet, isolated the monomer as a crystalline solid. The material is challenging in that the pale yellow liquid appears to have a viscosity less than that of Bis-GMA despite an expected two-fold increase in molecular weight.

c. Synthesis of Functional Monomers

Research to develop adhesive bonding to the dentin, the collagen-containing component of tooth structure, has progressed in several areas.

(1) Aldehyde Methacrylates

The natural reactivity of aldehydes toward collagen suggested the synthesis of aldehyde methacrylates as a potential means of coupling dental resins to dentin. We have previously [6] reported on the synthesis, purification, and characterization of the monomers p-(2-methacryloxyethoxy)benzaldehyde and 0-(2-methacryloxyethoxy)benzaldehyde. These were derived as crystalline solids (hence in high purity) which melted respectively at 47-48°C and 52-53°C. The meta isomer derived from m-hydroxybenzaldehyde melted below room temperature and was difficult to purify.

In the present report period we completed the purification and characterization of meta(2-methacryloxyethoxy)benzaldehyde (MMB). The isomer was isolated as a white crystalline solid, m.p. 21-22°C, after treatment with decolorizing charcoal in ethanol and after several recrystallizations from a mixed solvent of ethanol and m-hexane (1:1 v/v) at 20°C. Elemental analysis calculated for $C_{13}H_{14}O_4$ was C 66.7%; H 6.02%; found was C 66.8%; H 5.95%. In comparison with the para (PMB) and ortho (OMB) isomers, MMB is the lowest melting of the

(2-methacryloxyethoxy)benxaldehydes. Not only are ternary liquid mixtures of these isomers easily prepared, but binary liquid mixtures of MMB with the other two isomers are easily prepared. MMB itself is easily liquified by only slight warming (e.g. exposure to body heat).

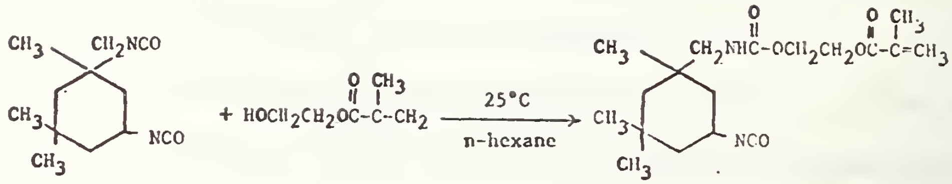
As expected, MMB undergoes free radical polymerization under a variety of conditions (e.g., by chemical initiation with benzoyl peroxide and N,N-dimethyl-p-toluidine, by modest heating in the absence of air, and by photoinitiation, e.g., exposure to ultraviolet light in the presence of methyl ether of benzoin.)

Photopolymerization can occur without the use of a photoinitiator (e.g. methyl ether of benzoin) but at a much slower rate. This system of aldehyde methacrylates is considered primarily as a promising candidate for evaluation as an adhesion-promoting agent although it may have further utility as diluent comonomer for dental composites and pit and fissure sealants since the monomers are miscible with Bis-GMA.

This work on aldehyde methacrylates was presented at the 1976 IADR Meeting in Copenhagen and a manuscript has been accepted by the J. Dent. Research.

(2) Monomers with Isocyanate Functional Groups

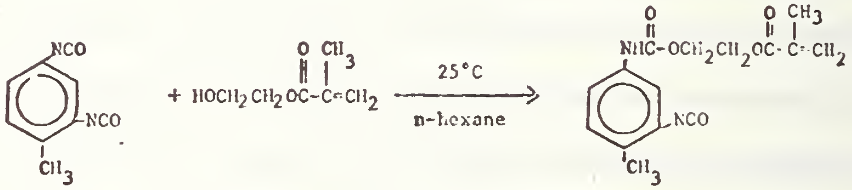
A second type of methacrylate monomer that we have synthesized to contain a functional group capable of reaction with the organic (collagenous) phase of bone or dentin is the isocyanate methacrylate. We have completed synthesis (as per schemes below) and isolation of five such functional monomers.



IPDI

HEMA

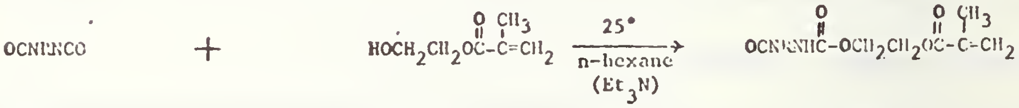
IPDI-HEMA
(MW ~ 352)



TDI

HEMA

TDI-HEMA (MW ~ 304)
m.p. 67-68°C



$$OCNRNCO + HOCH_2CH_2O\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[n\text{-hexane}\ (Et_3N)]{25°} OCNRNH\overset{O}{\overset{\|}{C}}-OCH_2CH_2O\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

HDI [$R=(CH_2)_6$]

TMDI [$R=CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2$]

DDI [$R=C_{36}$ Hydrocarbon]
MW ~ 600

HEMA

HDI-HEMA
(MW ~ 298)

TMDI-HEMA
(MW ~ 340)

DDI-HEMA
(MW ~ 730)

The physical state in which the three monomers were isolated is as shown below:

DDI-HEMA	Pale yellow liquid
IPDI-HEMA	Yellow viscous liquid
TDI-HEMA	White crystalline solid
HDI-HEMA	White solids
TMDI-HEMA	Pale yellow liquid

Elemental and NMR analyses were used to confirm the structures of TDI-HEMA and IPDI-HEMA. Infrared spectra on all five isocyanate methacrylates was consistent with assigned structures. Each was shown to polymerize in 2-8 minutes via chemical initiation by the benzoyl peroxide-amine catalyst system and to polymerize rapidly by photoinitiation in the presence of a photosensitizer. These monomers were also shown to be miscible and copolymerizable with the Bis-GMA system. In addition to evaluation as an adhesion promoter, DDI-HEMA deserves consideration as a component in a composite resin system since DDI-HEMA has very large bulk that can be expected to give low polymerization shrinkage while at the same time it possesses a workable viscosity.

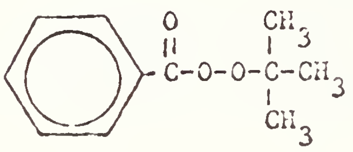
This work was presented at the 1977 AADR meeting in Las Vegas.

2. New Initiator/Accelerator Systems

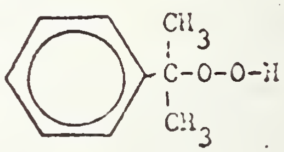
The storage stability of a typical paste-paste dental composite formulation depends to a large degree on the thermal and chemical stability of the peroxide component of the initiator system. Further, there is the relative color instability inherent in the tertiary aromatic amines used as accelerators of the polymerization. The discoloration observed when an otherwise acceptable composite resin system, i.e. the tertiary eutectic of the three isomeric dimethacrylate derivatives of phthalic acid, employed the benzoyl peroxide-tertiary amine catalyst has spurred a search for accelerators other than aromatic amines. Because many of the usual ambient temperature free radical initiations are based on some kind of oxidation-reduction reaction, we have begun an investigation of several types of organic peroxides and the natural non-toxic reducing agent, L-ascorbic acid. Progress in these areas is summarized in the following pages.

a. New Initiator Systems

We have begun an investigation of the feasibility of substituting for benzoyl peroxide, peroxides that have improved thermal (and hence storage) stability such as the organic peresters, e.g. t-butyl perbenzoate, and hydroperoxides such as cumene hydroperoxide. These chemical structures are given below:



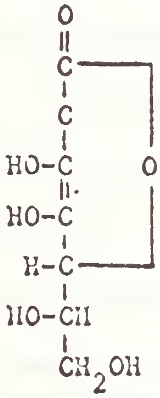
TBPB



CHP

The chemical activation of these types of peroxides to yield initiating radicals usually requires the presence of a redox metal compound such as iron, copper, cobalt, etc., salts. These metal salts are reductants in their lowest oxidation state (e.g. Cu^{+1}, Fe^{+2}, etc.) and can transfer an electron to the peroxide (oxidant) bringing about its decomposition to initiating radicals. They are considered extremely potent activators for peresters and hydroperoxides. However, there are several problems associated with the use of these redox metal activators in a dental monomer system. If the metals are used in the concentrations comparable to those employed with the amine type activators, both color and toxicity become problems. In addition, the metal activators which need to be in their lower oxidation states (e.g. Cu^{+1}, Fe^{+2}) to be effective, are susceptible to oxidation on storage to their higher valance state (Cu^{+2}, Fe^{+3}) which makes them less effective.

As a way of circumventing these problems we are investigating the natural relatively mild reducing agent, L-ascorbic acid (Vitamin C), as a possible activator for these peroxides. The chemical structure of ascorbic acid is



Ascorbic Acid
(Vitamin C)

Because of the limited solubility of ascorbic acid in most monomers, we also investigated ascorbyl palmitate, which has a better solubility in most monomers, as an activator for peresters and hydroperoxides. For the same Bis-GMA type monomer systems, we obtained cure times comparable to those obtained with ascorbic acid.

A comparison of the two activators is shown below for a monomer system consisting of 70% Bis-GMA and 30% triethylene glycol dimethacrylate. We used a powder/liquid formulation with the ascorbic acid and palmitate deposited on the silanized glass beads. The monomer contained the perester, t-butyl perbenzoate. By means of a cross slide immobilization technique, the working times were determined. Working times of 2-1/2 minutes are considered clinically acceptable. Table 3 and Table 4 summarize some of our results. As can be seen, the lowest working times were 4 minutes using ascorbyl palmitate as the activator. By using extremely small amounts of cupric and ferric salts the working time can be further reduced to the 2 to 3 minute range. Table 5 shows the typical effect of a redox metal compound such as cupric acetate on the working time with the same monomer system with 1.5% TBPB and glass beads (0.45% ascorbic acid). For composites prepared with glass beads (0.3% ascorbyl palmitate) the working times were extremely short (under 2 min.). Cupric and ferric salicylate in catalytic amounts also were effective in reducing the working times to under 3 minutes. Without the ascorbic acid or palmitate being present, no polymerization occurred in these systems.

To check for effects of other metal impurities, we obtained a standard reference material for copper, SRM-1080A, which is cupric benzoylacetonate. This copper compound is slightly soluble in the monomer and we prepared several solutions having from 0.001 to 0.0001% Cu^{+2}. A slight light blue coloration was noted in the more concentrated solutions but no coloration was visible at 0.0001% level.

In addition, it appears possible to combine the perester TBPB, with this cupric compound without encountering any storage problems. As indicated earlier, the redox metals are effective activators for these peroxides only in their lower oxidation states. The ascorbic acid or palmitate apparently reduces the cupric or ferric cation to the corresponding cuprous or ferrous state which will immediately activate the decomposition of the perester. Simultaneously ferric ions and cupric ions are reformed, which because of the presence of the ascorbic acid, are reduced again, thereby creating a chain activation mechanism for the decomposition of the peroxide. Composites prepared using these minute quantities of copper have shown no signs of extraneous coloration and appear similar to those prepared without these catalytic amounts of redox metal.

Using a liquid monomer formulation consisting of 70% Bis-GMA and 30% TEGDMA (triethylene glycol dimethacrylate) and a glass powder properly treated to enhance reinforcement we have prepared composite tensile strength specimens using various initiating systems. Comparison has been made with the conventionally cured material, e.g. benzoyl peroxide-dimethyl-p-toluidine. Representative values of the diametral tensile strength measured after 24 hours are given in Table 6. The highest values were obtained with monomer containing minute quantities of copper (as copper benzoyl acetonate) which may be indicative of a more efficient initiator system.

These new types of initiator systems, by employing more stable peroxides, e.g. peresters, and more "natural" reducing agents or accelerators (e.g. ascorbic acid) offer promise for improving the storage and color stability, the biocompatibility and other properties not only of dental composite and sealant materials but also other medical materials based on the concept of "cold-curing" resin systems.

Table 3

Working Times for Glass Beads (0.45% Ascorbic Acid)*
and Liquid Monomer (0.5% TBPB)**

Trial	Liquid/Powder Ratio	Consistency of Paste	Working-Time (min)
1	1/3	Thick	7
2	1/3	Thick	8
3	1/3	Thick	6
4	1/2	Fluid	6
5	1/2	Fluid	9
6	1/1	Very Fluid	8
7	1/1	Very Fluid	10.

* Glass beads (silanized) prepared by depositing ascorbic acid from 3% Ethanolic solution using a rotary evaporator.

** Liquid monomer consisted of 70% Bis-GMA and 30% TEGDMA and contained 0.5% TBPB
Bis-GMA = The adduct of bisphenol A and glycidyl methacrylate
TEGDMA = Triethylene glycol dimethacrylate
TBPB = t-butyl perbenzoate

Table 4

Working Times for Glass Beads (0.30% Ascorbyl Plamitate)*
and Liquid Monomer (1.5% TBPB)**

Trial	Liquid Powder Ratio	Consistency of Paste	Working-Time (min)
1	1/1.7	Fluid	11
2	1/0.84	Very Fluid	6
3	1/2.5	Medium	4
4	1/1.96	Medium	8
5	1/1.91	Medium	5
6	1/2.7	Thick	5
7	1/3.2	Very Thick	7
8	1/3.3	Very Thick	4
9	1/3.4	Very Thick	4
10	1/3.6	Very Thick	4
11	1/3.6	Very Thick	4

* Glass beads (silanized) prepared by depositing ascorbyl palmitate from 3% ethanolic solution using a rotary evaporator.

** Same monomer as in Table 3 except concentration of TBPB is 1.5%.

Table 5

Effect of Cupric Acetate [$Cu(OAC)_2$] on Working Time

Trial	Liquid/Powder Ratio	Percent [$Cu(OAC)_2$] in Composite	Working-Time (min)
1	1/3	0.057	2
2	1/3	0.029	3
3	1/3	0.019	2

For composites prepared with glass beads (0.3% ascorbyl plamitate) the working times were extremely short (under 2 min). Cupric and ferric salicylate in cataylic amounts also were effective in reducing the working times to under three minutes.

Table 6

Comparative 24-hour Diametral Tensile Strength of a Typical Dental Composite Prepared with Various Initiating Systems

Sample Number	Formulation	TS (psi)
1	A. (0.45% A. A.) 3 parts B. (1% TBHP) 1 part	5832
2	A. (0.45% A. A.) 3 parts B. (1% CHP) 1 part	5784
3	A. (0.45% A. A.) 3 parts B. (1% TBPB) 1 part	6631
4	A. (0.45% A. A.) 2-1/2 parts B. (1% TBPB + 0.0001 Cu^{+2}) 1 part	8277
5	A. (0.75 BP) 3 parts B. (0.23% DMPT) 1 part	6337

A = glass powder consisting of 67% fused silica plus 33% of an x-ray opaque BAF_2 containing glass, silanized with γ-methacryloxypropyltriethoxy silane and sieved (100 mesh). This glass was coated with ascorbic acid (A.A.) or benzoyl peroxide (BP).

B = liquid monomer consisting of 70% Bis-GMA [bis(3-methacryloxy-2-hydroxypropyl) bisphenol A] and 30% TEGDMA (triethylenegycol dimethacrylate).

Peroxides used:

TBHP = Tert-butyl hydroperoxide
CHP = Cumene hydroperoxide
TBPB = t-butyl perbenzoate
BP = benzoyl peroxide
Cu^{+2} = ion form of copper benzoyl acetonate

Typical amine accelerator = DMPT (dimethyl-p-toluidine)

b. Improved Amine Accelerators

A number of amines have been suggested as accelerators for dental resins but esthetic and biocompatibility requriements have greatly limited the number of compounds that can be used for this application. The currently used tertiary dialkyl aromatic amines that are used in the benzoyl peroxide initiated polymerization of methacrylates suffer from a basic color instability and relatively high toxicity index. Part of the discoloration problem of dental composites probably is traceable to the color-prone amine accelerators.

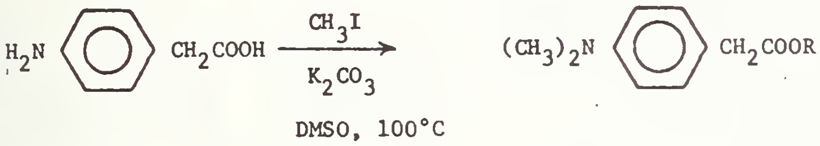
The amines investigated in this report period were either those used in current composite restorative materials, e.g. dimethyl-p-toluidine (DMPT), dihydroxyethyl-p-toluidine (DHEPT) dimethylsymxylidine (DMSX); those predicted to be highly reactive based on structure-property relationships, (i.e. free energy relationships) e.g. 4-N,N-dimethylaminophenyl acetic acid (DAPAA) or its methyl ester (MDMAPAA), methyl 4-N,N-dimethylaminoglutethimide (DMAG); or some amines previously synthesized in this laboratory which had not been evaluated, e.g. di-2-hydroxypropyl-p-toluidine (DHPPT), low and high melting isomers of bis(3- p -tolyloxy-2-hydroxypropyl)m-xylidine (BTX), dimethylaminobenzaldehyde (4-DMAB),tetramethylammonium 4-dimethylaminobenzaldehyde (TMADMAB) lithium 4-methylaminobenzoate (LDMAB), 3-dimethylaminobenzoic acid (3-DMABA) and dimethylaminopyridine (DMAP).

The structure-property relationships found in this laboratory [15] for correlating the reactivity of tertiary amines with benzoyl peroxide in vinyl monomers indicated that amines with aryl(ring) substituents have a σ^+ value [16] close to -0.20 would be the most reactive.

A library survey indicated that p-CH_2-$COOC_2H_5$ has a σ^+ value of -0.16, thus recommending the potential of phenylacetic acid or ester derivatives. The σ^+ for the aryl substituent of aminoglutethimide is not known but is expected to be near that of p-tert-butyl (-0.26).

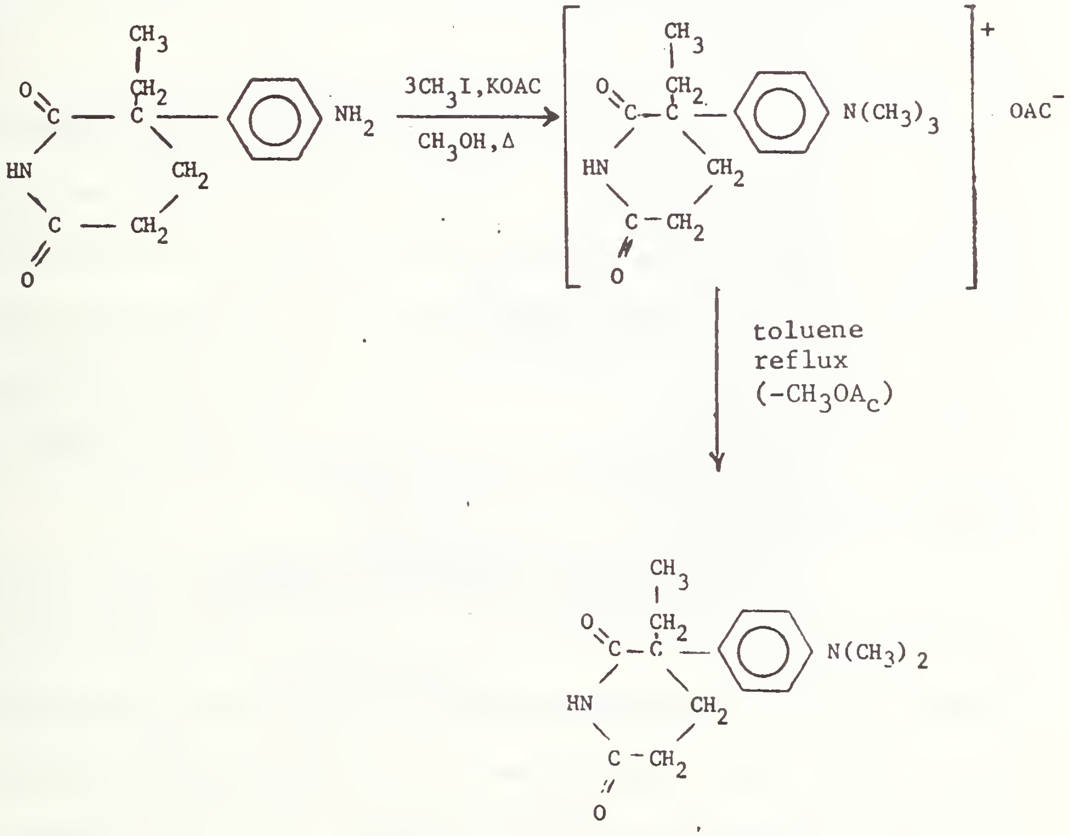
The several amine syntheses carried out in this report period are shown below:

DAPAA (and MDMAPAA)



R = H Crystalline solid, m.p. 110-112°C
R = CH_3 Pale Yellow liquid

DMAG



Beige crystalline solid
m.p. 147-149°C

The specification for Direct Filling Resins [17] requires a minimum working time of 1.5 min and a maximum hardening time of 8 min. Formulations containing DHPPT, BTX (low melting and high melting isomers), DMAB, 3-DMABA and MAP at the concentrations studied did not harden within the time limit. The effect of amine concentration on hardening time of the composites is shown in Fig. 1. Increasing the amine concentration to approximately 30 mm (millimolal) decreases the hardening time. At this molality the most efficient amines (DMPT, DMSX and DMAPAA) yield a polymer within 1 minute. As will be shown below composites with high concentrations of an amine accelerator have poor color stability. Thus, liquids with concentration greater than 50 mm amine were generally not employed in this investigation. It is likely that on incorporating larger concentrations of amine into the resin, the hardening time, after passing through a minimum, will increase.

Inspection of Fig. 1 indicates that shortest hardening times (1 min) are obtained with DMAPAA, DMSX and DMPT. Among these, resins containing DMAPAA give minimum hardening times at a lower molal concentration than those into which DMSX or DMPT are incorporated. Based on the results of this investingation it can be concluded that the approximate orde of the accelerating ability of the respective amines is DMAPAA > DMSX > MDMAPAA, DMPT>DMAG>DHEPT.

The effect of amine concentration on the tensile strength of the composite is shown in Fig. 2. Values of the tensile strength for DMAPAA could not be determined above 16.8 mm amine concentration because of the insufficient working time for the preparation of test specimens. Similarly, the hardening time of materials with 13.3 mm DHEPT was considered too slow for practical use. Therefore, the tensile strength of this formulation was not determined.

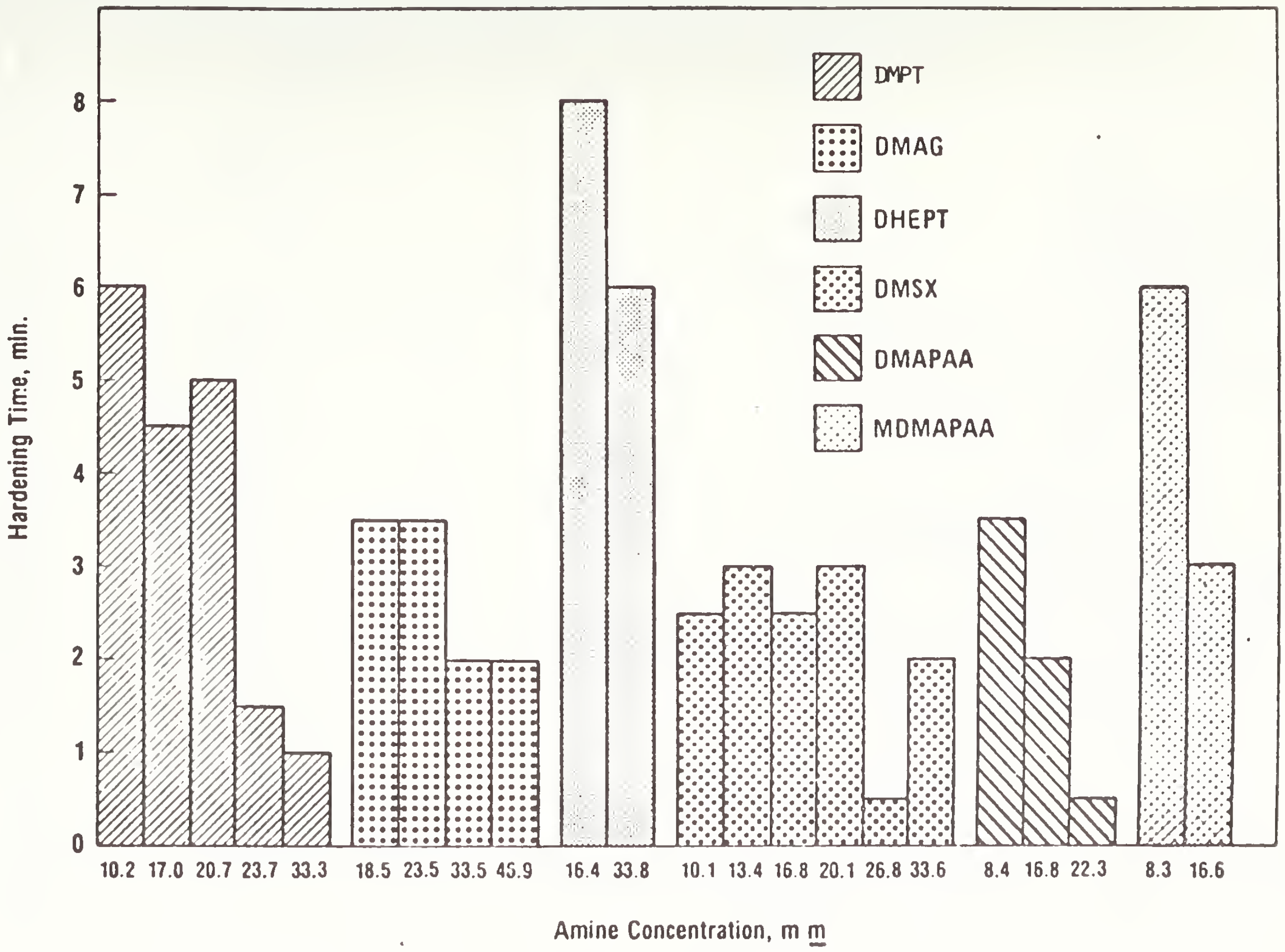


Figure 1: Hardening times of composites containing varying concentrations of tertiary amine accelerators

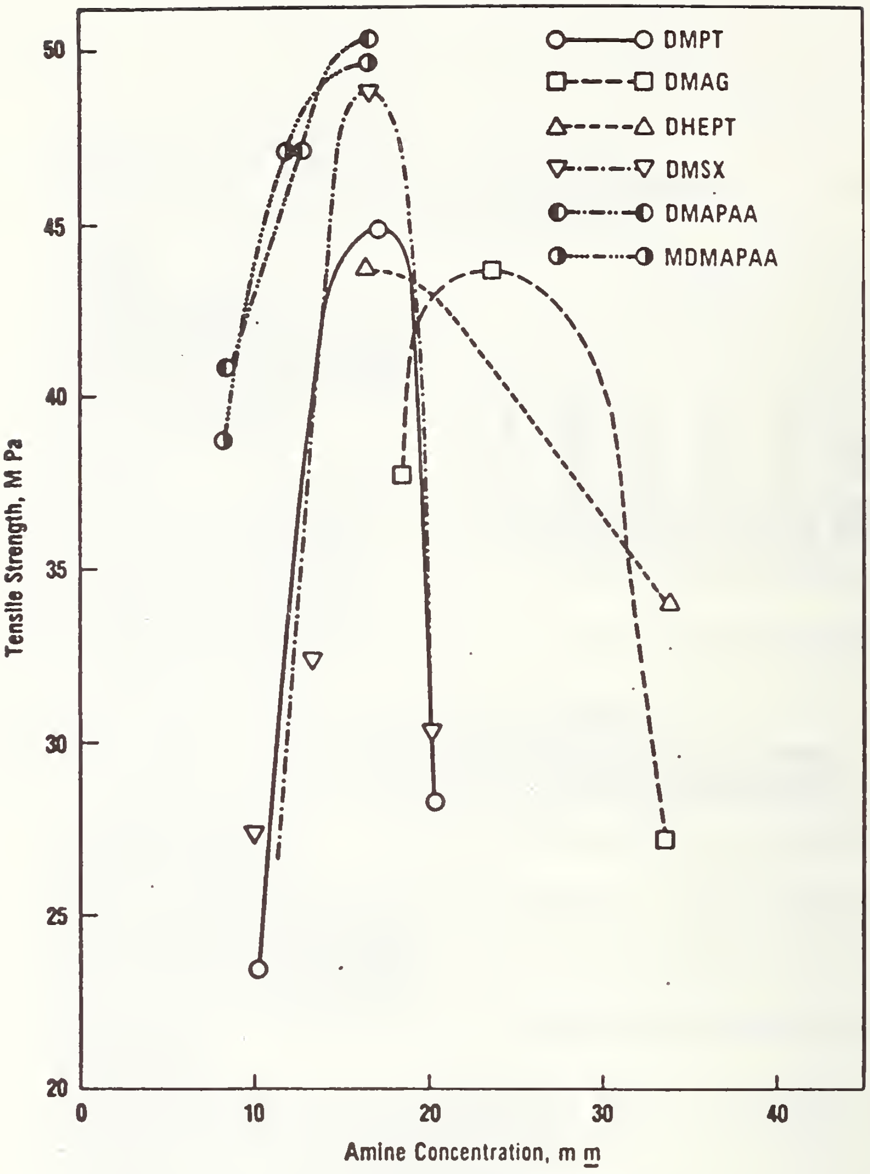


Figure 2: Tensile strength of composites as a function of the concentration of tertiary amine accelerator

A maximum tensile strength is observed in the 16.5 to 17 mm concentration range except for DMAG which yields a maximum at approximately 23.5 mm. The peaks are sharpest for DMSX and DMPT and appear to be much broader for DMAG and DHEPT. Maximum tensile strength of about 50 MPa is obtained with DMAPAA, MDMAPAA and DMSX. The tensile strength values obtained on incorporating DMPT, DHEPT and DMEG ranging from 43.6 to 44.8 MPa are slightly lower.

The compressive strength values of the composites are much less sensitive to changes in amine concentration than the tensile strength values. Thus between 10 and 35 mm amine in the liquid component the tensile strength of 6 amines shown in Fig. 2 varies from 23.4 to 50.4 MPa, a 115% increase whereas the compressive strength ranges from 147 to 221 MPa, i.e. a 50% increase. The compressive and tensile strength curve versus amine concentration in the liquid component are very similar. Compressive strength increases with amine concentration and reaches a maximum between 17 and 23 mm.

The DMAPAA proved to be the most reactive accelerator, yielding products of good mechanical strength and excellent color stability. The overall properties of composites with MDMAPAA and DMAG also proved to be very satisfactory. The 4-dimethylaminobenzoic acid and its tetramethylammonium and lithium salts cured fairly rapidly and had good strength, but their color stability and water sorption were only fair.

For unfilled resins, the rate of curing proceeds most rapidly using a molar peroxide-to-amine ratio between 1.10 and 1.50 [18, 19]. A composite formulation prepared from powder coated with 1% peroxide and 17.0 mm amine in the liquid has a molar peroxide-amine ratio of 6.5. Thus, for composites, a much larger molar excess of peroxide is required to obtain optimum hardening time. This much larger excess of peroxide is to be expected since only a small portion of the peroxide is accessible to the amine before the composite is cured.

A minimum of 34 MPa is required for the tensile strength of composite resins [17]. Practically all the composites prepared with the amines used in this study pass this specification test. The range of amine concentrations that yield cured resins with high strength is quite critical. Compressive strength is somewhat less dependent on the type and concentration of amine used. Maximum compressive and tensile strength are obtained in the same amine concentration range. Some of the amines, first evaluated in this study, especially DMAG, DMAPAA and BTX, show excellent color stability. Thus, proper quality control is required in the manufacture of these materials to assure that the liquid component contains the exact accelerator concentration.

Although the evaluation of some of these accelerators would indicate their potential usefulness, their biocompatibility will have to be established. In selecting tertiary amines to be synthesized consideration was given to compounds with promising toxicological characteristics, hopefully better than those of the presently used accelerators. The parent compounds, 4-aminophenylacetic acid, its derivatives and aminoglutethimide have been suggested respectively as anti-inflammatory agents [20, 21] and anticonvulsant agent [20]. The 4-aminobenzoic acid (Vitamin B, anticanitic agent) and its derivatives are employed as sunscreen agents, local anesthetics and to raise blood salicylate level [20]. The N,Ndimethylated derivatives of aniline or p-toluidine have toxicological properties similar or better than the parent compound [20]. Similarly, examination of a homologous series of 4-aminophenylacetamide and n,N-dialkylaminophenylacetamides shows that the toxicity (expressed in gm/kg of test animal) steadily decreases as the amine hydrogen is replaced by increasingly longer alkyl substituents [22]. Analogously, one would expect that the tertiary amine derivatives under investigation (DMAG, DMAPAA, MDMAPAA, 4-DMBA, TMADMBA, 4DMBA) will have the same order of biocompatibility as their unsubstituted primary amine homologues; but this awaits further investigation. Based on the results of this study we conclude:

1. The overall characteristics of composites (hardening time, strength and color stability) containing N,N-dimethylaminophenylacetic acid (DMAPAA), its methyl ester (MDMAPAA) or dimethylaminoglutethimide (DHAG) compare favorably to restorative resins cured with commonly used tertiary amines or other accelerators evaluated in this study.

2. Maximum tensile strength for the composite is obtained only over a narrow concentration range of accelerator.

3. Study of Properties of Sealants

A study of the properties of experimental sealants which had been started previously was completed. It was shown that on substitution of other monomers for methyl methacrylate as diluent for Bis-GMA-based sealant, properties of the sealant can be varied widely. Thin films of sealant on storage in water lose weight for many weeks after an initial weight increase. Unless a hydrophilic diluent such as glycidyl methacrylate is used the decrease is generally larger than the initial gain resulting from water sorption. Incorporation of a photocrosslinking agent, e.g. (1-azo-5-acryloxymethyl-3,7-dioxabicyclo [3,3,0] octane) (AADO) into the formulations lowers the water solubility of the UV-cured sealant, thus improving the dimensional stability of the adhesive. Measurement of the apparent water sorption on storage of specimens for 12 to 27 months showed a continuous loss in weight. These changes were much smaller in formulations containing the AADO crosslinking agent; e.g. the apparent water sorption of a formulation containing 66% Bis-GMA, 28% methyl methacrylate and 5% AADO was 0.2% after the 25 month observation period. This formulation would be expected to possess excellent dimensional stability in an aqueous environment.

In the preceeding study and in the follow-up investigation to develop and evaluate physical test methods to characterize sealants, a number of new tests were suggested which were shown to be valid as specification tests. Some of these tests are described in the following paragraphs

A gravimetric test which measures the amount of uncured monomer that remained at the sealant-air interface was developed. The sealant is cured in a brass ring on aluminum foil at 37°C and 100% RH. The ring and foil which have previously been weighed are removed from the bath. Foil, ring and cured and uncured material are weighed to the nearest 0.1 g two minutes after curing. The surface is then patted dry with filter paper and the weight of the disk is redetermined. The difference between the two weights gives the weight of residual monomer which can be expressed as percent of total weight of cured and uncured sealant.

Results for 5 determinations for a chemically cured sealant gave a mean of 1.76 % with a standard variation of 0.76 %. The mean value for uncured surface monomer of 6 commercial sealants ranged from 1.8% to 14.0%.

We have developed two simple tests for semi-quantitative evaluation of the penetration ability of sealants into fissures. The first test measures the flow of sealant into a capillary and is mainly dependent on the viscosity of the sealant. The exact bore of capillary tubing is measured with a measuring microscope. The tubing used is approximately 0.005 cm and is readily obtainable. A 4 cm length of this tubing is positioned vertically. By means of a micropipette with disposable tips, exactly 10 μl of sealant, mixed according to manufacturer's instructions, are placed immediately after mixing on top of the tubing before curing. The time between placing the sealant on the tubing and its hardening and the distance the sealant traveled are determined. The distance traveled varied from 0.5 cm to 4.0 cm.

A similar test is conducted for capillary rise. A vial (3 cm high, 0.8 cm in diameter) is filled with freshly mixed sealant up to a mark placed 0.2 cm from the bottom of the vial. Immediately, a 4 cm long capillary tube (0.05 cm in diameter) is placed through a plastic cap fitting the vial so that it penetrates 0.01 cm below the surface of the sealant. The maximum rise of sealant in the capillary tube above the level of the material in the vial is measured after curing of the material which usually occurs within 1 minute. Values ranged from no capillary rise to 2.0 cm. Thses simple tests were found to be fast and easily reproducible. They should correlate quite well with the penetration of sealant under clinical conditions which is greatly dependent on the viscosity and surface tension of the sealant.

We have also studied an indentation and recovery test for sealants as a measure of the gross mechanical properties of the sealant. This test is similar to the one described in the American Dental Association Specification No. 15 for Acrylic Resin Teeth [23]. Specimens are prepared by the procedure described for the residual monomer test. After removal of the monomer by blotting with filter paper and storage of the specimens in water at 37°C for 24 hours, the indentation resistance is measured with a Rockwell Hardness Tester with a steel ball 0.635 cm (0.25 in) or 0.158 cm (0.062 in) in diameter. The center of the top surface in contact with air during polymerization is subjected to a minor load of 3 kg by lowering the steel ball and the dial is adjusted to zero. Then a major load of 15 kg, which includes the minor 3 kg load, is applied for 5 min. After this time, the depth of the indentation is read from the dial gauge and recorded to the nearest 0.001 mm as Reading A. The major load is then released leaving the minor load on the specimen. Five minutes later the gauge is read and the value recorded as Reading B. Percent recovery is calculated as follows:

$$\text{Percent Recovery} = \frac{\text{Avg. Reading A} - \text{Avg. Reading B}}{\text{Avg. Reading A}}$$

The use of the smaller (0.158 cm) ball cannot be recommended since many of the specimens broke on application of the load. Smaller indentation resistance values were obtained with the larger diameter ball indenter. Even with the 0.64 cm ball indenter, different values for the various brands investigated were obtained. The results of the measurements of different specimens of the same brand were quite reproducible. Such tests measuring gross mechanical properties may be useful for predicting the clinical performance of a sealant.

D. Techniques for Bonding to Mineralized Collagen Surfaces

The goal of developing dentally applicable adhesive procedures has long been considered a worthy one [24]. Such procedures and materials would have ready application in restorative and preventive dentistry as well as in orthodontics.

The objective of the current effort has been to determine the feasibility of covalent or ionic bonding of polymer chains to the components of mineralized tissue such as bone or dentin. Where true chemical bonding cannot be confirmed we are interested in evaluation of the "adhesive" effect achieved through interpenetrating networks of natural and synthetic polymer. Additionally we are examining the stability of any attachment where the initial adhesive strength is promising.

While acid etch pretreatment of enamel has proven a successful means of adhering resins or composites to enamel surfaces, it has not been effective with collagen containing substrates such as dentin or bone. One approach, initiated in this laboratory, has been to generate grafts of polymer chains to such surfaces using ceric ammonium nitrate or persulfate-bisulfate initiated polymerization [25-27]. The formation of a true graft was shown to depend on the selection of monomer and the type of initiator employed.

1. Cyanoacrylates

In the Annual Report for FY 76 [6] we reported the following results of our initial research on cyanoacrylates:

1. With a commercially available methyl-2-cyanoacrylate

curing times under UV on dentinal or bone surfaces pretreated with dimethyl-p-toluidine ranged from 15 sec. to 1 minute.

2. Tensile strengths observed between bovine dentin treated with methyl-2-cyanoacrylates and an *in situ* curing composite were found to be less than those reported by others in the literature.

3. Evidence that the methyl-2-cyanoacrylate lacked gap-filling ability was demonstrated. This would be of more concern in restoration applications than in preventive techniques.

4. A bone/cyanoacrylate/bone tensile strength measurement technique was developed for rapid screening.

5. Using commercially available cyanoacrylates and several from the Army Medical R&D Laboratory more encouraging initial bond strengths to bone were obtained.

6. A modification of the Lee, Swartz and Culp [28] test procedure was developed for measuring adhesive strength between cyanoacrylate-treated dentin and an acrylic resin system.

We have continued the research on cyanoacrylates. NMR analysis was used to identify the nature of the alkyl groups in the commercial cyanoacrylates that were used. Room temperature curing times on bone of cyanoacrylates with 2-5 carbons in the ester side chain varied from a few seconds to less than 3 minutes.

a. Isothermal Aqueous Storage at 37°C

We measured the deterioration in bond strengths developed by cyanoacrylates in bond-cyanoacrylate-bone specimens as a function of storage time in water at 37°C. The data for up to one month storage periods is given in Table 7.

TABLE 7

Bond Strength of Various Materials to Bone

Temperature: 37°C

Material	Surface Pretreatment	H_2O Storage	Tensile Strength Mean	S.D.
		Days	MPa	MPa
Composite (control)	----	1	0.03	.07
Bonding resin (control)	acid etch (a)	1	0.06	.12
2-Cyanoacrylates				
Ethyl (product A)	---- (a)	1	0.92	.26
" (product B)	---- (a)	1	1.45	.61
" (dental adhesive)	---- (a)	1	1.82	.75
" (product C)	---- (a)	1	3.34	.69
" "	---- (b)	1	5.06	1.45
" "	---- (b)	7	4.21	1.21
" "	----	1	6.60	1.13
" "	----	7	3.88	1.36
" "	----	30	0.16	0.19
" " presence of arterioles		1	8.25	1.21
" "	ethanol	1	5.64	1.80
" "	1% alc DMPT (c)	1	6.38	1.95
" "	1% alc DMPT (c)	30	0.17	0.17
" "	modified aminofunctional silane	1	0.29	.10
n-Butyl	1% alc DMPT (c)	1	2.86	1.75
Isobutyl	1% alc DMPT (c)	1	6.04	2.20
"	1% alc DMPT (d)	1	6.44	2.79
"	1% alc DMPT (d)	30	3.87	1.27
" (commercial)	----	1	6.62	1.73
" (completely dry bone)	----	1	0	0
"	1% alc DMPT (c)	1	4.79	1.06
"	----	30	4.65	1.51
n-Amyl	----	1	6.62	1.75
"	1% alc DMPT (c)	1	5.94	2.23
" (arterioles)	1% alc DMPT (c)	1	7.84	1.42
"	1% alc DMPT (d)	30	2.53	.80
Isoamyl	----	1	6.27	0.94
"	1% alc DMPT (c)	1	5.57	1.15
"	1% alc DMPT (d)	1	5.43	.86
"	1% alc DMPT (c)	30	4.48	2.15
Isoamyl (viscous)	----	1	7.18	1.47
" "	(b)	1	4.72	1.27
" "	1% alc DMPT (c)	1	5.53	2.02
" "	1% alc DMPT (c)	30	4.70	2.04
n-Hexyl	1% alc DMPT (d)	did not cure in 3 min.		
Ethylcellosolve	----(b)	1	0	0
Fluorinated	----	1	1.34	1.04
"	1% alc DMPT	1	0.50	0:75

(a) Test specimens kept for 30 min. at 37°C and 100% RH. prior to storage in water.

(b) Test specimens kept for 3 min. at 22°C and 50% RH prior to storage in water.

(c) DMPT = N,N-dimethyl-p-toluidine.

(d) Only one mating surface treated.

The adhesive is seen to be nil for controls in which the bone cylinders were joined by a composite resin or a dental bonding resin even after acid etching of the bone surfaces. A dry bone surface resulted in no bonding. The ethyl cellosolve 2-cyanoacrylate treated specimens showed no improvement over the control. All cyanoacrylates with 2 to 5 carbon atoms in the alkyl group produced significant tensile adhesive values after storage of one day. A maximum bond strength of 7.2 MPa after one day water storage was observed with viscous isoamyl 2-cyanoacrylate. This tensile adhesion value is of the order of magnitude reported for etched enamel-composite bond strength.

After one months storage the strength of all specimens decreased. Over this time span it appeared that hydrolytic stability increased with the alkyl side chain length. Some bonds were completely disrupted in this time interval, e.g. ethyl-2-cyanoacrylate.

To explore further the relation of side chain alkyl group and hydrolytic stability, specimens were stored in water at 37°C for up to six months. This data is given in Table 8 and Fig. 3. It is apparent that the isobutyl, n-amyl and isoamyl cyanoacrylates, while losing strength as a function of time, do hold up much better than does ethyl cyanoacrylate. After the six month storage the n-amyl, isoamyl and viscous isoamyl 2-cyanoacrylate retained respectively 67, 70%, and 71% of their first day bond strength.

Pretreatment of the bond surfaces with 1% alcoholic dimethyl-p-toluidine, to speed up curing of the adhesive, slightly reduced the one-day bond strength. These treated surfaces gave much lower tensile adhesion values than the untreated substrate after one and three month water storage and retained only a small percentage of the original strength after a 6 month observation period. Again the n-amyl and the viscous isoamyl homologues exhibited the largest 6 month adhesive strength.

Table 8

TENSILE STRENGTH OF THE CYANOACRYLATE-BONE BOND

No Pretreatment

2 cyanoacrylate	Tensile Strength in MPa after H_2O Storage			
	1 day	1 month	3 month	6 month
Ethyl (Alpha Ace)	6.60	0.16	--	--
n-Butyl	2.86	--	--	--
Isobutyl	6.62	4.65	4.62	4.12
n-Amyl	6.62	--	3.80	4.84
Isoamyl	6.27	--	4.98	4.39
Isoamyl	7.18	--	6.33	5.14
Ethyl cellosolve	0	--	--	--
Bone pretreated with 1% alc. dimethyl-p-toluidine				
Ethyl (Alpha Ace)	6.38	0	--	--
Isobutyl	4.79	--	2.87	0.15
n-Amyl	5.94	2.53	1.12	1.57
Isoamyl	5.50	4.48	0.62	0.51
Isoamyl, viscous	5.53	4.70	4.21	2.06

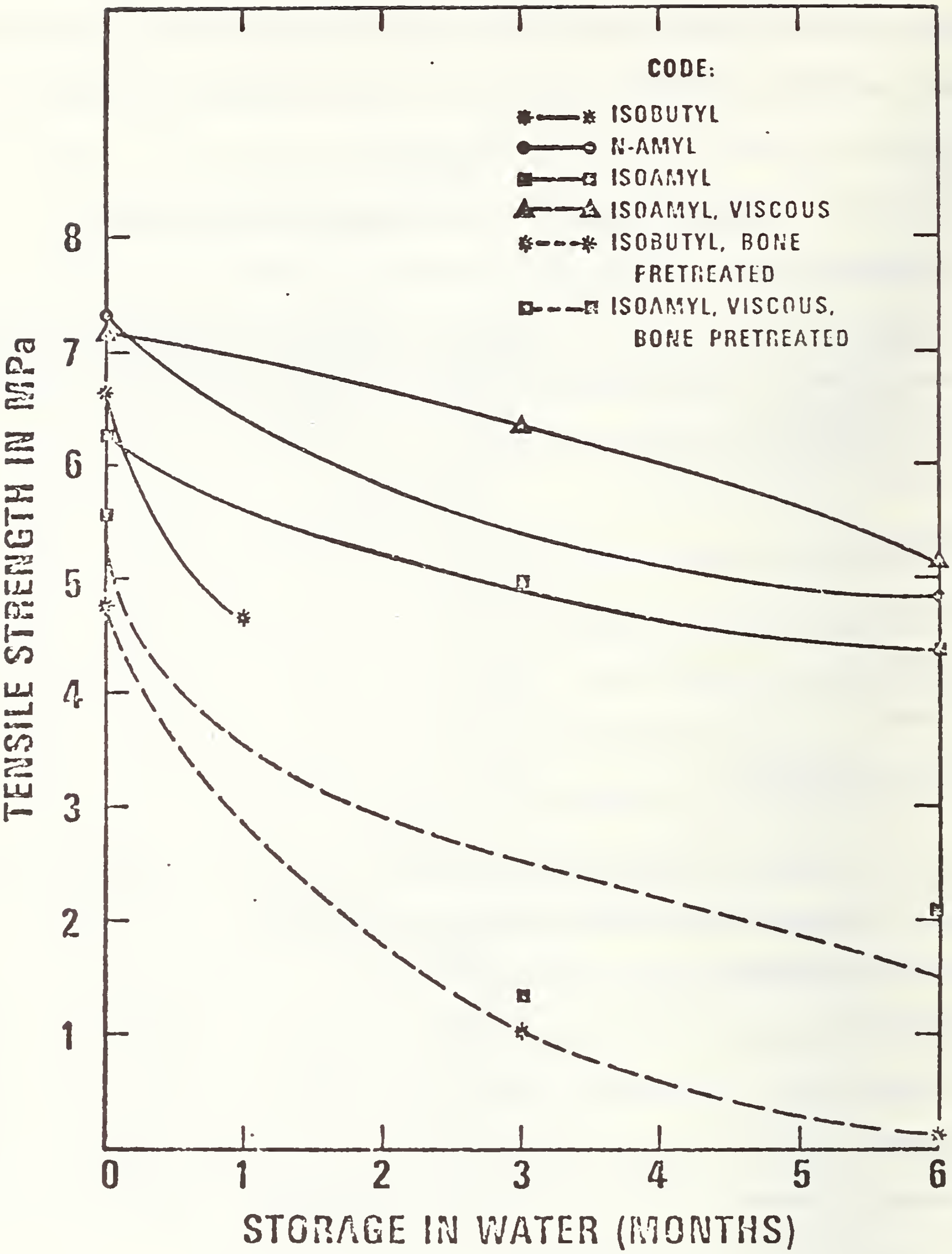


Figure 3: Tensile strength of cyanoacrylate to bone bond after storage in water

b. Accelerated Aging Test

With equipment built in the laboratory, bone-cyanoacrylate-bone specimens were subjected to a cyclic exposure to water at 5° and 55°C, the specimens being 70 s at each temperature with 10 s taken for the transfer. These results are given in Table 9. Isobutyl and viscous isoamyl 2-cyanoacrylates gave the highest one day tensile values. However all values were much lower than those obtained with the same specimen types when aged isothermally at 37°C. As was true in the isothermal aging, pretreatment to achieve rapid cure times significantly encouraged deterioration of bond strengths. The bond established by viscous isoamyl cyanoacrylate which appears to be the most hydrolytically stable is greatly deteriorated, e.g., by 67% of the 1 day 37° value of 7.2 MPa, in 30 days of cycle testing. The test correlates well with the long-term isothermal storage studies and should be of value in predicting lifetime behavior.

The viscous isoamyl cyanoacrylate with the highest initial bond strength to bone also shows the least bond strength deterioration in water. It has the further advantage that it should possess greater gap filling potential than the less viscous materials and is considered to be less toxic than the lower homologues of the 2-cyanoacrylate series. It may prove useful clinically where an intermediate term bone adhesive is indicated.

Table 9

TENSILE STRENGTH OF ADHESIVE-BONE BOND AFTER TEMPERATURE CYCLING

Temperature of Water bath: 5° & 55°C; Number of cycles per day: 540

Cyanoacrylate	Tensile Strength in MPa after cycling		
	1 day	12 days	30 days
Ethyl	3.90	0	-
Isobutyl	4.52	4.06	1.61
Isobutyl (a)	3.36	3.19	-
n-Amyl	4.59	2.92	0.59
Isoamyl	-	1.64	-
Isoamyl, viscous	4.40	2.73	2.32
Isoamyl, viscous (a)	3.97	2.37	-

(a) Bone pretreated with 1% alc. dimethyl-p-toluidine

c. Nature of Adherence of Cyanoacrylate to Bone

Ethyl 2-cyanoacrylates were spread on the surface of a bone slab primed with a hexane solution of tritheylamine. Infrared spectra taken 2 hours later clearly identified the cyanoacrylate. Upon extraction with acetone and dimethylsulfoxide an I.R. spectra of a fresh bone surface was found. Similar results were observed when the most hydrolytically stable cyanoacrylate, viscous isoamyl, was used. It appears that contrary to the reaction of amino acids with cyanoacrylates [28], covalent grafting of bone to cyanoacrylate does not occur.

Table 10

TENSILE STRENGTH OF THE DENTIN-ACRYLIC JOINT BONDED WITH VARIOUS CYANOACRYLATES

Temperature of water: 37°C

2-Cyanoacrylate	Treatment	Days in H_2O	Tensile Strength, MPa
Ethyl	--	1	2.80
Ethyl	DMPT	1	1.67
n-butyl	--	did not cure	--
Isobutyl	DMPT	1	3.50
Isobutyl	--	1	5.54
Isobutyl	37% H_3PO_4	1	7.23
Isobutyl	37% H_3PO_4	90	1.89
n-Amyl	--	did not cure	--
n-Amyl	DMPT	did not cure	--
Isoamyl	--	did not cure	--
Isoamyl	DMPT	1	3.22
Isoamyl, viscous	DMPT	1	2.29
Isoamyl, viscous	DMPT	1	2.65
Isoamyl, viscous	37% H_3PO_4	1	3.00
Isoamyl, viscous	37% H_3PO_4	90	0.25

Temperature Cycling

Temperature of water: 5°C and 55°C, Number of cycles: 540

2-Cyanoacrylate	Surface Treatment	Tensile Strength in MPa after cycling		
		1 day	7 days	30 days
Isobutyl		--	0.12	--
Isobutyl	37% $H_3P)_4$	5.65	3.32	0.25
Isoamyl	37% H_3PO_4	--	--	0.00
Isoamyl, viscous	--		0.00	--
Isoamyl, viscous	37% H_3PO_4	2.34	2.53	0.00

d. Cyanoacrylate Bonding of Acrylic Resin to Dentin

Results of the bond strength of the dentin joined to acrylic rod through cyanoacrylates are given in Table 10. Only the ethyl-, isobutyl- and viscous isoamyl 2-cyanoacrylate are cured within the 3 min. period that a force is applied to the assembly. By far the best bond strength (5.54 MPA) is obtained with the commercial isobutyl 2-cyanoacrylate. The bond strength for the 2-cyanoacrylates is higher for the bone to bone than for the dentin-poly (methyl methacrylate) joint. Pretreatment of dentin with dimethyl-p-toluidine lowered the bond strength. Acid-etch pretreatment of the dentin surface with 37% phosphoric acid surprisingly increased adhesion. Thus the one-day tensile strength of the dentin-acrylic rod is 7.23 MPa (1080 psi). However, as with bone, bond strength decreases greatly on storage in water. Thus after 90 days at 37°C tensile adhesion with the isobutyl- and viscous isoamyl-2-cyanoacrylate is reduced to 1.89 and 0.25 MPa, respectively. Thermocycling greatly reduced the bond strength. Acid-etched specimens showed minimal adhesion and the bond was destroyed completely on 30 days of thermocycling. These results indicate that the presently available non-filled 2-cyanoacrylates studied in this investigation could find only very limited usefulness, if any, as adhesives for cementing dentin to acrylic restoratives since (1) the bond degrades quite rapidly in an aqueous environment even after acid etching of the substrate and (2) the two mating surfaces must fit together closely without gaps or voids since these adhesives do not act as gap fillers, a quality usually required for clinical application.

Further studies to improve adhesion to dentin by incorporating (a) polymerizable crosslinking agents into the cyanoacrylate monomer and (b) by pretreatment of dentin surfaces with copolymerizable compounds are currently under investigation.

II. Physical, Mechanical and Physicochemical Properties of Dental Materials

A. Dimensional Charge Measurements

As part of a general investigation of the physical and clinical properties of amalgams made from some of the recently introduced alloys with high copper content, a study was concluded of the thermal expansion characteristics of the amalgams. The objective was to obtain information on the stability of amalgams at elevated temperatures rather than to determine coefficients of thermal expansion. The thermal expansion curves demonstrate that in addition to a "normal" reversible thermal expansion of about 25 parts per million per degree Celsius, some of the amalgams exhibit large dimensional changes that are time dependent as well as temperature dependent.

The thermal expansion apparatus used is a miniature vitreous silica dilatometer shown schematically in Fig. 4. The end of the silica tube containing the specimen was immersed in an ethylene glycol bath which provided heating or cooling rates between 10° and 19°C of approximately 0.35°C per minute. Openings in the tube permit the bath liquid to contact the specimen.

The compositions of the alloys on a weight percent are given in Table II. The alloys can be classified into three groups: first, those listed as "conventional" which fall into the composition limits given in

Table 11

COMPOSITION OF ALLOYS FOR AMALGAMS

Alloys	Silver %	Tin %	Copper %	Zinc %	Classification
ADA Spec. 1(1970)	≥65	≤29	≤6	≤2	
A	69.8	26.3	3.7	0.3	Conventional
B	69.0	27.4	3.4	1.2	Conventional
C	70.1	19.2	9.6*	1.1	9% Copper
D	70.0	20.1	9.5*	0.4	9% Copper
E	70.0	20.4	9.4*	0.2	9% Copper
F	42.2*	30.0*	27.8*	0.0	High Copper, Low Silver
G	58.5*	28.4	12.9*	0.1	High Copper, Low Silver
H**	60.2*	24.4	12.1*	-	High Copper, Low Silver
I	58.5*	28.4	12.9*	0.3	High Copper, Low Silver

* Differs from specification composition limit

** Contains 3.4% Indium

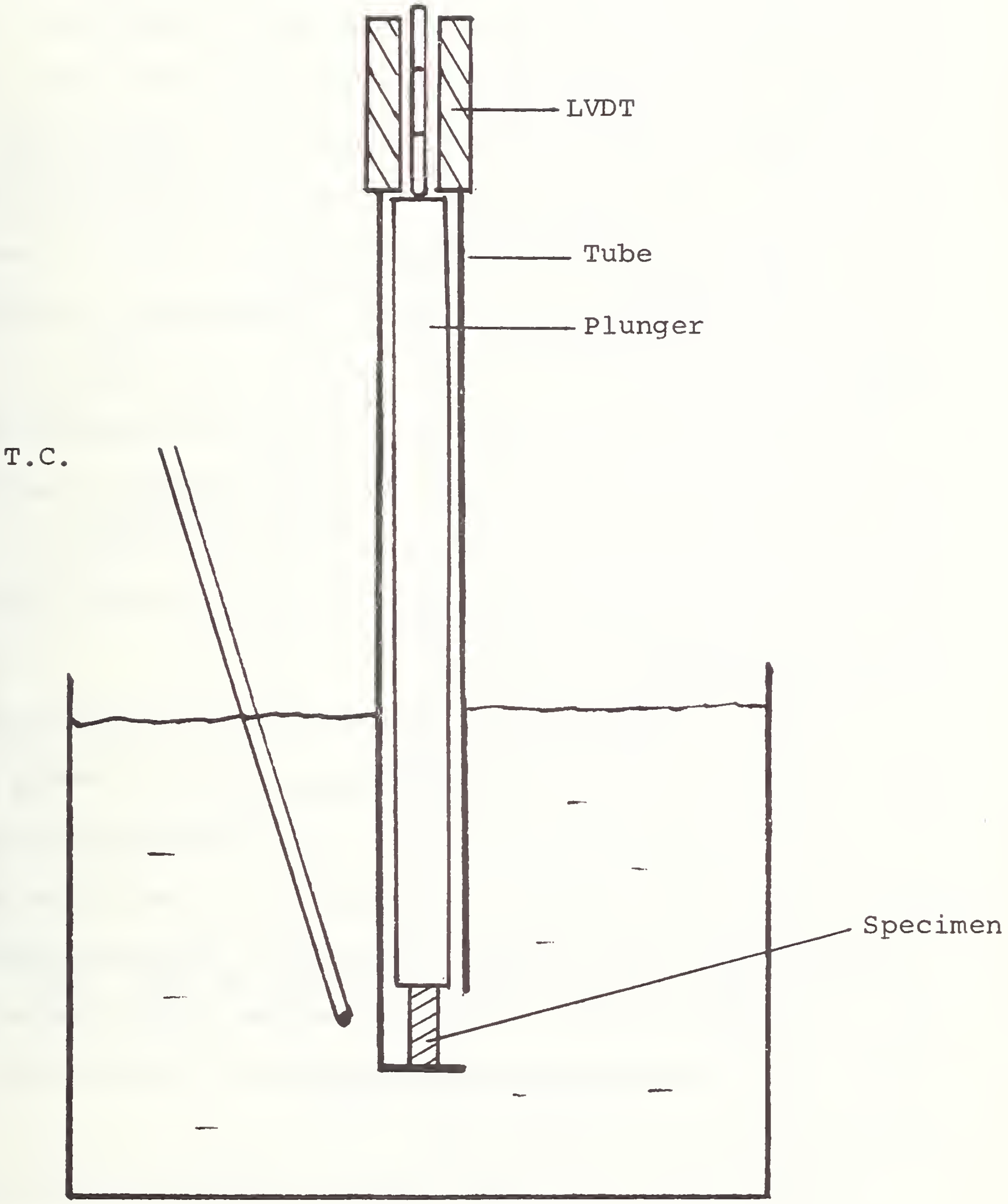


Figure 4. Vitreous silica dilatometer used for measurement of the thermal expansion of amalgam.

American Dental Association Specification No. 1 (1970); second, those listed as "9% copper" which contain more than the 6% maximum copper listed in the specification but comply with the other composition limits although they contain less tin than do the conventional alloys; and third, those listed as "high copper-low silver" which contain 12% or more copper and less than the 65% minimum silver listed in the specifications. The thermal expansion curves for amalgams within any one of the three composition classes are similar. There are, however, distinct differences between the thermal expansion curves for different classes.

The curves for the two examples of conventional amalgams (Fig. 5) are alike in that each shows a sharp shrinkage on heating at near 75°C and an expansion on cooling in the 50 to 40°C range. There is a difference above 75°C with an expansion occurring in amalgam A while a shrinkage is observed for amalgam B.

In Fig. 6, all three amalgams made from the "9% copper" alloys show irreversible expansion beginning near 55 or 60°C on heating and continuing, with some deviation near 75°C, until cooled to near 40°C. The decreased rate of expansion in amalgams D and E and the shrinkage in amalgam C near 75°C on heating, correspond to the sharp shrinkage observed in the conventional composition amalgams at this temperature. The specimen of amalgam E shows a growth of about 100 μm/cm or 1% during the heating and cooling cycle.

The four amalgams with high copper and low silver content (Fig. 7) are more stable dimensionally over the temperature range investigated than are the other amalgams. With the exception of amalgam I, which

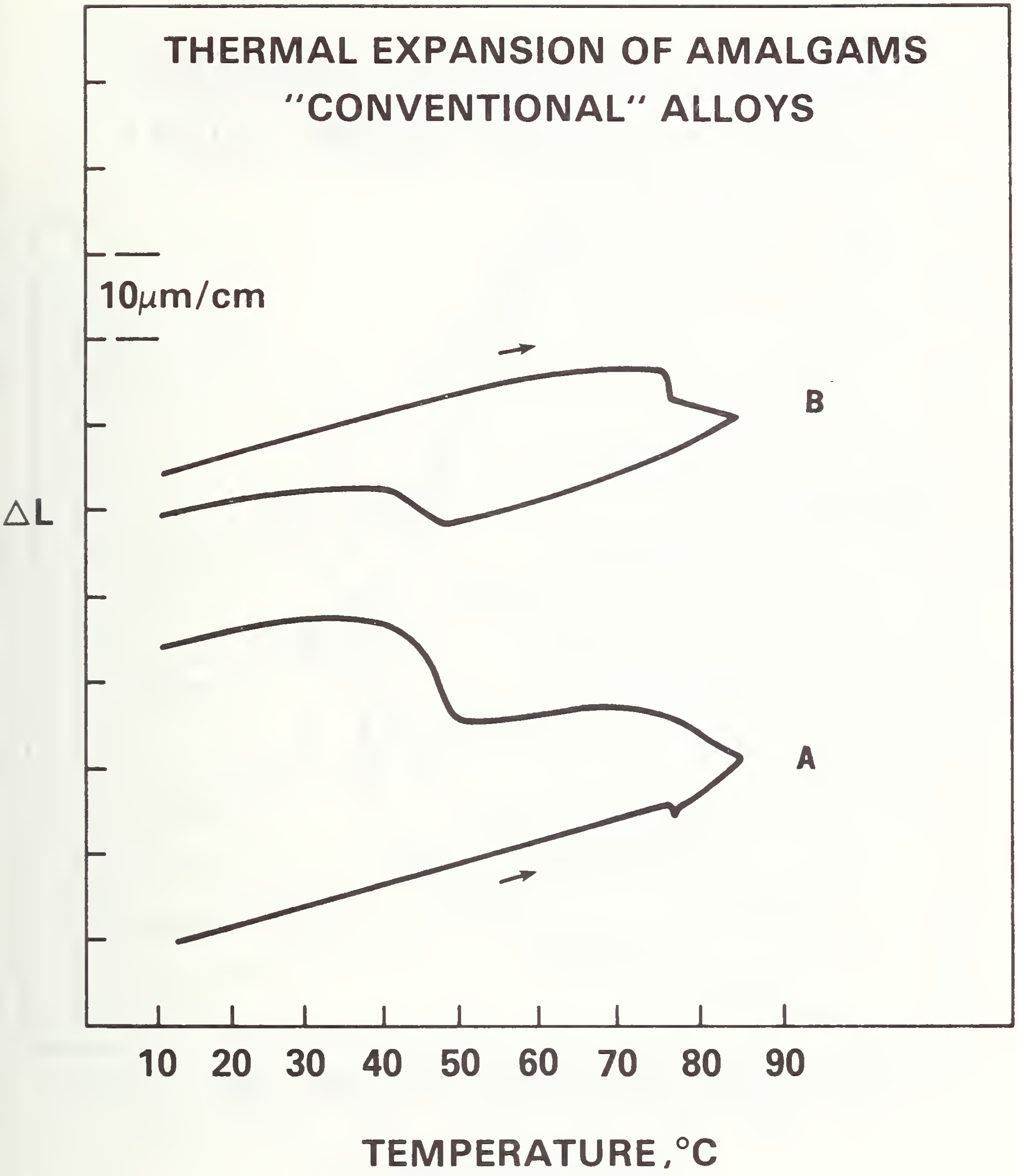


Figure 5: Thermal expansion of amalgams - "conventional" alloys

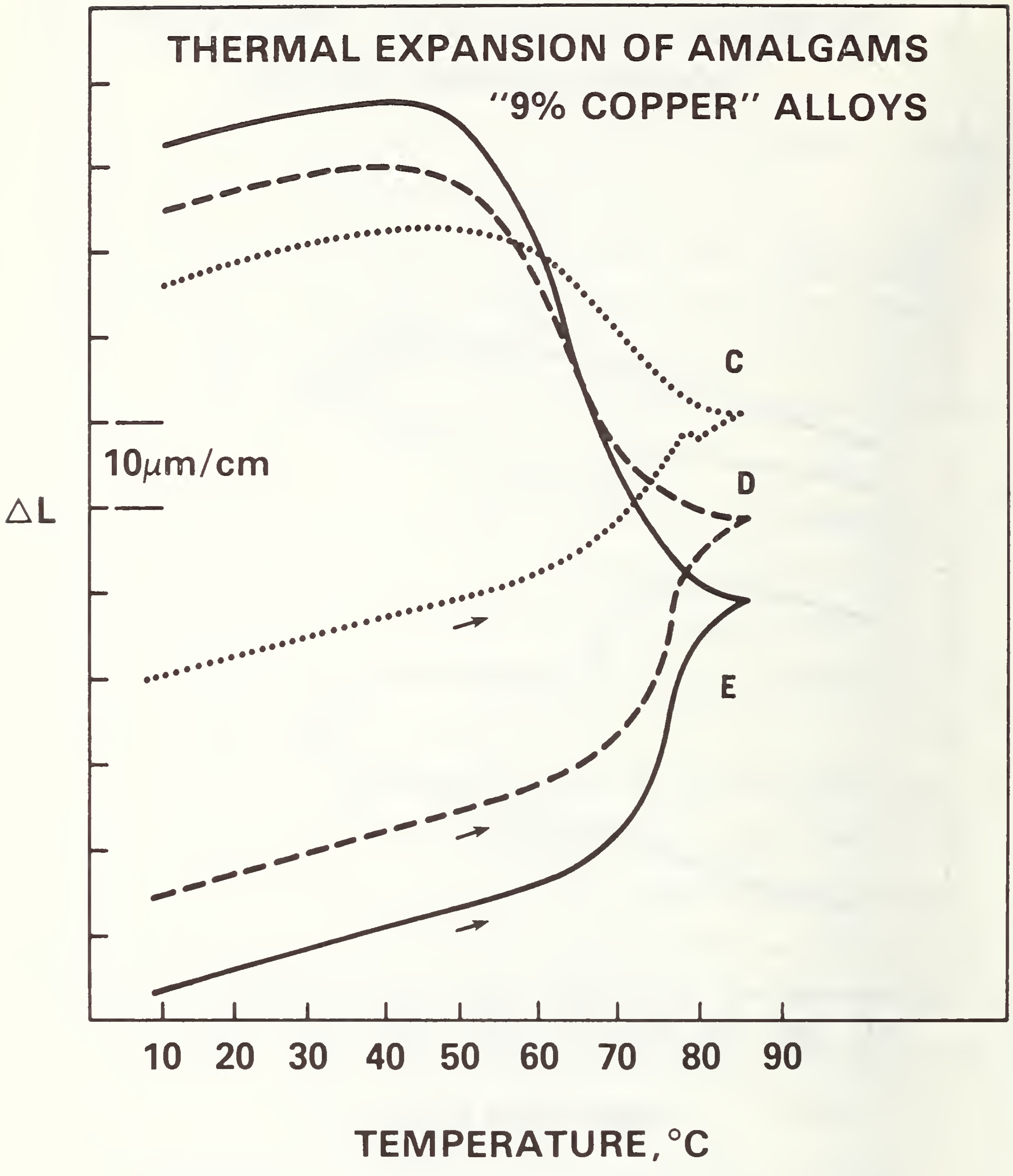


Figure 6: Thermal expansion of amalgams - "9% copper" alloys

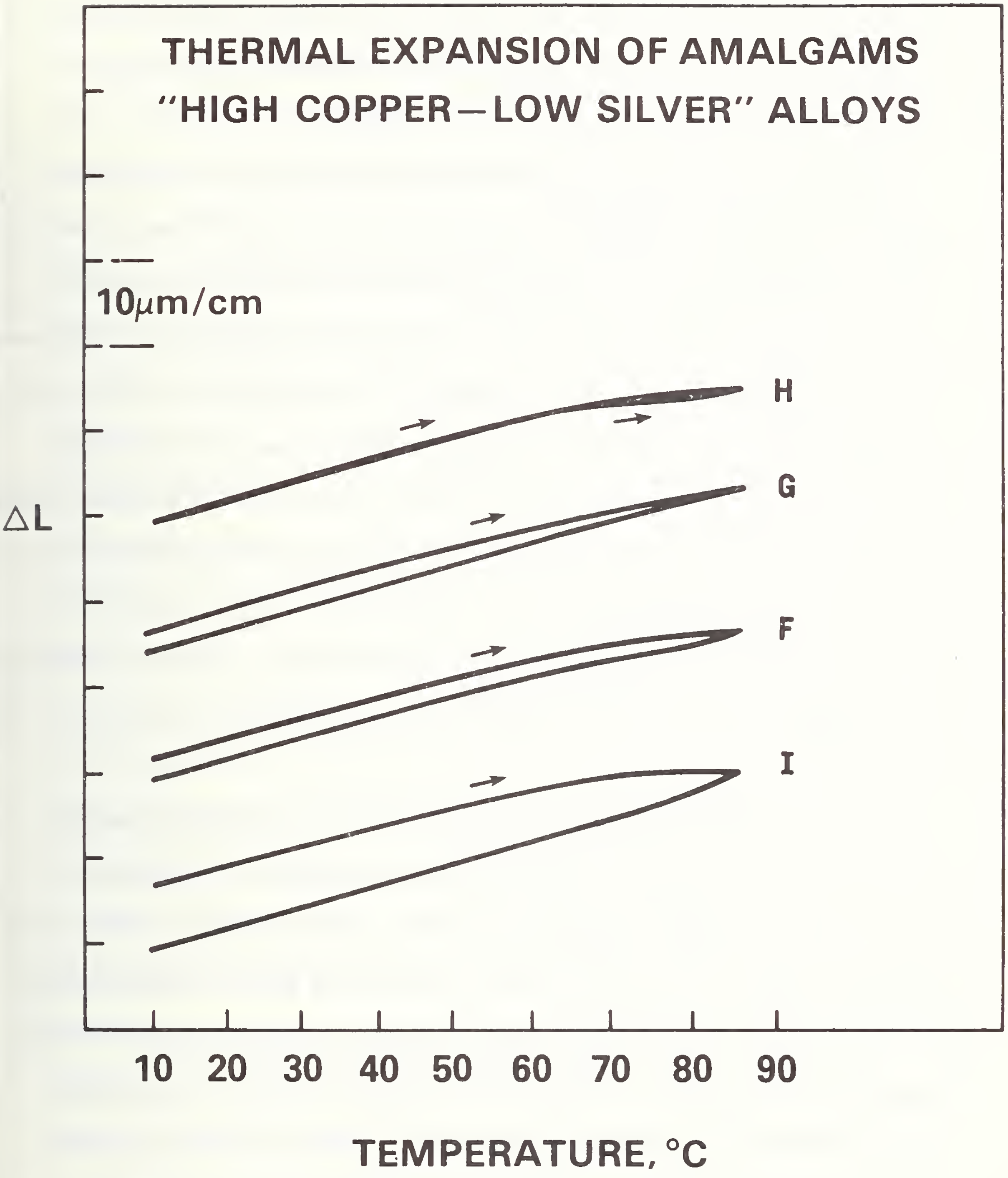


Figure 7: Thermal expansion of amalgams -"high copper-low silver alloys"

exhibited some shrinkage between 60 and 85°C, they show very little irreversible dimensional change. There is no evidence of the abrupt shrinkage at 75°C on heating or of the large expansion on cooling observed near 50°C with the conventional amalgams.

Although differences between the three classes of alloys investigated were readily observed, evaluation of the significance of the results and explanation of the differences in irreversible or time dependent dimensional changes are not so readily accomplished. In regard to those amalgams which begin to show growth near 60°C, the "9% copper" amalgams, it seems reasonable to expect that the same phenomena may occur to some extent in the mouth. On the other hand, dimensional changes that were observed only after heating to near 75°C would appear to be of limited clinical significance. As to the reasons for the differences between the "thermal expansion" curves for the three classes of amalgams investigated, the data were not decisive but do provide some guidance for speculation.

In conventional amalgams reacted at 37°C one generally observes residual particles of the γ phase (Ag_3Sn) in a matrix consisting mainly of the γ_1 phase (Ag_2Hg_3) and some γ_2 phase (Sn_7Hg). The γ phase and the γ_2 phase are reported not to undergo any phase transformations over the temperature range of these experiments and the observed sharp dimensional changes must therefore be accounted for mainly through phase transformations which occur in the γ_1 phase. If the γ_1 phase has the composition Ag_2Hg_3 in the amalgam, then the binary phase diagram predicts the transformation $\gamma_1 \rightarrow \beta$ + Liquid Hg would occur at about 127°C in heating. The γ_1 phase in conventional dental amalgams, however, is known to contain a few percent tin in solution, and this dissolved tin may lower the transformation temperature. The liquid mercury released by this transformation could react with residual γ phase particles in at least two ways;(1) it could dissolve in the γ phase and (2) it could also react with the γ phase to form the β phase ($Ag_{55}Hg_{45}$) which is stable at this temperature, and once formed would remain stable to room temperature unless sufficient liquid mercury remained to produce the reverse reaction β + Liquid Hg $\rightarrow \gamma_1$.

The appearance of the curves for conventional amalgams (Fig. 5) suggests that all of these mechanisms are operating to produce the observed behavior. The sharp decrease in volume occurring at about 75°C on heating is attributed to the $\gamma_1 \rightarrow \beta$ + Liquid Hg transformation occurring at this reduced temperature because of the presence of tin in the γ_1 phase. At this point droplets of mercury can often be seen to form on the surface of the specimen. The newly released mercury dissolving in the γ phase would be expected to produce an expansion above 75°C as seen in the curve of amalgam A. However, if both of these reactions and also the reactions of the liquid mercury with the γ phase to produce the β phase are going on simultaneously, the result might be the shrinkage seen in amalgam B. On cooling the reverse reaction β + Liquid Hg $\rightarrow \gamma_1$ may be responsible for the rather sharp expansion at about 50°C. The liquid mercury droplets disappear from the surface shortly before this expansion occurs (and crystals of γ_2 (Sn_7Hg) are left on the surface).

In the amalgams made from the "9% copper" alloys (Fig. 6) which are low in tin content compared to the conventional alloys, the γ_1 phase may contain sufficient copper to lower the temperature at which the solid state diffusion reaction, $\gamma_1 \rightarrow \beta + Hg$, begins to near 60°C tending to produce shrinkage. If however, at the same time the released mercury is dissolving in the γ phase, this may produce sufficient expansion so that expansion is observed in the curves. The slight shrinkage or reduced rate of expansion at 75°C may result from the equilibrium transformation $\gamma_1 \rightarrow \beta$ Liquid Hg as in the conventional amalgams. On cooling, these reactions continue until the temperature falls to about 60°C. The $\beta + Hg \rightarrow \gamma_1$ transformation cited as responsible for the expansion near 50°C in the "conventional" amalgams, perhaps does not occur in the "9% copper" amalgams because there is not sufficient liquid mercury. In fact, the droplets of liquid observed on the surface of the "conventional" amalgam were not observed on the "9% copper" amalgams.

In the amalgam made from "high copper - low silver" alloys (Fig. 7) the strong tendency toward formation of the compound Cu_6Sn_5 may mean that there is little incorporation of either tin or copper in the γ_1 phase. This phase would then be essentially a a binary Ag_2Hg_3 compound, and the transformation $\gamma_1 \rightarrow \beta + Hg$ would not occur below the equilibrium peritectic reaction temperature of about 127°C. The result would be the retention of the original structure throughout the temperature range of these investigations, and the thermal expansion curves should show no irreversible dimensional changes. This is essentially what is observed in three of the four amalgams of this class.

This work has been reported at the 1977 AADR meeting in Las Vegas.

B. Wear Resistance of Dental Materials

The objective is to assemble and perfect instrumentation and methods for the generation and precise measurement of relative wear of dental materials. Of major concern is the simulation of human masticatory conditions to such an extent that the *in vitro* wear data will be similar to that in the mouth, while reducing the period of years required for clinical evaluation to days or hours in the laboratory.

To further the attainment of this objective, the design and construction of a new device for measuring the wear resistance of dental materials was completed. The earlier wear machine designed and used in our laboratory demonstrated highly satisfactory wear generating characteristics [29], but had two disadvantages. First, it was a single-specimen machine on which not more than one specimen could be run each day; and thus an extensive period of time was required to obtain data on a sufficient number of specimens. Second, the data acquisition system assembled from components then available was subject to frequent malfunction with attendant loss of data necessitating preparation and running of additional specimens. The new wear apparatus was designed to overcome these difficulties and at the same time retain the wear generating characteristics of the previous device. In both the old and the new device, the design is of the classic pin-on-disk configuration. It incorporates a stabilized turntable which carries the specimen mounting cup. The pin, or enamel slider, is a round cylinder of enamel and underlying dentin and is suspended in a mounting cup from a vertically displaceable arm. The flat face of the slider rests on the flat of the restorative disk, with the center of the slider 6 mm off center of the disk. The arm is loaded to establish a stress of 1 kg/mm^2 (approx. 10 MPa) at contact between the members of the wear couple. A continuous stream of water lubricates the specimen. The rotation of the specimen produces an annular wear tract with a width of 1.5 to 2.0 mm and diameter of approximately 12 mm. The specimen rotates at 27 rpm, which gives a sliding speed of 1.7 cm/s. Wear is determined by intermittent measurement of the depth of the wear track.

To overcome one of the disadvantages of the previous apparatus, the new machine (Figs. 8,9,10) is a multispecimen device with three wear stations thus greatly reducing the time required for evaluation of a material. The mechanical features include higher tolerance bearing systems, greater horizontal rigidity in slider carrier arms and a direct gear drive to all turntables so aligned as to use gear thrust to maintain a good bearing seating force. Preliminary tests of the new device indicate it to be very stable and vibration free.

To overcome problems in data collection, the new device has a completely redesigned and much more sophisticated and versatile control system combined with a data acquisition system of high reliability. Data are automatically printed out at regular intervals during a run and are also recorded on magnetic tape for processing by computer.

All ancillary functions for the wear generator are electrically powered (LVDT lift, water solenoid, measurement stepping, etc.) as opposed to pneumatic and mechanical means used on the earlier testing device. As a result, all of these functions operate reliably under full program control. The new control circuitry has been designed so

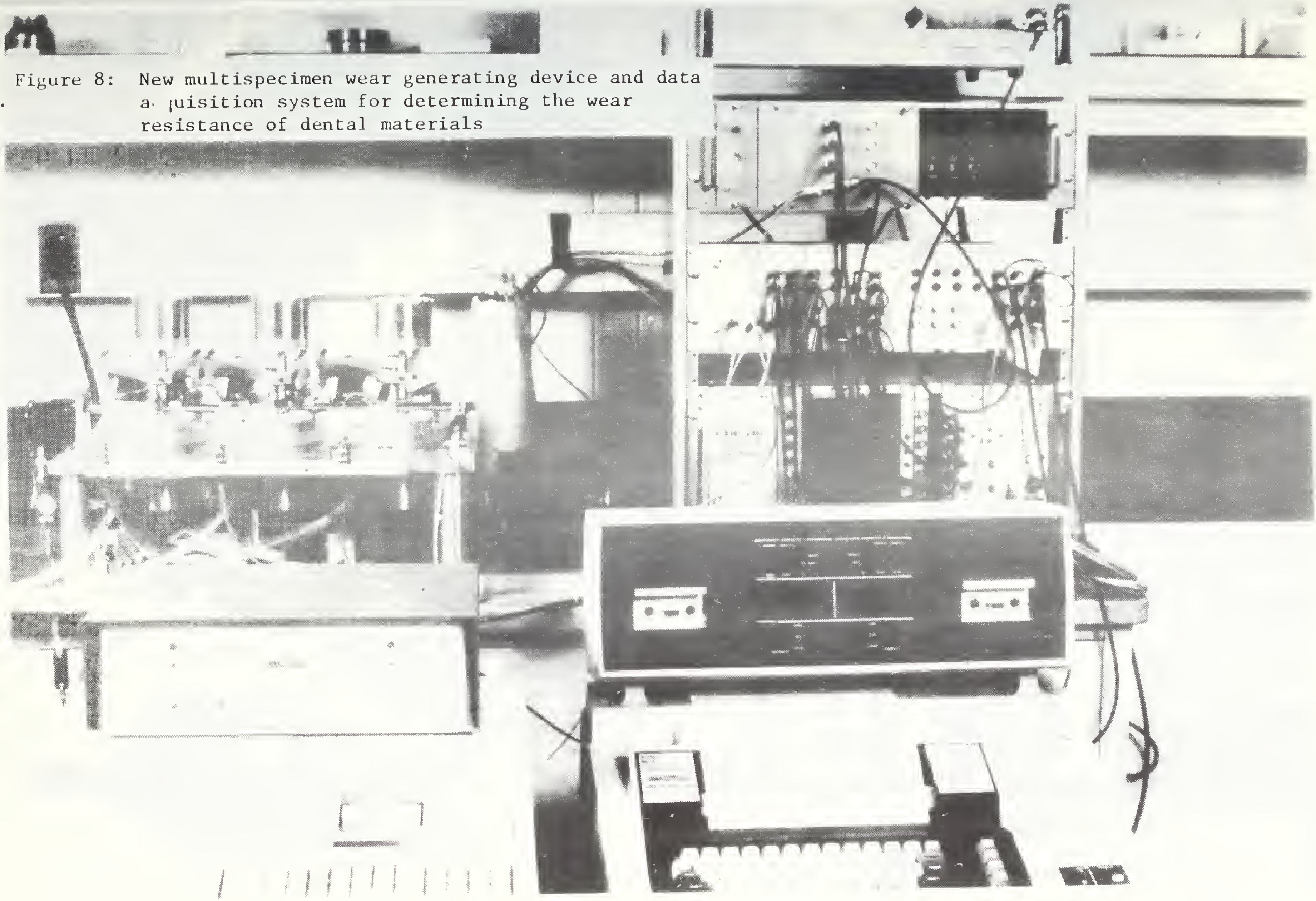
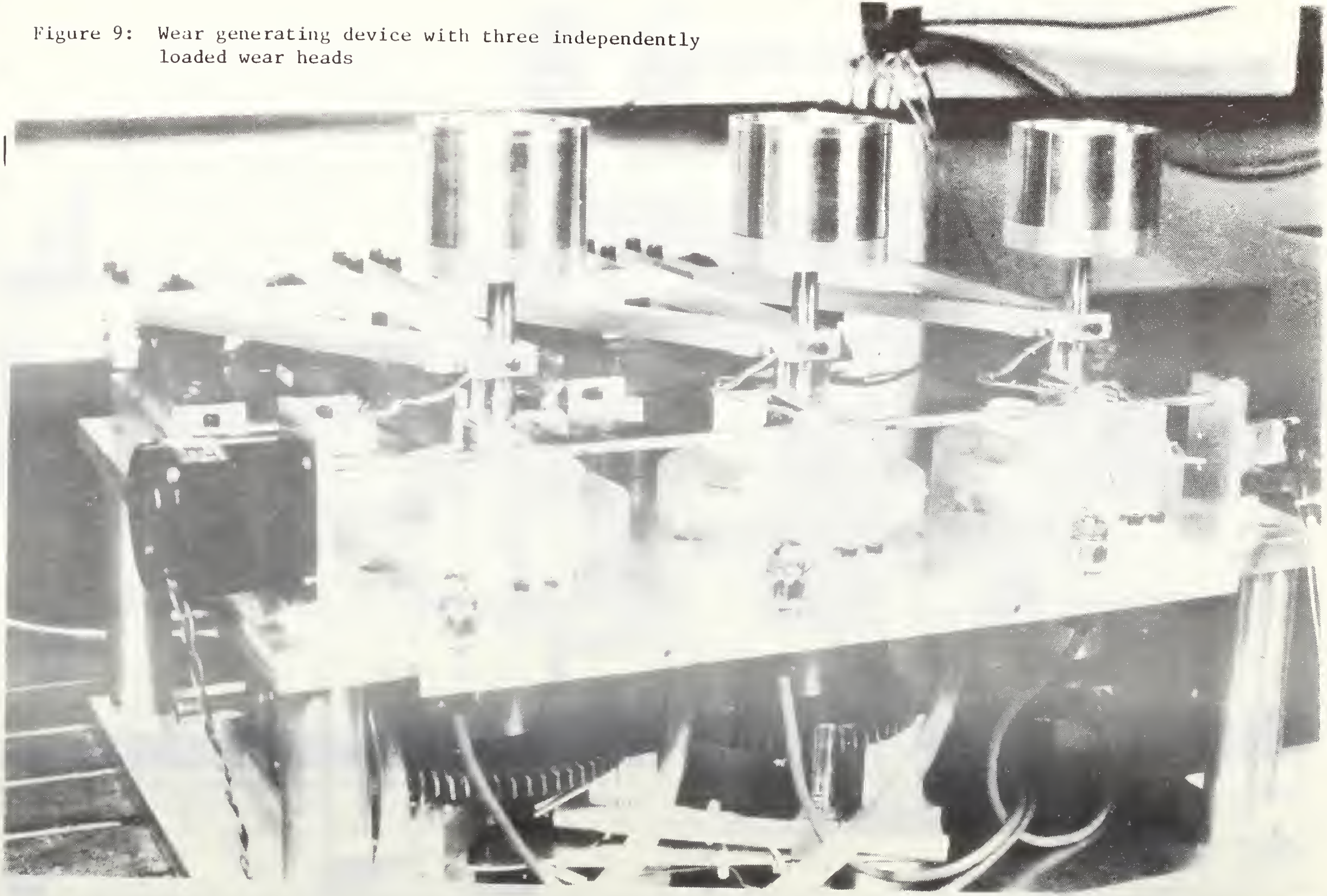


Figure 8: New multispecimen wear generating device and data acquisition system for determining the wear resistance of dental materials

Figure 9: Wear generating device with three independently loaded wear heads



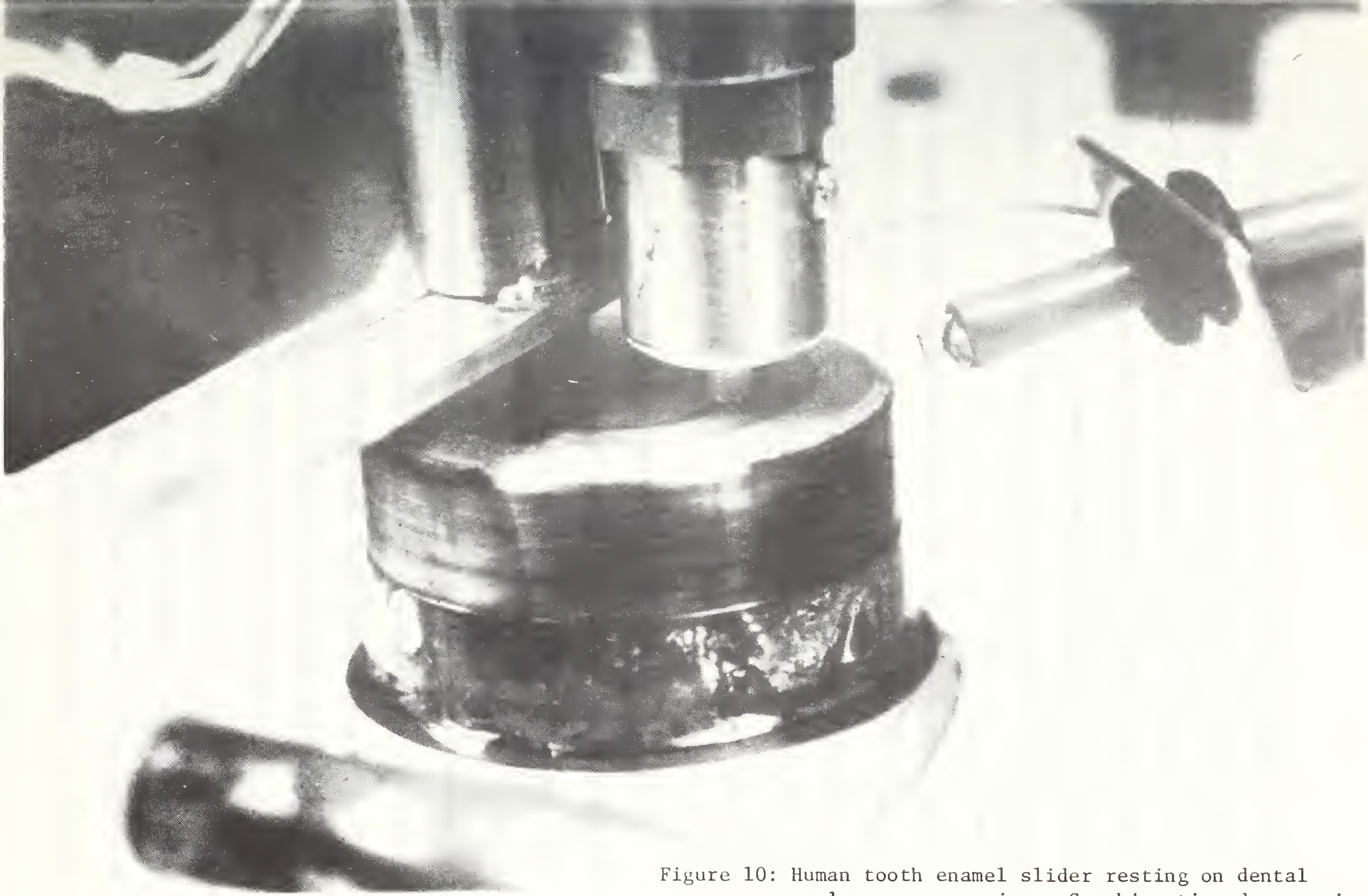


Figure 10: Human tooth enamel slider resting on dental amalgam wear specimen. Sapphire tipped measuring probes are beneath the LVDT on the left side of the specimen. During operation the nozzle on the right directs a jet of water on to the specimen

that all LVDT scanning functions are handled by solid-state switching, reducing the noise experienced previously. The digital voltmeter has been factory-modified so that measured values shown in the display register are passed directly through the BCD output to the printer instead of running one measurement behind as is common in many of these systems. This feature greatly reduces complexity of program assembly.

The data acquisition and control system has responded well to debugging. Programming is at present being done by repetitive magnetic tape command while awaiting a program module from the manufacturer. This module is the final piece of equipment needed for full utilization of the system. Until delivery of the programmer, work will continue by means of tape program control.

From preliminary reliability tests, the improved design of the fully automated instrument appears to have overcome all of the problems experienced in this area with the single specimen prototype device. Repeated measurements on non-wearing surfaces show that the instrument is capable of measuring to a level of ±0.7-0.8 micrometers when operated in circulating air whose temperature varies approximately ±2°C. It is anticipated that the instrument accuracy will be improved to ±0.3-0.4 micrometers in a more stabilized environment.

It is anticipated that newly acquired wear data will show an even more significant difference between classes of direct restorative materials and at a higher confidence level than was shown with the prototype single specimen device. Early results obtained with the new apparatus indicate that one source of variability in this recorded data previously obtained may be the adhesion of small amounts of wear debris to the surface of the contact probes used to measure wear track depth. During the time it is on the probe, the debris causes a false indication of reduced or negative wear as shown in Fig. 11 which is a plot of data for a short trial run on three amalgam specimens. The low points in two of the curves (at 260 and 340 minutes respectively) are apparently the result of gradual buildup of wear debris on the surface of the sapphire probes followed by rapid release of the debris. In order to prevent such irregularities, the measurement sequence is being changed to eliminate rubbing contact between measurement probes and specimens. Such changes are relatively easy on the new apparatus since they can be accomplished to a large extent by programming changes with a minimum of hardware alternations. The programmer now on order will further improve the versatility of the apparatus in this respect.

The first phase of testing with the new wear appartus will be directed to all types of amalgam alloys and composite restorative materials available to the practicing dentist. This phase of testing commercially available materials will be undertaken before the wear evaluation of experimental materials in order to build sufficient background data against which future developments can be compared. Such background data will serve another important purpose: that of test method simplification where needed. Also comparison of the wear resistance of these materials to their individual component makeup should provide highly pertinent data to dental manufacturers as a guide in formulation of improved materials.

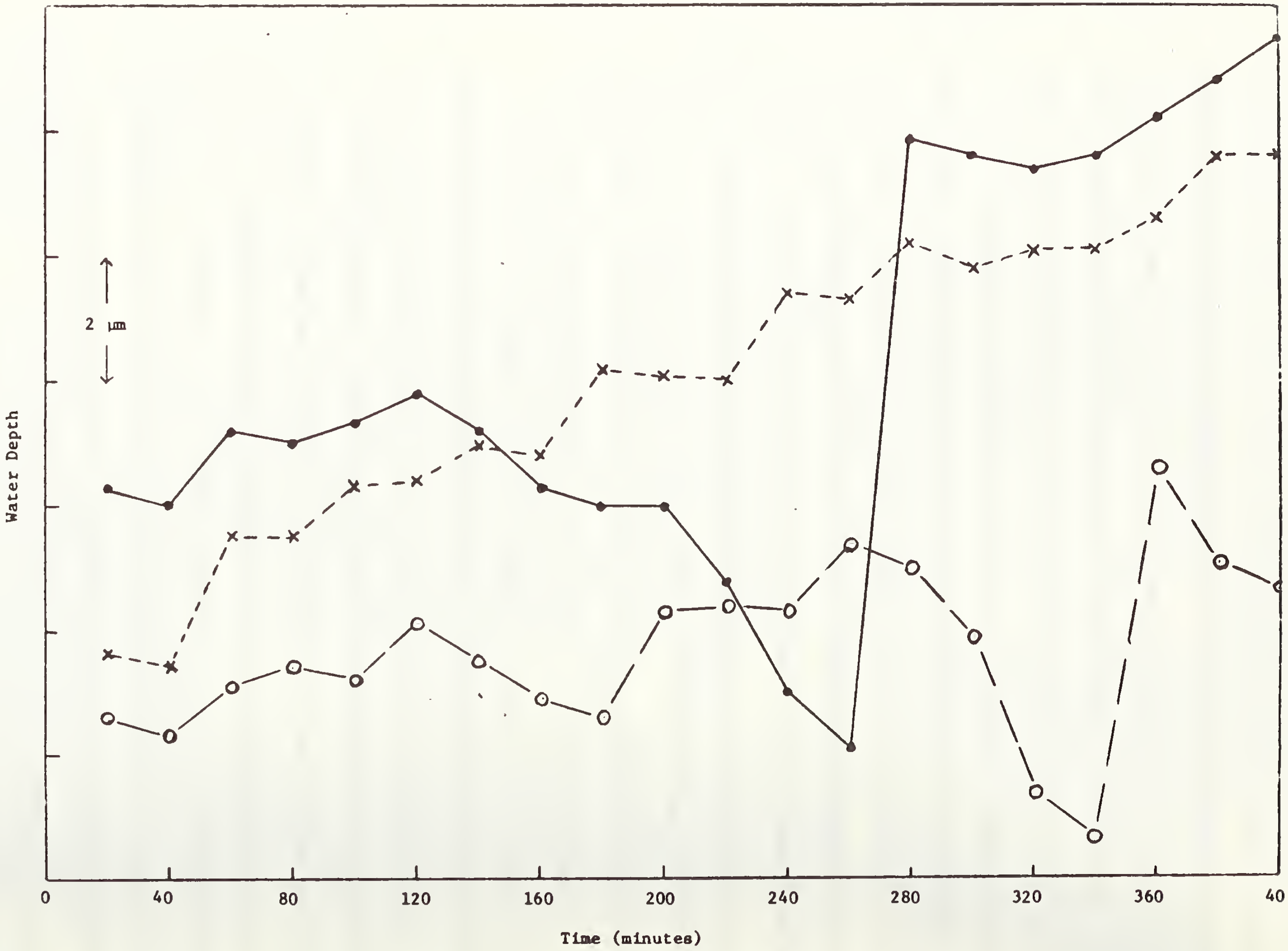


Figure 11: Example of problem encountered in preliminary trials. The low points on the "wear" curves at 260 and 340 minutes are artifacts produced by the build up of wear debris

As has been stated in earlier reports, perhaps the single most difficult phase of the wear measurement procedure is the preparation of human tooth enamel pins or sliders. Some priority must therefore be given to investigation of an enamel substitute in the wear couple.

In their work on characterization of surface failure of non-metallic single crystals under sliding, Powers and Craig [30] used large crystals of natural fluorapetite to attempt to identify the wear phenomenon of enamel. Both natural and synthetic fluorapatite crystals are available commercially and if comparable to enamel in wear response and effect would be a readily obtainable and easily managed substitute for slider heads used in this test method. Consideration should also be given to the sintered hydroxyapatite recently proposed by Rootare, Powers and Craig [31] for use in wear studies.

Other materials that may need to be considered are th ultra-high tensile strength fibers or whiskers of boron, carbon and glass, as a high pack density filler in a matrix of Bis-GMA, epoxy or other high strength resin. Any of the aforementioned substitute materials which produce wear values on the background data restorative materials comparable to that obtained with human enamel on level of significance of 95% or better could be considered acceptable.

C. Base Metal Alloy and Investment Research

The objectives of the research on base metal alloys and investments have been to determine the characteristics of these materials relating to the serviceability of the alloys for use in cast crowns and bridges, to determine the effect of fabrication techniques on the properties of the castings, and to utilize this information for the development of

Ni-Cr crown and bridge alloys. Each manufacturer, using the investment and technique of his choice prepared castings for our evaluation. These castings were prepared from Ni-Cr based alloys and also from various noble metal alloys; nine castings were made for each alloy examined:

Jelenko:	Jelenko-0*	98% Noble
	Cameo*	80% Noble
	Midas**	52% Noble
	Jel-Bon*	Ni-Cr
Howmedica:	Microbond #2*	98% Noble
	A-6**	78% Noble
	Microbond NP$_2$*	Ni-Cr
J. M. Ney Co.	SMG-W*	81% Noble
	Ney-Oro B-2**	78% Noble
	Neydium*	Ni-Cr
Johnson & Johnson Dental Products Div.	Bak-on-Yellow*	98% Noble
	Ceramalloy*	Ni-Cr

* Crown and bridge alloy for porcelain bonding

** Crown and bridge alloy not for porcelain bonding, Type III Gold or Type III Substitutes

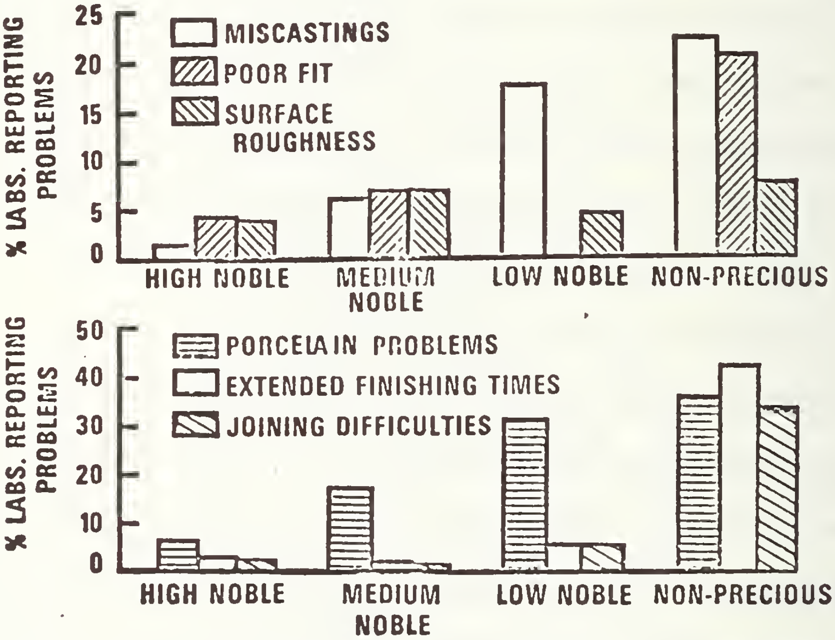


Figure 12: Problems encountered during fabrication with various ceramic alloys

improved techniques and to provide guidance for the development of improved alloys.

A comprehensive survey of the 3044 member laboratories of the National Association of Dental Laboratories (NADL) conducted by a Research Associate in this laboratory sponsored by NADL has revealed that 25% of all crown and bridge units fabricated by these laboratories are cast from Ni-Cr alloys. Although the Ni-Cr alloys have gained wide acceptance because of their lower cost, reporting laboratories list significant problem areas:

Miscastings	22% of Reporting Labs
Poor Fit	21% of Reporting Labs
Porcelain Problems	39% of Reporting Labs
Extended Finishing Times	45% of Reporting Labs
Soldering and Joining Problems	38% of Reporting Labs

As seen in Fig. 12 there appears to be a strong negative correlation between total noble metal content and the degree of difficulties experienced during fabrication of porcelain bonded to metal restorations.

1. Fit of Porcelain Fused to Metal Crown and Bridge Castings

Our most extensive work has been in the area of casting accuracy and castability. As noted in last year's report, the phosphate bonded investments necessary for use with the high melting porcelain bonding alloys are "technique sensitive." This technique sensitivity leads to castings which are generally undersize when made by us from Ni-Cr alloys using the instructions supplied by the investment manufacturer or the metal manufacturer. We have verified these "in house" experimental results through visits to major manufacturers of

Each manufacturer was asked to prepare castings from at least one gold based alloy, and a non-precious Ni-Cr alloy. Both categories have the same end use in the dental profession: metal substructures to which porcelain is bonded to produce functional and esthetic extracoronal restorations.

a. Methods and Materials

(1) Die

A hardened stainless steel die with dimensions approximating an upper anterior crown preparation (Fig. 13, Part 1) was used for wax pattern construction and casting size determinations. The surface of the die which contacted the pattern was a truncated cone with base diameter of 5.0 mm, height of 6.0 mm and an included angle of 5.7° (taper is 10%). This taper is within the critical range recommended for retention of clinical castings.

(2) Patterns and Sprue

Nearly invariant wax patterns[1] with a wall thickness of 1.0 mm were constructed using the total die assembly (Fig. 13). An amount of Kerr's[2] regular inlay wax slightly in excess of that needed for the pattern was warmed for 5 minutes along with the

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[1] $\frac{\text{std. dev. of wax pattern diameter } (n = 9)}{5.00 \text{ mm design diameter}} \times 100 = 0.02\%$

[2] Kerr Manufacturing Co., Romulus, Mich.

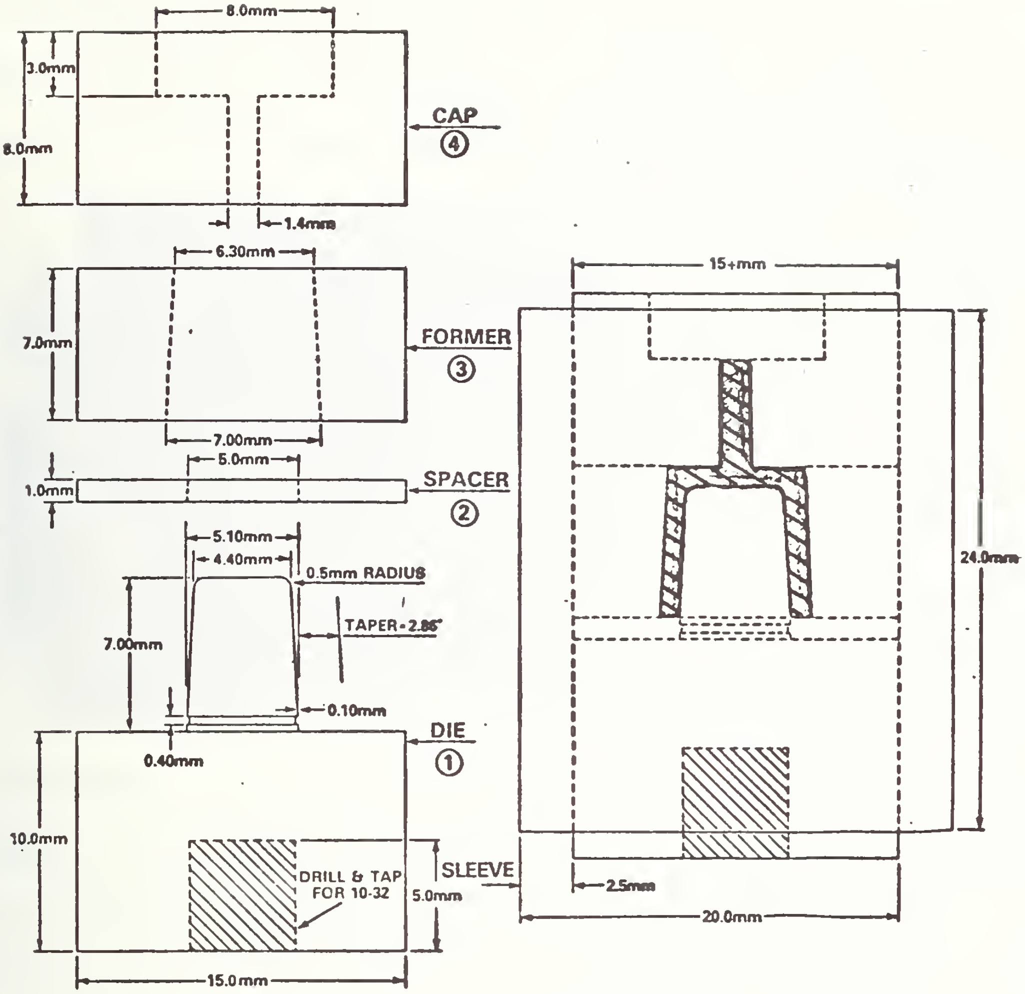

Figure 13: Die used for wax pattern construction and casting size determination

lightly lubricated[3] die assembly in an oven held at 50°C. The wax was placed in the former (Part 3) and all parts fitted into the sleeve. The sleeve aligned assembly was then compressed and held in a tightly closed bench vise at ambient room temperature (23 ± 1.5°C) for one minute. The vise pressure on the softened wax caused extrusion of excess wax through the 1.4 mm diameter vent in the cap (Part 1) and created a wax flash between the former (Part 3) and the spacer (Part 2). The assembly was removed from the vise, placed in room temperature water for two minutes, dried and the pattern removed from the die. The pattern was trimmed of flash, replaced on the die, rewarmed, repressed, and brought to room temperature in a water bath as described above. The second pressing frequently allowed metal to metal contact of the die parts, produced minimal flash at the pattern base and increased uniformity in wall thickness of the pattern. The stress relieved, annealed pattern was examined for defects and a 10 gauge hollow plastic sprue with a 6 mm diameter reservoir[4] located 1.5 mm from the point of attachment was luted to the center of the occusal surface of the pattern (Fig. 14).

(3) Mold Lining Material

The effects of restrictive stresses on setting, hygroscopic, and thermal expansion of typical phosphate and gypsum

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[3] # 4 compound, Dow Corning Corp., Midland, Mich.

[4] E-S Sprue Pins, Surgident Ltd., Los Angeles, CA

PRESSED WAX PATTERN

PRESSED WAX PATTERN, SPRUE, & CRUCIBLE FORMER

PRESSED WAX PATTERN CLOSE UP

Figure 14: Pressed wax pattern, sprue and crucible former

investments have been well reported. Minor restraint suppresses mold expansion markedly during hygroscopic set and to a lesser extent during thermal expansion of both investments. To minimize restraint and provide for greater mold expansion, the standard liner condition employed for castings prepared at NBS utilized two layers of asbestos (Table 12).

To further increase mold expansion by reducing restraint against the setting phosphate investment, 40 mil. (1.02 mm) or 80 mil. (2.03 mm) thick strips of highly resilient spun kaolin refractory furnace liner[5] were substituted for the stiffer and less yielding asbestos strips as mold liners. The Kaowool, cut in strips 4.1 cm wide, was used in the same fashion as asbestos. One strip of 40 mil. (1.02 mm) thick Kaowool was dimensionally equivalent to a double thickness (2 x 0.6 mm = 1.2 mm) of asbestos.

(4) Investing, Burnout and Casting

Manufacturers' technical personnel prepared several series of castings from patterns made on site by us. Each manufacturer was instructed to choose the conditions and techniques used with his alloys so that full size castings would result. Die assemblies had been supplied in advance to allow practice with the particular pattern configuration used in the test series. Using the same alloys

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[5] Kaowool, Babcock and Wilcox, Refractories Div., Augusta, GA.

Table 12

CASTING DETAILS

Casting Ring	Whipmix[*]	31.8 mm x 47.6 mm (1-1/4"x1-7/8") Pyronel
Asbestos	Whipmix[*]	41.3 mm x 0.8 mm (1-5/8" x 1/32") 2 layers, dry
Investment	Whipmix[*]	Ceramigold[*]
Liquid/Powder Ratio	16cc/100 g	Undiluted Investment Liquid
Spatulation	By hand-1 min.	(120 spatulations/min.)
Setting time before casting	45 min. 38°C (100°F) Hygrobath[*] followed by overnight bench set	
Burnout	1 h to 816°C (1500°F), 1 h heat soak at 816°C (1500°F)	
Placement of Ring in Casting Machine[**]	5 to 10 s before metal filled the mold cavity	

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[*] Whipmix Corp., Louisville, KY.

[**] Electromat-Howmedica Corp., Chicago, IL.

at NBS, we prepared comparable series of castings but used uniform mold conditions (Table 12) so that possible differences in casting size between alloys might be detected.

(5) Devesting and Surface Preparation

The hot casting rings were bench cooled to room temperature and the cylinder of investment pressed from the ring. The investment cylinder was cleaved along its axis and the casting lifted free. Adherent investment was removed from the casting with 50 µm alumina using an air abrasive unit with an operating pressure of 80 psi (0.55 MPa).

Bubbles and other irregularities characteristic of the surface of the phosphate investment mold were removed before measuring the casting. The casting was placed on the hardened steel die with moderate finger pressure and rotated. This produced shiny spots on the bearing surface of the casting which were easily identified under 5x magnification and removed with a #2 round bur. The process was repeated several times or until smeared areas of metal to metal contact indicated that isolated nodules or bubbles were not interfering with further seating of the casting. The bubbles and nodules were removed individually without wholesale grinding or machining of the casting surface. The hardened steel die surface was not abraded by this procedure.

(6) Measurement of Patterns and Castings

Completed patterns were placed on the die with the spacer (Fig. 13, Part 2) removed. Using a measuring microscope graduated to .00254 mm (0.0001 inch) the distance between the pattern base and the die base was measured at 120° intervals around the circumference of the pattern. The mean of the three measurements established the reference position of the seated pattern. The completed casting, with the top of any oversize casting removed to permit seating, was placed on the same die with 5 Kg of force and the distance between the casting base and die base measured as above. Because of the 10% taper of the die the displacement of the casting relative to the reference position of the pattern was equal to ten times the diametral change in an undistorted casting necessary to produce the measured displacement. Percent change in diameter of the base of the casting relative to the 5.0 mm diameter of the pattern from which it was made is given as the value of percent oversize or undersize of the casting.

All six series of precious PFM[*] alloy castings were oversize with the four high noble metal content (>90%) alloys slightly more oversize on average (+0.51%) than the two medium noble metal content (80%) alloys (+0.33%). All five series of Ni-Cr alloy castings were undersize (-0.31%) on average) and were smaller by 0.76% than the average of the six precious PFM alloys (+0.45%). Of the three Type III/Type III substitutes, all of which were cast into the same brand of gypsum investment, one series was oversize (+0.47%) and two (; Figure 15) were undersize (-0.41% and -0.76%). The -0.76% undersize Howmedica A-6 series had an extremely high standard deviation with individual casting size extremes of -2.67% and +0.91%.

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[*] Porcelain fused to metal.

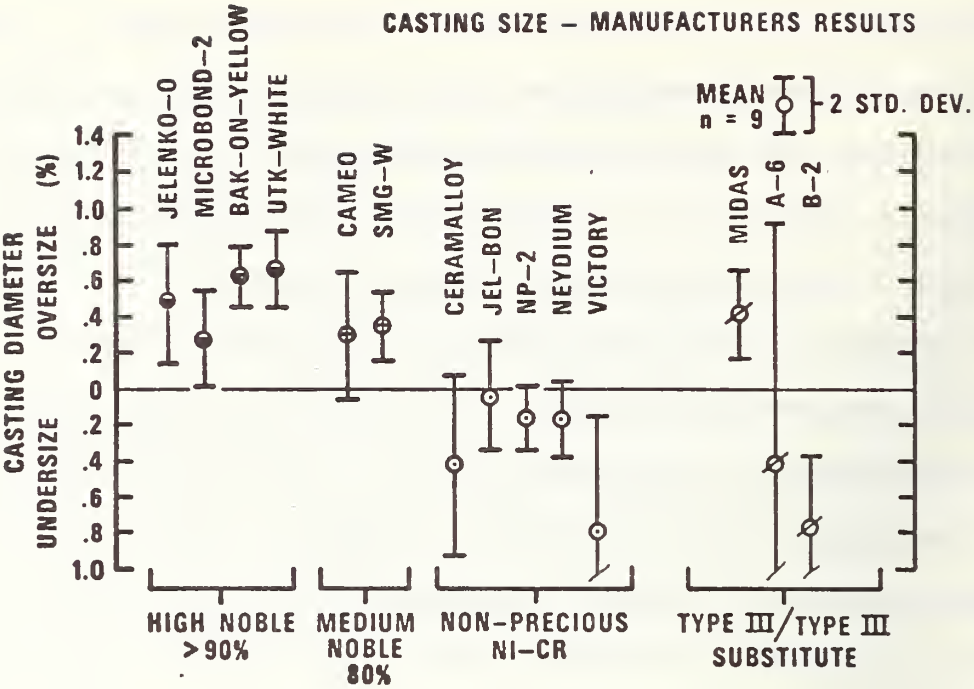

Figure 15: Casting size as a function of alloy type - manufacturer's results

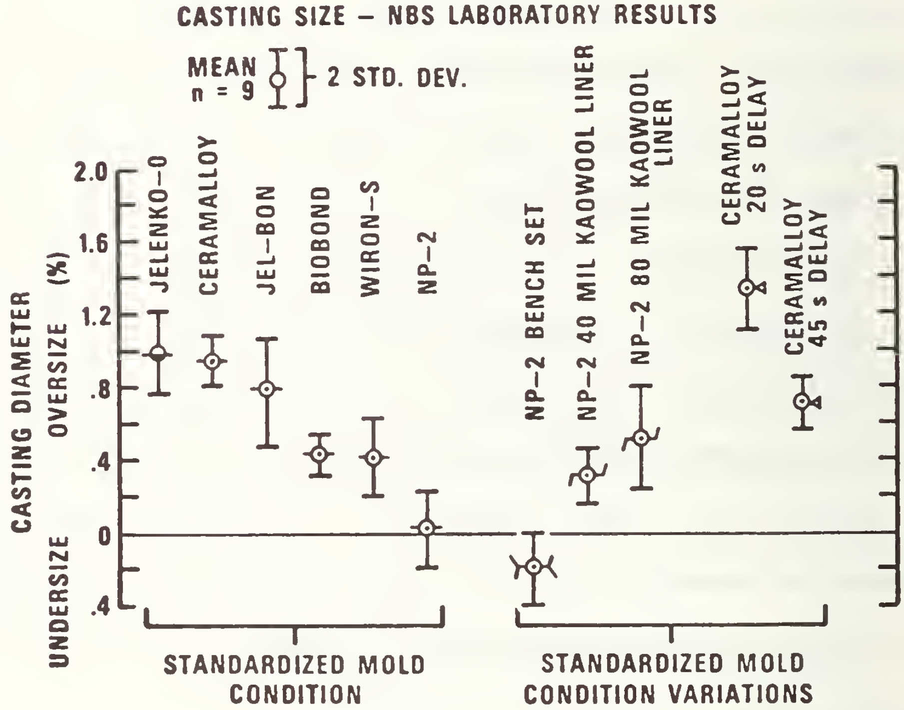

Figure 16: Casting size as a function of alloy type - NBS laboratory results

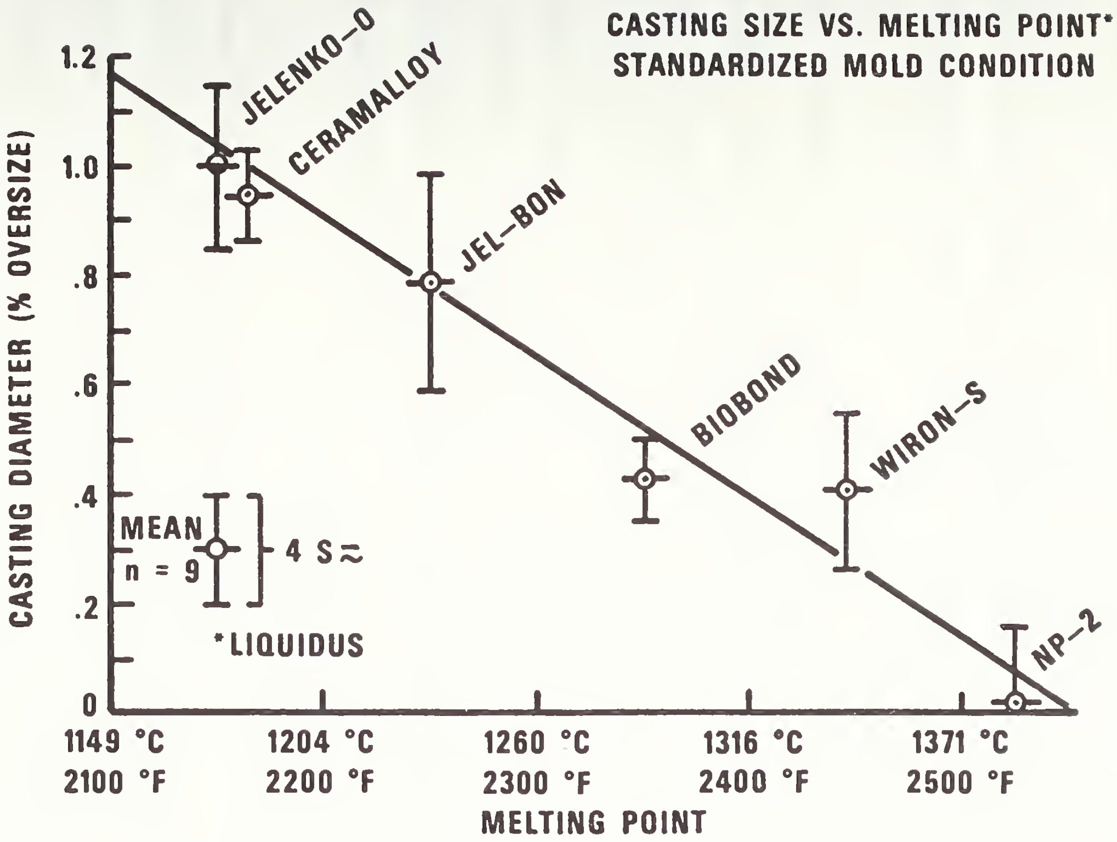

Figure 17: Casting size as a function of melting temperature

All six casting series made in our laboratory with the standardized mold technique (Fig. 16) were oversize with a range of +0.02% oversize for Howmedica NP-2 to 1.00% oversize for Jelenko O. The significant differences in degree of oversize were related to the melting points (liquidus) of the alloys. The least squares line in Fig. 17 shows the relationship of casting size to melting temperature for this mold condition. Degree of oversize decreased linearly with increasing melting point (liquidus) nearly 1.0% over a temperature range of 222°C (400°F).

Substituting Kaowool for the asbestos liner and with all other mold and melting conditions held constant resulted in increase in the mean size of NP-2 castings from +0.02% for a dry, double asbestos liner to +0.31% for a 40 mil. thickness Kaowool liner and to +0.52% for an 80 mil thickness liner (Fig. 16). Bench setting of the investment ring at ambient room temperature (23 ± 1.5°C) resulted in a reduction in mean size of NP-2 castings to -0.19% as compared to a mean size of +0.02% when the investment rings were allowed to set in the 38°C (100°F) waterbath (Fig. 16).

Ceramalloy castings made using the standardized method for this study in which the casting ring was removed from the 816°C burnout even just 5 to 10 seconds before molten metal entered the mold cavity were on average 0.95% oversize. Preliminary data show that increasing the casting delay time to 20 seconds was accompanied by an increase in mean size of Ceramalloy castings to +1.34%. Further increase in the casting delay time to 45 seconds was accompanied by a decrease in mean size of Ceramalloy castings to +0.72%.

c. Discussion

The inability to produce full size base metal (NiCr) castings is apparently a universal problem. Twenty percent of the laboratories responding to the survey on C & B alloys reported problems of fit when using Ni-Cr alloys while only 5% reported problems of fit when using precious PFM alloys (including alloys with total precious metal content of 70 to 90% and Pd-Ag alloys). Cooperating manufacturers in this study, without exception, produced undersize Ni-Cr PFM castings when they used laboratory techniques and investments of their choice to optimize results. The same manufacturers, without exception, produced oversize precious PFM castings again using laboratory techniques and investments of their choice. This consistent difference in casting size between the two alloy types under a wide variety of laboratory techniques could discourage use of Ni-Cr alloys for those operators unwilling to use shims or die coats (of questionable accuracy) or to machine out the interior of undersize castings to permit seating and cementation.

The technique modification involving hand spatulation, dry asbestos, and hygroscopic expansion described here (Table 13) provides sufficient expansion for one phosphate bonded investment at least, to permit fabrication of oversize Ni-Cr castings. The results are for one size, shape and composition of wax pattern but the general trends observed here can be expected to occur although influenced by these variables in castings made from patterns of other sizes and shapes. The reasons for the greater size mold cavity using this technique are not obvious, however it is felt that the use of relatively high energy mixing, such as results from using the blade

Table 13

MODIFIED TECHNIQUE FOR INCREASED EXPANSION (CERAMIGOLD INVESTMENT)

Requirements:

1. L/P ratio: 16/100
2. Dry asbestos: 2 layers
3. Hand spatulation: 1 min. (120 spat./min.)
4. Vibrate mix, flex bowl: 30 sec
5. Invest pattern
6. Hygroscopic set: 38°C, 45 min.
7. Overnight bench set

type Whip-Mix Vacuspat, may interfere with the full expansion potential of the bonded investment by accelerating the setting reaction. Additionally, the use of dry asbestos which neither perfectly adapts to the casting ring nor becomes reduced in thickness (as does wet asbestos when light finger pressure is used) in adapting the liner to the ring may be an important factor in increasing mold expansion. Our measurements indicated that the thickness of two layers of dry asbestos as used in this study was approximately 20% greater than that of two layers of the same asbestos wetted and lightly adapted to the casting ring.

The linear relationship between the melting temperature (liquidus) and the degree of oversize of castings is well supported by this study. This relationship would be expected. The coefficients of thermal expansion of the various PFM alloys must be approximately equivalent to provide compatibility with bonded porcelain veneers. It follows that high melting alloys which have a greater thermal differential between solidification and room temperature must exhibit greater casting shrinkages than alloys with lower melting points. A more complete explanation of the correlation between melting temperature and casting size would take account of the facts that:

1. None of the alloys examined is either a pure metal or of eutectic composition so that each of the alloys has a melting range (the temperature interval between the liquidus and solidus which was 26°C to 111°C for PFM alloys in the study).

2. The initial shape of the casting is determined somewhere between the liquidus and solidus temperatures where the growing dentrites interlock, become fixed in relation to one another and prevent further feeding from the sprue (riser) which still remains liquid.

3. Plastic deformation of the metal casting will occur until that temperature is reached at which the yield strength of the cooling metal is great enough to deform the investment.

The internal restraint to investment expansion in the casting ring may be reduced by the use of more resilient liners such as Kaowool, with consequent increase in casting size. This is critically important for high melting alloys such as Howmedical NP_2 which produced significantly smaller castings under the constant mold conditions employed than those Ni-Cr alloys and precious metal alloys with substantially lower melting temperatures.

The preliminary data for casting time delay indicate that allowing the hot casting ring to rest in the cradle of the centrifugal casting machine for 20 seconds before filling the mold cavity may further increase casting size. This paradoxical result which seems to be at variance with sensible physical reasoning is reported primarily for completeness sake but also to stimulate interest in a possibly important variable of casting production. The casting time delay of 45 seconds resulted in a decrease in casting size of 0.23% (Ceramalloy + .95% oversize for 5-10 second delay versus Ceramalloy + 0.72% oversize for 45 second delay). The investment mold cavity would be expected to be somewhat smaller after 45 seconds exposure to room temperature environment. Also the metal casting ring which is approximately 1.2% greater in diameter at the burnout temperature of 816°C than at room temperature (22°C) decreases about 0.1% in diameter for each 56°C drop in temperature[**]. The highly conductive metal casting ring would chill relatively more rapidly and might possibly exert a constrictive effect on the investment.

The non-uniformity of casting size determinations for Type III/Type III substitutes was not expected but reflects the variability in casting accuracy possible with accepted reliable materials which reportedly may be as great as 1% within a given technique for a single operator. The emphasis in this study was on fit of PFM alloys with the Type III alloys included only for comparison since casting accuracy for this type of alloy had already been well reported. It is probable that all three of the Type III alloys, which have equivalent melting temperatures, could have been cast equally oversize with available investing techniques that take account of both wax strength and pattern shape.

[**] Manufacturers Data.

d. Summary

1. The results of this study show that Ni-Cr castings produced in manufacturers' laboratories were consistently undersize and corroborate dental laboratory reports which identify fit of Ni-Cr PFM castings as a significant problem area.

2. A modified investing technique which involves hand mixing of investment and the use of more resilient and thicker ring liners permitted routine fabrication of oversize castings from a wide range of Ni-Cr alloys.

3. Casting size was dependent on melting point of the alloy with casting diameter decreasing lineraly with increasing melting point under fixed mold conditions.

2. Test for Castability of Dental Alloys

In a project carried out largely with Armed Forces Defense Personnel Support Center funding, U.S. Navy Research Associates and an NBS physicist and technician supported on NIDR funding, a procedure for determining the castability of either Ni-Cr or gold alloys has been developed.

Castings are made from a pattern constructed from No. 18 mesh (1.00 mm) polyester sieve cloth. This provides a grid of 100 open squares and 210 segments where a segment is defined as the part of a sieve filament connecting two adjacent parallel filaments. Determination of the percentage of complete squares or segments in a metal specimen cast from this pattern alloys a numerical value for "castability" to be assigned to the casting, and permits a quantitative definition of castability for a particular alloy under specified casting conditions. Preliminary castability data show Ni-Cr alloys to be more sensitive to the amount of superheat (temperature elevation above the melting temperature) at which the alloy is cast than are the gold based Type III alloys. Far greater amounts of superheat were necessary for the Ni-Cr alloy (Fig. 18) than for the gold based Type III alloy (Fig. 19) to obtain nearly equal castability values. Castability values for Type III gold alloys were significantly higher when these alloys were cast into gypsum molds burned out at 650°C (thermal expansion technique) than when cast into molds burned out at 480°C (hygroscopic technique).

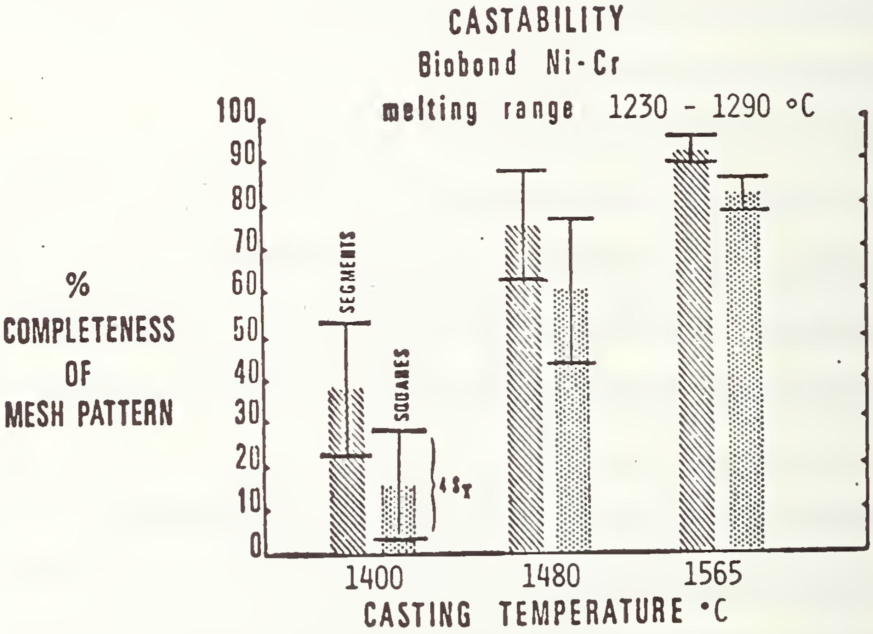

Figure 18: Castability test results for one Ni-Cr alloy as a function of casting temperature

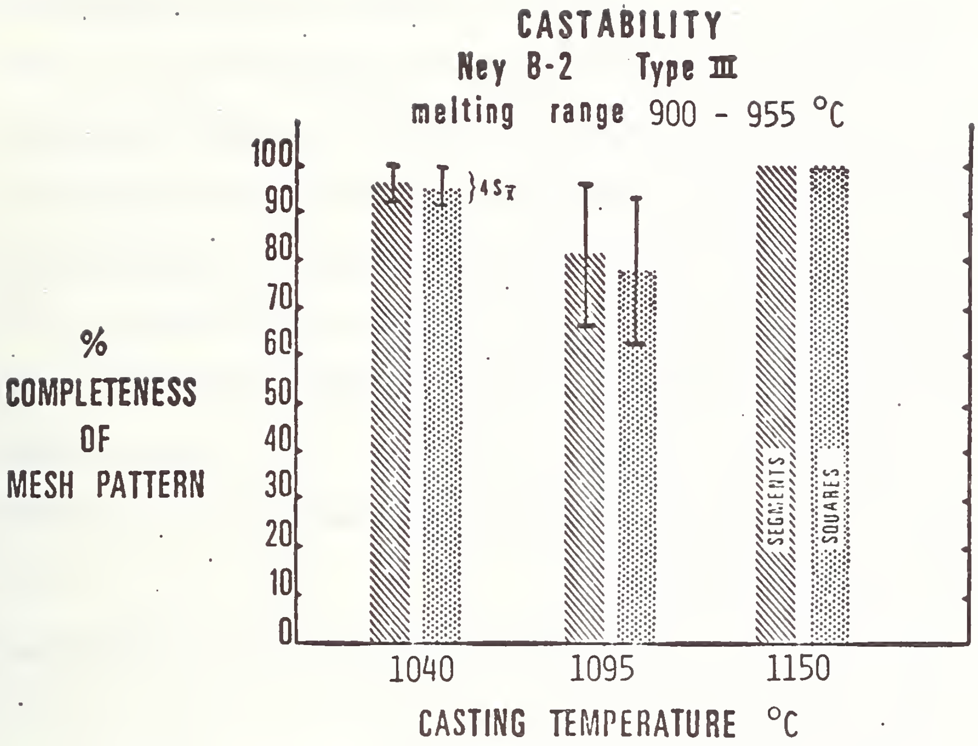

Figure 19: Castability test results for one gold based type III alloy as a function of casting temperature

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15. SUPPLEMENTARY NOTES

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.)*

Previous encouraging results with titanium and silicone based coating agents for coupling dental resins to tooth surfaces have been reinforced with accelerated aging data. Accelerated aging data for bone bonded to bone specimens indicates that a visc isoamyl cement may be worthy of clinical evaluation. Procedures for synthesis and purification of crystallizable aromatic aldehyde dimethacrylates are given. These highly purifiable materials offer promise as adhesion promoters through reaction with collagen and may have utility as diluent comonomers with Bis-GMA in composites or sealants. The feasibility of generating free radical induced polymerization of dental resins by using more thermally stable organic peresters or hydroperoxides and an ascor bic acid ester has been demonstrated. Design, assembly and debugging of a new multi-specimen wear instrument has been completed. Judging by their thermal expansion characteristics, high copper type amalgams show little or no evidence of phase changes at temperatures less than 90°C. The technique sensitivity of the higher melting non-precious procelain bonding alloys has been demonstrated by examining quantitatively the goodness of fit attained by manufacturers of such alloys who made castings to a standard die and wax pattern that we supplied. A technique to fabricate oversize Ni- crown castings is described.

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)* Adhesive; base metal; composites; dental materials; dental alloy; polymerization; resins; restorative materials; wear.

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