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Properties and Interactions of Oral Structures and Restorative Materials

James M. Cassel

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

Annual Report for period
October 1, 1977 thru September 30, 1978

November 1978

Issued: December 1978

Prepared for

National Institute of Dental Research
Bethesda, MD 20014

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Certain commercial materials and equipment are identified in this report to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the materials and equipment identified are necessarily the best available for the purpose.

Prepared for
National Institute of Dental Research
Bethesda, MD 20013

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ABSTRACT

To improve the storage stability of dental composite resin systems, alternative catalyst systems to the commonly used benzoyl peroxide-tertiary amine are being developed. Increased storage stability is attainable with organic peresters or hydroperoxides but these require more efficient accelerators than the presently used amines. Ascorbic acid or ascorbyl palmitate offer promise as useful accelerators which have good biocompatibility. To develop more reactive amine accelerators with perhaps less toxicity than those currently in use, p-dimethylamino-phenylacetic acid (or ester derivatives) and dimethylaminoglutethimide were synthesized and shown to yield composite restorative specimens of good mechanical strength and color stability. A wide range of cyanoacrylates from the simplest, 2-ethyl cyanoacrylate, to the more complex type such as a viscous isoamyl product have been examined for their capacity to achieve and retain bonding between acrylic resin and dentin. Very high initial bond strengths were achieved with isobutyl-2-cyanoacrylate on dentin pretreated with dilute acid but a one-month thermal cycling test in water indicated the bonding was not sufficiently stable. Initial synthetic hydroxyapatite pin on disc (dental amalgam) wear measurements have shown promise.

A pattern modification to reduce variability in the alloy castability test has been developed. Variations in the number of firing cycles and amount of condensation of green porcelain have been shown to cause significant differences in dimensional characteristics on cooling of fused dental porcelain.

SUMMARY

The research on dental materials that is described in this report is a part of a larger total effort that is carried out in collaboration with the American Dental Association Health Foundation. The Armed Services Dental Corps are also part of this collaborative effort through support funding and/or assignment of research personnel.

While the bulk of the research progress in this report represents 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 synthesis to improve today's composite restorative materials and pit and fissure sealants and investigation of new approaches to bonding restorations to tooth surfaces. A wear-generating and recording system is being developed to provide rapid laboratory assessments of the wear resistance of dental materials. Thermal expansion and contraction data are determined on base metal alloys and dental porcelains in order to assess the influence of this factor in the bonding of porcelain fused to metal.

A factor in the use of dental composite restorative materials, particularly paste-paste and paste-liquid systems, is the susceptibility of the peroxide component to deterioration and of the monomer to polymerization on storage where the temperature is not maintained at a sufficiently low level. Since any undesired pre-polymerization or decomposition involves the catalyst system, and therefore affects the in situ curing at the tooth surface, we have explored alternative catalyst systems to the normal benzoyl peroxide-tertiary amine type.

Increased stability is attainable by using organic peresters or hydroperoxides as substitutes for the benzoyl peroxide. This increased storage stability, however, demands a different accelerator component of the catalyst system than the tertiary amines normally employed. While certain multivalent metal compounds can be used to reductively activate these stable peroxides, their color and potential toxicity if used in concentrations comparable to those of amine accelerators could present serious problems. Alternatively, we found that the natural relatively mild reducing agent, ascorbic acid (Vitamin C) or its derivative ascorbyl palmitate, provides the required increase in accelerator activity.

The room temperature stability of ascorbic acid or ascorbyl palmitate toward oxidation when deposited on composite glass filler particles has been demonstrated to be excellent. While more work on the physical properties of composites prepared with the new initiator system needs to be done, the potential for improved storage and color stability, as well as biocompatibility, has clearly been demonstrated.

Tertiary aromatic amines have been employed for many years to

accelerate the peroxide-catalyzed polymerization of acrylic resins and composites. Although the accelerator comprises a minor component of a dental composite restoration, the type and concentration used not only affects the rate of hardening of an *in situ*-cured dental restoration, but also can affect other important properties such as initial color, color stability and strength. An increasingly important property of amine accelerators, as well as for all components of dental restorations, is their potential for toxic reaction with the body.

With an eye to developing more reactive amine accelerators and hence allowing lower concentrations to be employed, we synthesized a number of new amines using as a guide, structure-property relationships we had established previously. We find that the amines we have synthesized using p-dimethylamino-phenylacetic acid or its ester derivatives or dimethylaminoglutethimide are indeed extremely reactive and hence require relatively low concentrations in their role as accelerators. With these amines we have derived composite restorative specimens of good mechanical strength and excellent color stability which compare favorably to restorative resins cured with commercially used tertiary amines or other accelerators used in this study. Since related amines have found other applications in medicine, their toxicity would appear to be minimal. This will have to be checked, however, by valid testing elsewhere.

An additional important result that derived from this work is clear evidence from physical property determinations, e.g., tensile strength measurements, for the need on the part of a dental manufacturer to practice strict quality control in the concentrations of amine accelerators that are incorporated into this composite formulation.

Achieving adhesion between dental restoration and tooth structure could conceivably eliminate secondary caries-producing marginal leakage. It would also allow modified tooth cavity preparations so as to minimize removal of sound tooth structure. Reactions that proceed despite the ever present water molecules on a tooth surface are limited in number. Cyanoacrylates interact readily with the amino acid side chains of proteins and hence offer a potential means for bonding a composite dental restoration to the dentin component of a cavity surface. They also offer a means of supplementing the mechanical adhesion with enamel that is achieved through etching in both preventative and restorative application.

We have examined a wide range of cyanoacrylate types from one of the simplest, 2-ethyl cyanoacrylate, to the more complex type such as a viscous isoamyl product. An accelerated aging test provided an important means of assessing the durability of adhesive bonding that was achieved. The deterioration of initial bond strengths caused by cyclic exposure to water at 5° and 55°C could be determined in this test.

The isobutyl 2-cyanoacrylate has been demonstrated to develop the highest initial bond strength of acrylic resins to dentin. Further, a pretreatment of the dentin surface with a dilute acid such as 1% alcoholic citric acid significantly increases the bond strengths attainable, yielding in fact, greater adhesion (14 MPa, 2000 psi) to flat dentin surfaces than has been previously achieved.

However, debonding of the resin to dentin, as judged by accelerated (one-month thermal cycling) aging tests, occurs at too rapid a rate to make even the isobutyl 2-cyanoacrylate (at least in the form in which we experimented) an effective long term dental adhesive. Blending a

cyanoacrylate polymer with the isobutyl 2-cyanoacrylate or application of a protective coating increases the hydrolytic stability of the bond. At present, this improvement in the stability is not sufficient for the application of these materials where a permanent bond is required.

Despite excellent initial bonding that can be achieved by selection of the cyanoacrylate, it is apparent that a means must be achieved to stabilize this bonding. Further, before such techniques could be applied, the toxicity of the components would need to be assessed. From this point of view the isobutyl derivatives would appear to present less of a problem than the methyl ester which is considered to be toxic and on which most previous research has been done.

Development has continued of a laboratory wear test that will rapidly and cheaply generate wear resistance data on dental materials. Currently such data can be obtained only through time consuming and expensive clinical trials. An improvement in the precision of measurement has been made by redesigning to measure the wear track depth with the disc in a stationary mode as opposed to the slow rotational mode employed previously. Also redesigned was the means of mounting the transducers that are employed for depth of wear track measurement so that they were not contaminated with the water which is present to simulate oral fluid. This modification significantly improved the stability and precision of the measurements. Wear data acquisition equipment belonging to the Air Force has been replaced and the tape controlled approach changed to a computerized controller that will simplify programming and decision making during the measurement process.

Wear data on one amalgam type, one composite type and poly(methyl

methacrylate) indicate a high rate of wear in the enamel slider opposing the composite specimens. Slider pins have been machined from a synthetic apatite and will be evaluated as substitutes for human enamel. While the wear rates obtained initially with an amalgam-apatite couple are low, they fall within the range of those obtained with enamel on similar specimens. Further research on this aspect is required. A program to elaborate the micro-deformation mechanisms operable in the dental composite restorative system has been planned and will be initiated in FY79.

An additional Ni-based dental alloy has been examined for "accuracy of fit" and "castability" and found to be comparable with previously examined alloys of this type. A more predictable expansion has been shown to be attained by using a Kaowool ring rather than asbestos in the investing procedure. In response to an analysis that showed more completed vertical than horizontal segments in the "castability" test developed previously for dental alloys, a pattern modification has been developed which should serve to reduce the variability in the test results.

To more definitively characterize the state of bonding between porcelain fused to base metal alloy substrates, a study of six commercially available dental porcelains was initiated. Preliminary findings indicate that variations in the number of firing cycles and the amount of condensation of the green porcelain causes significant differences in dilatometrically-measured dimensional characteristics on coating of fused dental porcelain. Efforts to define a test procedure for measuring the wetting characteristics of base metal alloys by dental porcelain during fusion have not as yet produced a totally satisfactory method.

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 and the Armed Forces Dental Corps. The research reported in the following pages is only that portion of the dental program which is supported by interagency agreement with the National Institute of Dental Research.

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

I. Synthesis for Improved Composite Restorations and Sealants

II. Techniques for Bonding to Mineralized Collagen Surfaces

III. Wear Resistance and Mechanical Properties of Dental Materials

IV. Base Metal Alloy and Dental Ceramic Research

TECHNICAL REPORT

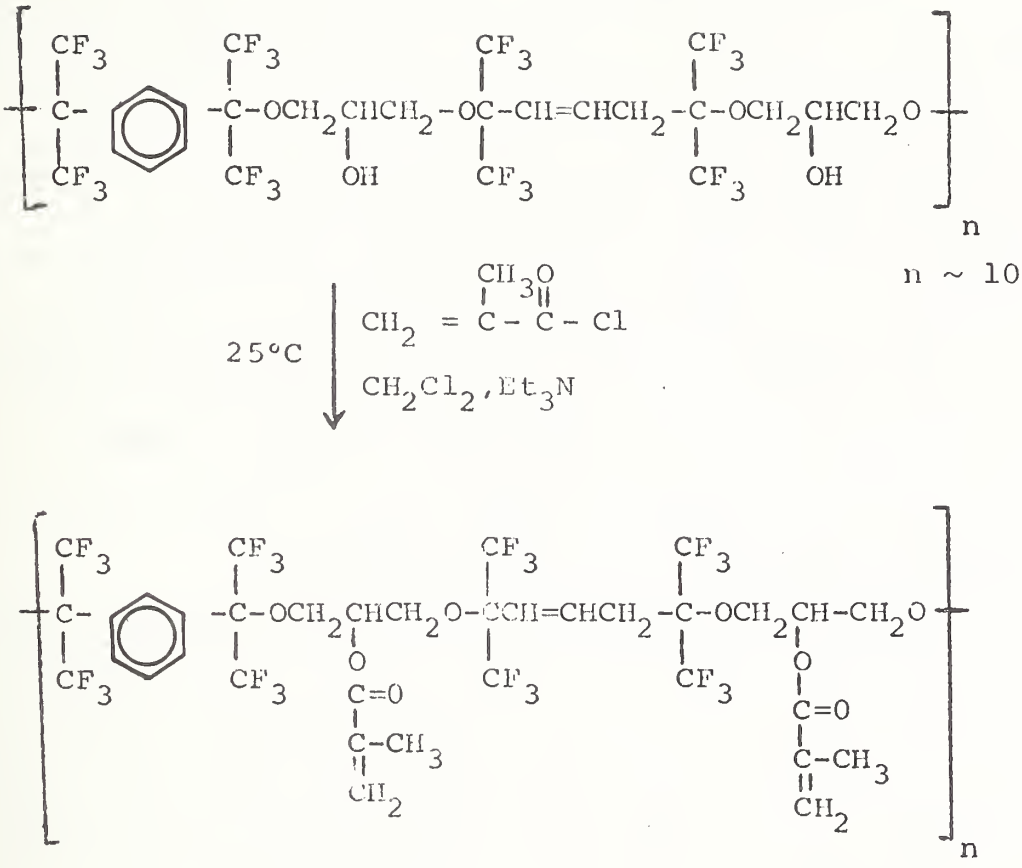
I. Synthesis for Improved Composite Restorations and Sealants

Early research of R. L. Bowen, Research Associate in this laboratory, resulted in a major breakthrough in the application of dental resin systems to both restorative and preventive dental practice (1-9). The objective of the current effort is to provide direction for improved composite restorations and pit and fissure sealants by synthesis and evaluation of monomers and other components of the resin matrix systems used in these restorative and preventive dental techniques. Special concern is for improvement in durability, color and storage stability, for development of materials with reduced toxicity levels and for development of techniques that will lead to a truly adhesive restorative or sealant material.

A. New Resin Monomers

1. Fluorinated Oligo (Ether Methacrylate)

To reduce polymerization shrinkage and introduce hydrophobic and oleophobic character into the resin system, we endeavored unsuccessfully to synthesize a fluorinated oligomethacrylate from the corresponding oligo(ether-ol) by a trans esterification reaction using excess methyl methacrylate with p-toluene sulfonic acid or tetraisopropyl titanate as the catalyst. However, direct esterification using methacrylol chloride, methylene chloride and triethylamine as shown below produced the desired product in excellent yield.



Infrared analysis of the viscous liquid was consistent with the assigned structure. This oligo methacrylate readily polymerized under U. V. irradiation in the presence of a photoinitiator (benzoin methyl ether). Thermal treatment (60°C) and the usual "cold-curing" procedures both resulted in the formation of polymer. The oligomethacrylate monomer appears to be more viscous than the corresponding acrylate, but not as viscous as Bis-GMA. For use in composite resins or sealants, some diluent monomer is necessary. We have determined that both these monomers are miscible with a variety of diluent monomers, such a methyl methacrylate (MMA), triethyleneglycol dimethacrylate (TEGDMA), neopentyl glycol dimethacrylate (NPGDMA) and octafluoropentyl methacrylate (OFPMA).

A series of composites was prepared using formulations based on monomer systems incorporating either the polyfluoroligomethacrylate (PFMA) or the polyfluoroligoacrylate (PFA) and the above diluent monomers. All the composites exhibited high contact angles with distilled water (80°-89°) and possessed excellent esthetics, especially those incorporating AA or AP as the accelerator. The diametral tensile strengths obtained with PFA and various diluent monomers are shown in Table I. The tensile strengths were considerably lower than those measured for Bis-GMA or urethane methacrylate type monomer systems, probably because of the relatively low glass transition temperatures (Tg) of the PFA copolymers.

Table 2 illustrates the tensile strengths obtainable using PFMA-based resin systems. Here the results are more encouraging presumably because of the probably higher Tg of the polymer (PFMA) compared to that of PFA, especially if, in addition, diluent monomers which give copolymers of still higher Tg's are used. The tensile strengths can be further augmented by the use of a finer glass filler (325 mesh) than the BaF_2 containing glass we have used previously. The last three results are particularly encouraging in that they indicate that it is possible to use low surface energy resin binders for dental composites and still maintain good mechanical strength (diametral tensile strength, DTS>34MPa). The aesthetics of these composites were excellent, especially with composites made with the blended glass formulation.

In addition, these results demonstrate the feasibility of using a prepolymer monomer (e.g. PFMA) as the major component of dental resins. This type of resin may offer a means of achieving minimal polymerization shrinkage which coupled with its hydrophobic/oleophobic

Table 1

TENSILE STRENGTH OF PFA EXPERIMENTAL COMPOSITES.

(Powder[1]/Liquid = 3)

Formulation	Monomer System		Acc.[2]		Hardening Time (Min.)	Diametral Tensile Strength (MPa)
1	PFA	6				
	TEGDMA	1	DMSX	0.22%	1.5	10.2 ± .14 (3)*
	OFPMA	1				
2	PFA	3				
	TEGDMA	1	DMSX	0.40%	1.5	19.1 ± 0.44 (3)*
	OFPMA	1				
3	PFA	7	AP	0.30%	8.0	17.6 ± 0.50 (4)*
	TEGDMA	3				
	(1.2% TBPM) (0.0005% CBA)	} in liquid				
4	PFA	5.3	DMAPAA	0.40%	5.0	20.9 ± 1.9 (4)*
	NPGDMA	1				

[1] The glass filler is coated with 1% benzoyl peroxide (BP) except in formulation #3 where it is coated with 0.3% ascorbyl palmitate (AP) and the liquid contains t-butylperoxy maleic acid (TBPM) and copper benzoylacetonate (CBA).

[2] Accelerators: DMSX = N,N-dimethyl-sym. xylidine
DMAPAA = N,N-dimethyl-p-aminophenylacetic acid
AP = ascorbyl palmitate.

*Numbers in ( ) refer to number of specimens.

TABLE 2

TENSILE STRENGTH OF PFMA EXPERIMENTAL COMPOSITES
(Powder[1]/Liquid = 3)

Formulation	Monomer System		Acc.	Hardening Time (min.)	Diametral Tensile Strength (MPa)
5	PFMA	3.4			
	TEGDMA	1	DMSX 0.37%	1.5	25.4 ± 0.42 (3)
	OFPMA	1.5			
6[2]	PFMA	3			
	TEGDMA	1	DMAPAA 0.40%	6.0	33.4 ± 0.86 (5)
7	PFMA	3	DMAPAA 0.40%	6.0	22.7 ± 1.3 (4)
	TEGDMA	1			
8	PFMA	7	DMAPAA 0.40%	7.0	27.4 ± 0.71 (4)
	NPGDMA	3			
9[2]	Same as 8		DMAPAA 0.40%	7.0	40.6 ± 3.4 (6)
10[2,3]	Same as 8		DMAPAA 0.40%	6.0	46.5 ± 2.1 (3)
11[2]	PFMA	2	DMAPAA 0.44%	2.5	44.6 ± 2.9 (2)
	MMA	1			

[1] Glass filler coated with 1% benzoyl peroxide, however see formulation 10.

[2] In formulations 6, 9, 10 and 11, a finer mesh (325) glass filler was used.

[3] In this formulation, the glass filler used was made by hand blending (spatulation) equal parts of two types of glass powder (silanized, 325 mesh). One glass was coated with 1% benzoyl peroxide (BP) and the other with 0.3% ascorbyl palmitate.

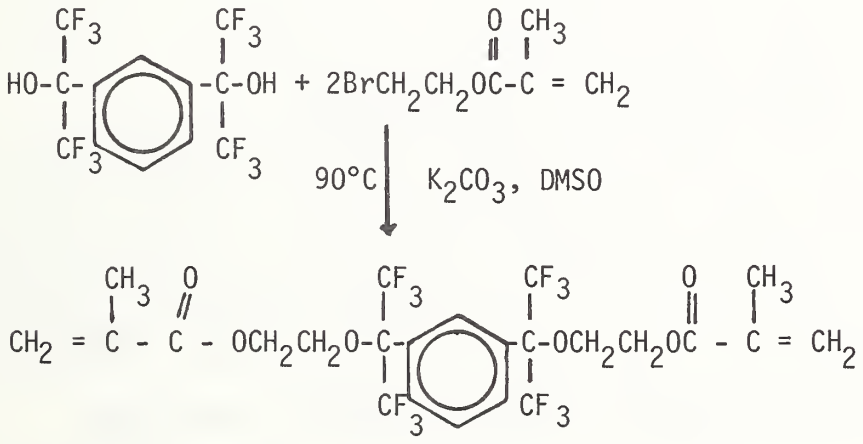
character may lead to composites and sealants of superior marginal integrity.

2. Fluorinated Dimathacrylates

Another approach to forming polymeric matrices having low surface energies and good mechanical properties is to use certain fluorinated dimethacrylates as part of the monomer system instead of PFMA. Two promising fluorinated dimethacrylates have recently been synthesized in these laboratories.

(a) Synthesis of Di-Methacryloxyethyl Ether of Meta-Bis(2-Hydroxyhexafluoroisopropyl)benzene - MEMFPB.

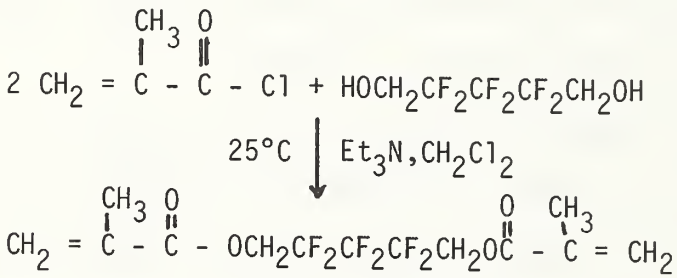
The method of synthesis is an extension of those described in previous publications (10,11) and is outlined below. The diol, synthesized by Dr. J. Griffith of Naval Research Laboratory, was a generous gift from that laboratory.



The dimethacrylate is a liquid with a viscosity less than that of Bis-GMA. The molecular weight of the fluorinated dimethacrylate is 634 vs 512 for Bis-GMA. Preliminary characterization by IR and NMR analyses supports the structural assignment.

3. 2,2,3,3,4,4-Hexafluoro-Pentanedimethacrylate

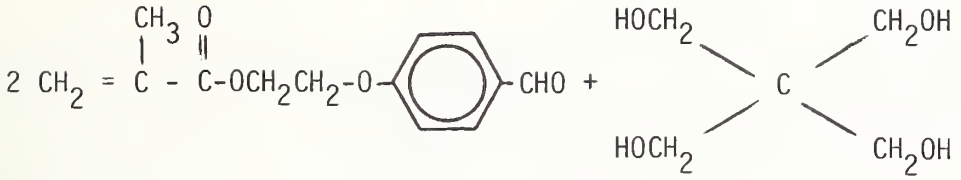
The synthesis of this fluorinated crosslinking monomer was accomplished by direct esterification of the corresponding hexafluoropentanediol with methacryloyl chloride as shown below:

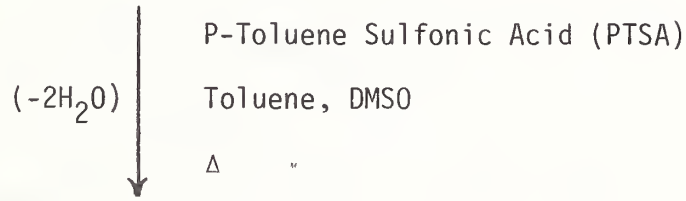


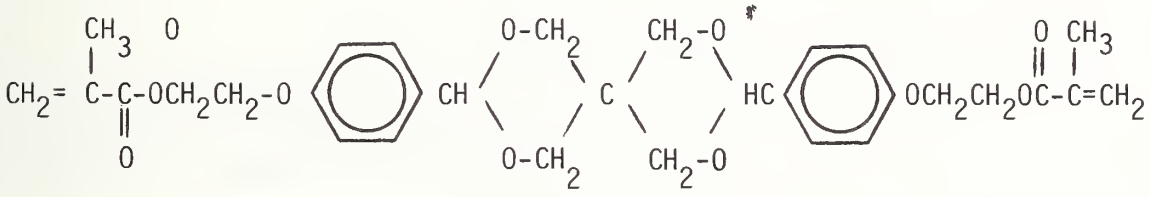
The product (MW=348) is a liquid of moderate viscosity. IR and NMR analyses supports the assigned structure.

4. Diacetal Benzaldehyde Methacrylates

Another attractive monomer system that should exhibit low polymerization shrinkage is that based on the cyclic diacetals derived from the various methacryloxyethoxy/benzaldehydes previously synthesized (12) and pentaerythritol. The synthesis of the para isomer (DAPMB) has now been accomplished in good yield by the reaction shown below:



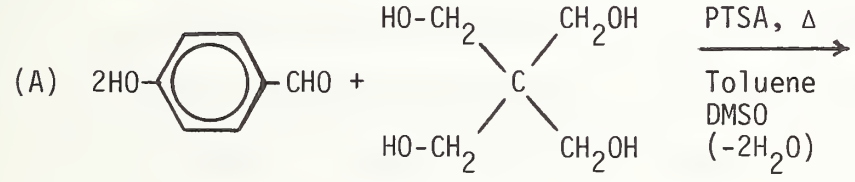


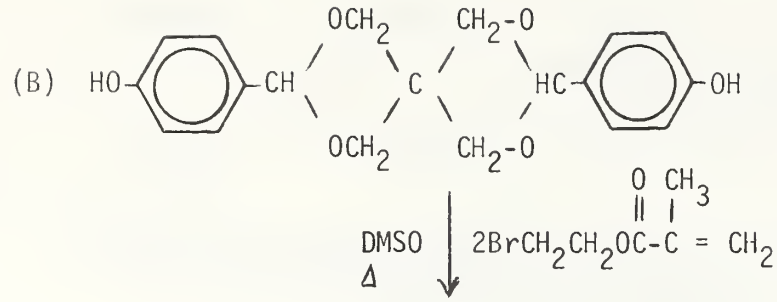


DAPMB

This monomer is a white crystalline solid, m.p. 104-06°C, which on heating above its melting point (140-50°C) polymerizes to a clear hard resin. Infrared analysis of the monomer supports the assigned structure.

An alternate synthesis of this monomer, shown below, also is under investigation. In this synthesis the cyclic diacetal of the p-hydroxybenzaldehyde is formed first in step A. In step B it is converted to the dimethacryloxyethoxy derivative.





DAPMB

Step A has been carried out and appears to be successful (IR Analysis).

B. New Initiator/Accelerator Systems

(1) New Initiator Systems Based on Ascorbic Acid (or Derivatives)

Dental monomers, such as those used in composite, sealant, cement and denture base materials, are commonly "cold-cured" by means of an initiating system consisting of a diacyl peroxide (e.g. benzoyl peroxide) and a tertiary aromatic amine accelerator (e.g. N,N-dimethyl-p-toluidine).

Although this type of initiator/accelerator combination has performed reasonably well in dental and medical applications, it does have shortcomings. For example, in composite restorative materials, due to the relatively low half-life temperature of benzoyl peroxide (Table 3), there exists a problem with regard to the storage stability of the peroxide component of these dental materials, especially in the case of paste/paste or paste/liquid formulations (13). At temperatures higher than those normally encountered in clinical use, the peroxide component undergoes accelerated deterioration, though to a lesser extent if a peroxidized

powder/liquid formulation is used (14,15).

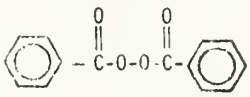
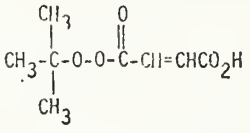
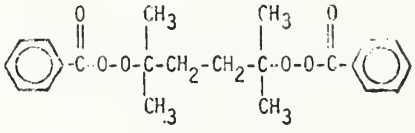
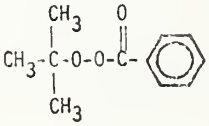
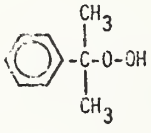
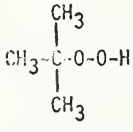
Another problem that can occur in these "cold-cured" dental composites and sealants is the development of undesirable colors, especially from exposure to sunlight and other U.V. sources. Although there can be other causes for the discoloration of dental resins, the inherent color instability of the usual tertiary aromatic amine accelerator is a likely contributing factor (16-20). In addition, although they have not been identified as causing a serious toxicity problem when properly used in dental and medical applications, the usual tertiary aromatic amine accelerators are not ideally biocompatible (21).

A general problem associated with the diacyl peroxide-amine initiator system is its relatively low efficiency (22,23). The presence of inhibitors in the dental monomers further lowers this efficiency. Also there is evidence that some tertiary aromatic amine accelerators themselves can have an inhibiting effect on the polymerization (24-26). The use by a manufacturer of more than the theoretical peroxide-amine concentration to overcome this reduced efficiency may further accentuate the stability, color and biocompatibility problems.

We have demonstrated that it is possible to devise alternative initiator systems based on the use of more stable peroxides, such as organic hydroperoxides and peresters, (Table 3), and less color prone and more biocompatible accelerators, such as ascorbic acid. Progress in this area is summarized in the following pages.

Table 3

RELATIVE THERMAL STABILITY OF PEROXIDES USED IN THIS STUDY BASED ON TEN HOUR HALF-LIFE DATA[13]

Name	Abbreviation	Chemical Structure	10 hr. half-life Temp. °C*
Benzoyl Peroxide	BP		73
t-butylperoxymaleic acid	TBPM		87
2,5-dimethyl-2,5-bis(benzoyl-peroxy) hexane	DMBBPH		100
t-butyl perbenzoate	TBPB		105
cumene hydroperoxide	CHP		158
t-butyl hydroperoxide	TBHP		172

* Ten hour half-life temperature is that temperature required for one-half of the peroxide to decompose in ten hours.

Mechanism:

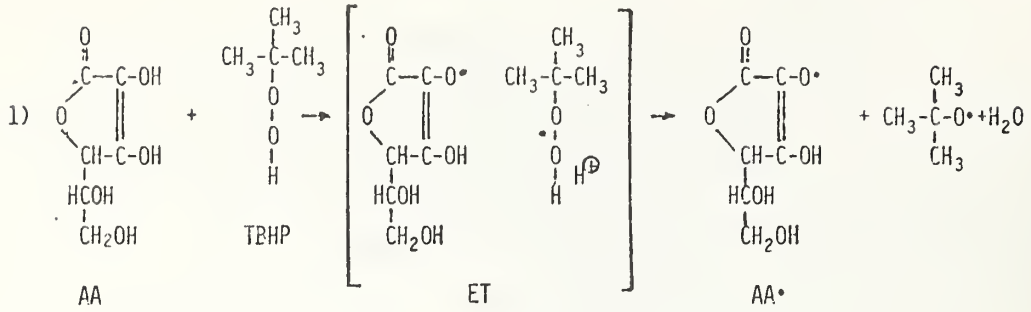
In Figure 1 is outlined a probable proton assisted one-electron transfer (ET) mechanism for the production of initiating radicals from the reaction of ascorbic acid (AA) or ascorbyl palmitate (AP) with organic peresters, hydroperoxides and diacyl peroxides. The partially oxidized ascorbic acid moiety $(AA)^{\cdot}$ in turn may act as an accelerator by a second proton assisted one-electron transfer to the peroxide.

Tertiary aromatic amines do not appear from our work to be very effective accelerators for the ambient free radical decomposition of organic peresters and hydroperoxides. However, these stable peroxides will undergo reductive activation to yield initiating radicals by means of certain multivalent metals (e.g. transition or redox metals such as copper, iron and cobalt) (27,28). These metals, in their lowest oxidation state (e.g. Cu^{+1}, Fe^{+2}) are extremely potent one-electron transfer agents for peresters and hydroperoxides.

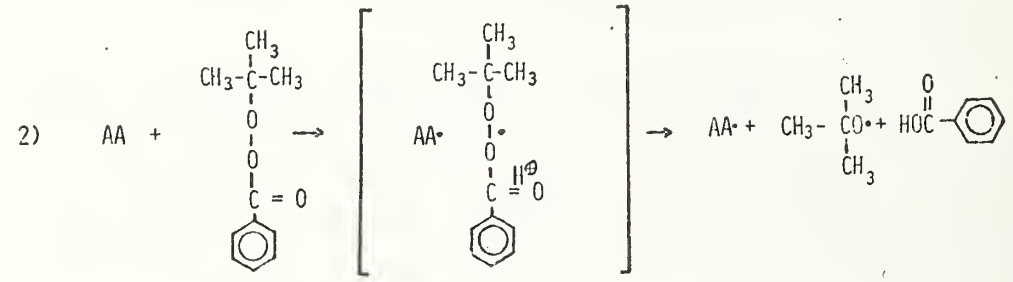
There are several problems associated with the use of these redox metal activators in dental or medical "cold-curing" applications. If these metal compounds are employed in concentrations equivalent to those used in the case of amine accelerators, then both the inherent color and toxicity of these metal cations would present serious problems. In addition, these metal activators need to be in their lower oxidation states (e.g. Cu^{+1}, Fe^{+2})to be effective accelerators for peresters and hydroperoxides. Unfortunately, in these states they are susceptible to oxidation on storage to their higher valence states (Cu^{+2}, Fe^{+3}).

However, an interesting extension of the redox metal system

POSSIBLE MECHANISM FOR REDOX REACTION OF
PERESTERS AND HYDROPEROXIDES WITH ASCORBIC ACID

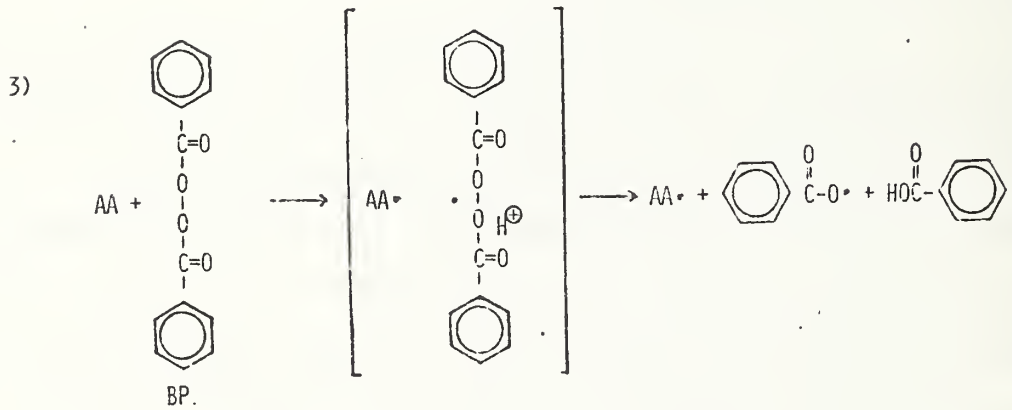


AA TBHP ET AA•



TBPB

POSSIBLE MECHANISM FOR REDOX REACTION OF
DIACYL PEROXIDES WITH ASCORBIC ACID



BP. ET

Figure 1: Possible Mechanisms for Redox Reaction of Peresters, Hydroperoxides and Diacylperoxides with Ascorbic Acid.

of activation is feasible by the addition of trace amounts of transition metals in their higher oxidation (Cu^{+2}, Fe^{+3}) to the perester or hydroperoxide component. On admixture with the AA or AP component, the metal cation is reduced to its lower oxidation state which, because it is a potent one-electron reductant, will rapidly activate the free radical decomposition of the perester, while it in turn is reoxidized to its higher oxidation state. Due to the presence of excess AA or AP and perester, this reduction-oxidation cycle is repeated many times, thereby creating a chain activation mechanism which requires very little metal activator to decompose much larger quantities of the peroxide. Because so little redox metal is used no color or toxicity problems arise. The chain activation mechanism is illustrated in Figure 2 for the initiator system consisting of Cu^{+2}, TBPB and AA.

A similar synergistic mechanism probably applies to the tertiary aromatic amine, BP and AA initiator system as shown in Figure 3. In this case the AA or AP regenerates the amine accelerator by reducing the transient aminium radical cation. This novel initiator system results in composites having improved color stability and biocompatibility compared to those prepared with the usual BP-Amine initiators because much less amine is employed.

Storage Stability

Most solutions of AA or AP in the monomer systems studied appeared to have good color stability on storage at room temperature and gave no signs of gelation after one year. If the monomer has formed peroxide (hydroperoxide) prior to the addition of AA, then gelation does occur. In most cases AA or AP will act as an effective antioxidant for

CHAIN ACTIVATION MECHANISM FOR THE REDOX

REACTION OF PERESTERS OR HYDROPEROXIDES

WITH ASCORBIC ACID AND TRACE OF REDOX METAL

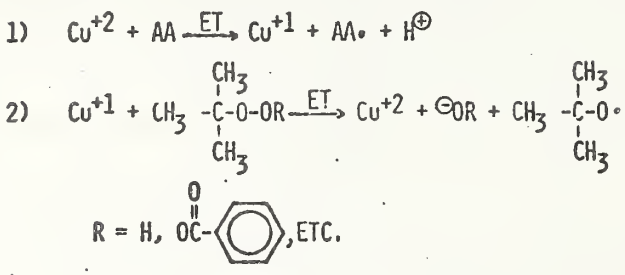


Figure 2: Chain Activation Mechanism for the Redox Reaction of Peresters or Hydroperoxides with Ascorbic Acid and Trace of Redox Metal

POSSIBLE SYNERGISTIC MECHANISM FOR THE REDOX REACTION

INVOLVING BENZOYL PEROXIDE, ASCORBIC ACID AND AMINE ACCELERATOR

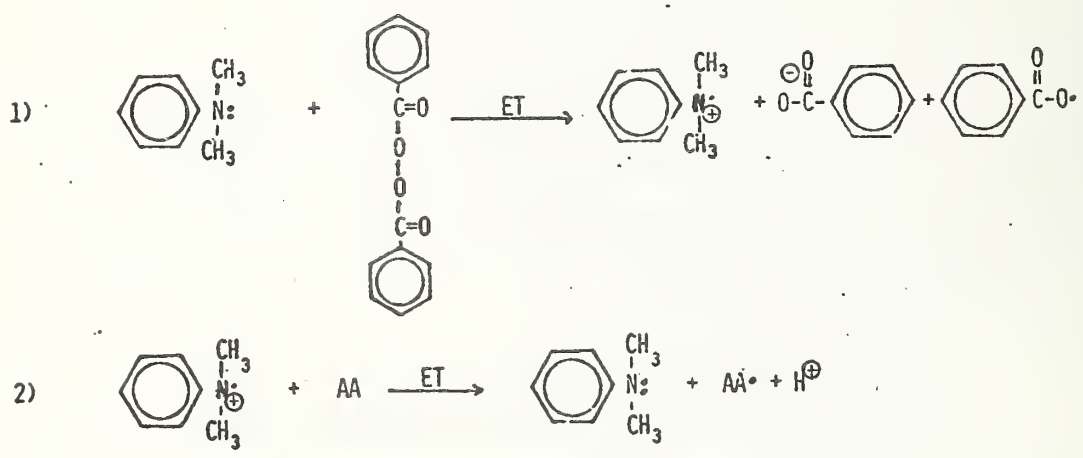


Figure 3: Possible Synergistic Mechanism for the Redox Reaction Involving Benzoyl Peroxide, Ascorbic Acid and Amine Accelerator

most monomers (29).

A problem with AA or AP solutions in monomers is a loss of accelerative activity with time. A similar problem exists with the sulfinic acid type accelerators (30). The loss of acceleration in AA solutions may be related to a number of factors. The principal factor, the well known reactivity of AA with oxygen in aqueous solution, apparently carries over to solutions in other media. However, the stability of AA appears to be better in alcohol and HEMA than in water or in Bis-GMA/TEGDMA. A study of the effect that other monomers have on the reductant activity of AA and derivatives may lead to more stable solutions. Also the use of certain stabilizing additives, such as cysteine, sulfur dioxide, etc., which are reported to stabilize aqueous solutions (31) of AA may further improve retention of its acceleration potential in monomer systems.

In contrast, the storage stability of AA or AP on glass filler appears to be excellent (>2 years at room temperature), and effective initiator systems for dental composites can be devised based on various powder/liquid formulations. Moreover, a storage stable paste-paste system may be feasible if a dual monomer system is used. One monomer system, designed to be a poor solvent for AA, is used to form the accelerator paste, while the other monomer used in the peroxide paste can dissolve AA. (The peroxide paste, if it is formulated with the more stable organic peresters and hydroperoxides, should show enhanced storage stability over paste-paste systems formulated with BP).

Another technique for utilizing these new initiator systems and enhancing storage stability is to use a two component premixed glass filler type formulation. The mixed glass, a blend of solid peroxide on glass filler and AA or AP on glass, is designed to be used with a monomer

system with or without a trace amount of redox catalyst. In the case of BP-AA blended glass, a small quantity of an amine accelerator may be included in the monomer (see formulations E and F in Table 7).

In some cases there appears to be a favorable synergistic effect on the polymerization with BP if AA or AP is used in conjunction with the usual amine accelerators. As noted previously (Table 2, compare formulations 9 and 10) the properties of composites (diametral tensile strength and aesthetics) are improved by the use of two types of accelerators. The same trend was noticed using a paste/paste formulation. With the accelerator paste containing only DMSX (N,N-dimethyl-sym-xylidine) a composite of diametral tensile strength of 40 MPa and with inferior aesthetics was obtained whereas if the paste contained AP as well as DMSX, the strength value was 48 MPa and the color of the composite was much improved.

Diametral Tensile Strength

The diametral tensile strength of composites prepared from some representative formulations based on these new initiator systems are shown in Tables 4-7. No attempt was made to optimize any of these formulations.

Blended Glass Formulations

It has been found possible to blend glass filler coated with a solid peroxide (e.g. peresters such as t-butylperoxymaleic acid and diacyl peroxides such as benzoyl peroxide) to obtain a stable mixed powder/liquid formulation. The liquid monomer system contains only an antioxidant (e.g. BHT) and, optionally a trace of redox compound. (In the case of BP-AA type of blended powders, a small quantity of a tertiary aromatic amine may be used as a synergistic accelerator). In Table 7 are

Table 4

SETTING TIMES[32] AND DIAMETRAL TENSILE STRENGTHS[33] OF EXPERIMENTAL COMPOSITE FORMULATIONS* BASED ON NEW INITIATOR SYSTEMS

Formulation	Initiator	Accelerator	P/L	Setting Time (min)	Diametral Tensile Strength in MPa (No. of Specimens)
A	1% TBHP	0.45% AA	3	7	38.1 ± 1.6 (3)
B	1% CHP	"	3	6	39.9 ± 0.1 (2)
B'	2% CHP CBA (0.0005%)	0.3% AP	2.75	6	43.0 ± 0.8 (3)
C	1% TBPB	0.45% AA	3	8	41.9 ± 3.0 (4)
C'	1% TBPB	0.3% AP	3	9	45.7 ± 1.6 (3)
D	1% TBPB CBA (0.002%)	0.45% AA	3	4	41.1 ± 9.1 (2)
E	1% TBPB CBA (0.0002%)	"	2.5	3	55.3 ± 1.9 (3)
F	0.65% TBPM CBA (0.005%)	"	3	7	38.4 ± 5.1 (4)
G	"	0.3% AP	3	8	42.4 ± 0.9 (5)
H **	0.75% BP (on glass)	0.3% AP 0.2% CYS	3	6	36.5 ± 3.1 (5)
I **	"	0.5% AP 0.15% CYS	3	6	34.2 ± 2.4 (5)

*Monomer System consisted of 70% Bis-GMA/30% TEGDMA with 0.2% BHT; Glass Filler consisted of 67% of a fused spheroidal silica and 33% of a BaF_2-containing glass, both silanized with γ-methacryloxpropyltrimethoxysilane and sieved (100 mesh).[34] Glass Filler had coating of 0.45% AA, 0.3% AP or 0.75% BP.

**In formulations H and I, accelerator components, AP and CYS, are dissolved in monomer system.

Table 5

SETTING TIMES AND DIAMETRAL TENSILE STRENGTHS OF
EXPERIMENTAL COMPOSITE FORMULATIONS* BASED ON NEW INITIATOR SYSTEMS

Formulation	Monomer System	Initiator	Acc.	P/L	Setting Time (min)	Diametral Tensile Strength in MPa (No. of specimens)
1[a]	Eutectic 92%[a] HEMA 8%	2.2% TBPB CBA (0.003%)	0.45% AA	3	6	31.5 ± 3.1 (4)
2*	Eutectic[a]	1.8% TBPB CBA (0.0014%)	0.3% AP	3	6	32.1 ± 1.8 (5)
3	THUDMA[b]	1.1% TBPM CBA (0.007%)	0.45% AA	2.5	3	52.6 ± 4.1 (5)
4	"	1% TBPM CBA (0.0006%)	0.30% AP	2.5	5	50.5 ± 1.2 (4)
5[d]	THUDMA 81% MEH 11% MEC 8% } [c]	1% BP	0.7% AP 0.001% CBA 0.001% CYS	3	6	35.1 ± 0.9 (5)

[a] In this formulation part of the monomer system consists of a eutectic monomer[34,35] (45.6% MEI 36.8% MEP, 14.5% MET and 0.2% BHT).

[b] THUDMA - Trimethylhexamethylene diurethane dimethacrylate (Vivadent).

[c] Ortho and para crystalline solid diether dimethacrylates.[36]

[d] In this formulation the initiator (BP) is on the glass filler and the accelerator components (AP, CBA, CYS) are dissolved in the monomer system.

*Same glass as in Table 4.

Table 6

SETTING TIMES AND DIAMETRAL TENSILE STRENGTHS OF EXPERIMENTAL COMPOSITE FORMULATIONS* BASED ON NEW INITIATOR SYSTEMS

Formulation	Monomer System	Initiator	Acc.	P/L	Setting Time (min)	Diametral Tensile Strength in MPa (No. of specimens)
1	Ester Eutectic[35] (9) HEMA (1)	2.2% TBPB CBA (0.003%)	0.31% AA	3	5	42.5 ± 0.7 (3)
2	Bis-GMA (7) TEGDMA (3)	1.0% CHP CBA (0.0005%)	0.31% AA	3	5½	50.6 ± 1.6 (4)
3	Bis-GMA (7) TEGDMA (3)	2.0% CHP CBA (0.0005%)	0.31% AA	3	7	49.7 ± 2.3 (5)
4	THUDMA	1% TBPM CBA (0.0006%)	0.31% AA	2.5	6	49.5 ± 1.9 (4)
5	THUDMA	1% TBPM CBA (0.0006%)	0.3% AP	2.5	5½	59.9 ± 2.7 (6)

*New glass (325 mesh) recently silanized according to procedure used in reference 34.

shown the setting times and diametral tensile strengths obtained from some typical blended glass formulations.

After several months at room temperature these blended powders appear to be unchanged (virtually same setting times and diametral tensile strength after two months), and this type of formulation may offer a means of further improving the storage stability of these new initiator systems.

Summary of Advantages of Initiator Systems Based on Ascorbic Acid/Ascorbyl Palmitate

1. Storage stability of dental composite materials is enhanced due to the use of more stable peroxides (e.g. peresters, hydroperoxides).

2. Cured resins have improved color stability resulting in dental composite restorations of enhanced aesthetics.

3. Improved biocompatibility of these materials results from the use of ascorbic acid type accelerators instead of tertiary aromatic accelerators.

4. The use of ascorbic acid type accelerators permits the use of a wide range of different types of peroxides (e.g. diacyl peroxides, peroxycarbonates, peresters, hydroperoxides, etc.) whereas the use of amine accelerators is limited to a relatively few types (e.g. diacyl peroxides, peroxycarbonates, which are not as stable as peresters and hydroperoxides).

5. The use of ascorbic acid/palmitate as an accelerator plus the use of trace amounts of redox catalyst (e.g. iron, copper compounds) probably provides an initiator system of improved efficiency (compared to the usual peroxide/amine systems).

6. The synergistic use of ascorbic acid type accelerators plus smaller amounts of tertiary aromatic amine accelerators with diacyl peroxides (e.g. benzoyl peroxide) gives a fast setting initiator system that results in resins and composite resins of improved color stability and biocompatibility.

7. For maximum storage stability of dental composite materials, powder/liquid formulations are used. One type is as follows: The powder consists of glass filler coated with the ascorbic acid accelerator. The liquid contains the perester or hydroperoxide with or without a trace amount of redox metal compound in its highest oxidation state. A novel type of powder/liquid formulation probably having still better storage stability consists of the following ingredients: A blended glass filler consisting of glass filler coated with a solid peroxide mixed with glass filler coated with the ascorbic acid type accelerator (e.g. the proportions may be glass coated with 1% peroxide blended with an equal quantity of glass filler coated with 0.3% ascorbic acid.)

C. Improved Amine Accelerators

Although the accelerator, normally a tertiary aromatic amine, comprises only a minor component of the composite, it significantly influences the properties of the cured material. Many amines have been suggested as accelerators (37-43), but aesthetic and biocompatibility requirements limit their number for dental applications. The N,N-dialkyl aromatic amines that are used in commercial dental composites have a relatively high toxicity index and are a main contributing factor to color stability problems associated with composites.

Our aim has been: (1) to be able to predict from structure-

property relationship highly reactive amine accelerators, (2) to synthesize new tertiary amines, that based on these theoretical considerations and results of previous studies, should be highly reactive and biocompatible and should give cured composites of greater color stability and (3) to compare these and other amines with presently used accelerators with regard to their effect on such properties of the cured composite as mechanical strength, color stability and water sorption. Based on structure-property relationships, p-dimethylaminophenylacetic acid, its methyl ester and dimethylaminoglutethimide were initially selected for their potential reactivity with benzoyl peroxide and their anticipated toxicological characteristics. Studies to determine the curing behavior and physical properties of the resulting composites were initiated in FY77 and are in part described in the annual report (44).

Evaluation of 15 amine accelerators in Table 8 has now been completed. The hardening times and compressive strength as a function of accelerator concentration are given in Figs. 4 and 5 for the most reactive amines. The physical properties of the cured composites are dependent on the type and concentration of amine used. Compositions containing DHPPT, BTX (low and high melting isomers), DMAB, 3DMABA and DMAP at the concentrations studied did not harden within the time limit imposed by the specification for Direct Filling Resins and their properties were not further investigated. From Fig. 4 it will be noticed that on increasing the amine concentration, a minimum hardening time is reached between amine additions of 20 mm (millimols) and 35 mm. With larger amine concentration the cure proceeds at a slower rate. One can conclude that the approximate order of the accelerating ability of the respective amines is

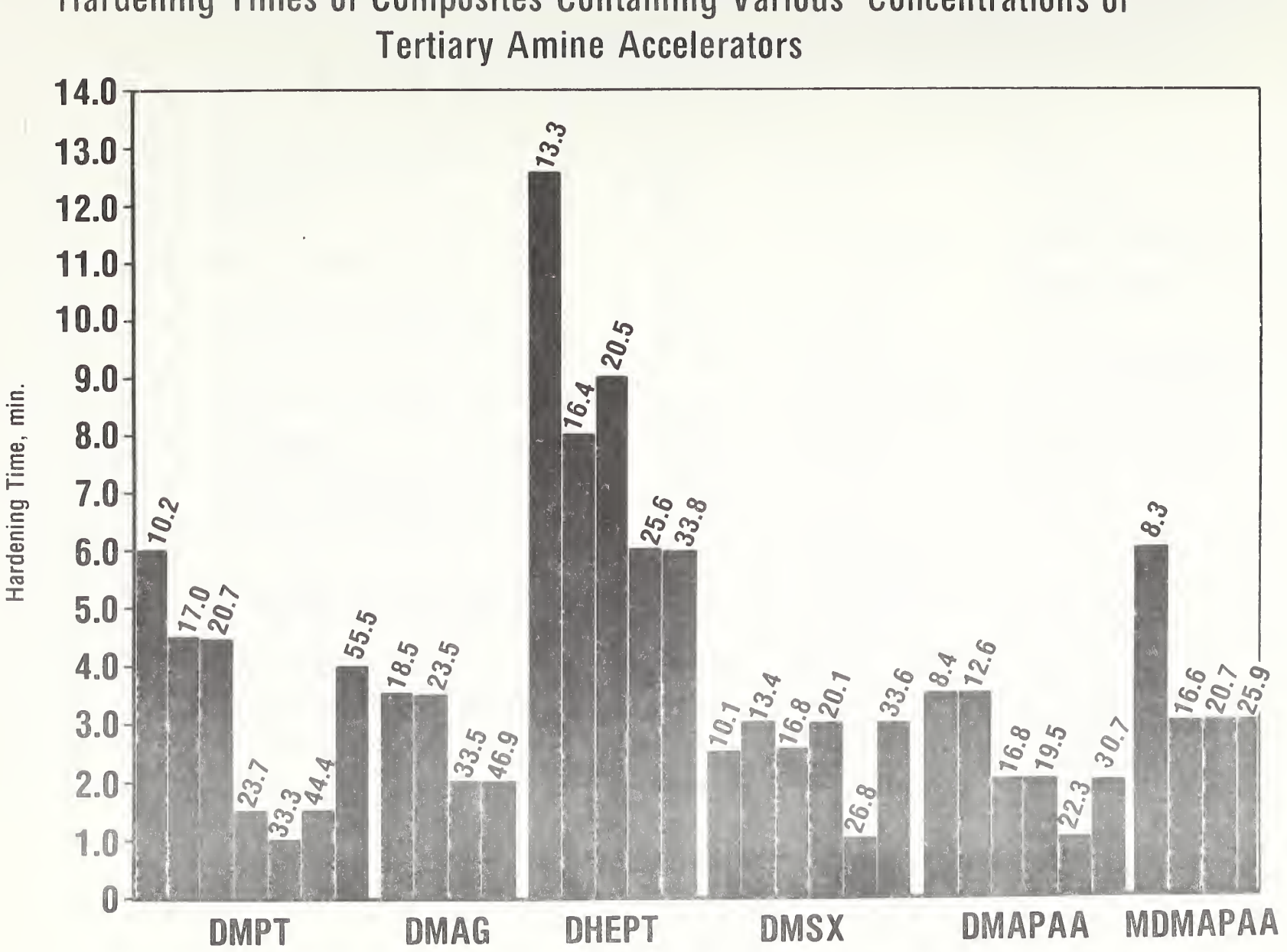


Figure 4: Hardening Times of Composites Containing Various Concentrations of Tertiary Amine Accelerators

Table 8

TERTIARY AROMATIC AMINE ACCELERATORS STUDIED

Amine Accelerator	Abbreviation	Melting or Boiling Point, °C	Source
N,N-Dimethyl-p-toluidine	DMPT	bp = 212	Commercial
N,N-Dimethylaminoglutethimide	DMAG	mp = 142-144	Synthesized from aminoglutethimide
N,N-Di-2-hydroxyethyl-p-toluidine	DHEPT	mp = 53	Commercial, recryst. from 1:1 cyclohexane-toluene
N,N-Di-2-hydroxypropyl-p-toluidine	DHPPT	mp = 109-110	Commercial
N,N-Dimethyl-sym-xylidine	DMSX	bp = 100-103/ $4x10^2$Pa	Commercial
N,N-bis(3-p-tolyloxy-2-hydroxypropyl)-sym xylidine (low-melting and high-melting isomers)	BTX	low melting: mp = 102.5-106 high melting: mp = 146.5-148	Syntnesized[45]
4-N,N-Dimethylaminobenzaldehyde	4-DMAB	mp = 73-75	Commercial
4-N,N-Dimethylaminobenzoic acid	4-DMABA	mp = 241	Commercial
Tetramethylammonium 4-N,N-dimethylamino-benzoate	TMADMAB	melts with decomposition	Synthesized from 4-N,N-dimethylaminobenzoic acid
Lithium 4-N,N-dimethylaminobenzoate	LDMAB	melts with decomposition 210	Synthesized from 4-N,N-dimethylaminobenzoic acid
3-N,N-Dimethylaminobenzoic acid	3-DMABA	mp = 150-152	Commercial
4-N,N-Dimethylaminophenylacetic acid	DMAPAA	mp = 110-112	Synthesized from 4-amino-phenylacetic acid
Methyl 4-N,N-Dimethylaminophenylacetate	MDMAPAA	bp = 107/1x10^2Pa	Synthesized from 4-amino-phenylacetic acid
Poly SAM-1	PSAA	mp = 81-92	Synthesized[46]
4-N,N-Dimethylaminopyridine	DMAP	mp = 112-113	Commercial

DMAPAA > DMSX > DMPT ≃ DMAG > MDMAPAA >> DHEPT.

The DMAPAA has a synergistic accelerating effect when added to the commonly used but relatively slow hardening DHEPT. Compositions with 16.8 mm DMAPAA or 16.4 mm DHEPT in the monomer liquid harden in 2 and 8 minutes, respectively. For a liquid containing 8.2 mm DHEPT and 8.4 mm DMAPAA, hardening takes place in 2.5 minutes yielding a product of high tensile (45.7 MPa) and compressive (215 MPa) strengths. Furthermore, with a monomer containing 13.1 mm DHEPT and 3.4 mm DHAPAA hardening occurs in 3.5 minutes.

Composites showed a rapid increase in tensile and compressive strength with increasing amine content and generally reached a maximum value with the liquid component of the mixture containing 16.5 to 17.0 mm of accelerator except for DMAG where a somewhat higher amine concentration (approximately 23.5 mm) was required for optimum strength. The tensile strength peak is sharpest for DMSX and DMPT amines and appears to be much broader for the DMAG amine. Maximum tensile strength of about 50 MPa is obtained with DMAPAA, MDMAPAA and DMSX. Composites with DMPT or DMAG have slightly lower tensile strength values (44-45 MPa). None of the composites containing the commonly used DHEPT passed the 34 MPa minimum tensile strength requirement for composite resins. Above 20 mm amine concentration the tensile strength increases again, but because of the poorer aesthetic properties the strengths of the resulting composites were not studied extensively. The curves relating compressive strength of the composite and amine concentration in the monomer (Fig. 5) are very similar to those obtained for the tensile strength correlation with amine concentration.

The initial shade of the cured specimens varied from

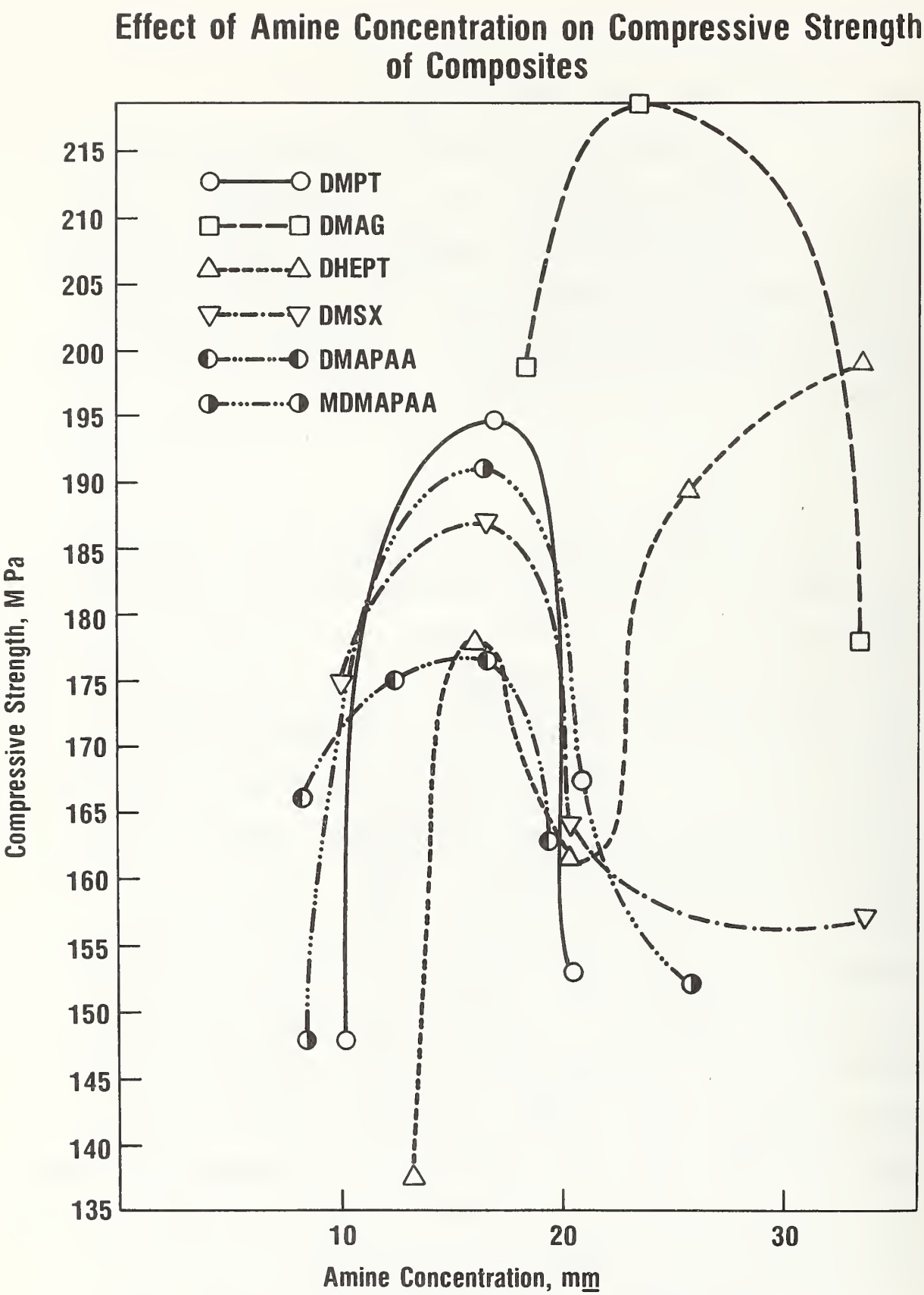


Figure 5: Effect of Amine Concentration on Compressive Strength of Composites

grayish to grayish-brown depending on the different amines used. A rating scale ranging from 1 (very large change) to 4 (no change) and based on comparison of exposed to unexposed specimens was employed. An increase in amine concentration lowers the color stability of the cured resin. Resins containing DMAB, BTX (high melting) and DMAPAA in concentrations of less than 20 mm have excellent color stability even though no ultraviolet absorber was incorporated in these formulations. The color stability of the cured composite after storage of the amine containing monomer at excessive temperature (60°C for 12 weeks) was especially good for MDMAPAA (Table 9).

The limited data obtained on the effect of amine accelerator on the water sorption of the cured resin are given in Table 10. The sorption values for composites with 17.0 mm DMPT, 16.8 mm DMSX or 16.8 mm DMAPAA are close to the value required in the specification (≤ 0.7 mg/cm^2). The water uptake of composites using salts of 4-dimethylaminobenzoic acid accelerators (LDMAD and TEGDMA) are too large for these composites to be useful for dental applications.

These experimental results proved indeed the theoretical assumption that the reactivity of tertiary aromatic amines with benzoyl peroxides reaches a maximum reactivity for amines with substituents on the benzene ring having an $\sigma+$ value (47) of approximately -0.20 (48). None of the accelerators yielded a composite that ranks highest in all properties. The DMAPAA proved to be the most reactive accelerator, giving products of good mechanical strength and excellent color stability. The overall properties of composites with MDMAPAA and DMAG also proved to be very satisfactory.

Table 9

COLOR STABILITY OF CURED COMPOSITES
AFTER STORAGE OF COMPONENTS

Powder-Liquid Ratio: 3 to 1 Amine Conc. in the Liquid: 16.8 mm

Amine	Color Stability[a] After Storage of Components		
	New Material	60°C/4 Weeks	23°/60°C[b]/12 Weeks
DMPT	2	2	2
DHEPT	3	2	1
DMSX	4	-	3
DMAPAA	3	4	3
MDMAPAA	4	4	4

[a]Color stability ranking: 1 - poor; 4 - excellent.
[b]Powder stored at 23°C; liquid at 60°C.

Table 10

WATER SORPTION OF COMPOSITES[a]

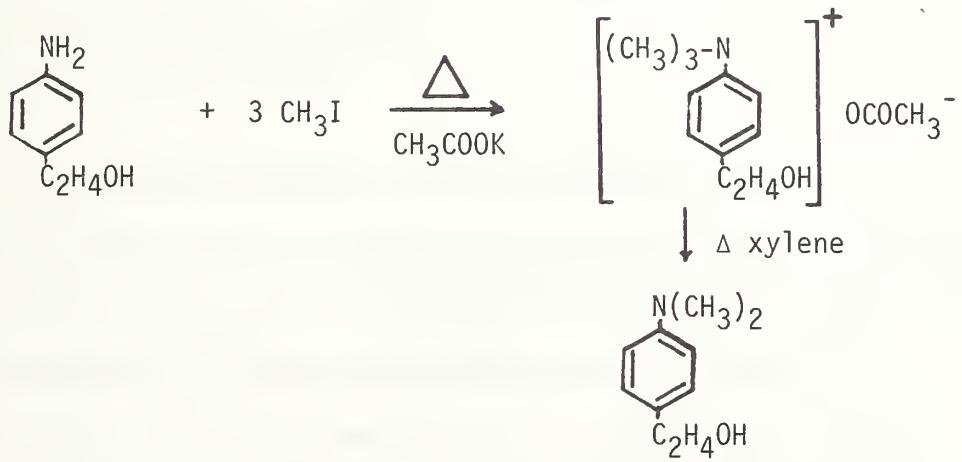
Amine	Concentration mm	Water Sorption mg/cm^2
DMPT	17.0	0.65
DHEPT	13.5	0.92
DMSX	16.8	0.75
TMADMAB[b]	16.4	1.32
LDMAB[c]	17.0	1.50
DMAPAA	16.8	0.77
MDMAPAA	16.6	0.97

[a]Composition of the liquid: 70% Bis-GMA, 30% TEGDMA to which 0.2% BHT was added.
[b]Diluent 20% HEMA, 10% TEGDMA.
[c]71.1% Bis-GMA, 14.3% HEMA, 14.3% TEGDMA and 0.2% BHT.

For a fixed peroxide content coated onto the powder, the amine concentrations range to produce cured resins with high strength is quite critical. Thus, strict quality control is required in the manufacture of these materials to assure that the liquid component contains the proper accelerator concentration.

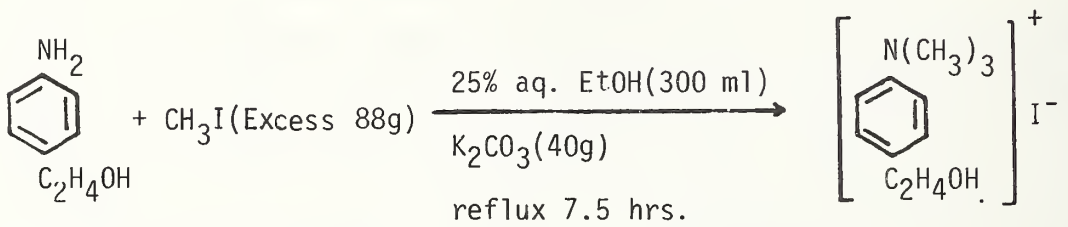
As has been outlined in the Annual Report of FY77 (44) there are good reasons to believe that these newly synthesized amines, in addition to their excellent reactivity, should have promising toxicological characteristics, hopefully better than those of the accelerators presently used. These assumptions are based on the fact that 4-aminophenylacetic acid, aminoglutethimide, 4-aminobenzoic acid and some of their derivatives are used as drugs. Efforts are being made to interest outside laboratories in assessing the toxicological properties of these more promising amines.

A few more amines, which one would predict from structure property relationships to be highly reactive, are being investigated. An attempted synthesis of p-dimethylaminophenethanol was made by the following reaction:



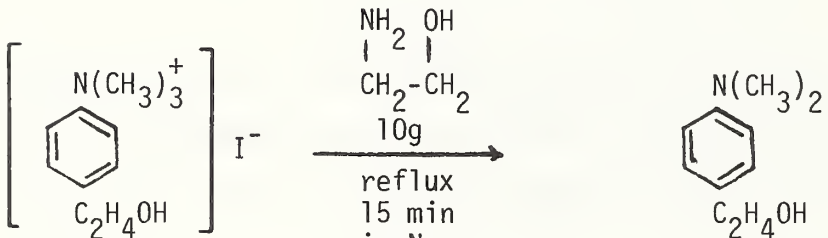
This gave a poor yield of product and an unidentified yellow liquid designated Amine X (approximate B.P. 97°C/7-8 mm Hg) which may be p-dimethylaminoacetaldehyde.

A successful synthesis employed a pure form of p-aminophenethanol and was as follows:



Recrystallized from EtOH and Toluene
20.7 g.

Recrystallized from H_2O - acetone; nearly white flakes
M.P. 172-173°C
Yield 100% (46.1g)



M.P. = 52-53°C after recrystallization from cyclohexane Yield 62.3% (3.3g)

Preliminary studies have been conducted to evaluate p-dimethylaminophenethanol and Amine X as accelerators for composite resin. The composite was prepared using the same formulation employed previously in our studies of amine accelerators except that the powdered glass was obtained from a commercial source (Corning Glass). Tables 11 and 12 give the results of the setting times, tensile and compressive

Table 11

Test Results for p-Dimethylaminophenethanol

Concentration of Amine in liquid, %	Setting Time min.	Tensile Strength MPa	Compressive Strength MPa	Color Stability*
0.20 (12mm)**	3	51.1±3.4†	266.7±4.9	3
0.28 (17 mm)	2 1/2	53.8±1.7	280.6±3.9	-
0.36 (22 mm)	2	56.3±2.1	-	-

* Color stability ranking: 4 = no visible change; 1 = large change

** Millimolal

†Standard Deviation

Table 12

Test Results for Amine X

Concentration of Amine %	Setting Time min.	Tensile Strength MPa	Compressive Strength, MPa	Color Stability
.2%	11.5+ (unacceptable)	-	-	-
.28%	10+ (unacceptable)	-	-	-
.36%	6.5	29.2±5.7 (unacceptable)	-	-
.44%	6.5	33.5±8.0 (unacceptable)	-	-
.6%	4	36.3±10.1	202.1±10.5	2.5

strength and color stability of the composites prepared with these amines. Tables 13 and 14 list properties of a widely used commercial composite (Adaptic) and an experimental composite, respectively, for comparison.

Of the two tertiary aromatic amines studied, only one, p-dimethylaminophenethanol, shows potential as a clinically useful accelerator. The other, Amine X, does not look promising, as it has performed relatively poorly on all tests conducted. Only the formulation containing 0.6% of this amine meets the minimum tensile strength requirement of 34 MPa of the ADA specification for composite filling materials. Investigation of Amine X has been terminated.

Para-dimethylaminophenethanol is the most reactive of any amine in a long series of previously conducted measurements as indicated by the setting times (Table 11). At optimum concentrations, composites containing this amine give tensile strength values that are somewhat higher than those exhibited by the commercially used composite and the commonly employed dimethyl-p-toluidine-accelerated composite (Tables 13 and 14). Compressive strength values are appreciably higher.

The color of the cured composite accelerated with the new amine is remarkably white, and its color stability rating of 3 is acceptable. Although the biocompatibility of p-dimethylaminophenethanol has not been tested, the low toxicity of its homologues would indicate it should have minimal toxicity.

The one problem posed by the p-dimethylaminophenethanol-accelerated composite is that in one series of measurements, within a few days of preparation of the formulation, the setting times of all

Table 13

Properties of a Commonly Used Commercial Composite*

Setting Time min	Tensile Strength MPa	Compressive Strength MPa	Color Stability
2-3	48.4±2.6	203.1±4.1	3 .5

*Adaptic employing a paste-paste system. Values given were previously determined in this laboratory.

Table 14

Properties of Composite made from Powder-Liquid Components Containing Dimethyl-p-toluidine as Accelerator*

Amine Concentration %	Hardening Time, min	Tensile Strength MPa	Compressive Strength Mpa	Color Stability
0.14 (10.2mm)**	6.0	23.8±4.8	147.7±12.2	3 .5
0.23 (17.0mm)	4.5	44.8±1.7	194.4±3.6	2
0.28 (20.7mm)	4.5	28.2±6.2	152.9±25.0	-
0.32 (23.7mm)	1.5	-	-	-
0.60 (44.4mm)	1.0-1.5	-	-	-
0.75 (55.5mm)	4.0	-	-	-

* Data taken from a previous study conducted at the National Bureau of Standards

**Millimolal

three concentrations accelerated to approximately 1 minute. This short setting time does not allow the clinician enough working time to place the restoration. This phenomenon will be investigated in much more detail Furthermore, this behavior probably could be modified or alleviated by the use of a more stable diluent monomer such as hexamethylene dimethacrylate instead of tetraethylene dimethacrylate or an increase in concentration of inhibitor (BHT). Further investigation is required to obtain a formulation with optimum properties.

Ionization Potential Measurements of Tertiary Amines

For better understanding of the mechanism of the amine-peroxide reaction and a more firm basis on which to select the most reactive amines, we began an investigation of the ionization potentials of selected tertiary amines. Ion cyclotron resonance spectroscopy, a novel procedure available to us, is employed.

The basic mechanism by which this system initiates polymerization involves charge transfer complexation. According to this mechanism, the aromatic amine and peroxide form a charge-transfer complex in solution. During this complexation, an electron migrates from the amine to the peroxide resulting in the breakdown of the peroxide into an anion and a free radical and the formation of a cation radical by the amine. One measure of the "driving force" that causes the electron to be emitted from the amine is its ionization potential. The lower the ionization potential the easier the electron loss.

In a previous paper from this laboratory, relationships were derived for correlating changes either in the aryl (ring) substituent or the N-substituent of the tertiary aromatic amine with the ionization

potential of the amine (49). The limited available data were correlated quite successfully using those derived relationships.

In turn, modification of these relationships could be used to predict maximally reactive aromatic amines. Three amines predicted to be maximally reactive were synthesized and tested. They did show high reactivity which were well within the requirements of the ADA specifications for self-curing resins.

The results previously obtained did not allow for estimation to be made for the effect caused by changing the aryl substituent simultaneously with changing the N-substituent. Thus, our first goal was as follows. By designing the experiment so that changes are made in both sets of substituents, the effect caused by these simultaneous changes upon the ionization potential can be determined. In this way it can be ascertained if changes in the two sets of substituents are strictly independently additive or whether an additional algebraic term must be employed to account for the "interaction" between these sets.

When electron loss occurs, it is not known if other changes in the amine occur, e.g., a simultaneous or subsequent proton loss. Since the experimental procedure is a spectroscopic one, breakdown of the cation radical derived from the amine or loss of the electron should be detectable. This information could provide additional insight into the nature of the amine-peroxide mechanism.

Techniques and Results

Ion cyclotron resonance (ICR) spectroscopy, a recent modification of mass spectrometry, is based on the dynamics of charged particles in magnetic and electric fields. The motion of the charged particles in

a uniform magnetic field is constrained to a circular orbit whose angular momentum, or cyclotron frequency, depends on the magnetic field strength and the charge to mass ratio of the ion.

Gas samples are introduced into the trapped ion analyzer cell through a vacuum inlet system. Positive ions are formed by collisions of the gas molecules with the electrons, which are emitted from a rhenium filament on the side of the cell in the direction parallel to the magnetic field. The motion of the ions thus formed by electron impact is constrained to a circular orbit in a plane normal to the direction of the uniform magnetic field by a radio-frequency (rf) electric field. The ions, then, react with neutral molecules present in the cell. Detection of the ions is accomplished by measuring the drop in the rf voltage. Ion abundance is observed on an xy recorder as a function of time.

In applying this technique to the present study, charge-transfer equilibrium reactions of tertiary aromatic amines, useful as accelerators for dental restorative resins, are being studied. Parent ions of two precursor molecules will form an equilibrium reaction in transferring their positive charges to one another. Thermodynamic and kinetic data can be obtained from such experiments. The most powerful feature of ICR spectroscopy is the double resonance or ion ejection technique. Using this method, direct relationships between reactant and product ions can be determined.

We have observed charge transfer reactions in several amine, or more specifically aniline pairs. The results for the various reactions investigated are shown in Table 15. These data are being examined critically for internal inconsistency and for possible utili-

zation in developing thermodynamic relationships pertinent to the amines.

Table 15

Equilibrium Constants and Free Energies ΔG for Selected Charge Transfer Reactions

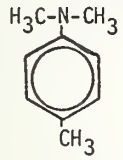
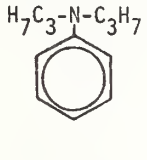
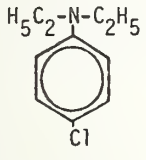
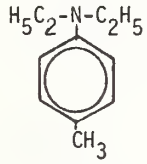
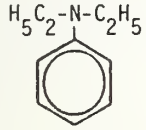
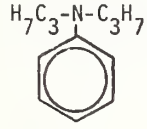
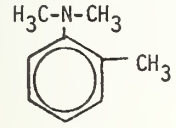
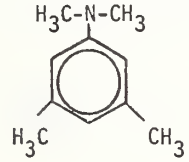
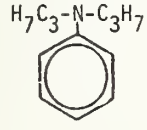
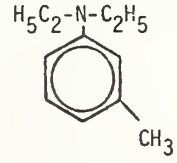
Reactant	Product	K_{eq}	Avg K_{eq}	ΔG	Avg ΔG
 11	 9	2.17 1.41 2.09	1.98	-0.49 -0.22 -0.46	-0.39
 10	 12	84.75 59.91	72.33	-2.76 -2.55	-2.65
 1	 9	4.79 3.84	4.32	-0.98 -0.84	-0.91
 15	 16	15.97 13.76	14.86	-1.74 -1.65	-1.69
 9	 13	4.30 4.06	4.18	-0.91 -0.87	-0.89

Table 15 (continued)

Equilibrium Constants and Free Energies ΔG for Selected Charge Transfer Reactions

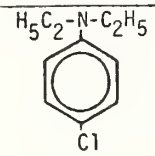
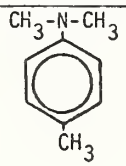
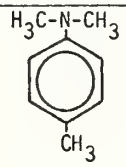
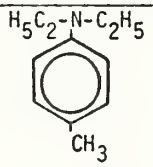
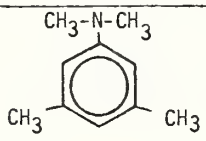
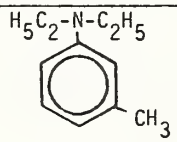
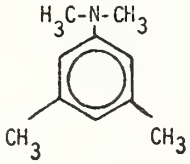
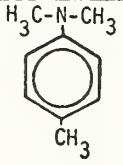
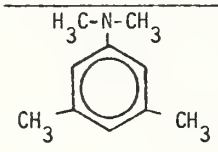
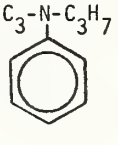
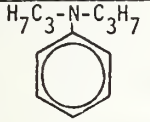
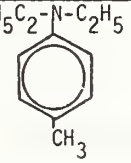
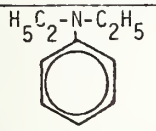
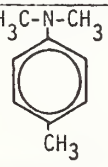
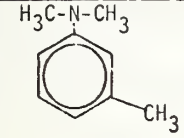
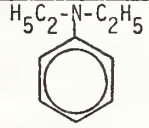
Reactant	Product	K_{eq}	Avg K_{eq}	ΔG	Avg ΔG
 10	 11	25.02	25.02	-2.01	-2.01
 11	 12	53.91 84.36	69.14	-2.49 -2.78	-2.64
 16	 13	26.47	26.47	-2.06	-2.06
 16	 11	2.31 1.92	2.12	-0.53 -0.41	-o.47
 16	 9	1.59 2.14	1.86	-0.29 -0.48	-0.38

Table 15 (continued)

Equilibrium Constants and Free Energies ΔG for
Selected Charge Transfer Reactions

Reactant	Product	K_{eq}	Avg K_{eq}	ΔG	Avg ΔG
		50.05 39.28	44.66	-2.24 -2.10	-2.17
9	12				
		4.08 1.34 4.79 5.71	3.98	-0.80 -0.18 -1.02 -1.10	-0.78
1	11				
		5.84 3.10	4.47	-1.10 -0.70	-0.90
5	1				

II. Techniques for Bonding to Mineralized Collagen Surfaces

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

A. Stability in Cyanoacrylate Bonding

An immediate objective of the present study was to improve the long-term adhesion of 2-cyanoacrylate to dentin by (1) modification of the adhesive, (2) pretreatment of the dentin surface to improve the adhesion to the modified substrate, (3) placing a protective water-repellent film around the joint so that the cured 2-cyanoacrylate adhesive is not exposed to water or at least the water permeation through the protective film to the exposed adhesive surface is minimal. Thus, it was hoped to avoid or at least to minimize hydrolytic degradation of the adhesive. In this study all tensile adhesion tests were performed using an accelerated aging thermocycling test employing 540 temperature cycles per day.

The preliminary results given in the FY77 Annual Report (44) indicated that the magnitude of the cyanoacrylate bond between dentin and acrylic is not equal to that found for bone cemented to bone. However, investigations were continued since modification of the

original procedure, i.e., pretreatment of the dentin surface with a very mild etching solution such as 0.1 or 1% citric acid, yielded excellent short-term adhesion to acrylates as evidenced by the tensile adhesion obtained after thermocycling the specimen in water for 24 hours.

Initial efforts to improve hydrolytic stability involved the incorporation of typical cross-linking agents into the isobutyl 2-cyanoacrylate monomer (which we previously had shown to be the most effective 2-cyanoacrylate adhesive for cementing bovine dentin to acrylic) so that after curing, an insoluble, more hydrolytically stable polymeric adhesive might be formed. However, addition of potential cross-linking agents such as 20% diallyl phthalate, 10% ethylene glycol dimethacrylate, 1% maleic anhydride or 1% itaconic anhydride, to the isobutyl 2-cyanoacrylate adhesive did not increase the strength of the dentin-poly(methyl methacrylate) joint (Table 16).

Thirty second pretreatments of the dentin with very dilute acid solutions were more promising than the incorporation of cross-linking agents into the monomer adhesive. Results of these tensile adhesion measurements for treated dentin surfaces are given in Table 17. Swabbing the dentin surface with diluted ethanol prior to bonding increased adhesion, due to the cleansing action of this pretreatment. Etching with 1% phosphoric acid prior to bonding the dentin to the acrylic rod yielded a bond strength of 12.4 MPa (1800 psi). Etching the dentin with 1% succinic, methacrylic or aconitic acid or maleic anhydride did not improve the tensile adhesion. Best results were obtained using a 1% solution of citric acid in dilute alcohol (1:2 ETOH/H_2O by volume). The bond strength after a 30-second pretreatment

Table 16

Strength of Dentin-Acrylic Resin Joint Bonded

With Modified Isobutyl 2-Cyanoacrylate

Joint was thermocycled in 5°C and 55°C water for one day (540 cycles)

Modifier Added to Adhesive*	Tensile Strength, MPa	
	Mean	SD**
- - -	5.38	3.00
20% v/v Diallyl Phthalate	0	0
10% Ethylene Glycol Dimethacrylate	0.58	1.00
5% Poly(methyl methacrylate) + 10% Dibutyl Phthalate	2.60***	3.40
1% w/v Itaconic Anhydride	3.12	1.47
1% w/v Maleic Anhydride	0	0

* Percentages given for solid modifiers dissolved in the monomer are in w/v,, for liquid modifiers they are in v/v.

** Standard deviation

*** Mean determined on 10 specimens rather than 5.

Table 17

Strength of Pretreated Dentin-Acrylic Resin Bond After Thermocycling for One Day

Adhesive: Isobutyl 2-Cyanoacrylate

Dentin Pretreatment*	Tensile Strength, MPa Mean	Stand. Dev.
Aq. Ethanol (1:2)	7.79	1.97
1% Phosphoric Acid	12.38	2.75
1% Alc. (1:2) Succinic Acid	2.83	3.89
1% Alc. (1:2) Methacrylic Acid	3.68	1.59
1% Alc. (1:2) Aconitic Acid	2.75	2.57
1% Alc. Maleic Anhydride	4.94	1.61
1% Alc. Abietic Acid	4.28	2.36
1% Aq. Citric Acid	12.60	3.62
1% Alc.(1:2) Citric Acid	14.10**	4.46
0.5% Alc. (1:2) Citric Acid	13.44	3.91
0.1% Alc. (1:2) Citric Acid	10.68	3.89
1% Alc. (1:2) Itaconic Acid	8.29***	3.25
1% Alc. (1:2) Itaconic Anhydride	5.80	2.42
1% Alc. (1:2) Citraconic Anhydride	11.13	2.83
1% Alc. (1:2) Tetrahydrofuran 2,3,4,5-tetracarboxylic acid	10.22	2.75
1% Alc. Triallyl Phosphate	2.51	2.84
1% Alc. Triallyl Cyanurate	4.25	4.31
0.5% Alc. Triallyl Cyanurate	1.17	1.69
0.2% Alc. Triallyl Cyanurate	2.51	2.84
1% Aq. Calcium Hydroxide	0.12	0.18
1% Aq. EDTA Tetrasodium salt	11.66	2.54

* Percentages given are weight of solids or volumes of liquids dissolved in volume of ethanol (1:2) or water

** Mean of 10 measurements

*** Mean of 20 measurements

of the dentin with this solution and after curing and thermocycling for one day was 14.10 MPa (2050 psi). This value is considerably higher than any adhesion to smooth dentin surfaces which has been previously reported. The bond strength was slightly decreased when more dilute citric acid solutions were used. Pretreatment with solutions containing 0.5 or 0.1% citric acid gave bond strength values of 13.4 MPa and 10.7 MPa, respectively. Other pretreatments yielding tensile adhesion values above 10 MPa included solutions of 1% alcoholic (1:2) citraconic anhydride, 1% alcoholic tetrahydrofuran -2,3,4,5-tetracarboxylic acid, and 1% aqueous ethylenediaminetetraacetic acid tetrasodium salt.

Pretreatment of the dentin with allyl compounds potentially capable of copolymerization with isobutyl 2-cyanoacrylate was not beneficial to adhesion. Addition of copolymerizable allyl compounds to the uncured adhesive coupled with 1% citric acid pretreatment of the dentin substrate did not improve adhesion (Table 18). Incorporation of a fluorinated 2-cyanoacrylate into the monomer or substitution of n-amyl 2-cyanoacrylate for the uncured adhesive did not increase the bond strength.

Extending the storage of the joined (citric acid pretreated) specimens in the thermocycled water bath to one week or one month considerably decreased the tensile adhesion. Seven-day bond strength values of 2.5 to 4.9 MPa were obtained with the pretreated specimens using the unmodified isobutyl 2-cyanoacrylate adhesive (Table 19). Again, addition of 2-5% cross-linking monomer such as diallyl maleate, triallyl phosphate or triallyl cyanurate did not appreciably increase the hydrolytic stability. Addition of from 3% to 30%

Table 18

Strength of Dentin-Acrylic Resin Bond After Thermocycling for One Day[+]

Dentin pretreated with 1% alc. (:2) citric acid

Adhesive: Modified isobutyl 2-cyanoacrylate

Adhesive Modifier*	Tensile Strength, MPa	
	Mean	Stand. Dev.
5% Triallyl Phosphate	7.77	1.57
5% Diallyl Maleate	8.03	2.15
5% Diallyl Phthalate	0	0
2% Triallyl Cyanurate	8.60	1.32
5% Allyl Methacrylate	7.95	3.41
10% Triethylene Glycol Dimethacrylate	0	0
20% Fluorinated 2-cyanoacrylate	7.22	1.48
100% n-Amyl 2-cyanoacrylate	3.97	1.22

* Percentages given for solid modifiers dissolved in the monomer are in w/v, for liquid modifiers, they are v/v.

[+] All results given in this and the following tables are mean values of 5 measurements.

Table 19

Strength of Dentin-Acrylic Resin Joint Bonded with Isobutyl 2-Cyanoacrylate after Extended Thermocycling

Adhesive Modifier[1]	Length of Thermocycling days	Tensile Strength, MPa Mean	Stand. Dev.
-[2]	7	2.57	1.73
-[3]	7	3.71	1.34
-[4]	30	0.12	0.25
-	7	3.87	1.78
-	7	2.98	1.72
-	7	4.88	1.98
5% Allyl Methacrylate	7	3.72	2.05
5% Allyl Methacrylate	30	0	-
5% Triallyl phosphate	7	2.89	1.35
5% Diallyl Maleate	7	3.18	2.61
2% Triallyl Cyanurate	7	4.35	2.34
3% Poly(ethyl 2-cyanoacrylate)	7	5.84	1.47
5% Poly(ethyl 2-cyanoacrylate)	7	8.67	1.68
12% Poly(ethyl 2-cyanoacrylate)	7	6.59	1.12
20% Poly(ethyl 2-cyanoacrylate)	7	6.77	1.92
30% Poly(ethyl 2-cyanoacrylate)	7	6.28	2.69
40% Poly(ethyl 2-cyanoacrylate)	7	1.51	0.82
50% Poly(ethyl 2-cyanoacrylate	7	1.18	0.88

[1] Percentage are given as weight of solids dissolved in volume of liquid and volume of liquid dissolved in liquid
[2] Dentin pretreatment: 0.5% alc. (1:2) citric acid
[3] Dentin pretreatment: 1% alc. (1:2) itaconic acid
[4] Dentin pretreatment: 1% alc. (1:2) citraconic acid

poly(ethyl 2-cyanoacrylate) to the isobutyl 2-cyanoacrylate monomer, however, yielded a bond with greater resistance to water. Thus, the seven-day bond strength of adhesive containing 5% poly(ethyl 2-cyanoacrylate) was 8.7 MPa compared to 3.7 MPa for the unmodified adhesive. Formulations containing more than 30% of dissolved polymer became quite viscous and their bond strength was quite low. The 30-day thermocycling tests employing isobutyl 2-cyanoacrylate with or without 5% allyl methacrylate resulted in a near zero bond strength for the unmodified adhesive.

In an attempt to reduce or eliminate debonding, a hydrophobic sealant was UV-cured around the dentin-methacrylate interface, the rationale being that the coating would seal off the adhesive from contact with water, or at least the water permeation through the protective film to the adhesive surface would be reduced. Suitable protective formulations should (1) cure within 1 minute, (2) be hydrophobic, (3) be compatible with the etched dentin and the cured cyanoacrylate adhesive, and (4) be storage stable for at least 24 hours. A number of monomeric resin formulations were prepared (Table 20) which are capable of polymerization after irradiation with UV light for 30 seconds. Four compositions with contact angles varying from 54 to 80 degrees were studied further. A thin film of these compositions was painted around the dentin-acrylate joint immediately after the adhesive had set. The protective coating was then UV-cured and the joints were placed immediately into water. A significant improvement in the shorter term stabilization of the bond was obtained with a composition containing 43% hexamethylene glycol dimethacrylate, 41% Bis-GMA, 12% 1H,1H,5H-octafluoropentyl

Table 20

Strength of Dentin-Acrylic Resin Joint Covered with a Protective Coating After Thermocycling

Adhesive: Isobutyl 2-Cyanoacrylate

Dentin pretreated with 1% alcoholic (1:2) citric acid

Protective Coating			Adhesive Tensile Strength, MPa	
Composition	Curing Time sec.	H_2O Contact Angle	7 day	30 day
60% Bis-GMA 25% Trimethylolpropane trimethacrylate 10% 2,2,2-Trifluoroethyl methacrylate 2% UV initiator; 3% photocrosslinking agent	30	59°	5.11 (2.00)	0.98 (0.68)
Same as above but adhesive containing 5% poly(ethyl 2-cyanoacrylate)	-	-	5.27 (2.77)	
41% Bis-GMA 43% Hexamethylene glycol dimethacrylate 12% 1H,1H,5H-Octafluoropentyl acrylate 2% UV initiator, 2% photocrosslinking agent	30	60°	8.92 (3.88)	0.59 (0.63)
43% Urethane dimethacrylate 43% Hexamethylene glycol dimethacrylate 10% Pentadecafluorooctyl methacrylate	30	54°	3.58 (1.06)	-
2% UV initiator; 2% photocrosslinking agent 70% Polyfluoropolyacrylate 30% Pentadecafluorooctyl methacrylate 2% UV initiator 0.3% Dimethylaminophenyl acetic acid	30	80°	4.40 (1.64)	-

acrylate, 2% benzoin ethyl ether, UV initiator and 2% of a UV photo cross-linking agent (oxa-5-acryloxymethyl-3,7-dioxabicyclo[3,3,0] octane. After seven days of thermocycling, the bond strength of dentin-resin joints coated with a protective film of this composition averaged 8.9 MPa (1340 psi). However, further thermocycling to 30 days reduced the adhesive strength to 1 MPa. The other formulations containing a urethane dimethacrylate or the most hydrophobic composition, which contained a fluoropolyacrylate, gave coatings that resulted in only marginal improvement in stability of the bond. Addition of polymeric 2-cyanoacrylate to the adhesive prior to applying the coating did not yield a statistically significant increase in the bond strength.

It should be realized, that the many abrupt temperature changes during the cycling procedure will result in considerable stress formation in the joined substrates that may not be encountered under clinical conditions; i.e., the accelerated test may be so excessively severe as not to be predictive of the clinical long-term applicability of this treatment. The present results indicate, however, that even after applying a protective coating the adhesive compositions studied cannot be recommended for use where a long term bond is required.

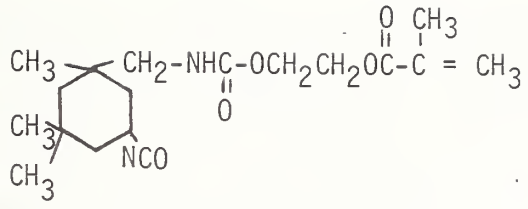
Studies, especially by Stanley and coworkers (50) have shown that etching of dentin with rather concentrated acid solutions, such as 37% or 50% phosphoric acid, gives an undesirable pulp response. The proposed dilute acid pretreatment may be applicable clinically where a strong, short-term attachment to dentin is desired provided that the very dilute (0.1 to 1%) citric acid solutions can be tolerated.

Prof. Cleaton Jones, Director of the Dental Research Institute of the University of the Witwaterstrand, South Africa, has expressed an interest in cooperating in a study of the pulp irritation by citric acid in low concentrations. He also plans to determine the effect of acid-etched dentin lined with an isobutyl 2-cyanoacrylate.

Two manuscripts, "Durability of the Bond Between Bone and Various 2-Cyanoacrylates in an Aqueous Environment" and "Bonding of Acrylic Resins to Dentin with 2-Cyanoacrylate," were prepared. These manuscripts have been submitted for publication. A paper, "Durability of the Bond Between Mineralized Fissures and Potential Adhesives," has been presented as part of the Symposium "Chemical and Physical Lifetime Limits of Macromolecular Materials" at the National Meeting of the American Chemical Society, September 1978. The proceedings of the symposium are scheduled for publication in the "Advances in Chemistry Series."

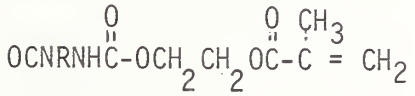
B. Urethane (Isocyanate) Adhesives

Studies to evaluate the adhesive properties of the previously synthesized urethane monomers having residual isocyanate as well as polymerizable methacrylate groups (51) were initiated. To speed up the initial appraisal, bone specimens were cemented together using formulations containing the urethane-methacrylate, diluent (methyl methacrylate or triethylene glycol dimethacrylate), benzoyl peroxide and dimethyl-p-toluidine. The urethane derivatives used were:

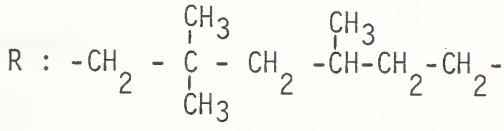


IPDI-HEMA

and



where



TMDI-HEMA

and R: C_{36} hydrocarbon

DDI-HEMA

In these exploratory studies little or no adhesion was obtained with formulations containing TMDI-HEMA and DDI-HEMA. Significant adhesion after storage in water was obtained with IPDI, but the magnitude of the bond strength (2-3 MPa) was considerably lower than the values obtained with the higher 2-cyanoacrylate esters. It appears that the -OH and $-NH_2$ groups in the dental collagen are either not readily accessible to the free -NCO groups or the reaction is too slow. In any case, an adequate bond is not formed within the 1 or 3 min. time limit in which we cement the specimens together before placing them in water. To alleviate this problem we are presently studying the effect of pretreating the substrate surface with very dilute decalcifying solutions (e.g., EDTA tetrasodium salt) and also with other solutions (bases and organometallic accelerators) which should speed up urethane formation.

Our investigations with the urethane-methacrylate adducts containing residual -NCO groups (the amount of which was determined analytically) have so far not yielded adhesion to smooth bone surfaces of the order of 4 to 5 MPa (580-720 psi), which we consider necessary for an acceptable clinical adhesive. By increasing the degree of isocyanate substitution it may be possible to increase adhesion. Furthermore, pretreatment of the collagenous substrate by mild demineralizing solutions should lead to a large increase in reactive sites. Another possible approach, especially when employing prepolymers of diisocyanates is using compositions containing a polymerizable solvent such as hexamethelene dimethacrylate and suitable chemical redox initiators or UV accelerators. Isocyanate prepolymers may also be prepared from amine terminated prepolymers and it may be beneficial to synthesize adducts from methacrylates containing amine substituents or acrylamide and/or polyisocyanates and study their adhesive properties. Such formulations generally contain an oligomer having reactive functional groups, acrylic crosslinking monomer, reactive acrylic monomer diluent to modify the viscosity and photoinitiator and photosensitizer additives. Control over the cured resin vehicle may be exercised by changing the structure of the oligomer backbone (type and number of functional groups present, degree of branching), functionality and level of crosslinking agent and the type and concentration of the reactive diluent. Some of these compositions are claimed to cure rapidly in air without leaving a residual monomeric layer which is always present in the dental pit and fissure sealants available today. Preliminary studies with IPDI-HEMA

indicate excellent adhesion to bone of UV cured coatings containing this adduct. Similar to our tensile adhesion studies candidate materials with desirable properties will be subjected to temperature cycling and other appropriate tests (such as changes in attenuated IR spectrum and changes in contact angle) which will detect any hydrolytic instability or other degradation of the adhesive.

If the true grafting is not obtained between the collagen component of hard tissues and the urethane, it is likely that permanent entanglement between the polymeric chains will result depending on the cohesive energy densities of the two macromolecules. Such interpenetrating networks, in which one is rubbery and the other is glassy, may yield additional reinforcement of the adhesive joint (52-54) without having covalent bonding. Indeed because of the in situ curing shrinkage of the composite an elastomeric phase may in fact be required to avoid the strain introduced on shrinkage. Polymeric compositions with long chain aliphatic diisocyanates such as DDI or HDI may prove most suitable since these groups impart greater flexibility because of the unusual ease of rotation provided by the CH_2 backbone. Thus, enhancement of a number of physical properties including tensile and impact strength and thermal resistance would be expected.

C. Aldehyde Methacrylates

An evaluation of the previously synthesized isomeric methacryloxyethoxybenxaldehydes (12) for their adhesion-promoting properties to dentin was begun. A modified test procedure similar to that employed for the cyanoacrylate adhesion studies reported earlier in this section was employed. The polished, flat ends of the plexiglass rods, threaded

at the opposite end, were wetted with the monomer system to be tested, pressed by finger pressure against the polished dentinal surface and polymerized by UV light through the rod. After storage for 24 hours at 37.5°C in a constant humidity chamber, the specimens were attached via the threaded ends to a jigscrew attachment designed for the Instron.

Two monomer systems were prepared. The control system consisted of Bis-GMA/TEGDMA in ratio 7:3 with 2% benzoin methyl ether as the photoinitiator. The experimental monomer system consisted of equal parts of the o-, m-, and p-methacryloxyethoxybenzaldehydes. No diluent is required with this monomer system nor was an added photoinitiator employed.

Neither control nor experimental monomer systems produced any measurable adhesion with or without mild pretreatment of the dentin with an aqueous $CaCO_3$(pH $\sim$ 8) solution. A mild denaturing pretreatment with a saturated solution of $Ca(OH)_2$ followed by a one minute rinse with distilled water also produced no measurable adhesion. Other types of pretreatment are planned to demineralize the surface layer of dentin and expose more effectively the collagenous surface layer. Also, the synthesis of more reactive aldehyde methacrylates (e.g., aliphatic aldehydes) is planned.

III. Wear Resistance and Mechanical Properties of Dental Materials

The principal objective of this work is to develop instrumentation and obtain appropriate wear data on dental restorative materials and to be able to correlate these data with those obtained from clinical tests. Thus, human masticatory conditions must be simulated to the extent that *in vitro* measurements taken over, say, one day may be correlated with *in vivo* data which require several years to obtain significant results.

The second objective is to adequately define the natural wear process in order to determine the test procedures to be made on various classes of materials in order to develop a correlation between physical properties and durability. Thus, some fundamental model involving various physical quantities may be useful, or necessary, to establish the desired correlations between *in vitro* and *in vivo* tests. Accordingly, the second objective may have to be met to satisfy the first.

The experimental details of the wear apparatus and measurement procedure, along with photographs of certain components of the apparatus were included in the last annual report (44). The system is fully automated and requires no attention during the wear and measurement processes. Basically, three loaded stationery sliders containing human tooth enamel make contact with three corresponding rotating platforms containing the dental materials to be evaluated. The depth of each circular wear track is measured at arbitrarily selected periods remaining between twenty minutes and one hour over 10 positions along the track circumference using linear variable differential transformers (LVDT's). Distilled water flows over the platforms to control temperature, lubricate, and wash away debris.

Prior to this fiscal year the principal investigator of the wear project was a USAF prosthodontist. At the time of his departure the apparatus was complete as intended, but not fully operational and reliable. Consequently, the wear research project was essentially interrupted until a qualified replacement could be found. The replacement problem was compounded by a hiring freeze in effect at that time. It was decided to hire a physicist in lieu of a materials scientist because it was assumed that a physicist would be more proficient in interfacing data acquisition equipment (including debugging), instrumentation, and conducting these experiments. It was also assumed that a physicist could obtain appropriate background while on the job and could collaborate with others more knowledgeable in the materials science area in evaluating the data.

Early in FY 1978, before the replacement arrived, a modification was made by another staff member to improve the measurement process. Prior to this change large amounts of apparent negative wear were sometimes observed which were attributed to the buildup of debris on the measuring probe tips. This problem was corrected by lifting the probes while the platforms are rotating between measurement stations and stopping the platforms when the probes make contact with the sample. Although less than two minutes are added to each measurement cycle, considerable improvement in precision was obtained.

In November 1978 a physicist was transferred into the wear project from another activity in the Polymers Division. His immediate concern was to become acquainted with the measurement system and then commence with debugging and further development necessary to obtain reliable data.

Another experimental problem, revealed by spurious results after attempting to take data for long periods of time, was the penetration of distilled water into the LVDT's. Modifications, including probe extension, were undertaken to improve performance. In addition the LVDT's were mounted in new housings which we designed and built. These proved more stable and facilitated critical adjustment of the transformer cores with respect to their coils. Later in this report data will be presented which depicts the stability and precision of these measurements.

Considerable effort has continued to be expended on debugging the electronic components of the data acquisition equipment in order to make them perform within the specifications of their manufacturers. Eventually the equipment was made very reliable in that it could obtain precise data over long periods of time without attention. This good performance continued until the activity suffered a serious setback which became effective in the beginning of August.

During December 1977 the USAF requested that all of their data acquisition equipment be returned as soon as replacements could be obtained. (Essentially all of the data acquisition equipment associated with the wear apparatus belonged to them.) Shortly after the USAF announcement NIDR approved funds for replacements. Since we have found the USAF's data acquisition equipment initially unreliable, we decided to replace it with different components made by other manufacturers in most cases. Also servicing by one of the makers of the USAF equipment has become difficult to obtain because of their recent move to a remote location. With the USAF equipment the experiment was controlled directly from a tape. In the replacements we have decided to use a computerized

controller, which will simplify programming and incorporate decision-making during the measurement process. We assume that the additional time and effort required to interface the new system will be offset by its advantages in performance over the old one.

After it became apparent that the wear apparatus (with the USAF equipment) was performing well enough to obtain reliable data, we decided to obtain as much as possible before the data acquisition equipment was reclaimed. Measurements were taken on three materials: poly(methyl methacrylate) (PMMA), Velvalloy amalgam, and Adaptic composite. The wear rates G = V/WL, where V is the volume loss, W is the normal force, and L is the total sliding distance, are tabulated in Table 21. In all cases the wear couples involved human tooth enamel (with underlying dentin) except where indicated otherwise. The three systems A, B, and C pertain to the three samples (worn and measured simultaneously) and their associated measuring devices. Positions 1 and 6, which are 180° apart, are two of the ten positions measured along the wear track circumference of each sample. The values of G were obtained from least square fits on the wear track data.

PMMA, which is a constituent of many restorative materials, was studied principally to obtain an initial evaluation of the apparatus. In this case the specimens were machined from an extruded rod. The data for systems A and B are not included in Table 21 because of an improper adjustment in their LVDT's which was corrected subsequently. The data are shown on Fig. 6 where the wear track depth is plotted against time. The sudden increases in wear of the order of several micrometers, particularly apparent in the lower curve, are typical of fatigue resulting in

Table 21

WEAR RATES FOR RECENTLY MEASURED MATERIALS

Material	Rotor	Position	$G \times 10^6$ mm^2/kg	$G_{av.} \times 10^6$ mm^2/kg
PMMA	C	1	1.81	
		6	0.97	1.39
Velvalloy	A	1	0.38	
		6	0.51	
	B	1	0.77	
		6	0.89	
	C	1	0.48	
		6	0.69	0.62
Adaptic	A	1	0.113	
		6	0.164	
	B	1	0.061	
		6	0.074	
	C	1	0.107	
		6	0.107	0.104
Velvalloy-Durapatite	C	1	0.43	
		6	0.38	0.41

surface flaking, where large chunks of debris are removed. The vast difference between the wear rates (proportional to the slopes of these curves) measured at the two positions shown, is tentatively attributed to density or structure gradients within the sample. Such behavior is commonly observed in wear measurements. It is clear from these observed irregularities that extensive data are required on several samples and many positions on each to obtain meaningful results.

The data for the three Velvalloy specimens are depicted in Fig. 7. The wear process for this material is more erratic, but appears to be more homogenous than that for PMMA. Surface flaking for Velvalloy comprises particles as large as 10 μm in thickness. Also, a healing or smoothing process is often seen from apparent negative wear, immediately after flaking, the void is partially built up from material in the neighborhood. The straight lines are obtained from linear regressions on each data set from which the wear rates (Table 21) are determined.

The results for the Adaptic specimens are displayed in Fig. 8. The wear process is slow with little or no flaking and shows little evidence of inhomogeneity. The Adaptic specimens produced more wear on the enamel sliders than the Velvalloy. The observed average slider wear rates are 2.1 μm/hr. against the Velvalloy and 6.5 against the Adaptic. The higher rates with Adaptic apparently result from the small quartz particles used as a constituent.

Periodically, highly polished brass flats are secured in the specimen cups and measurements are made over about one day without water.

The results indicate the quality of performance and give a measure of precision which we may relate to the irregularities in the wear data.

Figure 9 depicts an example of data obtained in this fashion. In this case the apparent wear depths (which is a measure of imprecision) are plotted against time. The standard deviations of the residuals about the means (displayed here as zero) for systems A, B, and C are 0.25, 0.26, and 0.30 μm, respectively. Somewhat paradoxically, the largest deviation 0.8 μm was obtained in position A which has the smallest standard deviation. Note that, in particular, the upper curve reveals an apparent decreasing trend corresponding to a slope of -0.033 μm/hr. obtained by linear regression. The slopes obtained from the wear data range from 0.14 for Adaptic to 3.5 μm/hr. for PMMA. Consequently, for low wear materials an improvement in drift stability would be desirable. The irregularities in the wear mentioned earlier, however, cannot be attributed to imprecision.

The recent results on Velvalloy and Adaptic are not in agreement with those obtained on the prototype (55) several years ago for which the values of G were 0.13×10^{-6} and 0.22×10^{-6} mm^2/Kg, respectively. At this time it is not appropriate to speculate on the reason for these discrepancies. We will attempt to resolve this when we repeat these measurements after the new apparatus becomes operational.

Obtaining satisfactory slider specimens from human teeth is a difficult and time-consuming procedure. Furthermore, even specimens obtained from the same tooth may have significantly different characteristics, as a consequence of different orientations with respect to the surface and variations in structure throughout the enamel region of the

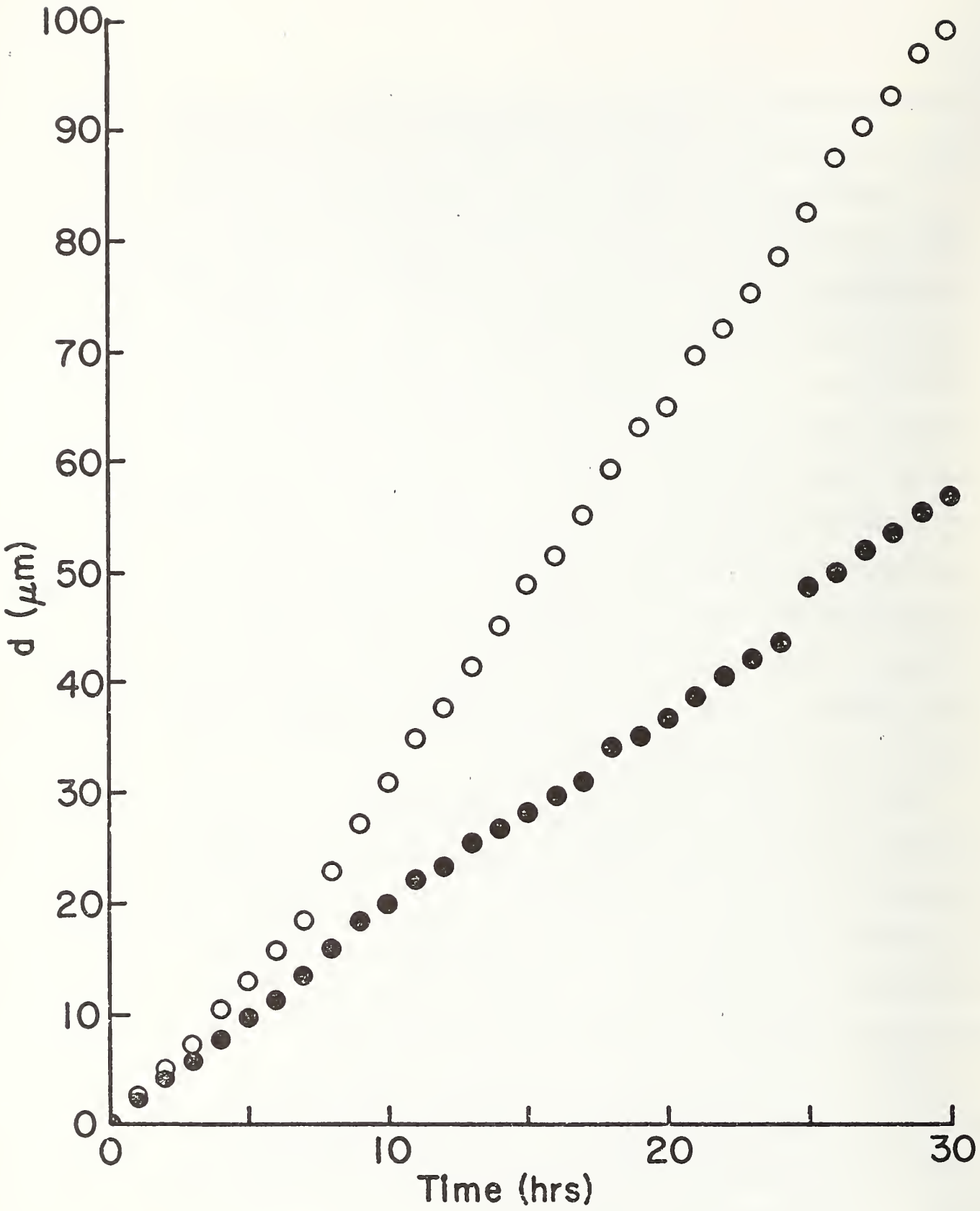


Fig. 6: Wear track depth d against time for poly(methyl methacrylate) measured at positions 1 (open circles) and 6 (closed circles).

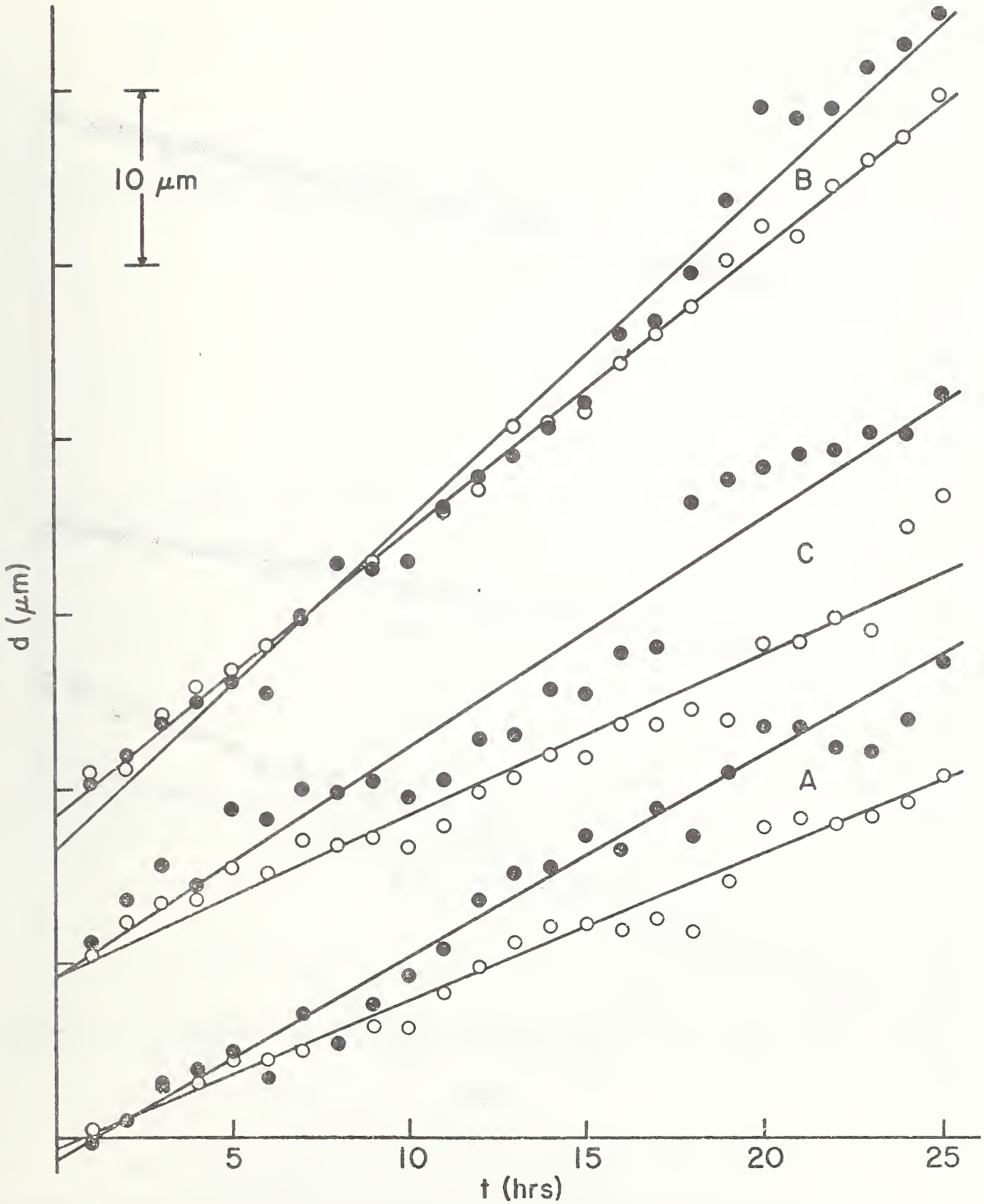


Fig. 7: Wear track depth d against time for Velvalloy (amalgam) measured on platforms A, B, and C at positions 1 (open circles) and 6 (closed circles).

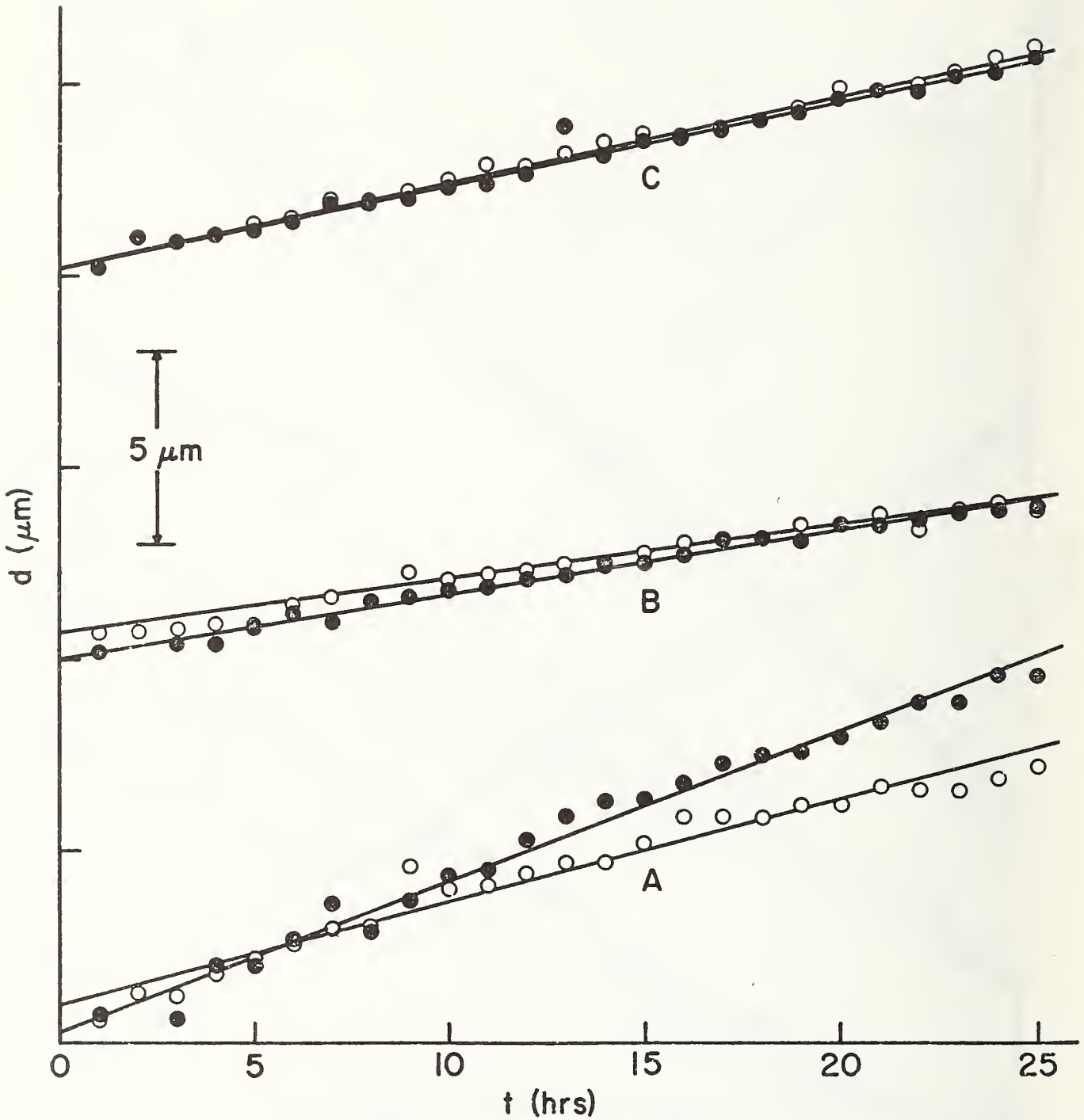


Fig. 8: Wear track depth d against time for Adaptic (composite) measured on platforms A, B, and C at positions 1 (open circles) and 6 (closed circles).

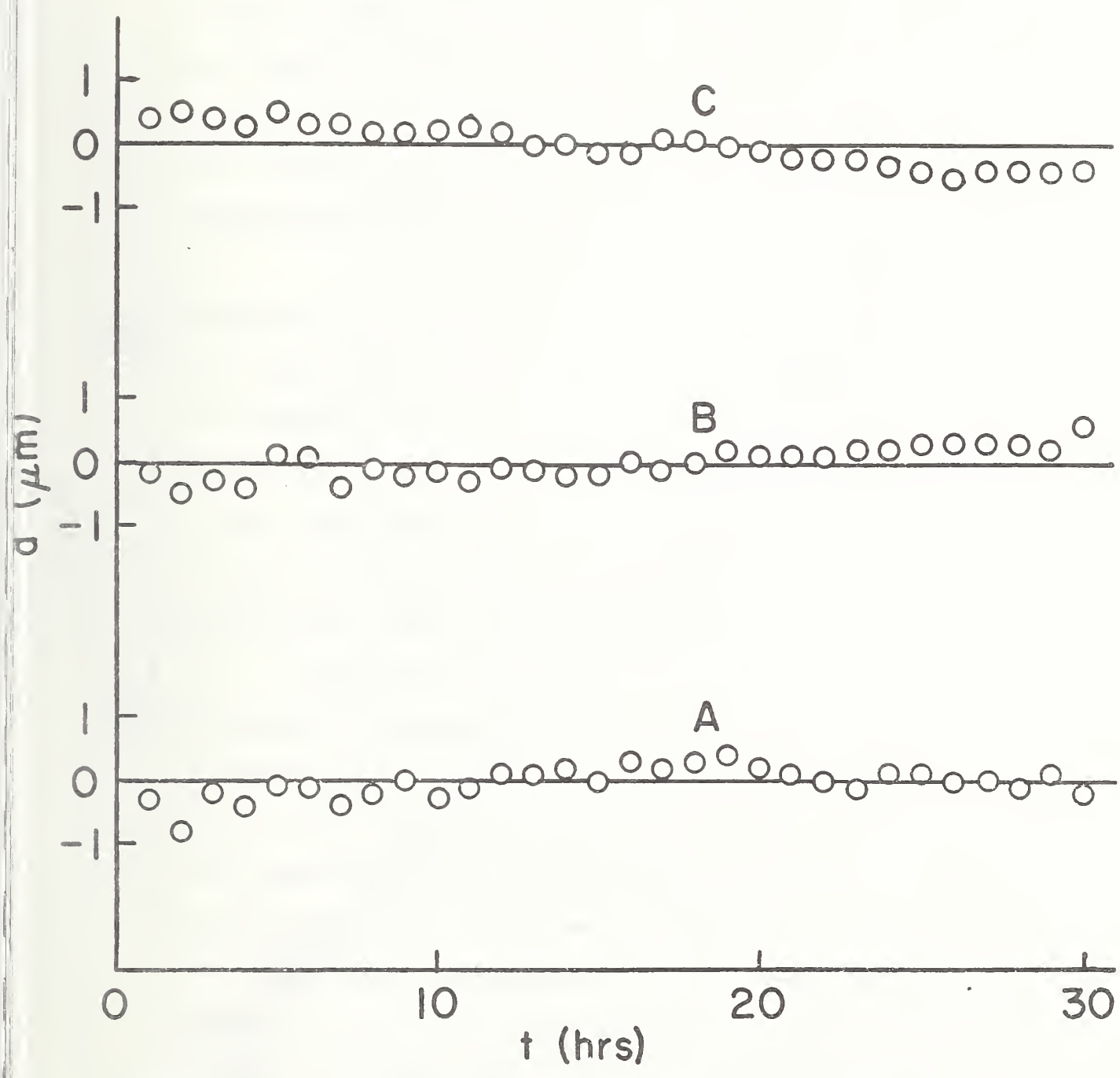


Fig. 9: Apparent wear track depth d against time using brass flats (in lieu of specimens) with no wear.

tooth. Also, during the wear process the investigator may not know when the enamel has been depleted and the underlying dentin has become a component of the wear couple. Accordingly, it would be extremely useful to have a substitute for enamel which resembles it in structure and properties of enamel and, unlike enamel, is homogeneous, isotropic, and consistent. A high priority should 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 (56) used large crystals of natural fluorapatite 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 the enamel sliders. Also, as an alternate, Rooture, Powers, and Craig (57) have suggested using sintered hydroxyapatite for this purpose.

In this connection we have obtained some Durapatite hydroxyapatite samples which were given to us by Dr. M. Jarcho at Sterling-Winthrop Research Institute. Some of these samples were in the form of cylinders but needed to be machined to smaller diameters to be satisfactory for our use as sliders. Subsequent wear measurements were made on using a Velvalloy-Durapatite wear couple. The results are shown on Fig. 10 where the wear track depth is plotted against time at positions 1 and 6. The wear rates are tabulated in Table 21. From comparison of these results with those from the Velvalloy-enamel wear couple displayed on Fig. 7, it is seen that the responses are similar. As seen in Table 21 the wear rates for the Velvalloy-Durapatite are low, but fall within the

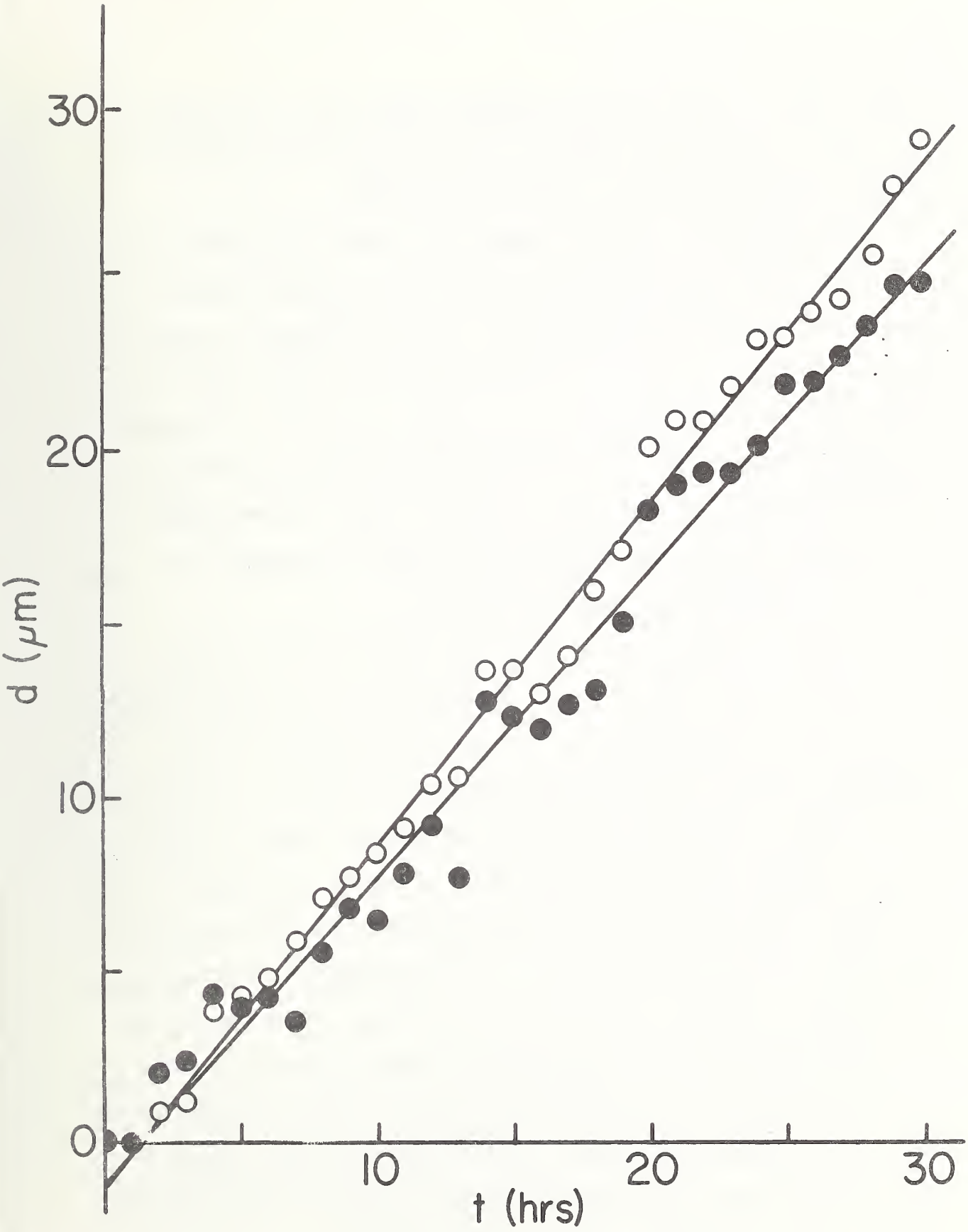


Fig. 10: Wear track depth d against time for Velvalloy (amalgam) measured at positions 1 (open circles) and 6 (closed circles) using Durapatite for the slider.

range of those obtained for the Velvalloy-enamel couple. This data is, of course, not conclusive; however, it does indicate the possibility of employing hydroxyapatite as a substitute for enamel.

The assembly of the new wear apparatus is about 95% complete. We still await delivery of a bus cable which has been delayed because of production problems at the manufacturer. Delivery has been promised by the end of October. The principal difference between this system and the old one is the implementation of a computer controller. The computer uses Basic language and has sufficient memory (24K bytes, expandable to 56K) to do the kind of data processing we anticipate. It is equipped with both EIA and IEEE-488 interfaces which makes it compatible with most interfacing equipment currently available.

The work on other physical properties related to wear will be initiated early in FY 1979. A materials engineer is being hired to work in this area. In connection with this activity a uniaxial universal mechanical testing machine has been ordered and delivery is expected in mid-November. The machine is hydraulically actuated, rated at 3300 lbs., and has separate, stroke, load, and strain controls. It has both static and dynamic modes, being able to generate periodic inputs (sine, square, and ramp) with amplitudes adequate for testing purposes at frequencies up to 300 Hz. Emphasis will be placed initially on elucidation of the micro-deformation mechanisms operable in the dental composite system under various applied stresses and environments. These micro-deformation mechanisms include craze and shear band initiation and their growth in the matrix materials, the interfacial failure between the plastic matrix and the inorganic reinforcement particulate materials.

IV. Base Metal Alloy and Dental Ceramics Research

The objectives of this research have been to determine the characteristics of base metal casting alloys and associated bonding porcelains in relation to the feasibility of their use in cast crowns and fixed partial dentures, and to utilize this information for the development of improved fabrication techniques for these porcelain to metal restorations.

Extensive work has been undertaken in this project and reported previously in the area of dental casting. Specific emphasis was directed toward "accuracy of fit" and "castability" of several dental alloys (44,58). However, several questions remained unanswered. One alloy, Ticon, in which there has been considerable interest was not included in the investigation. All castings were made in molds for which the investment material was mixed without the use of vacuum. Kaowool (59), a refractory felt-like material, was used as a ring-liner in the study and significant increases in mold expansion were noted with its use. Time, however, did not permit an analysis of its physical characteristics as compared with the traditional ring-liner, asbestos. Accordingly, work accomplished during this reporting period has been directed toward addressing these questions.

Consistently oversized (acceptable) base-metal castings are now produced routinely at NBS using investment techniques developed in this study. However, the surfaces of castings produced via this technique are frequently unacceptably rough; i.e., a relatively high number of surface projections and nodules are present on the castings. The

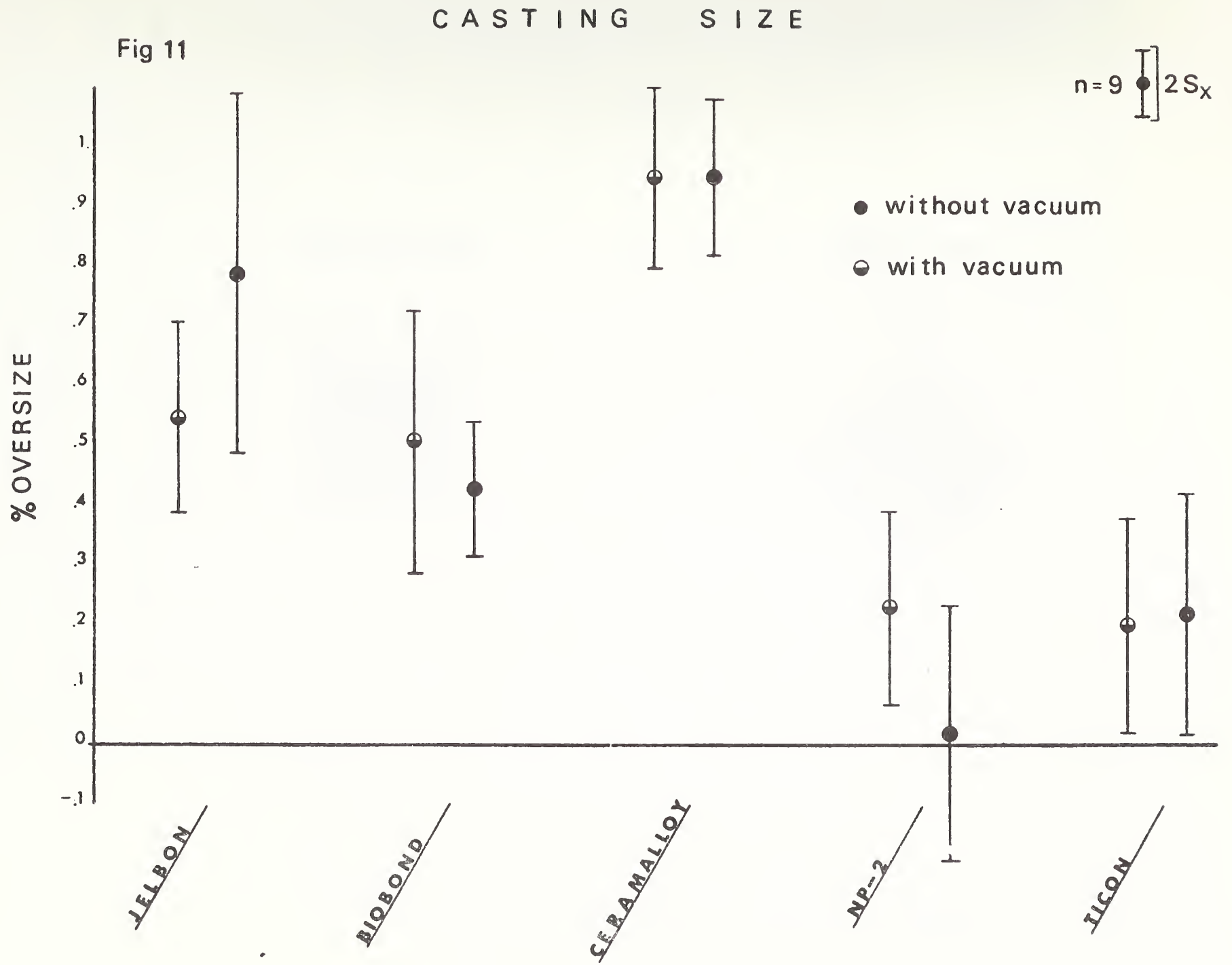
experiment has been repeated with several previously studied alloys using investment procedures that include the application of vacuum. An early trend observed with this technique refinement would suggest a possible improvement in surface smoothness. To date, no significant differences have been shown in either increased expansion or casting accuracy when recent experimental results have been compared with data reported previously in this project (Fig. 11).

The alloy, Ticon, has been evaluated in an identical manner as were all other alloys. Casting accuracy and castability data did not vary significantly from other alloys reported in the first phase of the project. Kaowool has been examined and our results confirm that the material is, indeed, significantly more compressible than asbestos. Further, and perhaps even more important, Kaowool is more uniform in its consistency, thereby providing more predictable expansion characteristics than asbestos when used as a ring-liner.

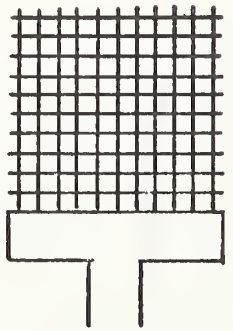
A system for measuring the castability of dental alloys has been developed as part of this project and identified in a previous report. Data collected from this work suggested that a rather wide range of variability might be inherent in the test procedure. Close examination of the grid-like castings revealed more completed vertical than horizontal segments. This observation is thought to be associated with inconsistencies in the sieve material which is used for the patterns. A pattern modification (Fig. 12) is being tested presently which should serve to reduce the variability in the test results.

Although work continues in the study of base-metal alloys, emphasis in the second phase of this project is being directed in the area of

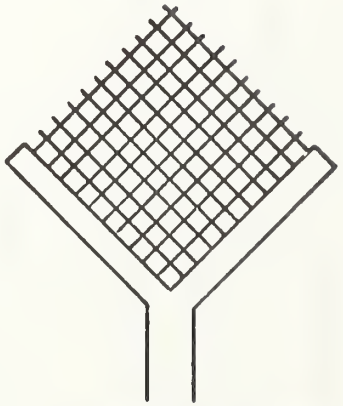
Fig 11


CASTING SIZE
n=9
2Sx
without vacuum
with vacuum
% OVERSIZE
1.
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
-.1
JELBON
BIOBOND
CERAMALLOY
NP-2
TICON

CASTABILITY PATTERN MODIFICATION



STANDARD



MODIFIED

Fig 12

dental ceramics. The study of six commercially available dental bonding porcelains has been undertaken. Dimensional changes resulting from heating and cooling cycles are being observed through the use of a differential dilatometer. Eight casting alloys will be examined in a similar manner. Variables include the total numbers of firings and differing load conditions. Preliminary findings indicate that variations in the number of firing cycles and the amount of condensation of the green porcelain cause significant differences in dimensional characteristics on cooling of fused dental porcelain. Early observations suggest that resistance of the porcelain to flow under load changes with repeated firings. Additionally, it would appear that ceramic materials from different manufacturers vary markedly in their dimensional responses to thermal changes. The data collected to date would suggest that varying degrees of residual stresses exist in different dental porcelains when cooling rates follow those prescribed by the respective manufacturers. The firing schedule followed under experimental conditions necessarily varies from commercial firing rates. These (slower) rates appear to effectively anneal the porcelain materials thereby changing their physical properties. These observed changes may have an effect on the compatibility of the porcelain materials with selected alloys. The significance of these data will be addressed during this phase of the investigation. The knowledge thus derived may serve as a basis for technique refinements aimed at improving the bond strength of porcelain-fused-to-metal restorations.

Initial observations suggest that the wetting characteristics of base metal alloys by dental porcelains during fusion may vary greatly

with differences in alloy composition as well as with surface preparation techniques. An investigation is in progress which will observe directly through scanning electron microscopy the influence of these variables on the wetting characteristics of selected porcelain/alloy combinations. Initial work has been directed toward the construction of a suitable specimen. The experimental procedure has involved fusing of the porcelain to a pre-treated (air-abrasive blasting) metallic surface, removal of the alloy from the fused porcelain via an electrolytic/chemical etching technique and SEM observation of the ceramic surface to ascertain the extent of reproduction of the metal surface by the fused material. Early findings from this method have been unsatisfactory. Neither the surfaces of the opaque porcelains fused to the base metal alloys nor those fired to the gold alloys reproduced the morphological structure of the metal as it was photographed after blasting. Generally, the ceramic surfaces appeared smoother than the original surface of the metal. Many voids (holes) could be seen on the Vita opaque no matter what alloy was used. These voids are thought to be inherent with the brush technique of applying the porcelain.

These initial observations have necessitated some major modifications in the experimental technique. Refinements of these procedures which presently are being examined include a metallurgical polish of the alloy surfaces followed by the controlled scoring of the surface, application of the ceramic material and SEM observation of cross-sections through the porcelain/alloy specimen. The information thus gathered will be extremely valuable in developing specific modifications of existing laboratory techniques.

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

To improve the storage stability of dental composite resin systems, alternative catalyst systems to the commonly used benxoyl peroxide-tertiary amine are being developed. Increased storage stability is attainable with organic peresters or hydroperoxides but requires more efficient accelerators than the presently used amines. Ascorbic acid or ascorbyl palmitate offer promise as useful accelerators which give good biocompatibility. To develop more reactive amine accelerators with perhaps less toxicity than those currently in use, p-dimethylamino-phenylacetic acid (or ester derivatives) and dimethylaminoglutethimide were synthesized and shown to yield composite restorative specimens of good mechanical strength and color stability. A wide range of cyanoacrylates from the simplest, 2-ethyl cyanoacrylate, to the more complex type such as viscous isoamyl product have been examined for their capacity to achieve and retain bonding between acrylic resin and dentin. Very high initial bond strengths were achieved with isobutyl-2-cyanoacrylate on dentin pretreated with dilute acid but a one-month thermal cycling test in water indicated the bonding was not sufficiently stable. Initial pin on disc wear measurements with a synthetic hydroxyapatite pin have shown promise.

A pattern modification to reduce variability in the alloy castability test has been developed. Variations in the number of firing cycles and amount of condensation of green porcelain have been shown to cause significant differences in dimensional characteristics on cooling of fused dental porcelain.

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)*

Accelerator; alloy; base metal; casting; composite; cyanoacrylate; dental alloy; initiator; resin; wear.

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