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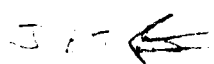
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ABSTRACT

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Various techniques are presently available that improve the bonding of filled and unfilled resins to base metal alloys in prosthodontics. A few of these techniques have focused on surface treatments of alloys suitable for use in removable partial denture frameworks and the resultant increase in bond strength between the alloy and acrylic resin.

The purpose of this study was to evaluate the tensile bond strength obtained when denture base acrylic resin was processed against Ticonium 100 under varied conditions. All specimens were etched with Quick-Etch, a commercially available chemical etchant. The etched surfaces were divided into three groups; 1) etched only, 2) treated with 4-META, a chemical coupling agent, and 3) coated with a bis-GMA bonding resin, Self-Cure, to promote adaptation.

Polymethyl methacrylate, Lucitone 199, was processed against all surfaces following standard laboratory procedures. Thermocycling of samples was conducted to incorporate the effects of intraoral temperature and water sorption on bond strengths. Tensile bond strengths were measured with an Instron machine. SEM (scanning electron microscope) analysis of the fracture patterns revealed a correlation between bond strength and amount of residual resin on the etched surfaces. 

No significant difference was found between the tensile bond

strength of the etched only and the bonding resin groups (6.39 +/- 6.04 MPa versus 6.81 +/- 7.73 MPa). The specimens treated with 4-META demonstrated significantly higher tensile bond strengths than either of the other two groups (24.30 +/- 11.29 MPa).

The results indicate that the use of a coupling agent would lead to a significant increase in tensile bond strength of etched alloy - acrylic resin systems.

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EFFECTS OF DIFFERENT SURFACE TREATMENTS ON THE
TENSILE BOND STRENGTH OF POLYMETHYL METHACRYLATE
PROCESSED AGAINST CHEMICALLY ETCHED TICONIUM 100

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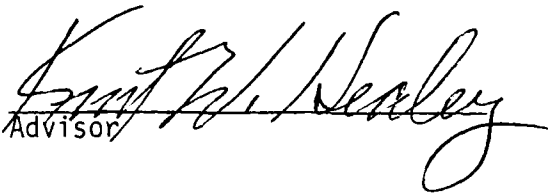
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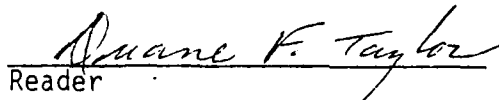
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of North Carolina at Chapel Hill in partial fulfillment
of the requirements for the degree of Master of Science
in the Department of Prosthodontics.

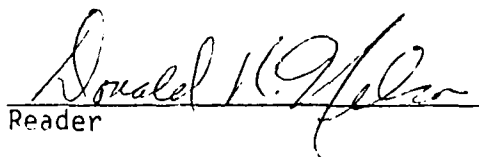
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Various techniques are presently available that improve the bonding of filled and unfilled resins to base metal alloys in prosthodontics. A few of these techniques have focused on surface treatments of alloys suitable for use in removable partial denture frameworks and the resultant increase in bond strength between the alloy and acrylic resin.

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The results indicate that the use of a coupling agent would lead to a significant increase in tensile bond strength of etched alloy - acrylic resin systems.

DEDICATION

To my wife, Kristi
For her patience and love

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INTRODUCTION

It has been estimated that over four million removable partial dentures are delivered each year in the United States¹. The use of denture base acrylic resins and base metal alloys in the fabrication of removable partial dentures necessitates appropriate physical retention measures to combine these materials in most final designs. Frequently, insufficient interarch space is available further compromising adequate retention. Though ingenious methods have been devised to circumvent these minimal space situations, esthetic and/or strength requirements are not always satisfied. Micromechanical retention techniques which were originally devised for etched enamel surfaces and composite resins have contributed significantly to the development of similar retention techniques for denture base acrylic resin to removable partial denture alloy. Many investigators, however, have expressed concern over the deleterious effects of contamination on eventual bond strength. In removable prosthodontics, contamination is encountered during many of the phases of laboratory processing, especially during the waxing, boil-out, and packing steps. Most research to date has focused on improving the electrolytic etching techniques. Chemical etching has also been attempted with results similar to the electrolytic approach.

Once uniform etching has been achieved, other factors at the interface govern the retention between materials. Recently, the

Japanese have devoted significant effort to developing agents which increase the wettability and the bonding at the interface by acting as "chemical" coupling agents.

The objective of this study was to compare the effects of various surface treatments on the tensile bond strengths between a denture base acrylic resin (Lucitone 199) and a chemically etched nickel-chromium removable partial denture alloy (Ticonium 100). The experimental design consisted of three surface treatments: 1) etched only, 2) etched and treated with 4-methacryloxyethyl trimellitic anhydride (4-META), and 3) etched and coated with a bis-GMA unfilled resin (Self-Cure).

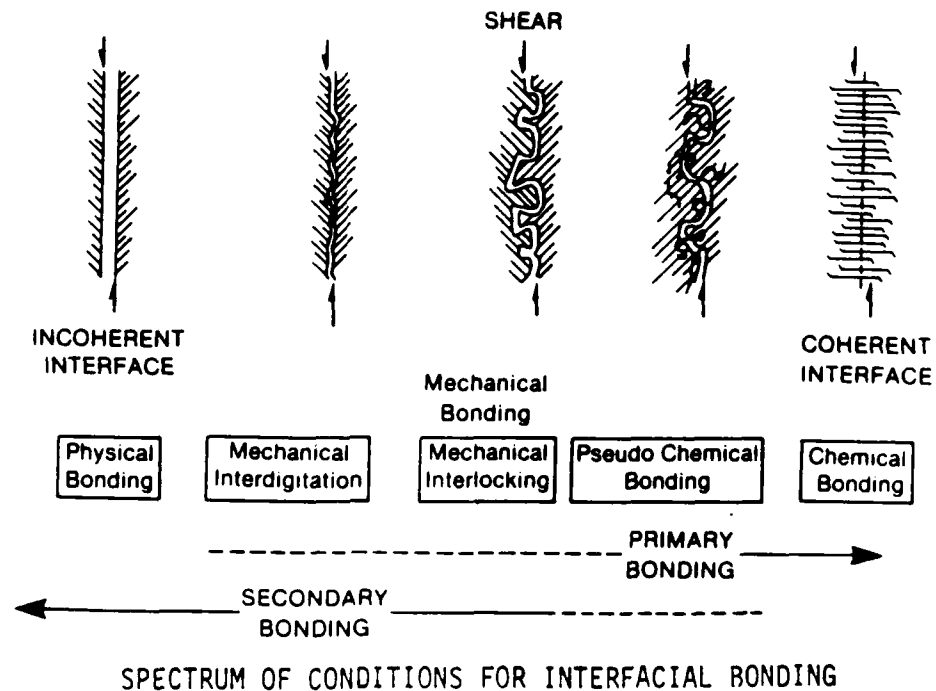
Improved bond strengths as achieved with chemical etching would significantly reduce the need for special designs often required to retain the denture base acrylic resin onto removable partial denture frameworks. Micromechanical retention attained with this technique would also facilitate removable partial denture repairs which involve the addition of acrylic resin to metal components. Relining metal denture bases, whether they involve complete denture or distal extension surfaces, could be accomplished quickly and with greater ease than by using other etching techniques or conventional repair methods.

REVIEW OF LITERATURE

Prior to reviewing the research on effects of surface treatments on bond strength, certain concepts of "bonding" or adhesion and metallurgy must be understood.

Adhesion

Bayne *et al.*² define adhesion as "the state in which two surfaces are held together by interfacial forces which may consist of valence or interlocking forces or both." These authors illustrate the conditions for interfacial bonding concisely by using this schematic (reproduced with permission of the authors);



Bonding may involve an incoherent interface in which weak intermolecular (van der Waals) forces lead to attraction between two surfaces. Van der Waals forces have been shown to be due to three actions: (1) orientation, (2) induction, and (3) dispersion effects³.(p.728) Or bonding may be totally chemical in nature, a situation creating a coherent, seemingly undetectable interface.

Primary bonding is thus seen as more chemical than physical, whereas secondary bonding is more physical. In dental bonding systems, primary bonding is the ultimate goal, though it is more likely that present systems are more of the mechanical interlocking variety.

Adhesion formation is dependent upon various factors. These include, but are not limited to, the availability of electrons in chemical bonding for sharing (covalent bonding) or transfer (ionic bonding), the surface free energy and surface tension, the contact angle at which the adhesive meets the adherend, and the viscosity of the adhesive.⁴

Surface free energy has been described in terms of energy per area. Most of the surface free energy is developed within a few molecular diameters of the surface. When compared to the surface free energy of liquids, that of solids is much higher, because of the ability of solids to support shear stresses.⁵ The higher the surface energy, the greater will be the capacity for adhesion.⁶

Surface tension, expressed in work units (force per length), has been described as that attraction of molecules within a liquid for each other. At the surface, a molecule is only partially surrounded by other molecules and experiences only an attraction toward the body

of the liquid.^{7(p.16)}

Contact angle is zero degrees when a liquid wets a solid completely. Spreading over the surface occurs at a rate depending on the liquid viscosity and solid surface roughness.^{8(p.2)} The contact angle is the result of an equilibrium between the surface free energies of the solid substrate, the liquid phase, and the gas phase. At equilibrium, the free energy of the interfaces between the phases is a minimum.^{8(p.11)} Changing any one of the phases changes the equilibrium and can affect the contact angle.

Viscosity is the resistance of a fluid to flow and is equal to the shear stress divided by the shear rate.^{9(p.87)} Buonocore ^{7(pp.17-19)} considers that the polymerization of a liquid adhesive may be a continuous process of viscosity increase until a rigid state is reached. He further states that some materials may, as a result of polymerization shrinkage, induce internal stresses at the bonded interface. These internal stresses or stress concentrators make the bond more susceptible to disruption than when the adhesive was in a less viscous state.

Asmussen¹⁰ noted that viscosity, surface tension, and contact angle are factors that influence the penetration of restorative resins into acid etched enamel. Contradictory results have been reported concerning the relevance of viscosity to penetration of etched surfaces and bond strengths.^{11-16,79} Asmussen¹⁷ also studied the effect of air entrapment within the low-viscous, bonding resins. He concluded that its application to etched enamel was not likely to improve the quality of the bond.

Metallurgical Concepts

Base metal alloys used in removable partial denture construction are generally comprised of more than one phase. In nickel-chromium alloys, it is common for the first phase to form a dendritic morphology upon solidification.^{18(p.640)} The dendritic structure is said to be accompanied by compositional segregation noted in the microstructure of alloy specimens treated with certain etchants.¹⁹⁻²⁰ Alloys containing beryllium are known to be the only ones with a large volume fraction of a solid solution as a secondary phase. Nickel-beryllium solid solution is located between dendrites of the gamma primary solution, which contains mostly Ni_3Al .^{18(p.641)}

In the as-cast state, base metal alloy surfaces are covered by oxides and irregularities. For most alloys, these irregularities and oxides are selectively removed by means of an electropolishing technique.^{21(p.1)} Electropolishing involves a deplating procedure which leads to "smoothing" and "brightening" effects with oxides sometimes creating a passivating film on the alloy surface.^{21(p.34)} In this fashion, the alloy becomes impervious to tarnish (surface discoloration) and less likely to corrode by further reacting with its environment.

Surface Treatment

The purpose of electrolytic etching is to selectively remove components of a surface without replacement, thereby increasing the area of the surface. Electrochemical corrosion, i.e., electrolytic etching, involves the process of local ion formation at the reactive surface in addition to a long range electron transfer.^{2(p.8-2)} Such reactions are dependent upon electrolyte temperature, current density,

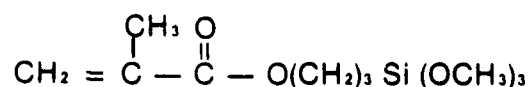
agitation of the electrolyte, initial surface preparation, time of treatment, and size of the specimen.²¹(pp.27-30)

The result of chemical corrosion is essentially the same as with electrochemical corrosion. However, there is no long range transport of electrons, since a solid solution reaction product forms at the surface.²(p.8-17) Electrons available for transfer are not replenished but are limited by the acid in contact with the surface. Except for current density, chemical corrosion is dependent upon the same factors as electrochemical corrosion. Nevertheless, McLaughlin and Masek⁷³ did point out that chemical corrosion does simplify the procedure and generally reduces the etching time.

Coupling Agents

Bowen and coworkers²² differentiated between surface active comonomers and coupling agents. The latter contain polar groups whereas the former do not. Historically, organofunctional silanes have been used to increase the cohesion of composite resins by reacting with the glass or water absorbed on the glass through the ethoxy-, chloro-, amino- groups, leaving the vinyl group to react and form a bond with the resin.²³ Bowen's resin was composed partly of silane treated glass particles.²⁴ Silanes have also been used to promote bonding between resins and ceramics and metals.

A common silane used in dentistry is the ester of methacryloxyalkylsilane:

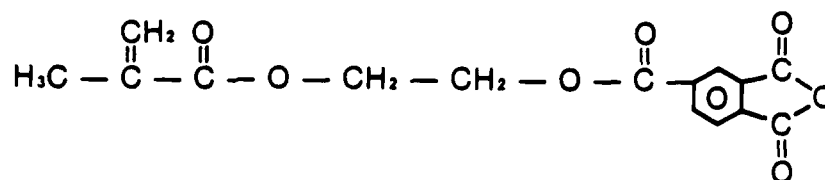


The coupling mechanism with such a compound is based on its dual

reactivity.²⁵ The methoxysilane groups can bond to certain surfaces. The methacrylic end can copolymerize with monomers.

The works of Johansson *et al.*²⁶ Kaas and Kardos,²⁷ and Plueddeman²⁵ support the theory that silane coupling agents actually form covalent bonds to both the glass surface and the resin. Studies have demonstrated improved adhesive strength due to the role of silanes.²⁸⁻²⁹

More recently, Japanese and American investigators have begun to use 4-META (4-methacryloxyethyl trimellitic anhydride)

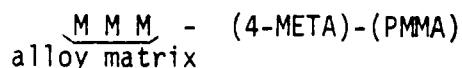


and other derivatives of glycidyl methacrylate directly on hard tooth and metal surfaces for purposes of creating chemical bonding.³⁰⁻³² Bowen³² theorized that the bond may result from the electron rich metal surfaces creating a charge transfer complex with the electron poor aromatic ring of 4-META, while copolymerization may take place with liquid resin of the composite. Atsuta *et al.*³³ observed that when 4-META was added to methyl methacrylate-based composite resin, gels are formed which are stable over long times in various solvents. This reaction, they feel, may be generally interpreted to mean that primary bond crosslinks are formed.

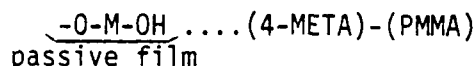
Ohno *et al.*^{31,34} were the first to study the adhesion of dental adhesives containing 4-META. They utilized adhesion models based on the measured bonding strengths and the details of Co-Cr alloy surface structures. By evaluating the results obtained from three surface

treatments, two of which included surface oxide formation after high heat exposure, these researchers theorized the possibility of six adhesion mechanisms:

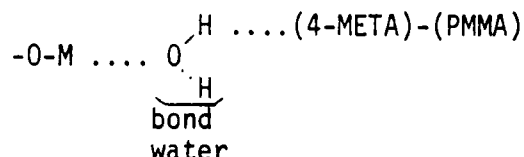
- (1) the possibility of primary bonds between the 4-META and the metal surface:



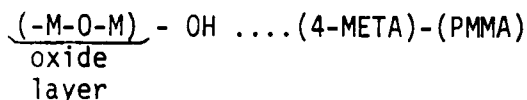
- (2) hydrogen bond between 4-META and the -OH in the passive film:



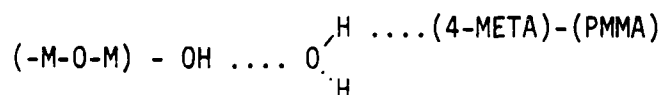
- (3) van der Waals interaction between water molecule and metal ion with hydrogen bonding of water molecule and 4-META:



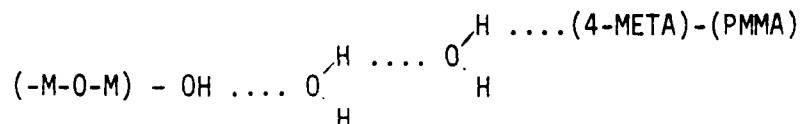
- (4) hydrogen bonding of 4-META with hydroxyl groups on the top surface of oxide layer:



- (5) one water molecule between the hydroxyl group and the 4-META:



- (6) several molecules of adsorbed water between the -OH and 4-META:

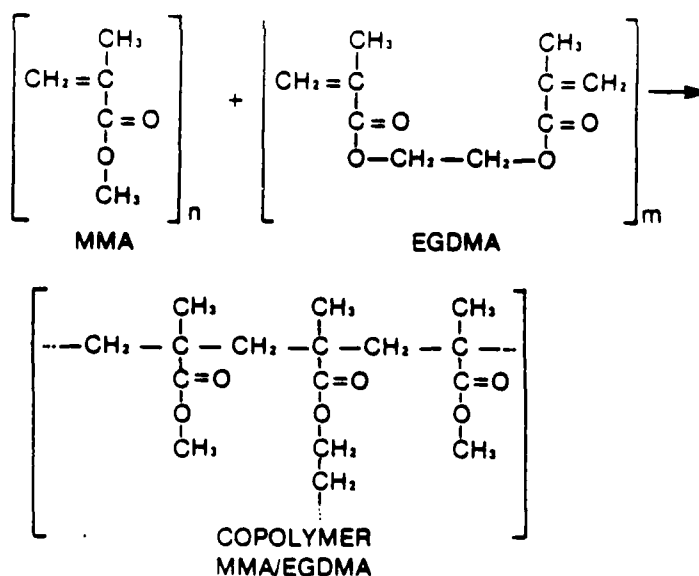


These researchers cited the presence of an amorphous passive film on as-polished surfaces as providing greater effectiveness in bonding with 4-META.

Based on the proposed effectiveness and availability of this coupling agent, 4-META was used in this study to evaluate its effect on bond strength.

Polymethyl Methacrylate

Polymethyl methacrylate has been used for denture bases since 1937.³⁵ Methyl methacrylate is a reaction product of acetone combining with hydrogen cyanide in the presence of methyl alcohol and sulfuric acid.⁵⁰ The liquid component of denture base materials includes methyl methacrylate monomer, an inhibitor (normally hydroquinone), and a cross-linking agent such as ethylene glycol dimethacrylate. When combined with polymer powder, benzoyl peroxide in the powder decomposes in the liquid to start the polymerization of polymethyl methacrylate.



Since the introduction of this material, various polymers have been explored to circumvent undesirable physical properties of PMMA.^{36-40,49} Problems associated with PMMA include inadequate tensile

strength, flexural fatigue, dimensional instability, and poor impact resistance. In this study, tensile strength and flexural fatigue of PMMA were factors to be considered.

Matthews and Wain³⁶ established that tensile fracture was the mode of failure under clinical conditions. They noted that internal residual stress is mainly due to thermal contraction of the plastic and to the temperature gradient which exists across the part that cools. Cornell *et al.*⁴⁹ reported on the disadvantages of single speed tensile tests, stating that such tests did not simulate oral conditions. Smith³⁷ noted that "tensile strength testing is superior (to flexural or bending tests) since it is less open to theoretical and practical objection." He further stated that caution must be used in applying the concept of maximum stress at failure. Smith concluded that tensile strength was lowered by the presence of pigments, by water absorption, and somewhat by the excess amount of residual monomer. Wollff⁵⁷ showed that the tensile strength of polymethyl methacrylate changed little with up to 25% cross-linking in the monomer, but decreased at higher concentrations. (Lucitone 199 is known to have a 10% cross-linking concentration.)

Stafford and Smith³⁸ demonstrated that water sorption had a large effect on reduction of tensile strength at a higher rate of loading. They attributed this to the plasticizing action of the water being more effective under lower loading rates. Braden⁵² studied the absorption of water by acrylic resins and cited the marked effect of temperature on the diffusion coefficient. Thus, the time to effect dimensional changes due to water absorption will be affected by temperature.

Johnson et al.⁴⁵ found that grafted (butadiene styrene) PMMA, such as Lucitone 199, exhibited the best resistance to flexural fatigue.

Bonding Agents

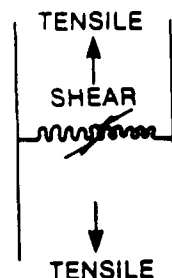
As developed by Bowen, the matrix phase for composite resins is a reaction product of bisphenol-A and glycidyl methacrylate.⁵³ Because of its extremely high viscosity, it is thinned with methyl methacrylate or some other comonomer of low viscosity, such as triethylene glycol dimethacrylate.^{54,55} The viscosity of composite resins varies depending on the proportion of bis-GMA to diluents.⁵⁶ It is evident to anyone who has ever processed dentures that the viscosity of denture base acrylic resin in dough form is greater than that of fluid resins (no data available).

The purpose of using a self-curing bonding agent in this study was to evaluate its role in providing greater adaptation between the metal adherend and the much more viscous ultimate adhesive PMMA resin. It would be reasonable to expect more intimate contact between the etched metal surface and the resin system if a low viscosity intermediate resin were included.

Tensile Testing

Three basic types of stresses occur when a force acts on a body. They are tension, compression, and shear.^{9(p.67)} Tension results when a system is subjected to two sets of forces that are directed away from each other in the same straight line. Stretching or elongation will result in tensile stress. Shear results when the forces are being directed parallel to each other. Twisting or a sliding of one portion of a body over another, will result in shearing stress. Due

to the mechanical interlocking occurring at etched alloy-resin interfaces, shear and tensile stresses are combined.



Measurement in pure tensile mode is not possible when evaluating mechanical interlocking. Most research dealing with measurement of bond strength is expressed in units which do not distinguish between tensile and shear stresses.

Great care has been taken to minimize the inclusion of unwanted stresses by various researchers. Bowen⁵⁷ felt that any testing method should incorporate uniformity of surface size among specimens, no projection of stress concentrations to the resin-substrate interface, and exposure of the periphery of the adhesive joint to water at any desired time.

Lee and coworkers⁵⁸ designed a testing method which allowed for application of a continuous or varying load to adhesive specimens. With this method it was possible to thermocycle the test specimens while a static load was applied. This was followed by dynamic tensile testing. Simulation of the oral environment with the interface under tension was thought to provide more meaningful results.

Eden et al.⁵⁹ sought to simplify previous testing techniques and to control the thickness of the adhesive resin. Though the jig they fabricated for maintaining uniform thickness was thoughtfully engineered, their approach to mounting on the universal testing

machine did not completely eliminate possible complicating torsional stresses.

Moser et al.⁶⁰ used link chain attached to each aluminum mount to reduce the rigidity of the jig assembly "so as to produce solely a tensile force." Similarly, Lee et al.⁵⁸ had relied on swivels built into the pneumatic gripping portions of their mounting mechanisms.

Kemper and Killiam⁶¹ addressed the problem of keeping the specimens properly aligned during mounting and testing to preclude the introduction of non-tensile elements into the tensile test. A machined alignment block with alignment rods to replicate the bonding action was transferred to a measurement block. The apparatus was not clamped into the testing machine. It was merely suspended to further reduce unwanted stresses during testing. Other workers⁷⁸ have used this design, or have modified it to include micrometers.⁷⁹

Fusayama and others⁶² created an elaborate system to test the non-pressure adhesion of specimens in a tensile mode. These researchers also relied on chain links and avoidance of direct clamping into the testing machine. Balance weights attached to the apparatus eliminated the influence of the weight of the pulley and enabled the determination of very low adhesion.

Hargreaves et al.⁶³ tested denture base acrylic resin in tension using a grip based on the anvil principle. To improve retention of the specimens in the grip, they inserted a dowel through the sample. Shackles and universal joints were used so that the load was applied axially to the specimen with the minimum of torsion or shear stressing.

The principles of alignment and minimal shear stress distribution

were considered in the development of the apparatus used in this study.

Etching for Micromechanical Retention

Etching of enamel for the purpose of enhancing retention of acrylic resin was initially proposed by Buonocore in 1955.⁶⁴ Acid etching of enamel to increase retention of a precious metal periodontal splint to resins was reported by Rochette in 1973.⁶⁵ He created mechanical retention between the undercut preparations of the splint and the unfilled acrylic resins. Additionally, a silane coupling agent was used to form a chemical bond between the acrylic resin and the metal.

Dunn and Reisbick⁶⁶ developed a method of etching a cobalt chromium alloy (Vitallium) in order to increase the surface area available for coating with ceramic. They immersed the preheated alloy in a 5N nitric acid solution through which a direct current was passed and noted varying degrees of corrosion depending on the current level and treatment time employed.

Tanaka et al.⁶⁷ described a method of utilizing a 5% sodium chloride solution to electrolytically corrode a nickel, chromium, copper alloy. They obtained greater retentive strengths (150kg/cm²) between the corroded alloy and a thermoset acrylic resin than they had achieved between beaded metal (86 kg/cm²) and powdered metal (135 kg/cm²).

McLaughlin⁶⁸ appears to have been the first to present an etched modification of the Rochette splint prosthesis. He noted that a multiphasic alloy was required due to the irregular crystalline formation created during freezing and solidification.

Tanaka et al.⁶⁹ added 4-methacryloxyethyl trimellitic anhydride to an opaque resin to create chemical bonding between the resin and the surface of a nickel chromium alloy. After thermal cycling, they noted a significant reduction in tensile bond strength between the two materials. 4-META is suspected of bonding to the oxide layer on the metal surface.

Livaditis and Thompson⁷⁰ explored the tensile bond strengths attainable between an electrolytically etched nickel-chromium-molybdenum alloy and composite resin. In later experiments, Thompson et al.⁷¹ investigated laboratory variables which might affect etching quality and consistency. Thompson⁷² pointed out, as a general rule, that micromechanical retention in nickel-chromium-beryllium alloys is achieved by removal of the lamellar interdendritic phases. He further stated that retention was enhanced to a lesser degree by removal of the intradendritic gamma-prime phase. However, this researcher also noted that Ticonium 100 did not exhibit a gamma prime phase and the dendritic arms were uniformly attacked.

McLaughlin and Masek⁷³, Love and Brietman⁷⁴, and Livaditis⁷⁵ studied the efficacy of chemical etchants and found them to be satisfactory. Others⁷⁶⁻⁷⁹ have tested the tensile bond strengths of a variety of resins to etched alloys. Still others⁸⁰⁻⁸⁴ have analyzed various surface treatments without etching to improve the mechanical bonding properties of acrylic and composite resins to metals. Of greater interest to the purpose of this particular study is the work of Zurasky and Duke⁸⁵. Their recently published findings revealed that the bond strengths between electrolytically etched Ticonium 100 and Lucitone 199 processed by standard laboratory methods were

significantly greater than beaded Ticonium/acrylic resin bond strengths (16.70 MPa +/- 4.60 MPa vs. 4.77 MPa +/- 2.68 MPa).

Garfield⁸⁶ applied the electrolytic etching technique to metal denture bases for relining purposes. De Delgado et al.⁸⁷ demonstrated that removable partial denture clasps may be camouflaged by etching and adding opaque composite resin to the etched clasps.

Table I summarizes the bond strengths obtained by various researchers.

MATERIALS AND METHODS

In this study, the technology of acid etching base metals as used in fixed prosthodontics was applied to a removable partial denture alloy, Ticonium 100 (CMP Industries, Albany, N.Y.). Manufacturers' guidelines were adhered to during the preparation of the alloy specimens and processing of the polymethyl methacrylate resin, Lucitone 199 (L.D. Caulk, Milford, Dl.), against the alloy. Associated or recommended auxiliary materials were also used. See Tables 2-4 for composition and properties of materials used and Appendix for list of technical references.

Preparation of the Ticonium 100 Specimens

Thirty cylindrical patterns of 6.3 mm diameter plexiglass material were cut to 23 mm lengths. Six patterns each were sprued and painted with a surface tension releasing agent (Ti-Sol, CMP Industries, Albany, N.Y.) and with Investic (CMP Industries, Albany, N.Y.) prior to being invested within a single flask. Painting an even layer of Investic was essential in obtaining uniform expansion of the investment. Additionally, this layer was kept thin to facilitate the escape of gases produced during burnout, casting, and cooling. After the paint-on layer reached the initial set, the patterns were dipped in water to prevent the set layer of investment from extracting water from the investment mix.

A Ticonium Burn-Out Oven (CMP Industries, Albany, N.Y.) was used

for burn-out, starting at room temperature going to 1350° F with a two hour heat soak at this temperature. The specimens were cast using a Ticomatic Auto Casting Machine (CMP Industries, Albany, N.Y.).

On recovery from the casting rings, the cast specimens were sandblasted (Zircon Grit, CMP Industries, Albany, N.Y.) to remove the powdered investment (Fig. 1). Once removed from their sprues, all thirty specimens were then cut in half and machined to a uniform size (6.0 mm in diameter by 10 mm in length) (Fig. 2). The ends of the specimens were smoothed with a carbide cutting tool. The machined specimens, now numbering sixty, were again sandblasted to eliminate shavings and debris on the cut surface. They were rinsed in tap water, dried, and electropolished using a Ti-Lectro polisher (CMP Industries, Albany, N.Y.) The solution temperature was set at 120° F, an ampere reading of 7, and a polishing time of 3 minutes per specimen. These settings and times were used to prevent excessive or uncontrolled etching during electropolishing.

To allow for proper accountability of the treated surfaces, the sides of the specimens were numbered sequentially from 1 to 120 ends of cylinders with a high speed handpiece and a #2 round carbide bur.

Etching of Specimens

Sticky wax was applied to the periphery of the surfaces to be etched. All specimens were then viewed under a stereomicroscope (Stereo Zoom 4 Microscope, Bausch and Lomb, Rochester, N.Y.) at 55X power to ascertain that sticky wax did not extend onto the surfaces to be etched. The surfaces to be evaluated were etched with Quick-Etch (Excelco International, Santurce, Puerto Rico) for twenty minutes (Fig. 3), followed by rinsing with tap water, ultrasonic cleaning in

ammonia, and again in distilled water. The etched surfaces were again viewed with the stereomicroscope at 55 X to assure that uniform etching of the specimens had been achieved. Scanning electron microscope (ETEC Autoscan, Coleman Systems, Irvine, Ca) photographs were made of representative specimens (Fig. 4-5).

Poly (Methyl Methacrylate) Processing

To facilitate fabrication of a wax pattern for Lucitone 199 processing, a teflon cylinder 4cm long was prepared with a 6 mm hole in the center. A plunger consisting of a 6 mm diameter Ticonium rod and a Duralay base (Reliance Dental Mfg., Worth, Il.) (Fig. 6) was inserted in one end of the teflon cylinder to a depth of 1 cm. The etched Ticonium specimens were warmed in a water bath at 140° F, dried and inserted into the other end of the cylinder. Warming the metal prevented premature solidification of the melted baseplate wax. Using a glass eyedropper, the open end of the teflon cylinder was filled with melted baseplate wax, creating a wax pattern 6 mm in diameter and 20 mm in length (Fig. 7). Following sufficient cooling, the wax pattern and metal specimen were ejected from the teflon mold (Fig. 8).

The specimens were flaked in a conventional maxillary denture flask (Hanau Engineering, Buffalo, N.Y.). In order to assure proper vertical orientation of the specimens, a customized technique was developed. 6 mm diameter holes were drilled with a drill press to a 12 mm depth into the dental stone within the lower portion (drag) of the flask. The metal/wax specimens were inserted into the holes, the depth of which allowed for the flash created during packing to remain at least 2 mm away from the joint area (Fig. 9). A total of six specimens were processed in each flask. The two Ticonium rods to be

etched only were set in the holes to the left. The two to be treated with 4-META were set in the center. The two to be coated with Self-Cure were set to the right (Fig. 10). Tincture of green soap (Concord Chemicals, Camden, N.J.) was applied to the dental stone surface prior to the pouring of a mixture of 50% dental stone and 50% plaster up to the level of the exposed ends of the wax portion of the specimens. After this mix was set, tincture of green soap was applied to this exposed surface of stone/plaster mix, followed by the addition of a dental stone cap to facilitate deflasking procedures.

Following setting, the wax was boiled out and detergent was used to remove any residue. The exposed etched metal surfaces were then steam cleaned and gently blown dry with an air syringe. Once the flask had cooled, Alcote separating agent (L.D. Caulk Co., Milford, D1.) was painted on the stone surfaces of both halves of the flask. Care was taken not to apply Alcote to the etched surfaces.

Two of the six exposed metal surfaces in each flask were painted with a 5% solution of 4-META in acetone (made by adding 0.5 gm of 4-META to 20 ml of acetone). Two other metal surfaces were coated with Self-Cure (L.D. Caulk Co., Milford, D1.), a bis-GMA resin. The third group of two exposed etched surfaces were otherwise untreated. Lucitone 199 was mixed according to the manufacturer's directions. Three trial packs were completed attaining pressures of 3000 psi. Once packed, the flasks were allowed to sit for one hour, to assure bonding between the two portions of resin created by the trial packing technique. The acrylic resin was cured for nine hours at 163° F in a Hanau curing unit (Hanau Engineering, Buffalo, N.Y.). After bench cooling, the specimens were recovered, shell blasted, and stored in

distilled water at 37°C until thermocycling was accomplished. Thermocycling consisted of the immersion of the specimens into a container of distilled water at 5°C for one minute, followed by their transfer to a 60° C solution for one minute, for a total of one thousand cycles. When not being cycled, the specimens were stored in distilled water at 37° C for a total of seven days, to allow for maximum water sorption to occur.

Tensile Testing

Tensile testing was done with an Instron Universal Testing Machine (Model TTLC, Instron Corp., Canton, Massachusetts) with a 500 kg load cell. The metal portion of each specimen was held with a 0-1/4 inch Jacobs chuck (Jacobs Mfg. Co., Clemson, S.C.) which was attached to a loop of 0.32 in. 1x3 twisted orthodontic wire (Unitek, Monrovia, CA) which was, in turn, attached to a metal swivel. The swivel was positioned within a holding device which was clamped to the Instron Machine using a self-centering, pneumatically operated clamp. The acrylic resin portion of each specimen was held by an Instron Wedge Grip (Series 2716-001) with a vee specimen holding face (Series 2703-008) (Fig.11-12). The tips of both the chuck and the vee holding faces were set 2 mm from the specimen joint. The chart paper speed was set a 5 cm per minute. Full scale load was 100 kg. The crosshead speed for the Instron was set at 10 mm per minute. The force in kilograms required to separate the acrylic resin portion from the metal portion was divided by the area of the etched metal surface, to obtain the tensile bond strength in kg/cm². This value was then divided by 10.19 to convert the tensile strength to MegaPascals (MPa).

Fracture Site Analysis

Following separation of the acrylic resin portion from the metal, all metal surfaces were viewed under the stereomicroscope to evaluate the predominant fracture patterns. Representative specimens (as determined by high, low, and average tensile bond strength values obtained) were sputter coated with a Polaron 5200 sputter coater (Hatfield, Pa) and photographed through a scanning electron microscope. Additional SEM photographs were made using the backscattered electron imaging technique (Fig. 13-22).

Statistical Analysis

The resulting data were subjected to three two-tailed Mann-Whitney U tests to determine if significant differences ($p < .05$) existed in the tensile bond strengths observed between the three treatment groups.

RESULTS

The results of the tensile bond strengths are shown in Table 5. The mean tensile bond strength for the etched only specimens was 6.39 +/- 6.04 MPa. For the specimens treated with 4-META the mean tensile bond strength was 24.30 +/- 11.29 MPa. For the specimens coated with Self-Cure resin, the mean tensile bond strength was 6.81 +/- 7.73 MPa.

Separation during deflasking occurred with five of the etched only specimens and four of those coated with Self-Cure. One specimen coated with Self-Cure separated during thermocycling.

Statistical analysis using two-tailed Mann-Whitney U tests (U value of 90) revealed that tensile bond strengths of the specimens treated with 4-META were significantly ($p < .05$) higher than either the etched only tensile bond strengths of those or the specimens coated with Self-Cure resin.

Examination of the fracture sites of all specimens using a stereomicroscope demonstrated that a predominantly mixed adhesive/cohesive failure occurred at the interface. Though minimal in a few cases, some denture base acrylic resin was retained on the etched surface of all specimens.

Not all specimens were evaluated with the scanning electron microscope. Specimens with low, average, and high tensile bond strengths were selected for further examination with the SEM (Fig. 13-21). Fracture site examination using a backscattered

electron technique revealed a lack of residual resin along the periphery of all surfaces. Specimens with higher tensile bond strengths exhibited greater apparent thickness of residual resin than did those with lower bond strengths. Representative specimens which separated during deflasking exhibited scattered and thinner residual resin, as did the specimens with low bond strengths. (Fig. 22) The only specimen to separate during thermocycling revealed good etching patterns but only one small island of residual resin. (Fig. 22)

DISCUSSION

The purpose of this study was to evaluate the tensile bond strength obtained when denture base acrylic resin (Lucitone 199) was processed against Ticonium under varying conditions. All specimens were chemically etched with a commercially available etchant (Quick-Etch). The etched surfaces were divided into three groups: 1) etched only, 2) treated with 4-META, a chemical coupling agent, and 3) coated with an unfilled bis-GMA resin (Self-Cure) to promote adaptation.

In previous studies which used a nickel-chromium alloy, 10% sulfuric acid was the electrolytic etchant of choice. In most of these research efforts, unusual care was taken to avoid contamination of the etched surface prior to application of the resin to be bonded. Only Zurasky and Duke sought to follow routine laboratory procedures without regard for the effects of contamination. The tensile bond strengths they obtained were 2.6 times higher than the tensile bond strengths obtained in this study for etched only specimens (16.70 MPa versus 6.39 MPa).

The difference in bond strengths may be due to different techniques. Zurasky and Duke relied only on the immersion in 37° distilled water for a relatively short time (17 days). Based on coefficient of thermal expansion and water sorption data, it appears that thermocycling and long term immersion may induce similar stresses. Since the time between deflasking and tensile testing in this study was seven days, the immersion time was not sufficient for complete diffusion to take effect. However, the stresses induced by

the 1,000 thermal cycles may have contributed to the variation in the results of the two experiments.

The etchant used in this study was a proprietary mixture of strong acids and viscosity builder. The appearance of the surfaces etched with Quick-Etch was similar to the patterns of electrolytically etched surfaces as depicted by Simonsen et al. No effort to determine the increase in surface area resulting from chemical etching was made in this study. Manufacturer's instructions specify that the gel should be applied for twenty minutes at room temperature. They also note to expect a greenish coloration as the etching activity occurs. Variation in intensity and rate of activity noted imply differences in the etching process between specimens. This variation may have been due to differences in cast structure and composition, as well as to the effects of prior electropolishing or mechanical distortion from machining. Visual examination of the etched surfaces at 55X with a stereomicroscope did not reveal unusual variation in etching patterns.

Improved wetting of the surface by the 4-META may have been one factor which contributed to the significantly higher tensile bond strengths of the specimens treated with this coupling agent. If 4-META does react with the oxide layer of metallic surfaces as theorized by Ohno et al. and Tanaka et al., a result of this activity might be to create an organic environment which would allow polymethyl methacrylate to readily wet the surface of the alloy.

Plueddemann and others have indicated that 4-META acted like a bifunctional silane coupling agent. The bond between the acrylic resin and the alloy was significantly higher when the etched alloy was treated with 4-META. The type and location of the bond within the

molecule of 4-META is not known with certainty. Thermocycling appears to have had a deleterious effect on the chemical bonds in the peripheral areas. These bonds may not be strong enough to withstand the stresses induced by oral thermal variations over time. Tanaka et al. found a significant decrease in tensile bond strength with an increase in the number of thermal cycles.

The purpose of using a low viscosity resin such as Self-Cure was to evaluate the effect of its increased penetrability when compared to polymethyl methacrylate alone. Though a slight increase in tensile bond strength was seen with this group compared to the etched only group, the difference was not significant ($p < .05$). When applying Self-Cure to the etched alloy surface, some difficulty in achieving wetting was seen. In order to get a uniformly coated surface, it was necessary to "spread" the resin repeatedly. Lucitone 199 was applied before the Self-Cure had time to set. The presence of air itself should have inhibited the polymerization of the Self-Cure. Whether bonding between Lucitone 199 and Self-Cure occurred was not determined. This researcher was unable to detect an interface between the resins. No significant difference in tensile bond strengths was found between this group and the etched only group. This seems to deny the effectiveness of, or requirement for, an intermediate resin layer.

The geometry of the specimens was selected for anticipated ease of handling and testing. For tensile testing purposes, this cylindrical geometry provided a method for taking into account torsional and shear elements frequently not considered in such testing. The use of multiple rotational elements in the upper segment

of the holding device coupled with the use of a stationary, yet adjustable, lower segment allowed for precise positioning of the specimens without inducing unwanted stresses. (Fig. 12) However, it is realized that the flat circular bond area is not likely to be found in clinical situations. Thinner specimens, resembling the retentive mesh or palatal major connector portions of removable partial dentures, might be more appropriate for comparison to oral situations.

Separation during deflasking occurred with nine specimens. Separation during thermocycling occurred with one specimen. None of the separated specimens were from the group treated with 4-META. The positional relationship of the specimens within the processing flasks involved a specific pattern: the two to be etched only were placed on the left, those treated with 4-META were in the center, and those coated with Self-Cure on the right. Random positioning may have eliminated any basis for questioning the influence of flask position on premature separation. However, the previous research by Tanaka et al. confirms the overriding effect of 4-META on tensile bond strength. The positional relationship of the specimens cannot be totally discounted since more stone had to be removed from the peripherally placed specimens than around the centrally placed ones. In the future, similar efforts should be based on random placement to avoid the inclusion of this factor as a possible variable.

Suggestions for Further Study

Future studies, using a flatter and thinner specimen, to evaluate the effect of 4-META on marginal seal are indicated. With a thin, flat geometry, it would be possible to section through a specimen to investigate the extent of penetration of a dye. The depth of

penetration would also assist in measuring the efficacy of the etchant. Use of such a design would also allow the investigator to study the effect of thermocycling on marginal seal. In addition, future research should include determination of bond strength between acrylic resin and an unetched alloy treated with 4-META. Shear tests are also indicated to evaluate the strength of the bond in this mode.

Future studies should also evaluate results using other removable partial denture alloys. If comparable bond strengths were achieved with other alloys, the theories relating to the mechanism of adhesion of 4-META would be reinforced. The versatility of the etchant itself would also be verified.

SUMMARY AND CONCLUSIONS

Cylindrical patterns were cast using Ticonium 100. Surfaces to be tensile tested were etched with a chemical etchant, Quick-Etch. The etched surfaces were divided into three groups: 1) etched only, 2) treated with 4-META, a chemical coupling agent, and 3) coated with an unfilled bis-GMA bonding resin. All specimens were flaked and polymethyl methacrylate was processed against the Ticonium cylinders. Thermocycling and immersion in water was done prior to testing.

Tensile bond strengths were measured with an Instron machine and results were statistically analyzed. Fracture sites were evaluated to determine the quality of the bond.

Within the limitations of the technical procedures and the experimental design, the following conclusions can be made from this study.

1. Tensile bond strengths were statistically higher for the group treated with 4-META.
2. There was no statistical difference between the etched only group and the group coated with a bonding resin.
3. 4-META significantly improves the bond strength between chemically etched Ticonium and polymethyl methacrylate.
4. The higher the bond strength, the greater the area of resin retained on the treated surface.

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TABLE 1

SUMMARY OF ACID ETCHED METAL/ADHESIVE TENSILE BOND STRENGTHS AS REVIEWED

<u>Researchers</u>	<u>Metal</u>	<u>Etching Agent</u>	<u>Adhesive</u>	<u>Tensile bond strength-Mpa (as reported)</u>	<u>Reference</u>
Thompson Livaditis	Ni-Cr-Be	10% H ₂ SO ₄	Comspan Only Self-Cure bonding agent/Comspan	16.1 +/- 4.8 21.2 +/- 3.2	16
Tanaka <u>et al.</u>	Ni-Cr-Be	5% NaCl	Thermoset acrylic resin	14.72 (150 kg/cm ²)	67
McLaughlin	Ni-Cr-Be (Rex. 111)	0.2M H ₂ SO ₄	Bonding agent	No test performed	68
Tanaka <u>et al.</u>	Ni-Cr	HCl	Opaque resin/ 4-META	24.53 (250 kg/cm ²)	69
Livaditis Thompson	Ni-Cr-Mo	0.5N HNO ₃	Composite resin	27.3 +/- 3.7	70
Thompson	Ni-Cr-Be (Titanium)	10% H ₂ SO ₄	Bonding agent/ Composite resin	25.0 +/- 3	72
Livaditis	Litecast B	FeCl ₃ + HCl + CH ₃ OH	Comspan	19.5 +/- 10.3	75
Hasiakos <u>et al.</u>	Litecast B	10% H ₂ SO ₄	Conclude Comspan	8.32 +/- 2.38 6.97 +/- 2.19	76
Wiltshire	Ni-Cr	10% H ₂ SO ₄	Self-Cure/ Comspan	12.15 +/- 4.7	78

TABLE 1 (Continued)

Haywood <u>et al.</u>	Ni-Cr-Be (Rex. III)	10% H ₂ SO ₄	Comspan only	32.21 +/- 9.70	79
Zurasky Duke	Ni-Cr-Be (Ticonium)	10% H ₂ SO ₄	Lucitone 199	16.7 +/- 4.6	85

TABLE 2

COMPOSITION AND PROPERTIES OF LUCITONE 199*LIQUID

Methyl methacrylate monomer
 Ethylene glycol dimethacrylate
 (cross-linking agent)
 Hydroquinone (inhibitor)
 N,N-dimethyl-para-toluidine
 (accelerator-for the peroxide decomposition)
 Dibutyl phthalate (plasticizer)

POWDER

Acrylic polymer beads (1)
 Benzoyl peroxide (initiator)
 Pigments
 Dyes (titanium oxide)
 Opacifiers
 Dibutyl phthalate (plasticizer)
 Inorganic particles

(1) may be treated with a coupling agent

PHYSICAL PROPERTIES

Mean particle size	73.68 microns
Average force at break	55.0 N
Modulus of elasticity	2220 MN/m ²
Compressive creep percentage	14.7%
Fracture toughness	1.99 MN/m ^{3/2}
Water sorption	0.56 mg/cm ²
Dimensional accuracy (shrinkage)	0.04%
Linear coefficient of thermal expansion	81.0 x 10 ⁶ /°C

*data taken from Stafford, G.D., Bates, J.F., Huggett, R., and Handley, R.W.: A review of the properties of some denture base polymers. J. Dent., 8:292-306 (December), 1980.

TABLE 3

COMPOSITION OF TICONIUM 100*
% of Weight

(1) Nickel	65.9
(2) Chromium	17.0
(3) Molybdenum	5.0
(4) Aluminum	5.0
(5) Manganese	5.0
(6) Beryllium	1.0
(7) Iron	0.5
(8) Silicon	0.5
(9) Carbon	0.1

EFFECTS OF ALLOY CONSTITUENTS**

- (1) leads to greater ductility than cobalt
- (2) by its passivating effect, insures corrosion resistance
- (3) effective solid solution hardener; preferred over tungsten
- (4) forms Ni_3Al -increases the ultimate tensile and yield strengths of alloy
- (5) oxide scavenger to prevent oxidation of other elements
- (6) added to reduce the fusion temperature; also acts as a hardener and grain structure refiner
- (7) aids in solid solution hardening
- (8) added to increase fluidity and ductility; acts like manganese
- (9) strengthens alloy, but very sensitive because of its ability for form carbides with any metallic constituent

*data taken from Craig, Ed., 7th ed., p. 386 (reprinted from Asgar, K.: An overall study of partial dentures, USPHS Research Grant DE-02017, National Institutes of Health, Bethesda, Md., September 1, 1968.)

**effects of alloy constituents taken from Skinner's Science of Dental Materials, Phillips, R.W., Ed., 7th ed., pp. 593-594.

TABLE 4

COMPOSITION OF SELF-CURE

2,2-bis 4(2-hydroxy-3-methacryloyloxy-propyl-oxy-phenyl propane (bis-GMA)	40-45%
Triethylene glycol dimethacrylate (TEGDMA)	30-35%
2-Hydroxyethyl methacrylate (HEMA)	15-20%
Organic Amine Accelerator	
Benzoyl Peroxide Initiator	

*from Personal Communication, P. Hammessahr, PhD, Dentsply Corp., York, PA, 1987.

Range of Physical Properties of Composites Made With Monomers
Containing Bis-GMA and Various Diluents**

Surface Tension (dyne/cm)	26.7 - 41.8
Viscosity at 37°C (cps)	117 - 4992
Diametral Tensile Strength (MPa)	15.6 - 51.3
Water Sorption (mg/cm ²)	0.45 - 1.17
Coefficient of Thermal Expansion (x 10 ⁶ /°C)	33.7 - 63.8

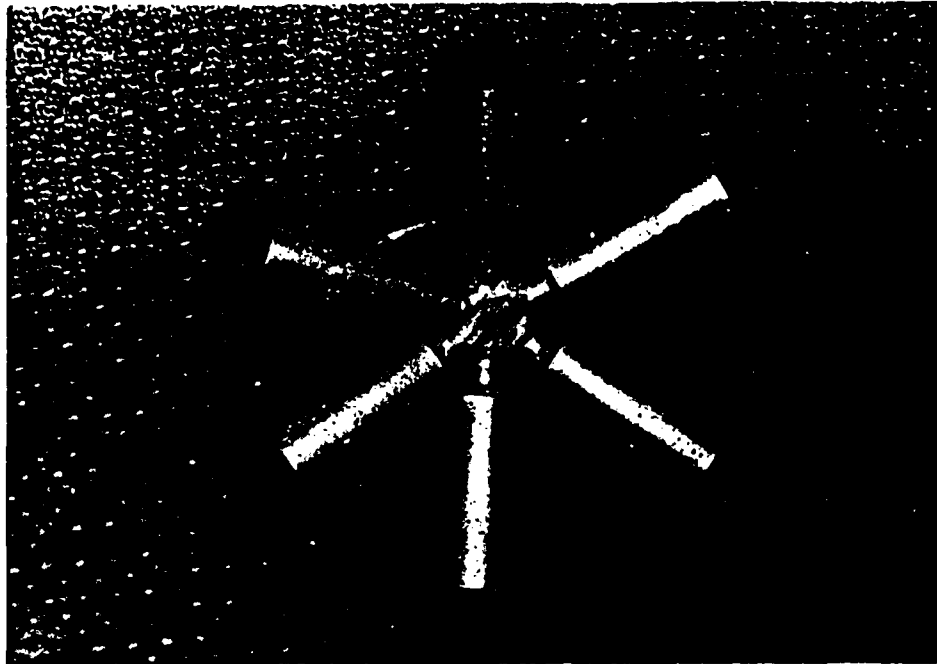
**from Dulik, D., Bernier, R. and Brauer, G.M.: Effect of diluent monomer on the physical properties of bis-GMA-based composites. J. Dent. Res., 60:983-989 (June), 1981.

TABLE 5
The Tensile Bond Strengths of Treatment Groups

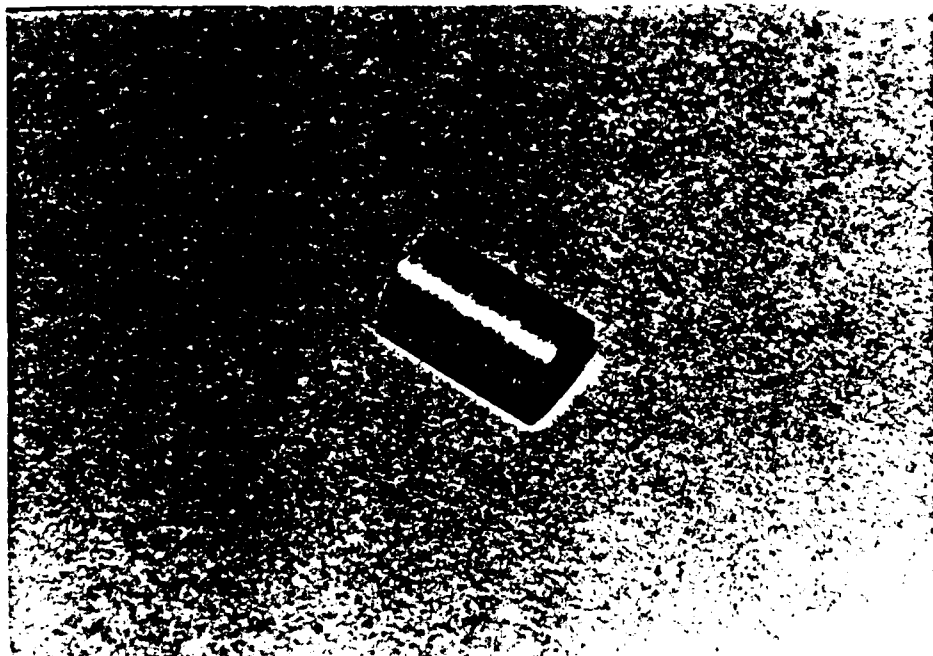
Flask Number	ETCHED ONLY		ETCHED + 4-META		ETCHED + SELF-CURE	
	Specimen Number	Tensile Bond Strength (MPa)	Specimen Number	Tensile Bond Strength (MPa)	Specimen Number	Tensile Bond Strength (MPa)
1	69	8.99	80	3.11	65	10.54
2	88	17.02	24	18.33	36	29.12
	71	6.99	74	1.25	92	11.93
3	84	6.05	51	34.58	62	1.80
	60	2.03	101	14.32	21	0.74
4	99	4.56	50	23.69	18	7.78
	42	*	64	37.01	119	*
	46	*	13	29.74	40	**
5	33	4.08	15	5.19	111	1.18
	4	0.81	76	32.10	10	1.42
6	94	5.76	19	35.97	89	6.35
	117	7.02	31	30.26	54	0.59
7	115	22.83	44	29.02	37	6.54
	47	3.54	104	33.54	28	*
8	55	1.14	81	31.47	12	3.10
	105	*	109	23.86	96	0.48
9	86	*	67	38.74	78	*
	5	*	98	11.59	7	*
10	2	0.88	26	25.07	114	16.46
	58	4.22	108	27.22	29	4.12
	N=15	Mean 6.39 MPa	N=20	Mean 24.30 MPa	N=15	Mean 6.81 MPa
		S.D. 6.04		S.D. 11.29		S.D. 7.73

* Separated during deflasking

**Separated during thermocycling

FIGURE 1

Cast and Sandblasted Ticonium 100 Rods Prior to
Removal from Sprues and Machining

FIGURE 2

Machined Ticonium Specimen (60mm diameter X 10mm length)

FIGURE 3



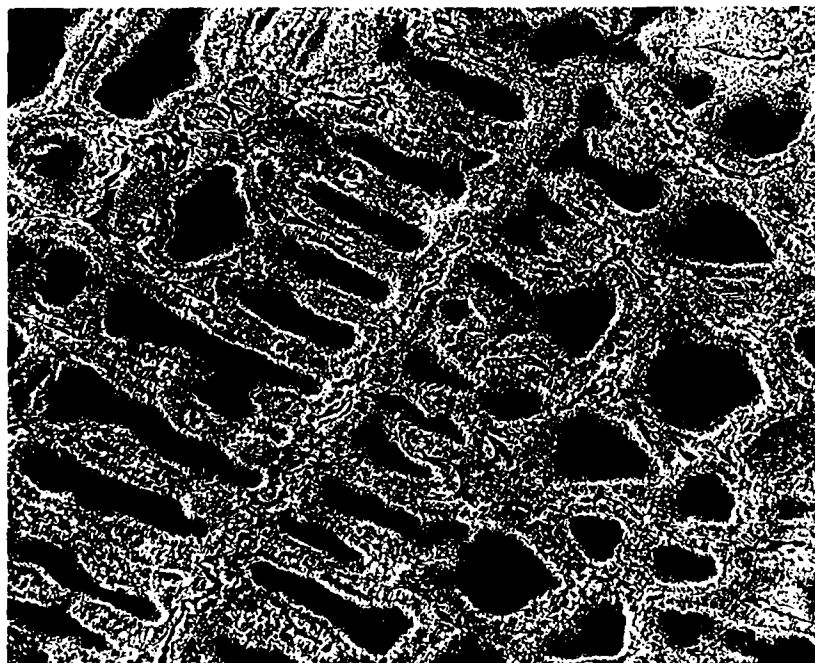
Quick-Etch Applied to Specimen Surfaces

FIGURE 4



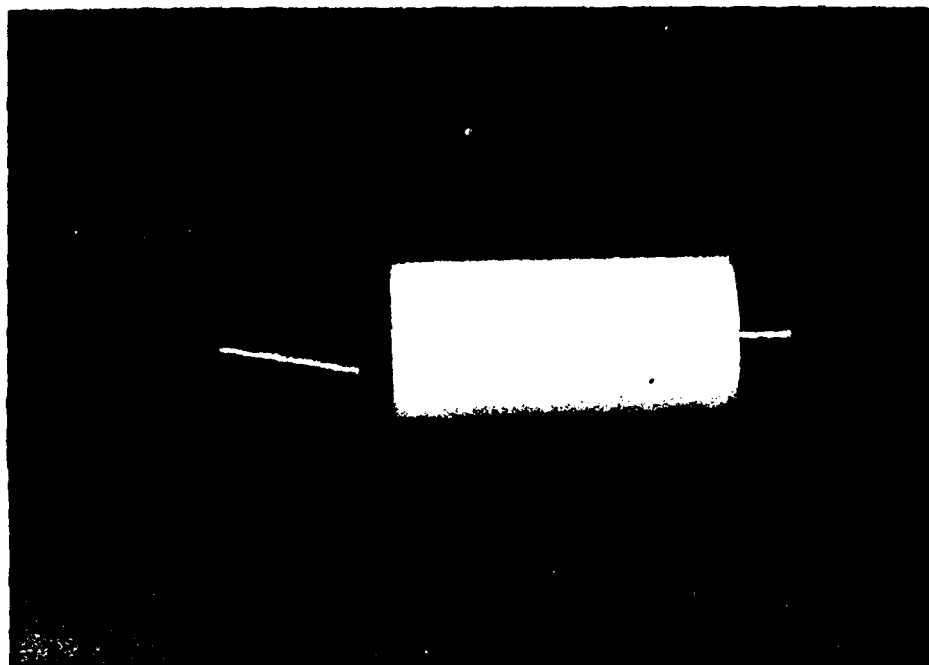
SEM Photograph of Etched Surface
(30X, 0° tilt, Specimen #91)

FIGURE 5



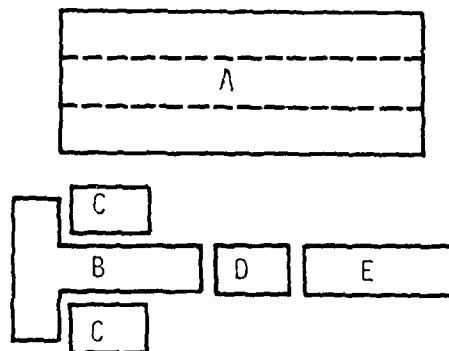
SEM Photograph of Etched Surface
(250X, 0° tilt, Specimen #91)

FIGURE 6



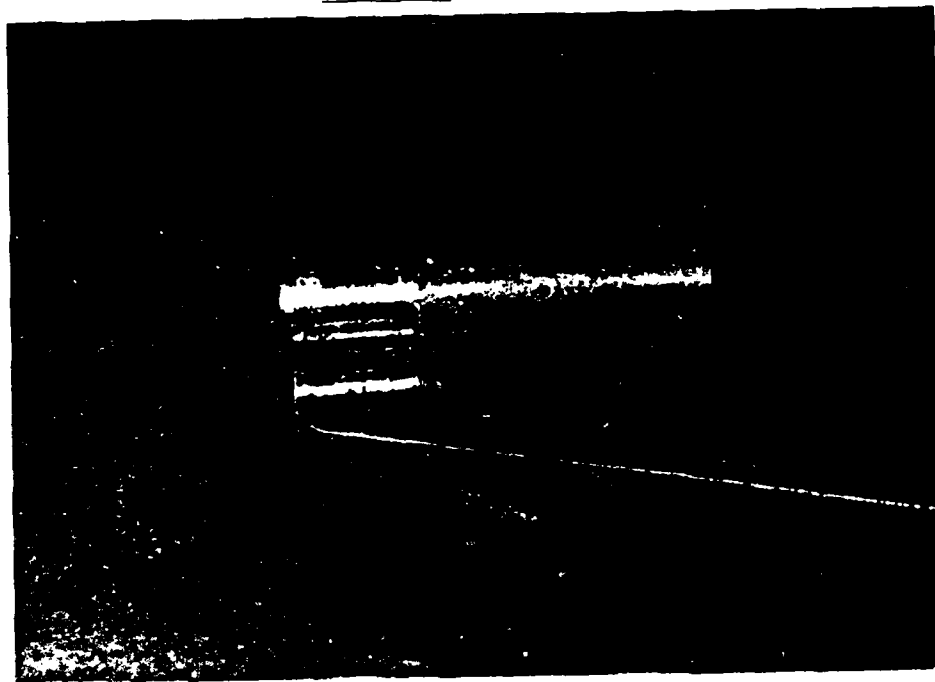
Plunger, Teflon Cylinder, Ticonium Specimen
Used in Preparation of Wax Patterns

FIGURE 7



- A - Teflon Cylinder
- B - Plunger (Duralay Base and Ticonium Rod)
- C - Plexiglass Spacers
- D - Ticonium Specimen
- E - Wax Pattern Against Etched Surface of Specimen

Diagram of Complete Apparatus Used in Preparation
of Wax Patterns

FIGURE 8

Ticonium and Wax Pattern Prior to Processing

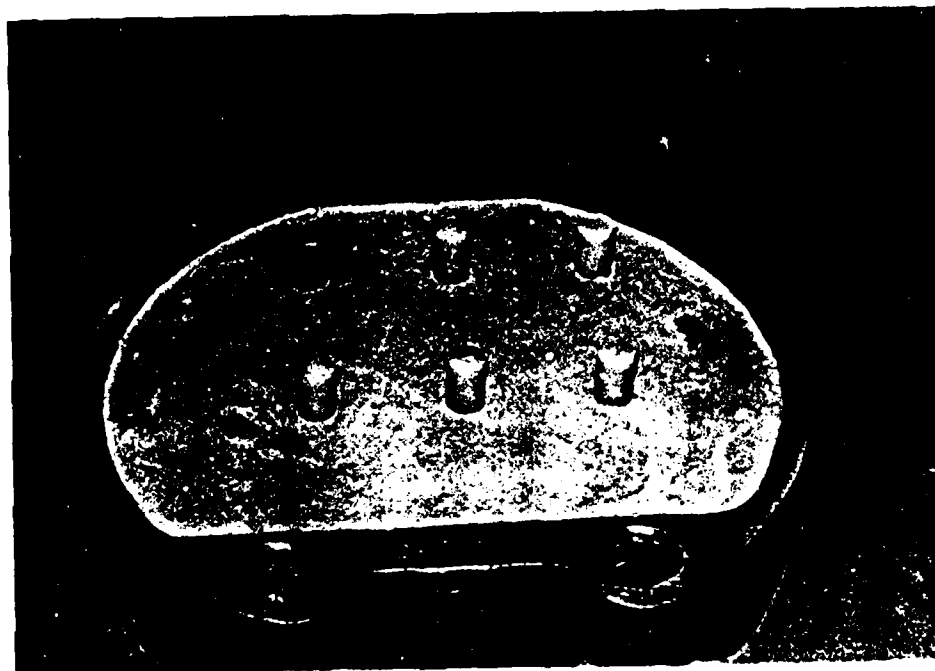
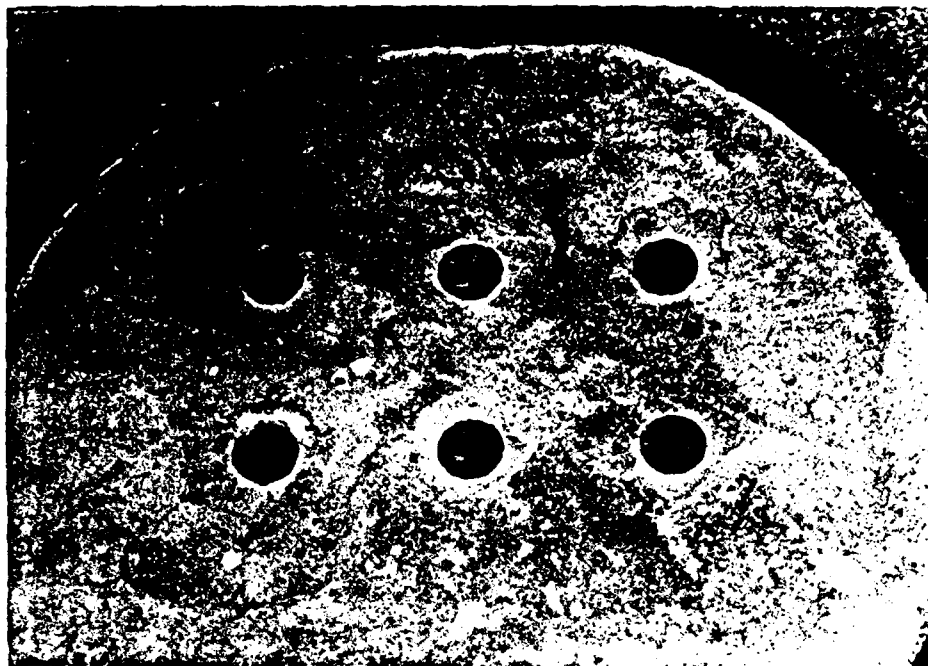
FIGURE 9Ticonium and Wax Patterns Set Into Pre-Drilled Holes
in Denture Flask

FIGURE 10

Etched Ticonium Rods Set in Drag After Boil-Out

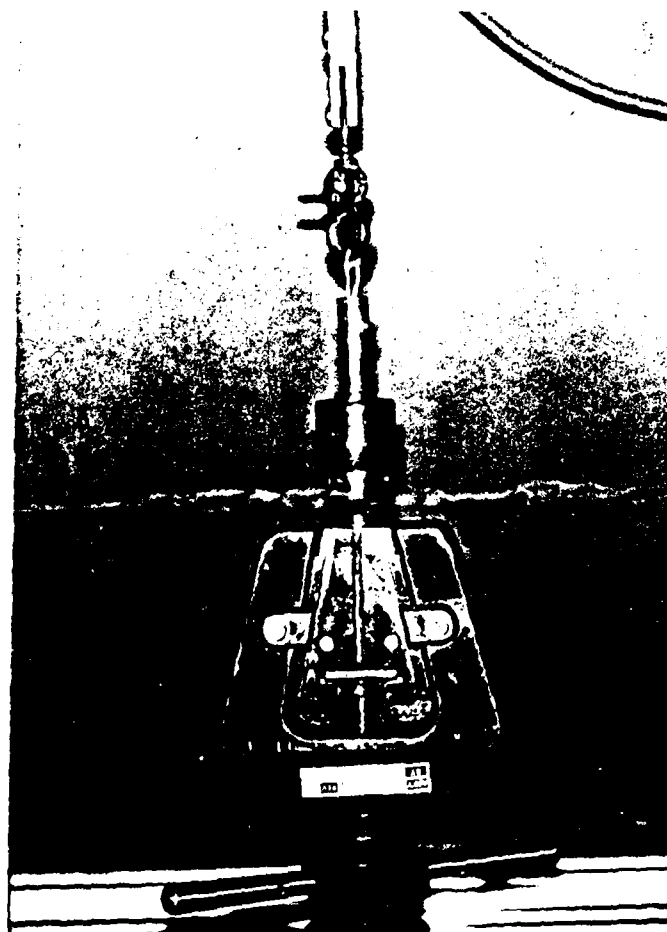
FIGURE 11Photograph of Tensile
Testing Apparatus in
Instron Machine

FIGURE 12

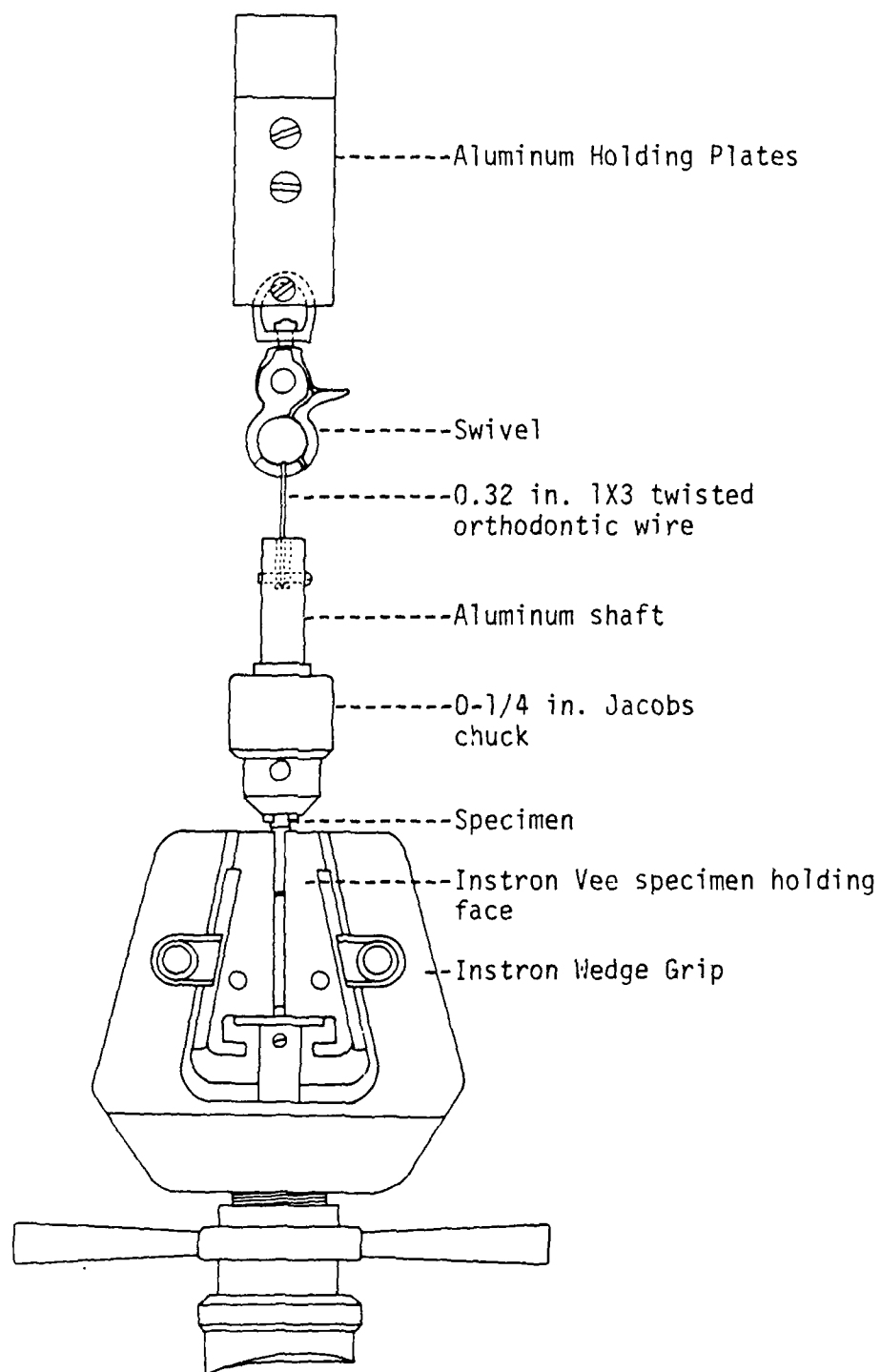


Diagram of Holding Device for Tensile Testing

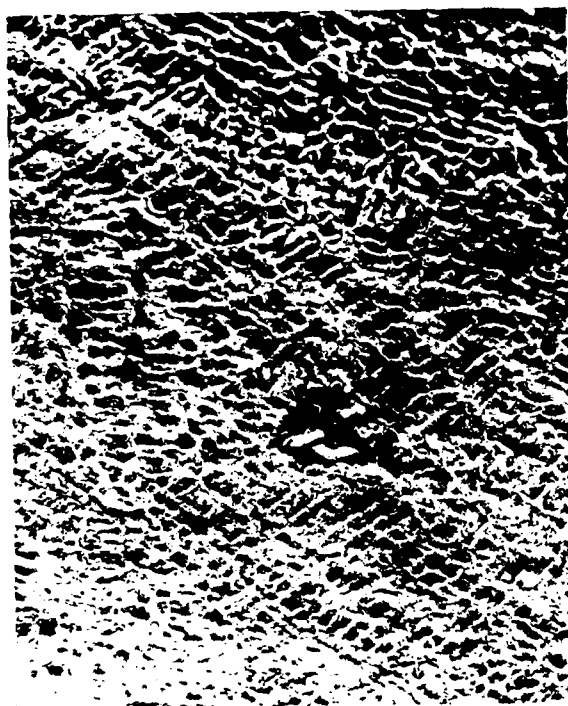
FIGURE 13

Etched Only Specimen #2
(0.88 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)

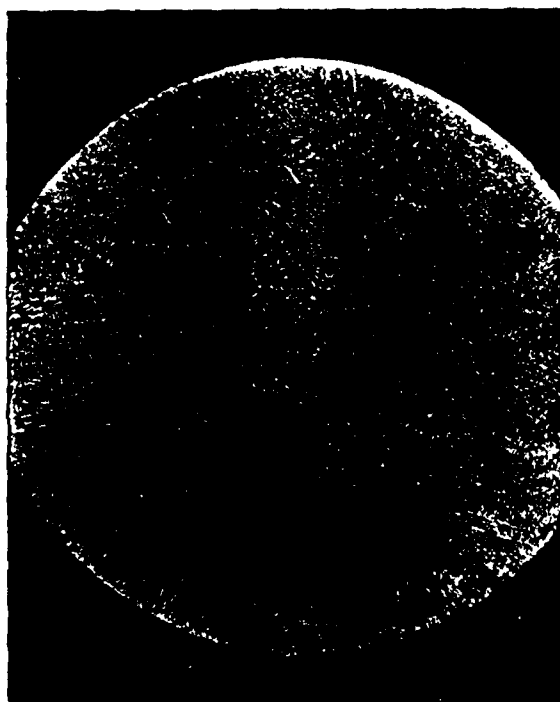


Secondary
Electron
Imaging
Technique

(60X magnification)

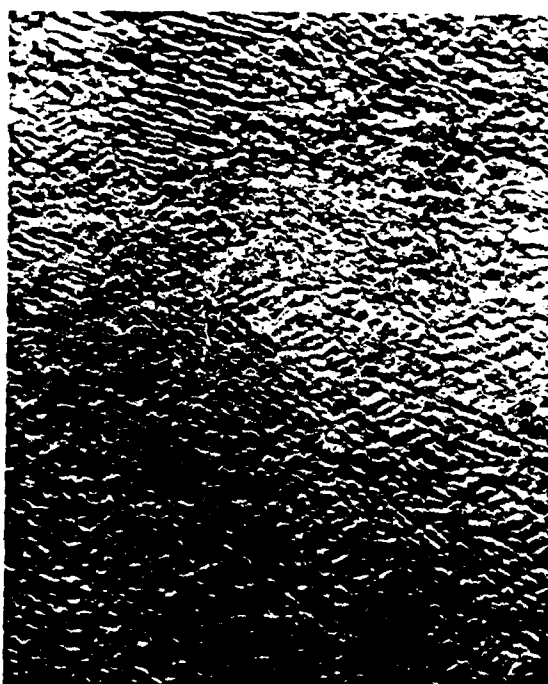
FIGURE 14

Etched + 4-META Specimen #74
(1.25 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)

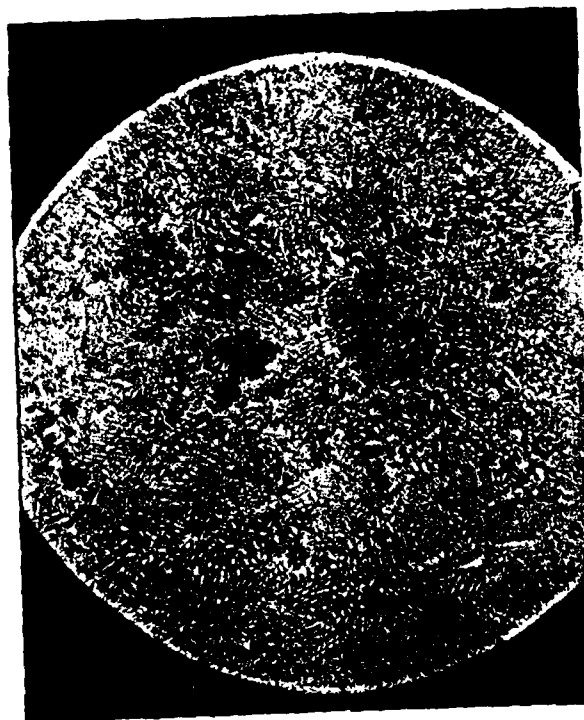


Secondary
Electron
Imaging
Technique

(60X magnification)

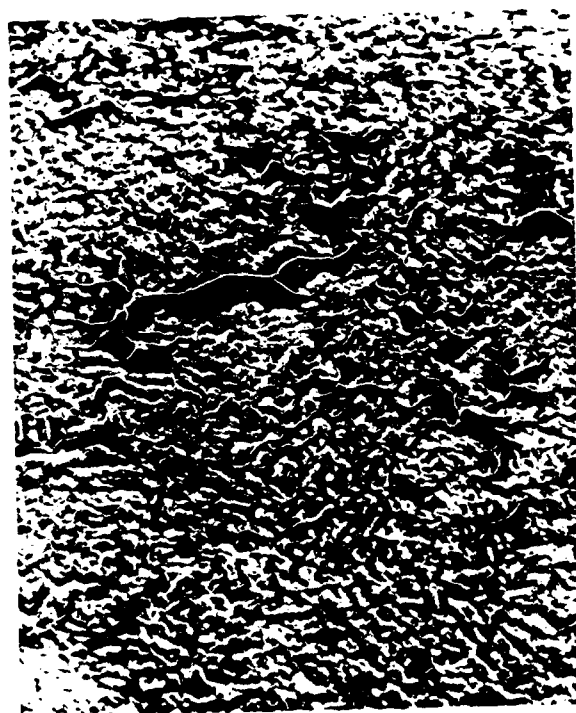
FIGURE 15

Etched + Self-Cure Specimen #54
(0.59 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)



Secondary
Electron
Imaging
Technique

(60X magnification)

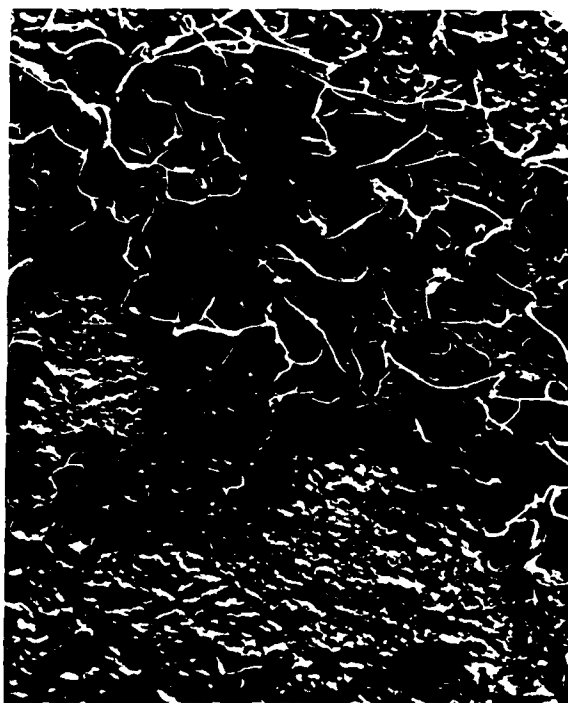
FIGURE 16

Etched Only Specimen #115
(22.83 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)



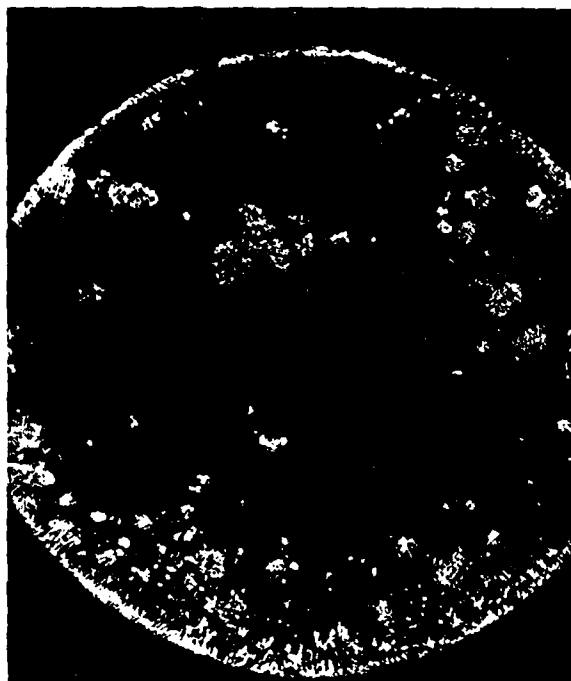
Secondary
Electron
Imaging
Technique

(60X magnification)

FIGURE 17

Etched + 4-META Specimen #64

(37.01 MPa)

Backscattered
Electron
Imaging
Technique

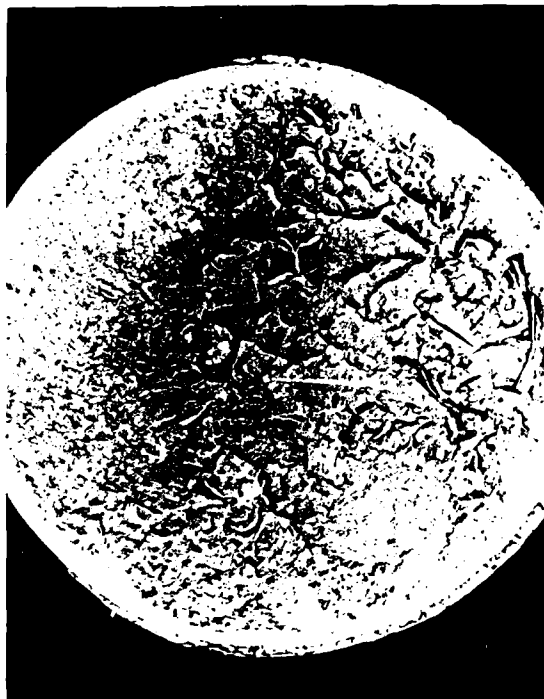
(13X magnification)

Secondary
Electron
Imaging
Technique

(60X magnification)

FIGURE 18

Etched + Self-Cure Specimen #36
(29.12 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)

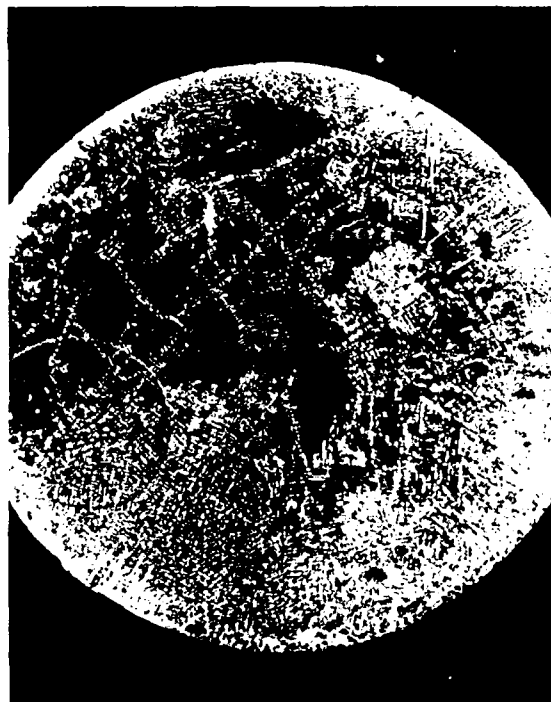


Secondary
Electron
Imaging
Technique

(60X magnification)

FIGURE 19

Etched Only Specimen #84
(6.05 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)

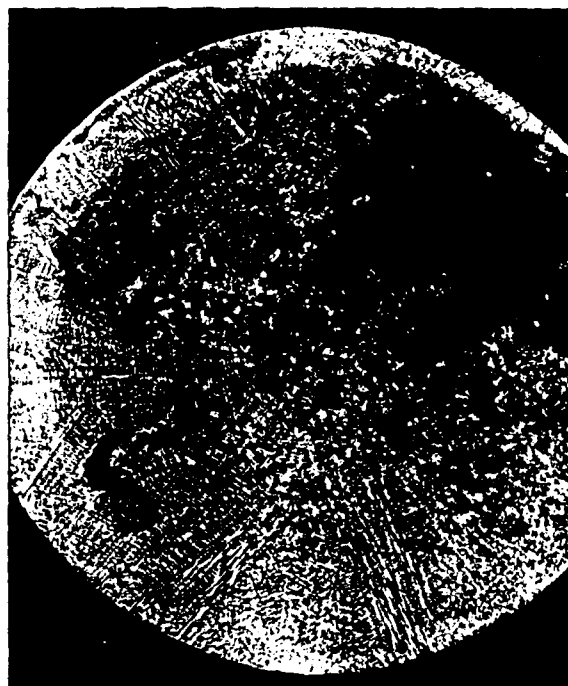


Secondary
Electron
Imaging
Technique

(60X magnification)

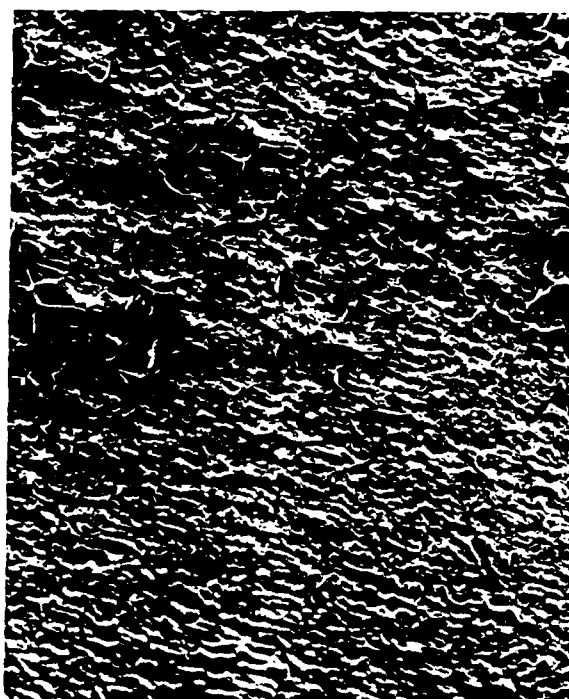
FIGURE 20

Etched + 4-META Specimen #101
(14.32 MPa)



Backscattered
Electron
Imaging
Technique

(13X magnification)



Secondary
Electron
Imaging
Technique

(60X magnification)

FIGURE 21

Etched + Self-Cure Specimen #114

(16.46 MPa)

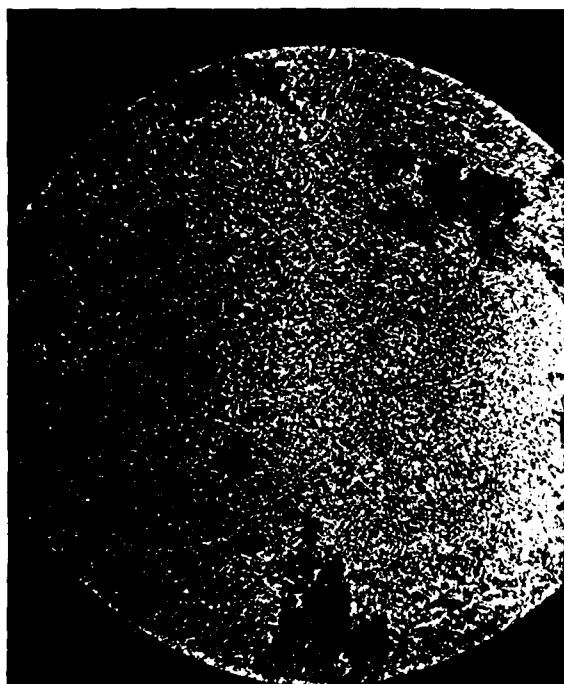
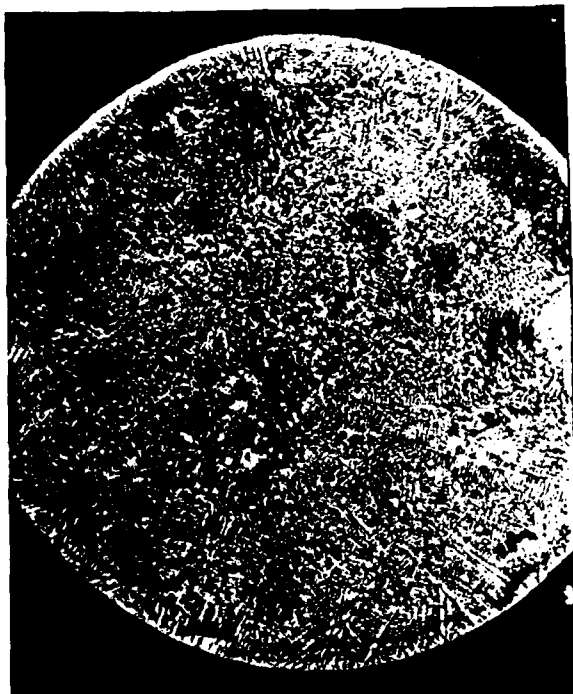
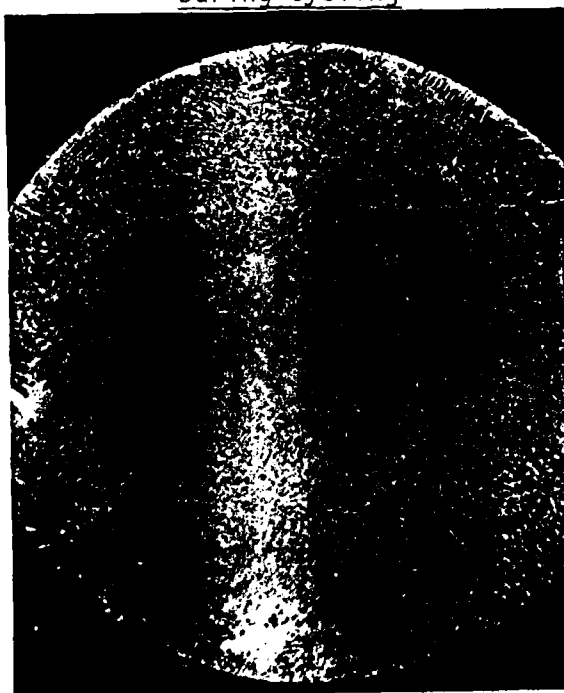
Backscattered
Electron
Imaging
Technique

(13X magnification)

Secondary
Electron
Imaging
Technique

(60X magnification)

FIGURE 22

Representatives of Separated SpecimensDuring Deflasking#42 Etched Only
(13X magnification)#28 Etched + Self-Cure
(13X magnification)During Cycling#40 Etched + Self-Cure
(13X magnification)

APPENDIX

TECHNICAL REFERENCES

Ticonium Company: Ticonium 100 Technical Manual, Albany, New York, June, 1966.

Rudd, K.D., Morrow, R.M., Eissmann, H.F.: Dental Laboratory Procedures, Removable Partial Dentures. St. Louis, C.V. Mosby, 1981.