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EFFECT OF PORCELAIN SURFACE PRETREATMENTS ON COMPOSITE RESIN-PORCELAIN SHEAR BOND STRENGTH

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By

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EFFECT OF PORCELAIN SURFACE PRETREATMENTS ON COMPOSITE RESIN-PORCELAIN SHEAR BOND STRENGTH

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Supervising Professor

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DEDICATION

I wish to dedicate this Thesis to my loving wife, Deborah, and our two sons, Matthew and Ryan. Their love, patience, and understanding helped me make it through the three years of my prosthodontic residency. My wife, Deborah, kept our home together and gave our sons the attention of two parents. To her, I dedicate this Thesis and my Love.

I would also like to dedicate this thesis to my mother, Carmen Breckner and my dearly departed father, Audelle (Harry) Breckner. Their love and guidance given to me throughout my life will be cherished always.

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EFFECT OF PORCELAIN SURFACE PRETREATMENTS ON COMPOSITE RESIN-PORCELAIN SHEAR BOND STRENGTH

Harvey Hamilton Breckner III

The University of Texas Graduate School of Biomedical Sciences at San Antonio

Supervising Professor: Barry K. Norling, Ph.D.

The bond between composite resin and dental porcelain has drawn much attention in recent years. This bond is important in dentistry because without it, porcelain restorations could not be bonded to tooth structure and it would be more difficult to repair defective porcelain restorations intraorally.

Previous studies of different methods for pretreating the porcelain surface, in general, have given conflicting and controversial results. Therefore, the objectives of this research were to determine the effects that six dental porcelain surface pretreatments, two types of silane, and thermocycling had on composite resin-porcelain shear bond strength.

To accomplish these objectives, this research was conducted in three parts; a pilot, a preliminary, and a principal study. The pilot study determined overall project feasibility, refined experimental protocol, and was used to determine the sample size used in the principal study. The preliminary study was conducted to establish the optimal hydrofluoric acid etch time and etchant concentration to be used in the principal study. The principal study compared six porcelain surface pretreatments, two silanes, and two specimen aging protocols. The six porcelain surface pretreatments compared were glazing, air-abrasion, air-abrasion/plasma cleaning, air-abrasion/sputter coating silica, air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating. The two types of silanes evaluated were Scotchprime™ prehydrolyzed silane and Silicoup™ nonprehydrolyzed silane. The two aging protocols consisted of hydration for 71 days in 37° C deionized water and hydration for 70 days in 37° C deionized water followed by 1000 thermocycles between 6 and 60° C. With few exceptions, the materials and methods were kept the same for pilot, preliminary, and principal studies.

In the principal study, porcelain coupon specimens were fabricated, pretreated by the six different methods, silane treated, bonded to composite resin, aged with and without thermocycling, and shear bond tested on a universal testing machine (Instron). Resulting fracture sites were examined under a stereomicroscope to determine mode of failure. Specimens representative of the different failure modes were further examined and photographed under a scanning electron microscope.

In comparing the porcelain surface pretreatments and silanes, statistical analyses were performed for nonthermocycled/thermocycled pooled data and thermocycled data. Because thermocycling better simulates the oral environment, conclusions were based on the thermocycled samples. The nonthermocycled data was used to determine the effects of thermocycling.

Statistical analysis and evaluation of the data resulted in the following main conclusions:

1. The optimal hydrofluoric acid etching time and etchant concentration for the porcelain evaluated in this study, VMK 68™, was a 2.5 minute etch time with a 10% solution of hydrofluoric acid.
2. The removal of the porcelain surface glaze is essential for successful composite resin-porcelain bonding.
3. One hundred percent of the thermocycled air-abrasion/HF etched and air-abrasion/silicoated specimens failed totally cohesively in porcelain or in porcelain/resin. It is anticipated that restorations bonded using air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating might be as strong as the porcelain from which they are made or the composite resin they are cemented with.
4. When comparing Silicoup™ to Scotchprime™ for each porcelain surface pretreatment, Silicoup™ was significantly more effective for glazed and sputter coated samples. Silicoup™ produced higher numerical composite resin-porcelain shear bond strengths than did Scotchprime after thermocycling for all surface pretreatments evaluated.
5. In general, thermocycling decreased the composite resin-porcelain bond strengths more for the Scotchprime™ samples than for the Silicoup™ samples.
6. Thermocycling significantly decreased the mean shear bond strength of the Scotchprime™-glazed sample but did not significantly affect the Silicoup™-glazed sample.
7. When comparing the different thermocycled silane-porcelain surface pretreatment combinations, as long as Silicoup™ silane was used on a once air-abraded porcelain surface, a significant difference between their means could not be

found. Regardless of the type of silane used, air-abrasion/hydrofluoric acid etching and air-abrasion/silicoating produced the highest four numerical thermocycled composite resin-porcelain shear bond strength means.

8. When comparing the silane-porcelain surface pretreatment combinations separately for Silicoup™ and Scotchprime™ silanes, for Silicoup, except for the glazed sample which had significantly lower shear bond strengths, a significant difference between the surface pretreatments could not be detected. For the Scotchprime™ sample, the best surface pretreatments were air-abrasion/HF acid etching, and air-abrasion/silicoating which were not significantly different from each other but produced significantly higher bond strengths than did glazing, air-abrasion-alone, air-abrasion/sputter coating , and air-abrasion/plasma cleaning. Clinically these findings suggest that if Silicoup™ were used as the silane coupling agent, air-abrasion-alone may be as effective as hydrofluoric acid etching when it comes to repairing porcelain restorations clinically. With respect to the laboratory pretreatment of porcelain restorations, in preparation for cementation, air-abrasion/silicoating appears to be just as effective in producing high bond strengths as air-abrasion/hydrofluoric acid etching and both would not be dependent on the type of silane used.

9. Because hydrofluoric acid use is fraught with potential medical hazards, the findings of this research suggest that Silicoup™-air-abrasion-alone be considered for repairing defective porcelain restorations intraorally. Extraorally, air-abrasion/silicoating should be considered a safe alternative to air-abrasion/hydrofluoric acid etching and is recommended over air-abrasion-alone, air-abrasion/plasma cleaning, and air-abrasion/sputter coating because it does not appear to be silane dependent.

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I. INTRODUCTION

Progress in esthetic dentistry is limited by the techniques and materials with which the dentist and dental laboratory technician have to work. An area that has drawn much attention in recent years has been the bond between composite resin and dental porcelain as it applies to bonded porcelain inlays, onlays, and laminate veneers. The method most widely used to create this bond involves pretreating the porcelain by acid etching the surface, followed by silane treatment. When these restorations are cemented to prepared tooth structure, a micromechanical-chemical bond is formed at the porcelain-composite junction (Horn, 1983a,b;Calamia, 1985).

Historically, this method evolved from techniques used in repairing fractured porcelain restorations (Nicholls, 1988). The fractured area was roughened with a diamond instrument, treated with a silane coupling agent, and then restored with composite resin. The silane reportedly promotes adhesion via a chemical bond between the composite resin and dental porcelain (Eames *et al.*, 1977; Eames and Rogers, 1979; Ferrando *et al.*, 1983; and Bello *et al.*, 1985). Horn (1983a,b) and Calamia (1983) popularized the use of hydrofluoric acid for pretreating the intaglio surface of porcelain laminate veneers. The use of this same technique for bonded porcelain inlays and onlays soon followed.

To date, there has been a great deal of conflicting evidence concerning resin-porcelain bond strengths and which porcelain pretreatments are most effective (Calamia and Simonsen; Nayyar *et al.*, 1985; Hsu *et al.*, 1985; Thomas *et al.*, 1987; Stangel *et al.*, 1987; Lacy *et al.*, 1988; Pratt *et al.*, 1989). These inconsistencies warrant continued study in this rapidly expanding area of dentistry. Any knowledge gained will be useful in understanding the nature of the resin-porcelain bond and the efficacy of the techniques used to create it. Two reasons for the lack of agreement in results among investigators in past studies, is that the composite resin-porcelain bonding process is affected by the silane chemicals involved (Culler *et al.*, 1986) and a precise acid etch time and concentration is needed for each particular porcelain evaluated (Calamia *et al.*, 1985; Stangel *et al.*, 1987). Both of these problems were considered in this study and investigated.

The evaluation of different porcelain surface treatments and pretreatments would obviously be beneficial to the dental community. Such an study could help to eliminate some of the present confusion in the literature concerning which silanes and pretreatments are most effective. Additionally, because of the well known potential medical hazards of hydrofluoric acid use, it would be beneficial if safe alternatives to hydrofluoric acid etching could be found.

The pretreatments investigated in this study were air-abrasion, air-abrasion/plasma etching, air-abrasion/sputter coating with pure silica and air-abrasion/silicoating. Glazed porcelain samples were included as an additional group to eliminate mechanical retention as a factor in the composite resin-porcelain bonding. This aided in evaluating the effectiveness of Silicoup™ and Scotchprime™ in promoting chemical bonding and determining the affect that roughening the porcelain surface had on composite resin-porcelain shear bond strength. It should be pointed out that plasma cleaning and sputter coating porcelain have not been investigated in past studies.

This study was divided into three parts: a pilot, preliminary, and principal study. The purposes of the pilot study were to determine the project's feasibility, refine the experimental protocol, and determine the appropriate sample size for the principal study. A definitive hydrofluoric acid etch time and concentration could not be found, in the literature, for the dental porcelain used in the principal study. Therefore, the preliminary study was designed to determine the optimal hydrofluoric acid etching time and concentration for the dental porcelain used in the principal study. In the principal study, dental porcelain coupons were fabricated, pretreated by six different surface pretreatments, silane treated with two different types of silanes, bonded to a composite luting resin, aged with and without thermocycling, and shear bond tested in a universal testing machine (Instron™). Each of the specimens shear bond tested was examined under x30 magnification using a stereomicroscope to determine mode of failure. Finally, a representative specimen of each different failure mode was selected and examined under scanning electron microscopy (SEM).

II. LITERATURE REVIEW

A. Composite Resin-Dental Porcelain Bonding Studies

Early studies of the composite resin-dental porcelain bond evolved from investigations in which acrylic resin was bonded to silane treated porcelain teeth (Paffenbarger *et al.*, 1967; Semmelman and Kulp, 1968; Myerson, 1969; Moffa *et al.*, 1975). The significance of these earlier studies was that when the bonded samples were strength tested, the fractures occurred in the porcelain teeth and not at the acrylic resin-porcelain interface. These were the first reports in the dental literature to demonstrate that the bond at a resin-porcelain interface was stronger than the cohesive strength of the porcelain itself. Armed with that knowledge, it was soon learned that composite resin could be bonded to dental porcelain using similar techniques. At this point, composite resin-porcelain bonding research, in general, can be divided into research evaluating porcelain repairs and research of porcelain restoration bonding.

1. Porcelain Repair Studies

Jochen (1973) was the first to describe a method for bonding composite resin to dental porcelain. He showed that a fractured porcelain denture tooth could be repaired by roughening the tooth with a green stone and restoring it with composite resin. In a subsequent study, Jochen and Caputo (1977) found that a course diamond worked better than a green stone, heatless stone, or carborundum disc for creating a roughened porcelain surface, because it produced significantly greater fracture strengths of composite resin to porcelain. The bonds created by these different abrasives were mechanical in nature and resulted in adhesive fractures of the specimens at the composite resin-porcelain interface.

In the search for a method to repair fractured porcelain restorations, Eames *et al.* (1977) were the first to evaluate the chemical bonding of composite resin to dental porcelain. They tested two porcelain repair systems: Den-Mat porcelain repair system and Fusion (George Tabb products) silane with Concise™ (3M Co.) composite resin. These systems were compared in their effectiveness to bond to porcelain denture teeth roughened with 240 grit silicon carbide paper. As was seen in the earlier acrylic resin-porcelain studies, the samples fractured cohesively in the porcelain. Hydration of the samples for one day, seven days, and thermocycling for one day did not reduce shear bond strength levels. Eames and Rogers (1979) later reported that specimens, prepared exactly the same way as was done in the Eames *et al.* (1977) study, resulted in shear bond strengths that actually increased in strength after one year's storage in 36.7° C water.

Based on the acrylic resin-porcelain bond studies, Newburg and Pameijer (1978) bonded composite resin to silane-treated porcelain denture teeth. They compared glazed to deglazed samples bonded with freshly prepared silane, two week old silane, and without silane altogether. In addition, half of the specimens from each sample was thermocycled to determine its effects on shear bond strength. They discovered that deglazed samples, bonded without silane, and glazed samples, bonded with silane, fractured adhesively at the composite resin-porcelain interface and were significantly weaker than deglazed samples bonded with silane. Again, thermocycling did not significantly reduce the shear bond strength of the deglazed samples bonded with silane and Nuva-Fil™ composite resin, but did affect the deglazed samples bonded with silane and Adaptic™ composite resin. The data from the two week old silane group was so variable that they did not attempt statistical analysis on them. They concluded that the removal of the glazed surface was essential and the use of fresh silane was critical for successful composite resin-porcelain bonding.

In a similar study, Burgar *et al.* (1980) examined the effects of thermocycling on the shear bond strength of composite cylinders bonded to wheel abraded silane-treated porcelain. This study differed from the work of Newburg and Pameijer (1978) in that metal ceramic squares, measuring 10mm x 10mm x 1mm, were used as the substrate instead of denture teeth. Fusion™ (George Tabb Products), an unspecified Den-Mat product (Den-Mat, Inc.), and Cervident™ (S.S. White Dental Products) repair systems were used according to the manufacturer's directions. For Fusion™ and Den-Mat specimens, no statistically significant difference was found between the thermocycled samples and non-thermocycled controls.

Highton *et al.* (1979) fractured, both, porcelain beams (control) and repaired porcelain beams in a three point bending test for fracture toughness. To ascertain the inherent bonding characteristics of the porcelain repair systems used, the fractured porcelain surfaces were not altered prior to the application of a silane. They reported that after 24 hours and 3 months storage in 37° C saline, 28% and 25% of the unrepaired porcelain strength was regained, respectively. These samples were repaired using the Den-Mat system with its own silane and composite resin. In this same study, porcelain beams were repaired using Fusion™ silane and acrylic resin. Again, specimens were stored for either 24 hrs or 3 months, but this time, 48% and 39% of the unrepaired porcelain strength was regained, respectively. For all groups of repaired samples, failure occurred adhesively at the resin-porcelain interface and increasing the storage time of the samples prior to testing did not significantly affect the flexural strengths. It was concluded from this study that porcelain repair systems using acrylic resin were significantly stronger than systems using composite resin.

In a similar study, Nowlin *et al.* (1981) compared the effectiveness of three commercial composite resin repair systems, and tested the affects of thermocycling. The specimens were either stored in 37° C water (1 day or 10 days) or thermocycled (2172, 3241 or 4737 cycles) between 5° C and 50° C with one minute dwell and a one minute travel time. The best system tested regained only 18% of the unrepaired porcelain flexural strength. Across all composite resin-porcelain bonds tested, the lowest bond strengths resulted from thermocycling 4737 cycles which was significantly weaker than the highest bond strengths tested after 10 days hydration. The Fusion™/Concise™ specimens were significantly stronger than the Den-Mat and Cervident™ specimens.

In contrast to the above two reports, Dent (1979), Ferrando *et al.* (1983), Nayyar *et al.* (1985), and Bello *et al.* (1985) roughened the dental porcelain surfaces to be repaired with a diamond bur prior to the bonding of silane and composite resin to the porcelain. Dent (1979) used the technique described by Newburg and Pameijer (1978) to clinically repair a fractured metal ceramic crown. Nayyar *et al.* (1985) concluded from repairing metal ceramic crowns that the initial tensile bond between porcelain and four repair materials was inferior to the metal ceramic bond. Using tensile bond tests, Ferrando (1983) found statistically different composite resin-porcelain bond strengths created by the following porcelain repair materials in the following order: Enamelite 500™ (Lee Pharmaceuticals) (9.8 MPa) > Fusion™/Adaptic™ (Johnson & Johnson Products Co.) (5.4 MPa) > Adaptic™ with no silane (control - 1.8 MPa) > Den-Mat (1.1 MPa) and Cyano Veneer™ (Ellman International Manufacturing Inc.) (.2 MPa). There was not a significant difference between bond strengths of specimens hydrated for 1 week and those hydrated for 4 weeks. Also using a tensile bond test, Bello *et al.* (1985) did find a significant difference between bond strengths of specimens hydrated for 1 week and those hydrated for 4 weeks in all four systems tested. Enamelite 500™, Enamelite 500™ with experimental silane, and Den-Mat systems all increased in bond strengths while Silanit™ (Vivadent) decreased. At the 4 week interval, there was not a significant difference between the mean bond strengths of the Enamelite 500™ (12.6 MPa), Enamelite 500™ with experimental silane (10.2 MPa), and Silanit™ (9.3 MPa) specimens, while the Den-Mat specimens were statistically weaker (7.3 MPa).

Using transmission infrared spectroscopy, Culler *et al.* (1986) determined that the molecular structure of the major active ingredients in five porcelain repair kits was a silane coupling agent. A correlation was shown between the degree of hydrolysis of the silane and the shear bond strength of composite resin bonded to silane primed porcelain teeth (Trubyte, Dentsply International, Inc.). The silanes with the highest degree of hydrolysis caused cohesive failure in the porcelain. The bond strengths decreased significantly when the concentration of monomers was reduced by condensation of silane molecules. It was concluded that stronger and more reproducible bonds to porcelain can be achieved through proper control of the degree of hydrolysis and polymerization of the silane priming agent.

The effects of hydration on porcelain to composite resin bond strengths were studied by O'Kray *et al.* (1987) and Bailey (1989). When comparing Porcelite™ (Kerr) and Scotchprime™ (3M) repair products, O'Kray *et al.* showed that Porcelite™ repaired porcelain specimens stored in 37° C water for one day had significantly lower shear bond strengths (2.3 MPa) than those stored in air for one day (10.7 MPa). Hydration did not affect the Scotchprime™ samples' mean shear bond strengths for both water and air stored samples. Fractures were cohesive in porcelain for only the nonhydrated Porcelite™ specimens, while being cohesive in porcelain for all Scotchprime™ specimens.

Before storage, all specimens were roughened with 320 grit metallographic paper, silane treated, and bonded with composite resin. Bailey (1989) compared Scotchprime™, Ultrafine™ (Kerr), Fusion™, and Ultrabond™ (Den-Mat) organosilanes and found that 7 day hydration of porcelain samples roughened with a coarse diamond before bonding, significantly decreased flexural bond strengths.

The effects of varying hydration times on shear bond strengths of porcelain samples repaired by various porcelain repair systems [Fusion™, Scotchprime™, and Cerinate Prime™ (Den-Mat)] was investigated by Diaz-Arnold *et al.* (1989). Half of the samples were roughened with 220 grit wet-dry silicon carbide paper and half were left with glazed bonding surfaces. After bonding, half of both types of samples were hydrated in 37° C water for 1 day and half for 30 days. Scotchprime™ and Fusion™ deglazed samples did not show a significant decrease in shear bond strengths with the increased storage time (13.1 and 11.2 MPa respectively). However, Scotchprime™ samples were the only ones that were not significantly affected by the presence of an autoglazed surface with the majority of fractures occurring in porcelain for both storage times (100% and 83% respectively).

The effects of thermocycling on composite resin-porcelain shear bond strengths created by four porcelain repair systems was reported by Diaz-Arnold and Aguilino (1989). The products tested were Command Ultrafine™, Enamelite 500™, Fusion™, and Scotchprime™. After being roughened with 220 grit silicon carbide paper and repaired, all specimens were stored in 37° C double deionized water for 1 day. Before being shear bond tested, half the specimens were stored an additional 2 days in the same water while the other half were thermocycled between 5° C and 60° C for a total of 1776 cycles over a 2 day period. Thermocycling caused a statistically significant decrease in the mean shear bond strengths of all the systems tested except the Scotchprime™ system. Even though the mean shear bond strengths decreased from 17.8 MPa to 12.9 MPa due to thermocycling, all of the Scotchprime™ specimens fractured 100% cohesively in porcelain.

The effects of varying hydration times, in conjunction with thermocycling, was investigated by Pratt *et al.* (1989) and Beck *et al.* (1990). Pratt *et al.* evaluated six porcelain repair kits with bonded samples stored for up to three months. Flattened porcelain surfaces roughened with a course diamond were bonded according to manufacturer's directions. Half of the samples were hydrated in 37° C water for 48 hrs while the other half were hydrated in 37° C water for three months. Immediately prior to shear bond testing, all of the samples were thermocycled between 6° C and 60° C for 24 hours (500 cycles). Except for the Den-Mat specimens, all specimens fractured cohesively in porcelain, with Scotchprime™ producing the highest shear bond strength (11.2 MPa). At 3 months, Scotchprime™ specimens had a majority of cohesive fractures and had significantly higher shear bond strengths (6.2 MPa) than the other five systems. All products, however, had a statistically significant decrease in bond strengths over time. This led the authors to conclude that porcelain repair might be considered as an interim procedure. Beck *et al.* (1990) tested two organosilane repair systems (Cerinate Prime and Fusion™) at 1, 7, and 30 days storage in 37° C water. The 7-day and 30-day samples were thermocycled between 14° C and 60° C for 500 cycles. They concluded that shear bond strengths were higher at the 1-day and 7-day period than at the 30-day period.

Due to the unpredictable clinical results of repairing porcelain by the technique of mechanically roughening the porcelain surface with a rotary instrument, Lacy *et al.* (1988) sought to determine whether acidulated phosphate fluoride (APF) would be an effective porcelain surface pretreatment for porcelain repairs. They combined the knowledge that hydrofluoric acid (HF) etching creates high composite resin-porcelain bond strengths (Horn, 1983a,b; Calamia and Simonsen, 1984; Calamia *et al.*, 1985; and

McLaughlin, 1984), with the knowledge gained from studies that showed APF to etch and damage cameo porcelain restoration surfaces (Copps *et al.*, 1984; Wunderlich and Yaman, 1986; and Sposetti *et al.*, 1986), to deduce that, perhaps, APF could be used as a porcelain surface pretreatment for composite resin-dental porcelain bonding. To test APF's effectiveness, Lacy *et al.* (1988) took metal ceramic tabs roughened with a fine diamond and pretreated them in five different ways before bonding them with composite resin. The porcelain used was Will-Ceram (Williams Dental Company) low fusing dental porcelain. The pretreatments and resultant mean planar shear bond strengths are as follows: silane (15.1 MPa), 1.23% APF (8.0 MPa), 1.23% APF and silane (38.7 MPa), 9.5% HF (9.4 MPa), 9.5% HF and silane (46.8 MPa), and no pretreatment (6.9 MPa). Prior to testing, the samples were stored in 37° C water for 1 day. The etching times used for APF and HF were 10 minutes and 4 minutes, respectively . Silane treatment significantly raised shear bond strengths irrespective of how the porcelain surface was treated. Etching without a silane coupling agent provided no greater bond than mechanical roughening with a fine diamond. Only the etched and silanized samples demonstrated cohesive fractures in porcelain. They concluded that APF could be substituted for HF when bonding composite resin to porcelain. It should be noted that it has been shown that the planar shear test used by Lacy *et al.* results in significantly higher mean bond strengths than the conventional lap shear test (Watanabe *et al.*, (1988). This could account for the high composite resin-porcelain shear bond strengths obtained by Lacy *et al.*, relative to other studies in this literature review.

The use of topical fluoride in porcelain repairs was also studied by Abbasi *et al.* (1988) and Tomasovic and Glace (1989). Abbasi *et al.* found that HF, APF, and silane were significant in increasing composite resin adhesion to porcelain. Tomasovic and Glace compared several etchants in their ability to promote high composite resin-porcelain bond strengths. Dental porcelain samples (Cerinate™, Den-Mat) were etched and bonded with Ultra-Bond™ (Den-Mat). The etchants and mean shear bond strengths were reported as follows: Topical fluoride gel (4.1 MPa), 9.5% HF CeramEtch™ (11.9 MPa), 11.7% HF Stripit™ (12.5 MPa), 3% HF Porcelock™ (10.3 MPa). The authors did not report what kind of topical fluoride they used or the manufacturers of the etchants tested besides Den-Mat. They did report that the Porcelock™ (3% HF) was about as safe as topical fluoride, for use intraorally, and could be used as a porcelain etchant.

A new silane-activated phosphonate ester porcelain repair system (Clearfil Porcelain Bond™, A. Kuraray Co.) was evaluated by Anusavice *et al.* (1989). This relatively new repair system was compared to a system (Kerr Porcelain Repair System) using silane-only as a porcelain priming agent. Opaque porcelain embedded in resin was polished through 320 grit, and air-abraded. After application of priming agent and bonding with light-activated composite resin (Photo-Clearfil, A. Kuraray Co.), samples were stored for 3 weeks prior to being shear bond tested. Shear bond strengths showed that the silane-activated phosphonate ester samples (20.5 MPa) were significantly stronger than the silane-only samples (1.9 MPa).

The Clearfil Porcelain Bond porcelain repair system was also investigated by Matsumura *et al.* (1989). This system consists of a two liquid primer consisting of 5% 4-methacryloxyethyl trimellitic anhydride (4-META) in methyl methacrylate (MMA) and 4% 3-trimethoxysilylpropyl methacrylate in MMA. Following application of the primer, an autopolymerized opaque resin (4-META/MMA-TBB) is applied and is used as an adhesive to bond to the last component, the light-activated composite resin (Photo-Clearfil™). In this investigation, feldspathic porcelain (Vita VMK 68) samples were roughened with a diamond bur, repaired with the Kuraray system, thermocycled for

20,000 cycles and shear bond tested. All samples fractured cohesively in the porcelain with a mean shear bond strength of 32.5 MPa.

2. Porcelain Restoration Bonding Studies

Luting porcelain restorations to tooth structure was first reported by Charles Land. He used porcelain veneers, luted with zinc oxyphosphate cement, to restore broken down teeth (Land, 1903). The inner surface of the veneer was pretreated with "oxids combined with a suitable flux". When heated to a temperature equal to the melting point of gold and then cooled, a "film or coating that is homogeneously combined with a vitreous mass" was formed. The phosphoric acid in the cement used to lute the restoration would then purportedly form a chemical bond to the "coating of oxyphosphate" created by the porcelain surface pretreatment. Lands' procedure, however, soon lost favor with the dental profession because the "bond" formed was not a stable one and the restorations did not last.

The use of composite resin as a luting agent for the bonding of silane-treated porcelain restorations to etched enamel was first reported in the literature by Jenkins (1981). He described what led him to this treatment modality as "The availability of a resin capable of bonding to fractured dental porcelain and the possible clinical applications of such a material warranted an investigation of its tensile bond strength to porcelain and etched enamel". He attributed the "bond of the resin" to the application of an organo-functional silane (Den-Mat silane) to a non-glazed porcelain surface. In his study, Jenkins bonded composite resin (Den-Mat Porcelain Repair Composite Resin) to porcelain with and without silane. He also bonded the composite resin to etched enamel. After storage in 37° C water for one day, the tensile bond results were:

resin/porcelain (2.3 MPa), resin/silane/porcelain (25 MPa, all specimens fractured in porcelain), resin/etched enamel (27 MPa). After the in vitro tests, porcelain laminate veneers were bonded to tetracycline stained teeth in vivo using a silane coupling agent. At the time of writing of his report, six restorations remained bonded 20 months in one patient and four restorations were intact 12 months in another.

Horn (1983a,b) and Calamia (1983) were the first to bond *etched* porcelain laminate veneers to teeth in vivo. They used porcelain laminates as an alternative to acrylic resin laminate veneers, which they report were limited by their color instability, poor resistance to abrasion, and a weak chemical bond at the composite-laminate interface.

Simonsen and Calamia (1983) were the first to quantify, in vitro, the effectiveness of etching porcelain so that a strong composite resin-porcelain bond could be achieved for the purpose of bonding porcelain laminates to tooth structure. They assessed the effects of etching dental porcelain with 7.5% hydrofluoric acid for 0, 2.5, 5, 10, or 20 minutes. SEM analysis of various etch times showed a porous-like porcelain surface. After coating this surface with an unfilled resin followed by bonding of composite resin, the samples were tensile bond tested. Highest reported numerical tensile bond strengths (7.5 MPa) were obtained from the 20 minute etch. SEM analysis of the fracture sites showed that for all etched samples, fractures occurred cohesively in dental porcelain. Fractures of unetched porcelain occurred adhesively at the resin-porcelain interface.

In 1983, Calamia air-abraded the porcelain surfaces to be bonded with aluminum oxide prior to acid etching. While Calamia was developing a mechanical bond of composite resin to porcelain, Horn (1983a) was the first to described a technique for bonding porcelain laminate veneers to enamel using *both* mechanical *etching* and *silane* chemical bonding of composite resin to the porcelain. Using the knowledge gained from prior porcelain repair studies, (Eames and Rogers, 1979; Highton *et al.*, 1979; Johnson, 1980; and Barreto and Bottaro, 1982), Horn (1983a) was the first to bond a light-activated composite resin luting agent to hydrofluoric acid etched, silane-treated, feldspathic porcelain. In a follow-up article, Horn (1983b) reported that satisfactory etching can be accomplished with either a 10% solution of hydrofluoric acid for 15 minutes in an ultrasonic bath or in hydrofluoric acid substitute (Stripit™, J-Pin-Co) for 20 minutes in an ultrasonic bath. It is important to note that his report appears to be based on clinical experience.

Calamia and Simonsen (1984) studied the effects of silàne coupling agents on tensile bond strengths of etched dental porcelain disks mounted on non precious metal alloy stubs. The porcelain was etched for 20 minutes with a solution of hydrofluoric and sulfuric acids (concentrations not reported). They bonded composite resin to three groups of porcelain samples that were either silane treated, etched then silane treated or etched only (followed by application of an unfilled resin). The resultant tensile bond strengths were 8.2 MPa, 14.3 MPa and 11.4 MPa respectively. They concluded that the best results were obtained from using a combination of etching and silane treatment. Interestingly enough, etching was more important than silane treatment in obtaining high bond strengths. Calamia (1985) later reported in a clinical technique article, that the silane-only treated group was lightly air-abraded with aluminum oxide before silane application.

To determine the optimal etching time and solution of hydrofluoric acid needed to etch porcelain, Calamia *et al.* (1985) evaluated 5%, 7.5%, and 10% concentrations of hydrofluoric acid on four commercial porcelains using 2.5 and 20 minute etch times. Three feldspathic porcelains (Biobond™, Ceramco™, and Vita VMK 68™) and one aluminous porcelain (type not specified) were used as substrates. Shear bond tests demonstrated that substrates etched for 2.5 minutes had significantly stronger bonds and the feldspathic porcelain samples were stronger (17, 21, and 18 MPa respectively for 2.5 minute etch) than the aluminous sample (11.7 MPa). The salient point drawn from this study is that "To maximize bond strengths of etched porcelain veneers, one must use different etchant concentrations and etching times for different porcelains" (Calamia *et al.*, 1985).

A clinical evaluation of 116 etched porcelain laminate veneers was reported by Calamia *et al.* (1987). The restorations were evaluated over a 3.5 year period. During this time, none of the restorations debonded. This was the first controlled longitudinal clinical study that supported the conclusions of two earlier studies (Simonsen and Calamia, 1983; and Calamia and Simonsen, 1984) that the bond strength levels obtained in those studies would be of the magnitude expected to be clinically successful in the intraoral retention of porcelain restorations.

In a study aimed at determining the effects of silane on composite resin-porcelain shear bond strengths, Hsu *et al.* (1985) compared etched and non-etched porcelain (Microbond Natural Ceramic, Austenal Products) samples with and without silane (Porcelain Bonding Agent, Den Mat) treatment. An SEM pilot study determined the optimal etch time to be 2.5 minutes with commercial hydrofluoric acid (Stripit™). After hydration for seven days, the following mean shear bond strengths resulted: etched only (20.0 MPa), etched and silanated (24.0 MPa), silanated only (6.7 MPa), non-etched, and non-silanated (3.9 MPa). The use of silane significantly improved the composite resin-porcelain bond strength for porcelain etched with Stripit™.

A study by Stangel *et al.* (1987) also demonstrated that etching porcelain was the most significant factor in producing high shear bond strengths. They bonded etched and unetched Microbond Natural Ceramic porcelain with unfilled resin, silane (Porcelain

Bonding Agent, Den Mat), or silane with dentine adhesive (Creation Bond, Den Mat) prior to application of composite resin (Ultra Bond, Den Mat). The bond strengths increased significantly, from unetched to etched samples, for all three bonding conditions as follows: unfilled resins (3.0 to 15.6 MPa), silane (5.0 to 18.7 MPa), and silane/dentine bonding agent (8.8 to 19.4 MPa). All bonding conditions were equally effective in bonding composite to the etched samples. However, for unetched samples, the use of silane with dentin bonding agent was more effective than silane alone. The least effective method was found with unetched samples bonded with unfilled resin. Testing conditions for all samples consisted of hydration in room temperature water for seven days without thermocycling.

Through efforts on evaluating the effects of thermocycling on composite resin-porcelain tensile bond strengths, Thomas *et al.* (1987) showed that silane treatment did not significantly increase the bond strengths. Ceramco porcelain was fired with the surface to be bonded maintained against a phosphate-bonded investment tray. After divesting, the porcelain was etched with Stripit™ for 2.5 minutes. Half of the samples were bonded to Silar™ (3M) composite resin while the other half were silane treated (Fusion™) and then bonded to the composite resin. Thermocycling significantly decreased bond strengths as follows: non-silane treated (14.0 to 9.8 MPa), Silane treated (19.3 to 13.9 MPa). Although silane improved bond strengths, it was not statistically significant ($P=0.059$).

In a subsequent study comparing the effects of four commercial silane coupling agents on Ceramco™ porcelain etched for 2.5 minutes with Stripit™, Thomas *et al.* (1988) discovered that there were no significant differences between the tensile bond strengths they produced. Prior to testing, the samples were hydrated in 37° C distilled water followed by thermocycling between 5° C and 55° C for 100 cycles. The silanes compared were Fusion™, Kerr Porcelain Repair Primer, Prilane™ (Gresco), and Cerinate Prime™ (Den-Mat).

In light of the fact that many different porcelains and etching agents were being used for laminate restorations, Chan *et al.* (1987) investigated etching patterns and shear bond strengths of 12 porcelains and 3 etching agents. Bonded samples were thermocycled between 5° C and 55° C for 500 cycles. Significant differences were found for type of etching agent ($p=0.03$), type of porcelain ($p=0.0004$), and the etching agent-porcelain combination used ($p=0.01$). SEM analysis of etching patterns could not be correlated with the shear bond strengths. This investigation corroborated the findings of Calamia *et al.* (1985) that both the type of porcelain and etchant are significant in obtaining optimum composite resin-porcelain bond strengths.

In comparing retention of Vita Hi-Ceram™ and Vitadur N porcelain laminates pretreated by air-abrasion, silanation, 6% hydrofluoric acid etching or no pretreatment, Saunders and Adamson (1988) concluded that the important factor in providing an adequate bond was the differences in the roughness of the porcelain surface. Tensile peel impact retentive strengths revealed the Hi-Ceram™ veneers to be significantly ($p< 0.05$) more retentive than the Vitadur N™ veneers. They did not report any bond strength values. They also concluded that for veneers made from these types of porcelain, it may not be necessary to pretreat the porcelain prior to luting. The samples were not, however, hydrated or thermally stressed.

Sheth *et al.* (1988) supported the findings of Hsu *et al.* (1985) and Stangel *et al.* (1987) that silane treatment of etched porcelain significantly increases composite resin-porcelain bond strengths. Mirage™ (Chameleon Dental Products) feldspathic porcelain rods etched with hydrofluoric acid (Super Etch™, Chameleon) for 1.5 minutes were bonded, with and without silane (Bond Enhancer, Chameleon Dental Products), to etched enamel surfaces with an unfilled and a filled luting resin. After subjecting the bonded samples to thermocycling for 600 cycles between 5° C and 55° C, the mean shear bond strengths of the silane specimens (29.8 MPa) were significantly greater than those of the non-silane treated specimens (3.4 MPa). The silane was the critical step in obtaining high shear bond strength.

Tjan and Nemetz (1988) evaluated the ability of Porcelite™ (Kerr) and Recover™ (Teldyne Getz) luting resins to bond to etched porcelain with and without silane. Prior to etching, the samples were roughened with 240 grit silicon carbide abrasive paper. An unfilled resin was used for all samples prior to bonding. Shear bond strengths showed that samples bonded with Porcelite™ (without silane - 12.3 MPa; with silane - 12.3 MPa) were significantly greater than those bonded with Recover (without silane - 6.8 MPa; with silane - 8.3 MPa). Prior to bond testing, the samples were stored in 37° C water for 7 days. It was interesting to note that for both resins, the silane was not significant, which contradicts the findings of Hsu *et al.* (1985) and Stangel *et al.* (1987).

In a similar study, Sorenson *et al.* (1991) evaluated eight porcelains which were air-abraded and pretreated by either silane, hydrofluoric acid for 3 minutes or both hydrofluoric acid followed by silane. Each brand of porcelain came with its own silane. The bonded samples were stored in 37° C water for 7 days and thermocycled between 5° C and 50° C for 1000 cycles prior to being shear tested. The authors concluded that for most of the porcelains tested, etching significantly increased shear bond strengths. It is interesting to note that high mean shear bond strengths were achieved by etched and silane treated Optec™ HSP (23.47 MPa) and Mirage™ (20.66 MPa) porcelains. Results for Vita VMK 68™ porcelain were: silane (6.59 MPa), etched (10.88 MPa), etched and silane (9.42 MPa).

Nelson and Barghi (1989) measured mean shear bond strengths of composite resin bonded to acidulated phosphate fluoride (APF) and hydrofluoric acid etched feldspathic porcelain (Mirage™). The highest mean shear bond strength using 1.23% APF (12.0 MPa) resulted from an optimal APF 10 minute etch time which was not statistically different from the mean shear bond strength resulting from a 1 minute 10% hydrofluoric acid etch (11.9 MPa).

In a four part study, testing several porcelain surface pretreatments in dry and wet conditions, Kanchanatawewat and Stannard (1989) concluded that the type of porcelain, hydrofluoric acid etch times, type of silane, hydration, and methods of storage all had significant effects on tensile bond strengths. They contended that a number of variables need to be considered when evaluating the bonding of composite resin to porcelain.

The need to use an unfilled resin when bonding porcelain restorations with and without silane was investigated by Ross *et al.*, (1990). G-Cera™ composite resin (GC International Corp) was bonded to GC™ porcelain which was etched for 10 minutes with hydrofluoric acid. Immediately prior to bonding, the samples were surface pretreated by application of either unfilled resin (unspecified product), silane (unspecified product), or silane followed by unfilled resin. After bonding, the samples were stored in a humid atmosphere for 3 days. The mean shear bond strengths were reported as follows: unfilled resin (19.4 MPa), silane (19.5 MPa), silane/unfilled resin (10.4 MPa). The samples bonded with both silane and unfilled resin were significantly weaker than the other samples. Diaz-Arnold and Aquilino (1989) also found that the use of an unfilled resin after silane application caused a decrease in composite resin-porcelain bond strengths. Since there was not a significant difference when unfilled resin or silane was used alone, Ross *et al.* (1990), questioned the need for silane.

Reagan *et al.* (1990) evaluated the shear strengths of two composite luting resins (Porcelite™ and Insure™) bonded to porcelain disks (Vita VMK 68™ and Vitadur-N™) etched by two etching agents (Cerametch™ or Stripit™). Prior to testing the samples were stored for three days. The co-workers did not report what the samples were stored in. The mean shear bond strengths revealed that the composite luting resins and the etching agents were not significantly different. The VMK 68™ specimens were significantly stronger than the Vitadur-N™ specimens.

The effects of silicoating (Kulzer, Inc.) and hydrofluoric acid etching combinations on planar shear bond strengths of porcelain bonded with silane and composite resin were evaluated by Stannard and Kanchanatawewat (1990). They also evaluated the bonding of porcelain to acid etched enamel using unfilled resin as a luting agent. Prior to testing, samples were hydrated in 37°C water for 1 week. The porcelain surface treatments and resultant mean shear bond strengths and standard deviations for samples bonded to enamel or composite resin are listed as follows: samples bonded to enamel - no treatment (3.9 MPA), 30 second Stripit™ etch/silicoat (3.0 MPa), 30 second concentrated hydrofluoric acid etch/silicoat (7.5 MPa), silicoat (2.4 MPa); porcelain bonded to composite resin samples - no treatment (3.1 MPa), 30 sec concentrated hydrofluoric acid etch/silicoat (2.5 MPa) and silicoat (7.5 MPa). There were no significant differences in the bond strengths between the groups. Half of all of the silicoated samples fractured cohesively in the composite resin.

3. Summary of Composite Resin-Porcelain Bond Studies

a. Etching vs. Silane Treatment

To date, there has been a great deal of conflicting evidence as to composite resin-feldspathic porcelain bond strength and which bonding procedures are most effective. When comparing acid etching, silanization, and the two techniques combined, Calamia and Simonsen (1984) concluded from tensile bond strength tests that even though the greatest bond strength resulted from the combination (14.33 MPa), the etching alone (11.46 MPa) was the single most important factor in achieving initial dry bond strength. Ferrando *et al.* (1983) and Nayyar *et al.* (1985) obtained high hydrated (9.8 MPa) and dry tensile bond strengths (19.7 MPa) respectively, simply by roughening the porcelain surfaced with a diamond followed by silane treatment. Hsu *et al.* (1985) concluded that silane treatment can significantly increase the hydrated resin-porcelain shear bond strength. This conclusion was supported by Sheth *et al.* (1988) when they reported that etched and silane treated samples had a significantly greater thermocycled mean shear bond strength (29.8 MPa) than etched only samples (3.4 MPa). The silane, here, was the critical step in obtaining high composite resin-porcelain bond strength. Tjan and Nemetz (1988) and Sorenson *et al.* (1991), on the other hand, reported findings directly opposite to the findings of Hsu *et al.* (1985) and Sheth *et al.* (1988). Tjan and Nemetz showed that the mean hydrated shear bond strength of etched samples bonded without silane (12.3 MPa) was literally the same as those bonded with silane (12.3 MPa). Sorenson *et al.* (1991) demonstrated that, under conditions of hydration followed by thermocycling, the mean shear bond strength of etched only samples (10.88) was actually greater than samples which were etched and silane treated (9.42 MPa). Ross *et al.* (1990) even questioned the need for silane when they showed that the mean shear bond strength of etched porcelain samples bonded to composite resin using an unfilled resin (19.46 MPa) was virtually the same as those of samples bonded using silane (19.47 MPa). The worst bond strengths were found for samples that were bonded with silane followed by unfilled resin (10.46 MPa). It should be noted that Diaz-Arnold and Aquilino (1989) also found that when unfilled resin is used in combination with silane, significantly weaker composite resin-porcelain bonds result.

When considering whether there is a need to etch at all, a study by Lacy *et al.* (1988) concluded that etching without silane treatment (9.40 MPa) did not promote a stronger bond to resin than mechanically roughening the porcelain followed by silane treatment (15.09 MPa). These findings were corroborated by O'Kray *et al.* (1987) and Diaz-Arnold and Aquilino (1989) when they showed, also using a shear test, that the mean hydrated bond strength of porcelain samples repaired by roughening the surface and silane treatment were relatively high (13.44 MPa and 14.17 MPa respectively per study). One must also remember that Jenkins (1981), the first to document the use of composite resin for bonding porcelain laminates to enamel, reported a mean tensile bond strength of 25 MPa when he bonded composite resin to silane only treated porcelain.

b. Etching and Silane Treatment

When considering which bonding procedures yield the highest shear bond strengths, many studies show that the combination of etching and silane treatment ranks best ie. 14.33 MPa (Calamia and Simonson, 1984); 24.03 MPa (Hsu *et al.*, 1985); 15.09 MPa (Lacy *et al.*, 1988); 20.66 MPa (Sorenson *et al.*, 1991); 29.8 MPa (Sheth *et al.*, 1988). In obtaining high bond strengths, Sheth *et al.* (1988) demonstrated that neither the contributions of the physical microporosities in the etched porcelain nor the chemical bonding of the silane on an unetched porcelain surface were statistically significant. They concluded that high composite resin-porcelain bond strengths are due to the synergistic effects of the etching and silane combined. The wide range of bond strength values reported above serve to illustrate a point made by Calamia *et al.* (1985). They concluded that etchant concentrations and etch times need to be calibrated for different porcelains. Their findings were corroborated by Chan *et al.* (1987) who conclude that, both, the type of porcelain and etching were significant in obtaining optimum composite resin-porcelain bond strengths. The fact that no study in this review calibrated or optimized these factors may account for the confusion that exists in the literature about which porcelain surface pretreatments work best. Kanchanatawewat and Stannard (1989) concluded that the type of porcelain, hydrofluoric acid etch times, hydration, length of hydration, and type of silane had significant effects on tensile composite resin-porcelain bond strengths.

c. Type of Silane Coupling Agent

The type of silane used was taken into account by many investigators when comparing porcelain surface pretreatments. In general, they found that different silanes resulted in different bond strengths for mechanically roughened feldspathic porcelain bonded to composite resin (Nowlin *et al.*, 1981; Nayyar *et al.*, 1985; Bello *et al.*, 1985; O'Kray *et al.*, 1987; Nicholls, 1988; Bailey, 1989; Diaz-Arnold *et al.*, 1989; Diaz-Arnold and Aquilino, 1989). When using silane coupling agents, control of the degree of hydrolysis and polymerization are the two most important factors in the success of the silanization process (Culler *et al.*, 1986). In studies by O'Kray *et al.* (1987), Diaz-Arnold *et al.* (1989), Diaz-Arnold and Aquilino (1989), and Pratt *et al.* (1989) a prehydrolyzed form of silane (Scotchprime™) promoted higher shear bond strengths than non-prehydrolyzed silane products. In the Diaz-Arnold study, one non-prehydrolyzed silane product (Command Ultrafine™) promoted bond strengths statistically equivalent to those of Scotchprime™. When hydrofluoric acid etched porcelain surfaces were silane treated with four nonprehydrolysed commercial silane coupling agents, a statistically significant difference could not be found in their effectiveness to promote composite resin bonding (Thomas *et al.*, 1988). It should be pointed out that a prehydrolyzed form of silane, such as Scotchprime™, was not one of those compared in the Thomas *et al.* (1988) study.

The silane promoted composite resin-porcelain bond, in particular, is subject to potential hydrolysis induced degradation (Craig, 1989). Many of the studies in this review measured the effects that hydration and/or extended hydration had on composite resin-feldspathic porcelain bond strengths. The results on the effects of hydration were clearly inconsistent. Bailey (1989) found that hydration significantly reduced flexural bond strengths whereas Eames *et al.* (1977) showed no significant difference between hydrated samples and nonhydrated controls. O'Kray (1987) discovered that hydration degraded the mean shear bond strength promoted by Porcelite™ silane but not the mean shear bond strength promoted by Scotchprime™ silane. On extending hydration times, Highton (1979), Eames *et al.* (1977), Nowlin (1981), and Nayyar *et al.* (1985) found no significant differences between bond strengths of repaired porcelain samples hydrated for 1 day versus 3 months, 1 day versus 1 week, 1 day versus 10 days, and 1 week versus 4 weeks respectively. Eames and Rogers (1979), in a follow-up study to the Eames *et al.* (1977) investigation reported that extending the hydration for one year actually significantly increased bond strengths. When comparing hydration times of 1 week and 4 weeks, Bellow (1985) found that the increased storage time did not significantly affect bond strengths for samples repaired using Enamelite 500™, Enamelite 500™ with experimental silane or Silanit™ products, but significantly decreased bond strengths for Den-Mat repaired specimens.

d. Thermocycling Effects

The effects that thermocycling has on composite resin-feldspathic porcelain bond strength was investigated by Eames *et al.*(1977), Newburg and Pameijer (1978), Burgar *et al.* (1980), Nowlin (1981), Thomas *et al.* (1987), Diaz Arnold and Aquilino (1989), and Beck *et al.* (1990). Again, inconsistencies between studies are evidenced by their results. Eames *et al.* (1977) showed that thermocycling repaired porcelain samples for 1 day had no effect on shear bond strengths. Nowlin *et al.* (1981), showed that thermocycling for 4737 cycles significantly degrades repaired composite resin-porcelain flexural strength. Thomas *et al.* (1987) showed that thermocycling degrades both the bond created by etching alone and the bond established by etching followed by silane application. In a study by Burger *et al.* (1980), thermocycling decreased shear bond strengths of Cervident™ specimens but had no affect on Fusion™ or Den-Mat specimens. Since neither the silane nor the composite resin used were kept constant, one cannot attribute the less resistant Cervident™ bond to the silane or the composite resin. Diaz-Arnold and Aquilino (1989) compared samples, repaired by one of four porcelain repair systems, in their ability to withstand thermocycling. The only samples not affected by thermocycling were the Scotchprime™ samples. In one study thermocycling affected the bond strength generated by two different composites in different ways (Newburg and Pameijer, 1978). Thermocycling did not have a significant effect on the silane/Nuvafil composite resin-porcelain bond, but significantly weakened the silane/Adaptic™ composite resin-porcelain bond. This finding points us to the fact that the composite resin is another variable that could affect overall bond strength.

The effects of extending hydration times on thermocycled composite resin-feldspathic porcelain bond strengths was investigated by Pratt *et al.* (1989). They found that extending hydration time from 2 days to 3 months caused a significant decrease in composite resin-porcelain mean shear bond strengths for all four bonding systems, which included the Scotchprime™ system. In a similar study, Beck *et al.* (1990) concluded that thermal cycling and aging had an unclear influence on bond strength.

e. Mode of Failure

Most studies reviewed, when describing the mode of failure of the composite resin-porcelain bond, reported that when the bond interface was stronger than the adhesive (composite resin) or adherend (feldspathic porcelain), the fractures occurred in the adherend (Eames *et al.*, 1977; Jenkins, 1981; Simonsen and Calamia, 1983; Ferrando *et al.*, 1983; Bello *et al.*, 1985; Stangel *et al.*, 1987; O'Kray *et al.*, 1987; Thomas *et al.*, 1987; Lacy *et al.*, 1988; Tjan, 1988; Diaz-Arnold *et al.*, 1989; Diaz-Arnold and Aguilino, 1989; Pratt *et al.*, 1989). The only co-workers who did not report cohesive failures in porcelain , under these circumstances, were Stannard and Kanchanatawewat (1990). They reported 50% of cohesive fractures as occurring in composite resin.

f. New Treatments

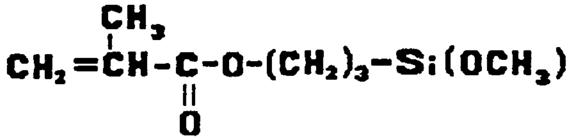
New composite resin-porcelain bonding techniques, which include a silane-activated phosphate ester (Anusavice *et al.*, 1989), a 4-META/MMA-TBB system (Matsumura *et al.*, 1989), Silicoating (Stannard and Kanchanatawewat, 1990) and the use of topical fluoride to replace hydrofluoric acid when etching porcelain (Lacy *et al.*, 1988; Abbasi *et al.*, 1988, Tomasovic and Glace, 1989), all show promise and should be investigated further.

B. Composite Resin-Porcelain Bonding Mechanism

Many analogies can be used to describe the bond between composite resin and porcelain as it is used for porcelain repairs and porcelain restorations. One such comparison is composite resin itself which is made up of bonds between organic polymers, silane couplers, and inorganic fillers. Both chemical and mechanical bonds exist in the composite resin system. The silane, being a bifunctional molecules, bonds chemically to both the organic polymer and the inorganic filler, while mechanical bonds exist due to interaction of the reinforcing filler particles and the surrounding matrix polymers (Sarkar *et al.*, 1984). The bonding mechanisms by which composite resin can be bonded to dental porcelain closely parallel those just described. The bond between composite resin and porcelain can be classified as either chemical, mechanical or a combination of the two (Calamia, 1983; and Horn 1983a,b).

1. Chemical Bonding Mechanism

The chemical bond between composite resin and porcelain has evolved from chemical adhesion methods for bonding glass fillers to polymers using silane coupling agents (Newman *et al.*, 1984). The principle work done in this area was accomplished in the glass and plastics industry (Vanderbilt and Simko, 1960; Pleuddemann *et al.*, 1962). Bowen (1963) recognized the potential dental use of the reinforced plastics industries' resin systems, which had improved laminate water resistance from the treatment of the glass reinforcements with vinylsilane, and developed dental composite resin using similar reinforcements. Bowens' composite resin was made by mixing an organic polymer (Bisphenol A Glycidyl Methacrylate or Bis-GMA) with an inorganic filler (silica) which had undergone treatment with an aqueous solution of 2 - methoxy ethoxy vinylsilane (silane coupling agent). The mechanism by which composite resin chemically bonds to porcelain also involves a silane coupling agent. In defining a coupling agent, it is an agent which acts by adsorbing onto and altering the surface of a solid to facilitate either a chemical or physical process (Sterman and Marsden, 1963; Arkles, 1977). The most common silane coupling agent used to bond composite resin to porcelain is 3 - methacryloxypropyl - trimethoxysilane which has the following structural formula:



$$CH_2=\overset{CH_3}{\overset{|}{C}}H-\underset{O}{\underset{\|}{C}}-O-(CH_2)_3-Si(OCH_3)_3$$

This silane is a bifunctional organosilane molecule having one end that bonds to an inorganic substrate (dental porcelain) and another end which bonds to a cross linked polymer (composite resin) (Stangel *et al.*, 1987; Diaz-Arnold, 1989). Figures 1 and 2 illustrate the chemical reactions that takes place in the coupling process. In reaction 1, the S-OCH_3 bond undergoes hydrolysis upon exposure to either aqueous solutions or water adsorbed at the substrate surface (Vanderbilt and Simko, 1960). Hydrolysis is a process in which cleavage of a molecule is accomplished by the addition of one of two components of a water molecule, H- and -OH (Solomons, 1976). In the hydrolysis of 3 - methacryloxypropyl - trimethoxysilane, one to three of the methoxy groups (CH_3O-) are cleaved and replaced by H-. The end group of the silane coupler thus becomes a reactive silanol. The silanol is the reactive funtionality that bonds to the porcelain surface. The silanol group condenses with Si - OH groups made available on the

Figure 1. Silane Coupling Mechanism

Reaction 1 - *Silane Hydrolysis*

Reaction 2 - Silane Condensation

Reaction 3A - Polymerization Initiation

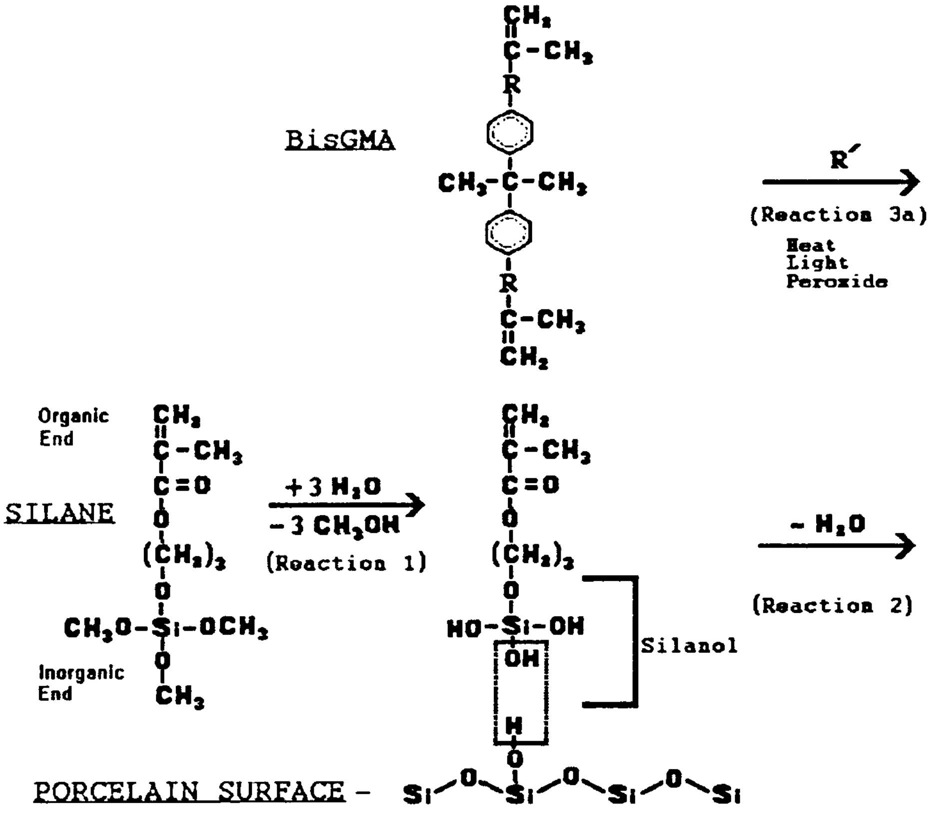
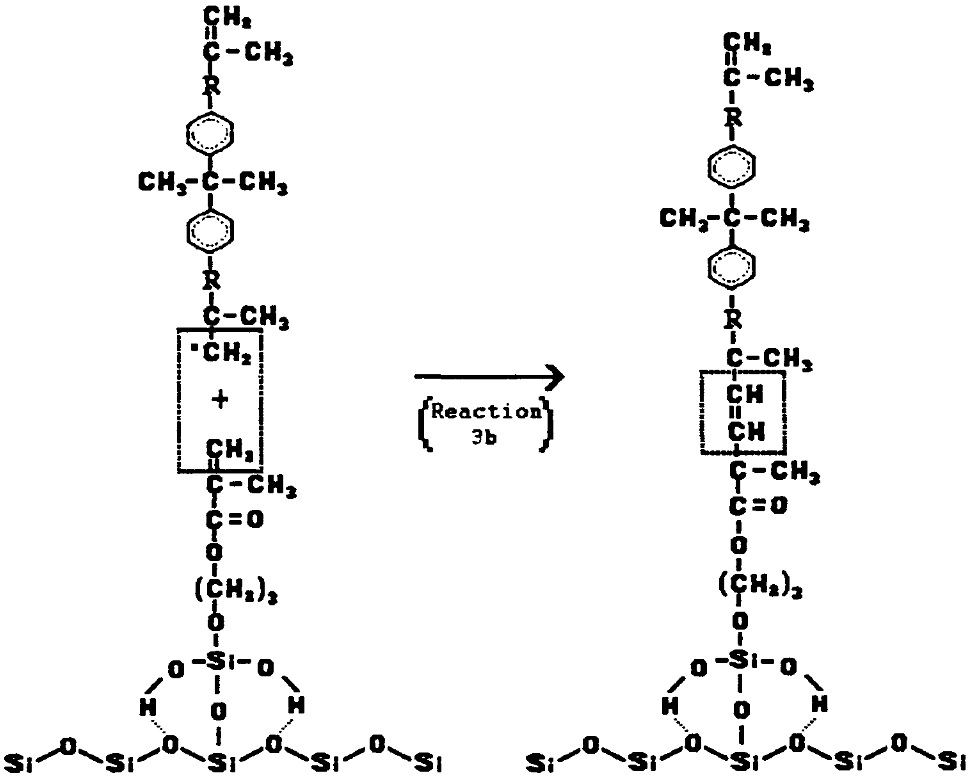

BisGMA
R´
(Reaction 3a)
Heat
Light
Peroxide
Organic End
SILANE
Inorganic End
+3 H₂O
-3 CH₃OH
(Reaction 1)
Silanol
- H₂O
(Reaction 2)
PORCELAIN SURFACE -

Figure 2. Silane Coupling Mechanism (cont.)

Reaction 3B - Polymerization of Bis-BMA With Silane Coupling Agent


CH₂
C−CH₃
R
CH₃−C−CH₃
R
C−CH₃
·CH₂
+
CH₂
C−CH₃
C=O
O
(CH₂)₃
O
Si
O
H
Si
Reaction
3b
CH
CH

porcelain surface from chemisorbed H_2O (Reaction 2). A condensation reaction is one in which two compounds became covalently bonded through the loss of H_2O or some other simple molecule (Solomans, 1976). In the final reaction (reaction 3b), composite resin (Bis-GMA) becomes copolymerized with the alkene (-C=C-) end of the silane coupling agent. The resultant alkene polymerization is a free radical (R') initiated addition reaction (reaction 3a). The free radical can be initiated by heat, light, or traces of peroxides (Craig 1989).

2. Mechanical Bonding Mechanism

Mechanical bonding simply implies a mechanical interlocking of two different materials (Sarkar *et al.*, 1984). One obvious example of a mechanical bond is the use of diatorics in porcelain denture teeth to retain acrylic resin which locks the teeth in the denture base. Jochen and Caputo (1977) used mechanical bonding to repair fractured porcelain teeth with composite resin. A coarse diamond on the porcelain created a surface better suited for the composite resin to interlock with. It should be pointed out, however, that the repaired porcelain samples fractured adhesively at the composite resin-porcelain interface during shear testing. It was not until 1983 that Simonsen and Calamia (1983) showed that mechanical bonding alone could create high shear bond strengths that were greater than the cohesive strength of the porcelain itself. To produce these results, they etched the porcelain surface with hydrofluoric acid. This method of roughening the porcelain surface creates microdefects in the porcelain into which low viscosity resin can flow. Once the resin fills these microdefects, they harden and lock into them (Nathanson, 1983). Roughening the porcelain by any means, low viscosity adhesives can spread and penetrate to interlock over a greater surface area. Once the adhesive (ie. composite resin) coats and penetrates the porcelain substrate, hardens, and interlocks over this greater surface area, greater bond strengths can be attained by virtue of the greater surface area (Sarkar *et al.*, 1984). Several investigators have shown, with SEM analysis of etched porcelain surfaces, that certain components of the porcelain substrate are preferentially etched away, thus leaving the microdefects needed for bonding (Calamia, 1983; Horn, 1983a; Tjan and Nemetz, 1988; Sheth *et al.*, 1988; Lacy *et al.*, 1988; Edris *et al.*, 1990). Hydrofluoric acid etches dental porcelain by selectively degrading the silica component (Timokhin and Komarova, 1985).

Even though SEM analysis can reveal porcelain surface morphology conducive to bonding, Chan *et al.* (1987) showed that etching patterns can not be correlated with shear bond strengths. Calamia *et al.* (1985) found that when acid concentrations and etching times are kept constant, different types of porcelain gave different bond strengths. They recommended that to achieve optimal bond strengths, the acid concentration and etching time be determined for each specific type and brand of porcelain used. Stangel *et al.* (1987) discovered that the initial surface morphology created by porcelain firing conditions plays an important role in the development of an appropriate microstructure for bonding. Having to control these variables makes acid etching somewhat material and protocol dependent, thereby increasing the possibility for error. Even with established guidelines, it is imperative that etching times and acid concentrations be closely followed (Calamia *et al.*, 1985).

3. Chemical-Mechanical Bonding Mechanism

When investigations using both chemical and mechanical retention were reviewed in the following section on composite resin-porcelain bonding studies, they all showed that high bond strengths are attained by the use of the combination of chemical and mechanical retention. These results can be attributed to the additive affect of the two processes combined.

Using SEMs, Sheth *et al.* (1988) showed that surface microporosities created by hydrofluoric acid etching are not obstructed by the application of a silane coupling agent. In fact, they contended that the chemical action of the silane on the energized surface of etched porcelain acted synergistically to improve composite resin-porcelain bond strengths. These results are consistent with a study by Brownd (1982) which concluded that effective wetting of dental porcelain with composite resin is promoted by the prior application of a silane coupling agent.

In summary, the bonding mechanisms involved when combining chemical and mechanical retention are the same mechanisms when chemical and mechanical retention are used individually. However, the added surface area and increased surface free energy created by the mechanical retention used in conjunction with silanes' wetting and chemical bonding characteristics increase overall bond strength.

C. Hazards of Hydrofluoric Acid

Horn (1983a,b) and Calamia (1983) popularized the use of hydrofluoric acid as a dental porcelain surface pretreatment for porcelain restorations to be bonded to tooth structure using composite resin. The problems with this surface pretreatment method, however, are the well known hazards that are presented by the use of hydrofluoric acid (Lacy *et al.*, 1988). Hydrofluoric acid inhalation or skin exposure can cause serious injury, disability, and if not promptly treated, possibly death. Burns by hydrofluoric acid produce a greater medical hazard than other chemicals because of the two-stage process of injury it causes. In the first stage, this acid causes a dehydration induced necrosis of the skin. In the second stage, it actually penetrates into the deep subdermal layers. Because of its solubility in tissues, it penetrates slowly and insidiously with a delay of symptoms. This is especially dangerous, because if left untreated it can cause deep tissue injury and bone destruction. Especially note that dilute solutions could be present on the skin and left unnoticed for hours until extreme pain and tissue necrosis occurs (Flood, 1988). For etching porcelain restorations, recommended concentrations of hydrofluoric acid range from 5% to 9.5% (Simonsen and Calamia, 1983; Hsu *et al.*, 1985; Calamia *et al.*, 1985; Thomas *et al.*, 1987; Tjan and Nemetz, 1988; Reagan *et al.*, 1990). Personnel handling this material must wear a lab coat or apron, safety glasses, and rubber gloves. Storage and disposal precautions are mandatory (Horn, 1983a,b; Harbert and Dudek, 1985). It is even recommended that at minimum, coveralls with long sleeves made of impervious material, face shields, and leather safety shoes with special impervious soles be worn as well (Flood, 1988).

Jochen (1973) was one of the first to discourage the use of hydrofluoric acid in the dental laboratory. No matter how dilute a concentration of hydrofluoric acid used, treatment of exposed sites requires immediate copious irrigation with water followed immediately by emergency referral to a physician for examination and treatment (Flood, 1988). Alternatives to chemicals using hydrofluoric acid as a porcelain surface pretreatment are needed (Lacy *et al.*, 1988; Edris *et al.*, , 1990). Products labeled as hydrofluoric acid substitutes may be just as hazardous and should be avoided if possible (Edris *et al.*, 1990).

D. Substrate Surface Pretreatment Methods

1. Silicoating

In search for a method to eliminate the need for mechanical retention of composite resin veneers, a new method for chemically bonding resin to alloy was presented by Musil *et al.* (1982). Developed in East Germany, this new system (Silicoater®, Kulzer Inc., Irvine, CA) pyrolytically applies and binds a silicon-oxide-carbon (SiOx-C) coating to air-abraded metal substrates (Musil and Tiller, 1984; Laufer and Nicholls, 1987; Barzilay *et al.*, 1988; Laufer *et al.*, 1988; Hansson, 1989). The pyrolytic system works when a silane, tetraethoxysilane, is transported via oxygen to a gas burner where it is mixed with propane. Upon gas ignition, the silane decomposes into its SiOx-C constituents and becomes deposited onto the metal substrate in molecular layers (Hansson, 1989). Since the SiOx-C constituents are only 10 to 20 Angstroms in size, these constituents become intimately associated with the metal substrate molecules and cover 100% of the roughened surface. This promotes excellent chemical and mechanical adhesion, and hence bonding, of the SiOx-C coating to the substrate. The adhesive bonding provides shear bond strengths of 24 MPa for precious metals and 15 to 20 MPa for base metal alloys. The estimated thickness of this SiOx-C layer is 100 to 1000 nanometers (Musil and Tiller, 1984). Since composite resin cannot bond to the -OH terminals of the SiOx-C molecules, a silane coupling agent is used for this purpose. Composite resin is then applied to and bonds with the silane coupling agent (Blanco, 1988; Hanson, 1989). Silicoating in effect turns a metal substrate into a silica (porcelain like) substrate (Musil and Tiller, 1984) with the silane and composite resin bonding processes proceeding as described earlier in the composite resin-porcelain bonding mechanism section. One major difference between a pure silica (glass) surface and a silicoated surface arises in their chemical structures. A pure silica surface has in it each

Si atom bonded to four oxygen atoms. This results in a rigid framework and gives this surface an embrittled character. The silicoated surface has this same basic structure, however there is an addition of carbon and hydroxyl groups amongst the tetrahedral Si framework. These additions cause a reduction in the silicoated surfaces' rigidity and conversely increase it's elasticity. This increased elasticity purportedly permits a distribution of strains caused by intraoral shearing and thermal expansion forces. This prevents loss of adhesion between the composite resin and the silicoated (siliceous) substrate (Musil and Tiller, 1984; Hansson, 1989).

To date, there has been only one published report on the effects silicoating porcelain has on the composite resin-porcelain bond strength (Stannard and Kanchanatawewat, 1990). The results of that study appear promising. It should be noted, however, that the bonded samples in that study were not thermostressed or hydrated for a prolonged period of time.

Studies on the effects that silicoating has on the bond strength of composite resin bonded to metal have been performed by Laufer *et al.* (1988), Barzilay *et al.* (1988), Naegeli *et al.* (1988), and Caeg *et al* (1990). Laufer *et al.* (1988) compared silicoating to electrolytic etching in their ability to bond four composite resins to five different alloys which were heat treated to simulate the metal preparation for a resin retained fixed partial denture. Tensile bond strengths of samples measured at 30 minutes and at 3 days in 37° C water revealed the silicoated samples to be significantly stronger than the electrolytically etched samples. A similar study was accomplished by Caeg *et al.* (1990). They evaluated a combination of electrolytic etching and silicoating as well as electrolytic etching alone and silicoating alone.. All bonded specimens were thermocycled 1000 times between 5° C and 55° C. The pretreatments were performed on three alloys (Vitallium™/Austenal Co., Ticonium™/Ticonium Co., and N-7™2/Pentron Corp.) using three luting agents (Comspan™/L.D.Caulk, Conclude™/3M, and Retain™/Pentron). When data were pooled for silicoating alone versus electrolytic etching alone, silicoating produced an average 87.9% increase in tensile bond strengths. Mean bond strength for Vitallium™ alloy (28.1 MPa) was significantly greater than those for Ticonium™ (23.8) and N-72™ (20 MPa) alloys. When the data were pooled for all of the pretreatments, the bond strengths for the etched and silicoated samples was not significantly greater than the bond strengths for samples that were etched only. SEM of the fracture sites showed that the silicoated only samples failed totally cohesively in resin, whereas the etched only and etched/silicoated samples failed cohesively and adhesively. The co-workers concluded that a reduction in surface energy of the metal, caused by etching, may account for the lack of adhesion of composite resin to the etched-silicoated samples. The lack of adhesion was illustrated by gaps between the resin veneer and metal for the etched samples when viewed by SEM. Even though the mechanical interlocking bonds were strong, the absence of molecular attraction between resin and metal precluded bond strengths equivalent to those attained by the silicoated only samples. Barzilay *et al.* (1988) compared silicoating to another adhesive bonding system 4-META (4-methacryloxethyl trimellitate anhydride, Super Bond C&B™, Kyoto, Japan) and found that both the silicoating and 4-META retentive systems were superior to conventional mechanical techniques (electrolytical etching, small beads, and large beads) for bonding light cured composite resin to metal.

An extensive assessment on the mechanisms of silicoating bonding was performed by Hero *et al.* (1987). They compared composite resin-metal alloy bond strengths produced by silicoating and conventional bead retention. The silicoated samples were air-abraded with 250 micrometer aluminum oxide. Hydration of samples for 90 days caused a 30% decrease in flexural bond strengths for silicoated samples. The samples bonded using bead retention were not affected by the hydration. To investigate the importance of mechanical bonding, they also silicoated , silane treated, and bonded composite resin to highly polished metal specimens. The Silicoup™ (Kulzer, Inc.) silane could not effectively wet the highly polished specimens. After applying composite resin to these specimens, it was evident that no bonding between the composite resin and substrate occurred. All specimens fractured adhesively during handling. This finding supports statements by Musil and Tiller (1984) that increased surface free energy achieved by air-abrasion is important for increased wetting and adhesive bonding when using the silicoating process. Further analysis of samples by SEM, electron spectroscopy for chemical analysis (ESCA), and microprobe analysis was performed. SEM of air-abraded/silicoated specimens, before bonding, showed silica particles embedded in the surface of the alloy. SEM of fractured dry and hydrated silicoated samples showed a thin uniform composite resin layer remaining on the dry surfaces while spots of composite resin remained on hydrated surfaces. The authors explained that this was possibly due to hydrolysis of the silica-silane bond. ESCA and microprobe analysis showed that carbon could not be detected in the air-abraded/silicoated metal layer. In fact, none of the metal elements present in the alloy were oxidized. From this, the authors concluded that the silane is chemically bonded to the silica particles which are mechanically bonded to the metal.

From the findings presented in the above studies, it can be safely assumed that silicoating, like silane coupling to porcelain, is molecularly a complicated process depending on mechanical and chemical bonding mechanisms.

2. Plasma Cleaning

Plasma cleaning or glow discharge cleaning is a method by which substrate surfaces can be cleaned at the molecular level. A cleaner surface has a greater surface free energy which enables it (the adherend) to become better wetted by an adhesive (Dahlquist, 1969). This increased wetting can increase chemical and mechanical bonding between adhesive and adherend by promoting intimate contact between the adhesive and adherend (Sarkar, 1984). Plasma cleaning has been used to clean glass. It is also useful in making hydrophobic surfaces of polymers and other materials wettable by aqueous reagents (Hollahan and Bell, 1974).

The process of plasma cleaning rids the substrate surface of microscopic debris through vaporization of the debris. This is effected by exposing the substrates to the plasma of a glow discharge which supplies the energy needed to break bonds between contaminant molecules as well as between the contaminant and the substrate (Brown, 1970). Plasmas are produced when an electrical potential is applied, across a gap in a vacuum, to a gas. If the applied voltage is high enough, this results in the formation of the plasma by the ionization of excited gas molecules (Boenig, 1982). These ionized gases can effect the removal of impurities and produce other beneficial changes to the substrate surfaces in many ways. Brown (1970) lists the following mechanisms by which plasma cleaning can accomplish this:

1. Straightforward heating due to impingement of charged particles and their recombination.
2. Impurity desorption through electron bombardment
3. Impurity desorption resulting from low-energy ion or neutral-particle bombardment.
4. Volatilization of organic residues by chemical reaction with dissociated oxygen

5. Modifications of glass surfaces through the addition of oxygen

Mechanism (5) is particularly important for substrates such as porcelain which have high silica content, where it appears to aid in subsequent adhesion by the formation of oxide bridges on the substrate surface (Brown, 1970). Plasma cleaning of porcelain substrates to promote better adhesion and consequently better composite resin-porcelain bonding, has not been investigated prior to this study.

3. Radio Frequency Silica Sputter Coating

Sputter coating silica is essentially a purer form of silicoating. Sputter coating is the nonpyrolitic deposition of silica onto a given substrate (Boenig, 1982). Sputter coating is a phenomenon in which high velocity inert gas ions are produced which strike a target electrode causing ejection of surface atoms from the target. These atoms then become deposited onto a given substrate (Hinson, 1982). To promote adhesion of the target atoms to the substrate, the substrate is sputter-cleaned by ion bombardment before sputter deposition (Wehner and Anderson, 1970; Maissel, 1970).

Sputtering was initially reported by W.R. Grove in 1852, who observed the deposition of metal from the cathode of a glow discharge onto the tubes' glass walls (Wehner and Anderson, 1970; Stuart, 1983). In 1962, according to Stuart (1983), Anderson was the first to show how radio frequency could be applied to the outside of a sputtering discharge tube to effect the cleaning of the inside walls of the tube. He suggested that this technique could be used for the deposition of insulating films, which was subsequently developed by Davidse and Maissel (Maissel, 1970).

There are many uses for thin films, which include coatings for resistance networks, corrosion resistance, integrated circuits, and electrical insulation (Stuart, 1983). Sputtering is an atom by atom deposition process which results in nonporous films with surfaces closely reproducing the surface of the substrate (Wehner and Anderson, 1970). The nonporous nature of sputtered silica makes this an excellent electrical insulating coating (Stuart, 1983). The potential outstanding sputtered film-substrate adhesion coupled with the ability of the sputtered film to obtain strengths up to 200 times that of the corresponding bulk material (Campbell, 1970) makes sputtering a potentially viable technique for dental bonding applications. Norling and Bugg (1980) and Norling *et al.* (1988) investigated the effects that silica sputter deposition had on composite resin-stainless steel crown bond strengths. Norling and Bugg (1980) found that the bond achieved by bonding composite resin to silica coated, silane-treated stainless steel crowns (15.9 MPa) was higher than those resulting from composite resin bonded to diamond stone roughened or aluminum oxide coated, silane treated stainless steel crowns. Norling *et al.* (1988) in a similarly designed study compared silica sputter coating to silicoating and 4-META (Cover Up™, Parkell) as stainless steel crown surface pretreatments. In addition, they investigated the effects that thermocycling would have on resultant composite resin-stainless steel crown shear bond strengths, all stainless steel crown surfaces to be bonded were wet ground through 240 grit silicon carbide paper and air-abraded with 50 micrometer aluminum oxide. They were then treated by silicoating, sputter coating, or 4-META application. Silicoating was accomplished per manufacturer's directions. The sputter group was coated with silica for 3.5 minutes at 500 Watts RF power in 95% argon/5 oxygen. The silicoated and sputter coated samples were additionally treated with silane, which promotes coupling of the composite resin to the respective coated surfaces. Shear bond tests showed that non-thermocycled silicoated

(16.5 MPa) and sputter coated (15.9 MPa) stainless steel crowns were significantly stronger than the 4-META stainless steel crowns (11.4 MPa). However, thermocycled silicoated samples (15.1 MPa) were significantly stronger than both 4-META (9.7 MPa) and sputter coated (11.1 MPa) stainless steel crowns. Thermocycling significantly degraded the silica sputter coated stainless steel crowns.

In a recent study, Norris *et al.* (1990) compared shear bond strengths between mechanically retained, silicoated, and sputter coated orthodontic brackets cemented with three different cements. Across all cements tested, the silicoated and sputter coated samples produced the statistically strongest mean shear bond strengths.

The above three studies are the only ones reported in the dental literature to have bonded composite resin to silica sputter coated substrates. There have not been previous studies on bonding composite resin to silica sputter coated dental porcelain.

III. RESEARCH OBJECTIVES

The objectives of this study were to compare the effects that six dental porcelain surface pretreatments, two types of silanes, and thermocyling had on the shear bond strength of composite resin bonded to dental porcelain. Three ***null hypotheses*** were formulated from these objectives as follows:

1. Porcelain surfaces pretreated by glazing, air-abrasion, air-abrasion/plasma cleaning, air-abrasion/sputter coating with pure silica, air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating, followed by application of a silane coupling agent, will produce composite resin-dental porcelain mean shear bond strengths that are not significantly different.

2. The type of silane used will not effect the composite resin-dental porcelain shear bond strength.

3. Thermocycling will not have an effect on the composite resin-dental porcelain shear bond strength.

IV. MATERIALS AND METHODS

A. Experimental Plan

This study was conducted in three parts; a pilot, a preliminary, and a principal study. The purposes of the pilot study were to determine overall project feasibility, refine experimental protocol, and determine the sample size to be used in the principal study . The pilot study was especially apropos since sputter coating and plasma cleaning porcelain has not been reported to date. Silicoating porcelain was not reported in the literature until after the data collection phase of the principal study had begun (Stannard and Kanchanatawewat, 1990). Dentin porcelain specimens were fired, surface pretreated, silane treated, and bonded to composite resin. They were then subjected to shear testing for evaluation of the resin-porcelain bond.

The preliminary study was needed to determine the optimal hydrofluoric acid etch time and concentration which was used in the principal study. This approach was deemed necessary to increase the internal validity of the principal study and was performed as recommended by Calamia *et al.* (1985). The optimal acid etch times and concentration reported for the porcelain used in this study (Vita VMK 68™, Vita Zahnfabrik Co.) had not been reported previously. The principal study compared six different porcelain surface pretreatments, the use of two different types of silane coupling agents, and the effect that thermocycling had on composite resin-porcelain bond strengths. To eliminate any confusion, in the remaining text, the application of silane is referred to as a porcelain surface *treatment.* Any porcelain surface treatment performed in preparation for silane application will be referred to as a porcelain surface *pretreatment.* In addition to shear bond strength evaluation, a steremicroscopic evaluation was performed to determine the mode and site of fracture. Specimens representative of the different failure modes were further examined under SEM. This experimental design, in general, is consistent with previous studies by Bround (1982), Stangel *et al.* (1987), Tjan and Nemetz (1988), Diaz-Arnold and Aquilino, (1989), Pratt *et al.* (1989), and Beck *et al.* (1990). The methodology used for porcelain sample fabrication, silane application, composite bonding, and shear testing, unless otherwise stated, was consistent throughout the pilot, preliminary, and principal studies. The methodology is reported in the principal study section (Subheading D).

B. Pilot Study

For the pilot study, 20 porcelain coupons were fabricated and air-abraded. The coupons were divided randomly into five groups of four coupons each and then surface pretreated by either silicoating, sputter coating, plasma cleaning, or hydrofluoric acid etching. The fifth group was not pretreated, but left as air-abraded to control for any additional pretreatment effect from silicoating,sputter coating, plasma cleaning and hydrofluoric acid etching. All of the aforementioned pretreatments were performed as described for the principal study. One difference to be noted is that instead of using prepared hydrofluoric acid solutions, as in the preliminary and principal studies, a proprietary 9.5% hydrofluoric acid solution (Ceram Etch™, Gresco Products Inc., Stafford, TX.) was used. Immediately following surface pretreatments, the respective groups were treated with Silicoup™ silane, bonded with composite resin (Porcelite™ Dual Cure, Kerr Co.), hydrated for one day, and shear bond tested in a universal testing machine (Instron™, Instron Corp., Canton, Mass. The results of the shear bond testing are listed in the Appendix, Table I. From these results it was concluded that this was a feasible study, the materials and methods were appropriate, and the results would be meaningful. In addition, from the reported shear bond strengths, an appropriate sample size for the principal study was calculated from a power analysis.

C. Preliminary Study

1. Introduction

As recommended by Calamia *et al.* (1985), the optimal hydrofluoric acid etching times and concentrations were determined for Vita VMK 68™porcelain so that valid bond strengths resultant from this mode of porcelain surface pretreatment would be reported.

2. Sample Selection

The samples compared in the preliminary study were porcelain coupons which were air-abraded with 50 micrometer aluminum oxide, acid etched with hydrofluoric acid, silane treated, and bonded to composite resin. The samples varied by acid etch concentrations and times used to pretreat the porcelain surface. The etch times evaluated were 1 min, 2.5 min, and 5 min. using hydrofluoric acid concentrations of 5%, 10%, and 15%. These etch times and acid concentrations were selected based on previous findings as described by Calamia *et al.*, (1985). Power analysis based on similar previous studies (Stangel *et al.*, 1987 and Bailey, 1989) dictated a sample size of seven. Therefore, sixty-three Vita VMK 68™porcelain coupons were randomly divided into nine groups of seven samples.

3. Preparation of Hydrofluoric Acid Solutions

A 48% solution of hydrofluoric acid (Monsanto co.,) was diluted with deionized water to make up 5%, 10%, and 15% solutions of hydrofluoric acid as follows:

5% SOLUTION

Dilution ratio equation

$48x = 0.05\ (50g)$

$48x = 2.5g$

$x = 5.21g;\ y = 44.8g$

Hence, 5.21g HF + 44.8g H_20 = 50g of a 5% HF acid solution

10% SOLUTION

Dilution ratio equation

$48x = 0.10\ (50g)$

$48x = 5.0g$

$x = 10.42g;\ y = 39.58g$

Hence, 10.42g HF + 39.58g H_20 = 50g of a 10% HF acid solution

15% SOLUTION

Dilution ratio equation

$48x = 0.15\ (50g)$

$48x = 7.5g$

$x = 15.63g;\ y = 34.38$

Hence, 15.63g HF + 34.38g H_20 = 50g of a 15% HF acid solution

4. Hydrofluoric Acid Etching Procedures

After air-abrasion and cleaning, each specimen was acid etched using the etching times and hydrofluoric acid concentrations described in the sample selection section. The groupings are illustrated as follows:

		Hydrofluoric acid concentration		
		5%	10%	15%
	1 min	7	7	7
Etch time	2.5 min	7	7	7
	5 min	7	7	7

The specimens were etched by group, one at a time. A stopwatch was used during the etching procedure to ensure time of etch. After etching, the specimen was immediately rinsed with a copious amount of deionized water for fifteen seconds followed by rinsing with acetone for three seconds. After rinsing, the specimen was air dried with oil free compressed air. Immediately after drying, each respective specimen was treated with silane (Silicoup™), bonded with composite resin (Porcelite™ dual cure, Kerr), hydrated at room temperature for one day, and shear bond tested in a universal testing machine (Instron™).

5. Statistical Analysis

A two factor 3 X 3 (HF acid concentrations X etch times) experimental design was selected for the preliminary study. The shear bond strength data were analyzed by a two-way analysis of variance (ANOVA): HF acid concentrations (5%, 10%, and 15%)

X etch times (1 min, 2.5 min, and 5 min). A Newman-Keuls multiple comparison test was made on all group means to identify significant differences.

6. Results

Shear bond strength raw data are recorded in the Appendix, Table II. The raw data, as recorded by the Instron™ machine in Newtons, were used for all statistical analyses. This was deemed appropriate because the bonded area at the composite resin-porcelain interface was considered the same for all specimens (refer to Materials and Methods, Specimen Preparation for Bonding). Hence, the bonded surface area were also the same for all specimens.

The results of the two-way ANOVA (Table 1) revealed that time was statistically significant ($F_{2,54} = 5.546$, $P = .0064$) while concentration was not ($F_{2,54} = 2.653$, $P = 0.0791$). The Newman-Keuls post-hoc analysis for time indicated that a 1-minute etch time yielded the weakest bonds ($P < 0.05$), while for concentrations of 5 and 10%, etch times of 2.5 and 5 minutes yielded bond strengths which were not statistically different ($p > 0.05$). Consequently, the time-concentration was selected for the principal study which produced the highest mean bond strength, 2.5 minutes and 10%. The means, standard deviations, and significant differences between means can be found in Table 2.

Table 1. Two Way Analysis of Variance Summary
(Preliminary Study)

Source	df	SS	MSS	F	P
Between Subjects	62	255777.98			
HF[1] Concentration (C)	2	17819.94	8909.97	2.65	0.0791
HF[1] Etch Time (T)	2	37258.13	18629.07	5.55	0.0064
C x T	4	19311.87	4827.97	1.44	0.2326
Subjects within Groups	54	181388.03	3359.04		

[1] Hydrofluoric acid

Table 2. Summary Results of Newman-Keuls Multiple Comparison Test of Hydrofluoric Acid Etch Time X Etchant Concentration Combinations (Preliminary Study)

			SD)	
[HF][1]	ETCH TIME[2]	n	NEWTONS	MPa
5%	1 min	7	206.3 (75.6)	11.40 (4.18)
5%	2.5 min	7	*255.4 (37.4)	14.11 (2.07)
5%	5 min	7	*243.6 (64.9)	13.46 (3.58)
10%	1 min	7	208.8 (24.4)	11.53 (1.35)
10%	2.5 min	7	*280.6 (74.7)	15.50 (4.13)
10%	5 min	7	*258.1 (49.4)	14.26 (2.73)
15%	1 min	7	*176.8 (38.9)	9.77 (2.15)
15%	2.5 min	7	*188.7 (29.7)	10.42 (1.64)
15%	5 min	7	260.3 (88.9)	14.38 (4.91)

[1] Hydrofluoric acid concentration

[2] Hydrofluoric acid etch time

* No significant difference between indicated means within each group ($p < 0.05$).

D. Principal Study

1. Sample Selection

The samples compared in the principal study were porcelain coupons bonded to composite resin. These samples varied by surface pretreatments, silane treatment, and thermocycling. Two hundred and forty Vita VMK 68™ porcelain coupons were randomly divided into 6 groups of 40 coupons each (Fig 3). The first group remained as glazed specimens. Any surface pretreatment effect on this group would result from glazing. The glazed samples were included in the study primarily to control for mechanical bonding. The remaining groups were air-abraded using 50 μm aluminum oxide. All but the last of these groups received surface pretreatment by either plasma cleaning, sputter coating with pure silica, silicoating, or hydrofluoric acid etching. The last group remained as air-abraded samples. Specimens in each of these 6 groups were then randomly divided into groups of 20. One half of the specimens (20) received silane treatment with Scotchprime™ (3M Dental Products Division, St Paul, Minnesota) and the other half (20) received silane treatment with Silicoup™. All of the samples then had composite luting resin (Porcelite™ Dual Cure, Kerr) bonded to them. Next, specimens in each group were randomly subdivided into groups of 10 samples that were hydrated and 10 samples that were hydrated and then thermocycled. The end result compared twenty-four groups with 10 samples in each group.

Figure 3. Principal Study Experimental Flowchart

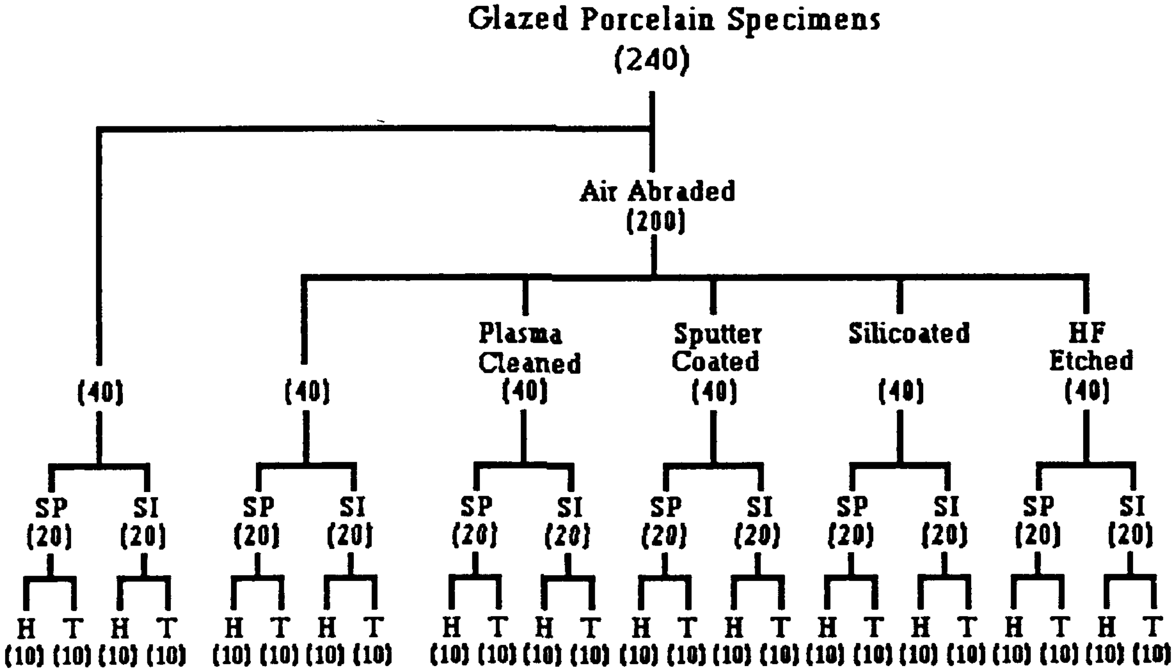
Key: HF = Hydrofluoric Acid

SP = Silicoup silane

SI = Scotchprime silane

H = Storage in 37° deionized water for 71 days

T = Storage in 37° deionized water for 70 days followed by 1000 thermocycles

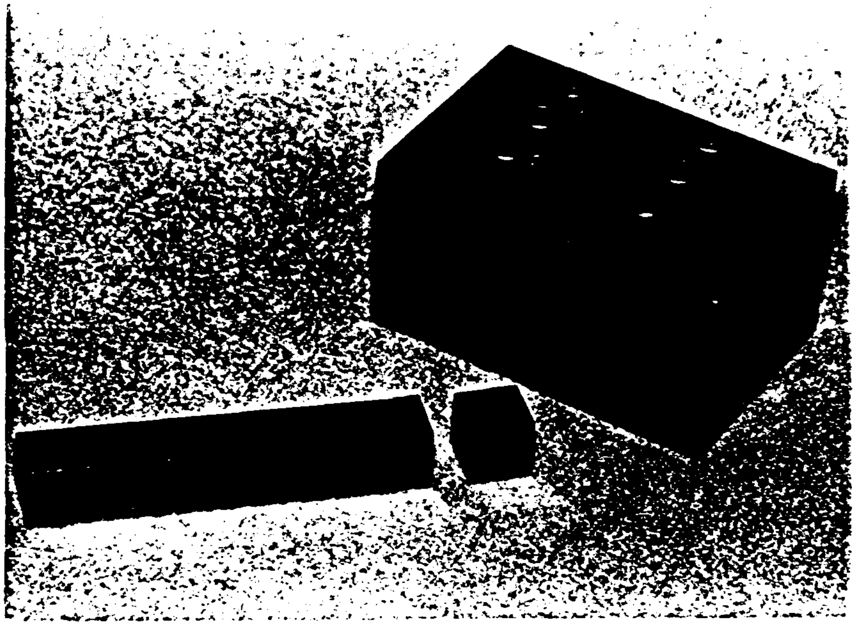

Glazed Porcelain Specimens
(240)
Air Abraded
(200)
(40)
(40)
Plasma Cleaned
(40)
Sputter Coated
(40)
Silicoated
(40)
HF Etched
(40)
SP
(20)
SI
(20)
H
(10)
T
(10)

2. Fabrication of Porcelain Coupons

Standardized porcelain coupons were fabricated of uniform size and geometry. Commercial dental porcelain (Vita VMK 68™ dentin porcelain, shade A-2) and a sintering aid were mixed by weight, two parts porcelain to one part sintering aid. The sintering aid itself consisted of a mixture of 10 percent poly (vinyl acetate-ethylene) copolymer and 90 percent paraffin diluted to 10 percent in xylene. Over a period of three days, the xylene was allowed to evaporate under a fume hood. The coated porcelain was then mixed and repowdered.

Porcelain coupon samples were formed by compacting the repowdered porcelain in a special four piece metal die constructed for this purpose (Plate 1). One gram of porcelain was weighed on an electronic scale (Sartorius Electronic Scale, Gottengen, West Germany) and placed in the die. The plunger was then loaded to 30,000 psi in a hydraulic press (Specimen Mount Press, Buehler LTD., Evanston, IL). This compaction resulted in uniformly sized coupons with sufficient pre-fired "green" strength to withstand transfer to a porcelain oven for firing (Nowlin *et al.*, 1981; Brownd, 1982). The pre-fired compacts were placed directly on the porcelain oven's ceramic table which had been lightly dusted with 50 micrometer aluminum oxide particles to prevent sticking. The compacts were placed in an opened wax burnout oven (Jelenko Model TFA, Jelrus Technical Products Corp., New Hyde Park, NY), set at 1200°F, for 10 minutes under a vacuum hood to allow the sintering aid to burn off. The ceramic table with compacts were then transferred directly to a newly calibrated automatic porcelain furnace (Penwalt Jelenko Auto Lt II VPF, Jelrus Technical Products Corp., New Hyde Park, HY) and heated for 5 minutes at 1200°F, in a closed muffle. The coupons were subjected to three successive vacuum firings to duplicate the porcelain building technique. The first two

Plate 1. Coupon Dies



firings were vaccum firings with a two minute entry time. The low temperature setting was 1200° F. The compacts were fired to 1760° F with a 32°/min rate of climb. During the third firing, the coupons were air fired with a two minute hold at 1760°F to simulate a natural glaze. Once cooled, the porcelain coupons were inspected for surface irregularities or voids. Post-firing coupon dimensions were approximately 11mm X 11mm X 3mm.

3. Substrate Surface Preparation

Air-abrasion was used to simulate divesting procedures. The air-abrasion was accomplished using 50 micrometer aluminum oxide under 40 psi air pressure. The coupon surface air-abraded was the glazed side which was facing up during oven firing. Uniform air-abrasion was performed on each coupon by moving the air abrading tip in a back and forth sweeping motion for 10 seconds, after which the coupon was rotated ninty degrees and air abraded again for 90 seconds. This technique was used for a total of three rotations or put in other terms, for a total of four directions for 10 seconds each. The air-abrader tip was held a constant two inches from the specimen to ensure even and uniform air-abrasion. The porcelain coupons were then ultrasonically cleaned for 30 minutes in an alkaline detergent solution (Alconox, Alconox Inc., New York, NY), followed by copious rinsing with deionized water once and acetone once. The coupons were then dried with oil-free compressed air.

4. Substrate Surface Pretreatments

Immediately prior to the application of the silane coupling agent, 160 of the air-abraded and cleaned porcelain coupons were surface pretreated by either sputter coating with pure silica, plasma cleaning, silicoating, or hydrofluoric acid etching (Fig 3) as follows:

Sputter coating with pure silica - The porcelain coupons were placed in a radio frequency (RF) sputter coating apparatus (Vaccum Technology Associates Inc., Boulder, Colorado) (Plate 2) and sputter etched at 250 RF voltage with a plate current of 75 mA in a 95% argon/ 5% Oxygen atmosphere. Silica sputter deposition then occurred for 3.5 minutes at 500 watts of power, at 1 micrometer atmospheric pressure, and 55 voltage at 18.85 loading and 2.6 turning. Silane was applied to the sputter coated surface within three minutes of the porcelain coupon's removal from the sputtering apparatus.

Plasma cleaning - The porcelain specimens were placed in the plasma cleaning apparatus (Plasma Cleaner, Harrick Scientific Corp., Ossining, NY) on a glass plate in a vacuum tube (Plate 3A). A vacuum was achieved and the specimens were plasma cleaned for 20 minutes. The vacuum was slowly released over a 2-minute period and the silane was applied to the freshly plasma cleaned surface within 90 seconds of the porcelain's removal from the vacuum tube.

Silicoating - According to the manufacturer's directions (Kulzer Product Information), in preparation for the silicoating process, the porcelain coupons in this group were placed in a jar and cleaned with ethyl acetate (Siliclean™, Kulzer Inc., Laguna Hills Calif.) for three minutes. Each porcelain coupon was placed in the Silicoater® machine (Plate 3B) and, as recommended by the manufacturer for metal pretreatment,

Plate 2. Radio Frequency Sputtering Apparatus

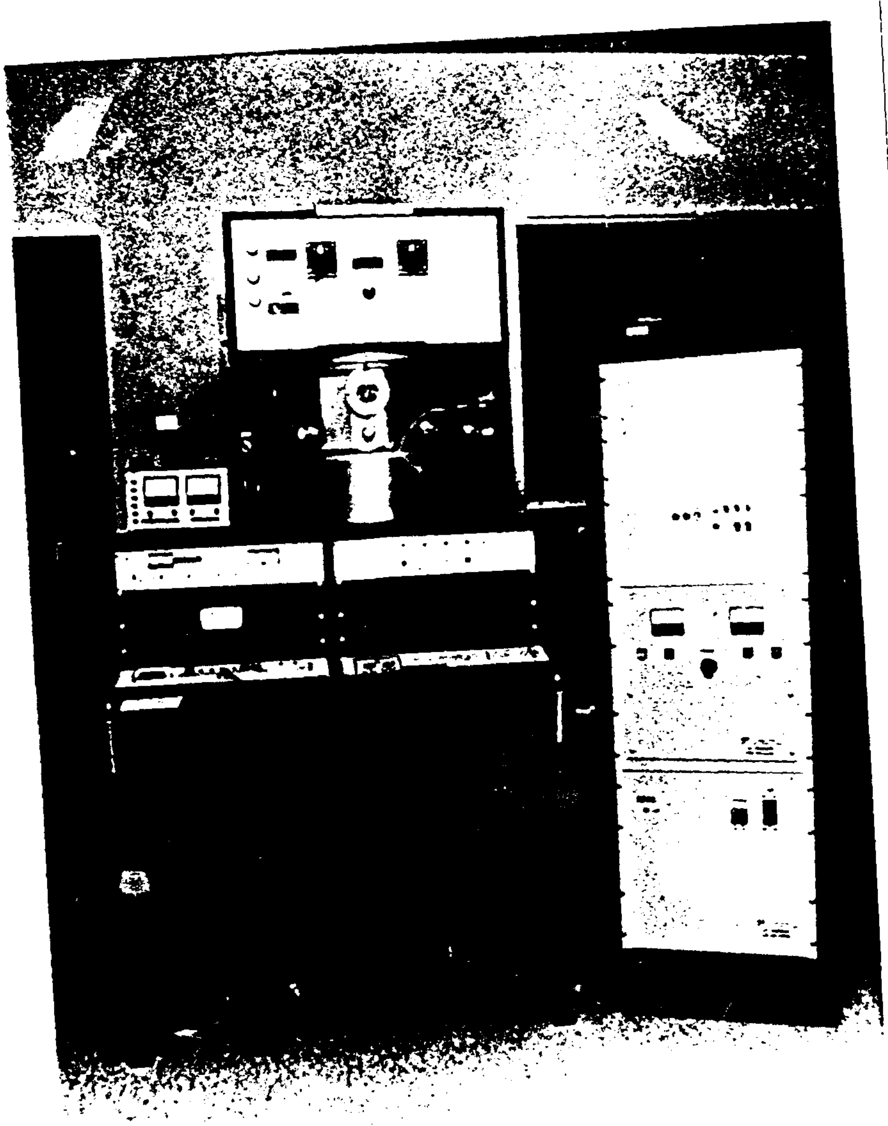
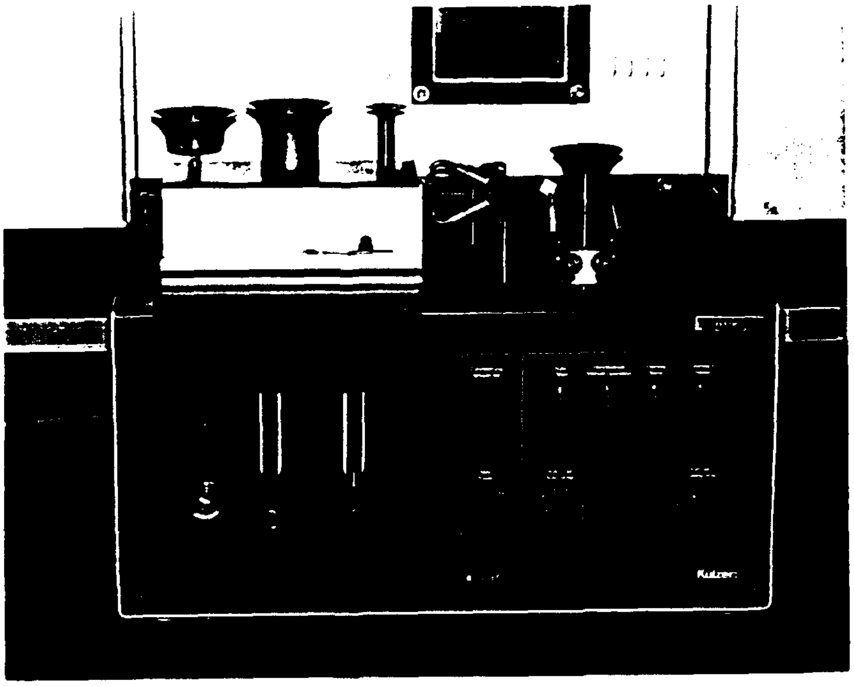


Plate 3. Plasma Cleaner and Silicoater

A. Plasma Cleaner

B. Silicoater


PLASMA CLEANER
PDC 3XG
OFF
LO
MED
HI
RF
LEVEL
ON
RF
HARRICK


Kulzer

repeatedly passed through the oxidizing region of a propane/tetraethoxysilane/oxygen flame for 5 minutes to pyrolytically deposit Siliflam™ (Kulzer, Inc.) silica onto the air-abraded porcelain surface. To complete the automatic cycle set on the machine, the porcelain coupon was then cooled for 3 minutes. Silane was promptly applied to the silicoated surface within 3 minutes of its removal from the Silicoater®.

Hydrofluoric acid etching - Porcelain coupons in this group were acid etched with a 10% solution of hydrofluoric acid for 2.5 minutes. Immediately following etching, each coupon was thoroughly rinsed for 15 seconds with deionized water followed by rinsing for 3 seconds with acetone. The porcelain specimens were then dried with oil free compressed air. A stopwatch was used during the etching and rinsing procedures to ensure standardized etching and rinsing times over all etched samples. The 2.5 minute etch time and the 10% hydrofluoric acid concentration used were determined from results of the preliminary study previously discussed.

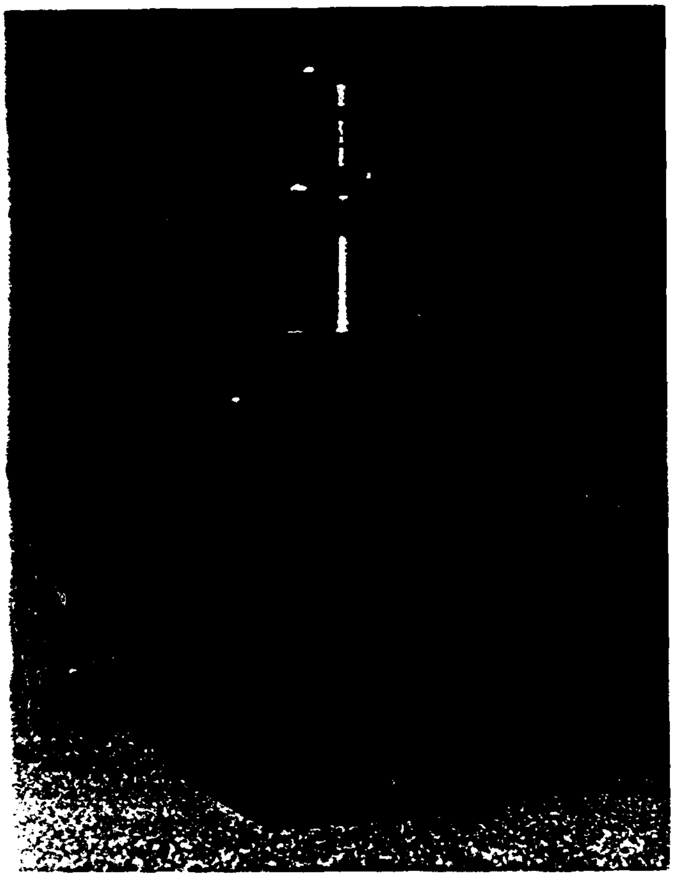
5. Specimen Preparation for Bonding

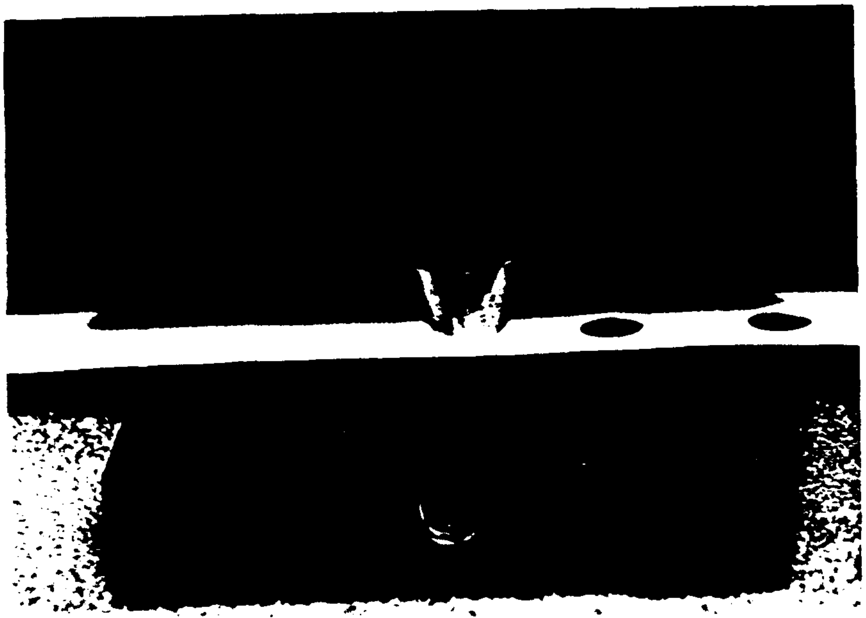
Immediately following porcelain surface pretreatment, a 10 mm square piece of Teflon™ tape (Type VF-81, FEP/VINYL, Chemplast Inc., 150 Dey Road, Wayne, New Jersey) with a centrally located 4.8 mm hole, was centered and attached to the 11 mm square coupons. The tape is a .008" vinyl film with a protective overlay of .001" Teflon™ film. The purpose of the standardized hole was to standardize bonding surface area by delimiting the area of composite resin application (Ferrando *et al.*, 1983; Horsley, 1989). The 4.8 mm holes were hand punched by a specially designed punch apparatus fabricated by the USAF Dental Investigation Service, Brooks Air Force Base (Plates 4A and 4B). The punched Teflon™ tape squares were placed on the coupons, adhesive side

Plate 4. Punching Standardized Holes in Teflon™ Tape

A. Customized Punch Apparatus

B. Punching Holes in Teflon™ Tape





down (Plate 5A).

Next, a translucent Teflon™ tube (Chemplast Inc., 150 Dey Road, Wayne, New Jersey) having a 6mm outside diameter and a 4.85 mm inside diameter was centered over the hole in the Teflon™ tape under a stereomicroscope (EMT-Widefield Stereo Microscope, Meiji-Labax Co., Ltd., Tokyo, Japan). The Teflon™ tube was then luted to the Teflon™ tape with sticky wax (Sticky Wax, J.F. Jelenko & Co., Armonk, NY) (Plate 5B).

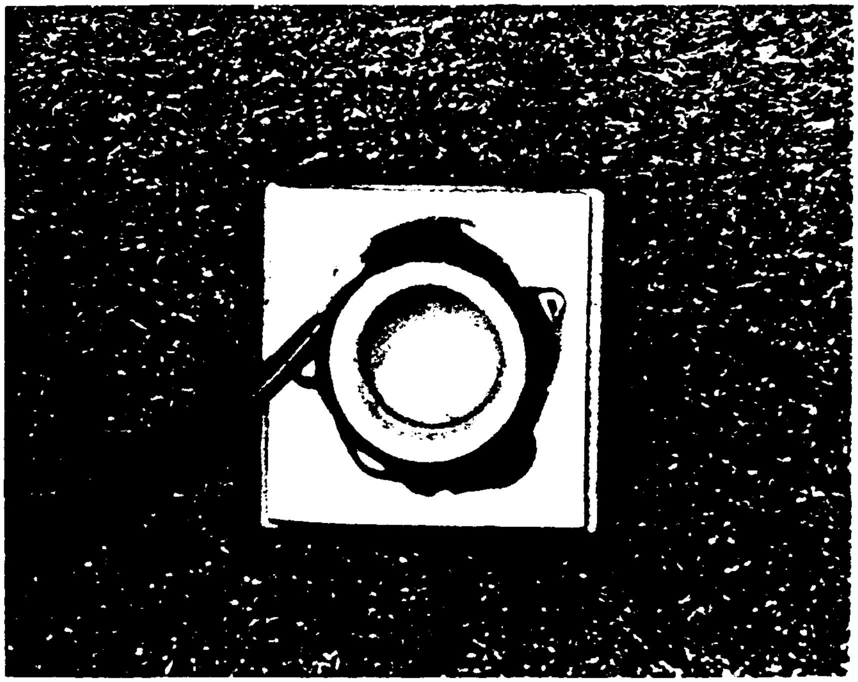
6. Resin and Silane Coupling Agents

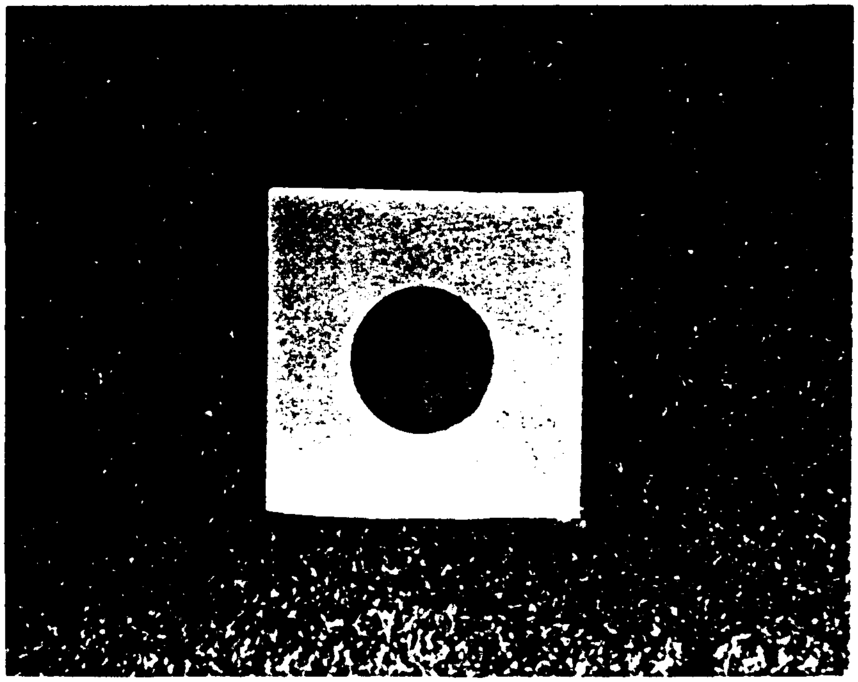
A commercial composite luting resin (Porcelite™ Dual Cure) and two commercial silane coupling agents (Silicoup™ and Scotchprime™) were used in this study. The Scotchprime™ silane coupler, which comes packaged in the pre-hydrolized form, was used according to the manufacturer's directions. The Scotchprime™ silane was applied straight from the bottle to the porcelain surface in three succesive thin layers. According manufacturer's directions, the Silicoup™ silane was prepared by mixing solutions A and B, as supplied in vials by the manufacturer. This allows for the hydrolysis reaction necessary for it to bond with porcelain. This freshly mixed silane was then applied to the porcelain surface in one thin layer.

Plate 5. Delimiting Area of Bonding

A. Application of Teflon™ Tape to Substrate Surface

B. Teflon™ Tube Sticky Waxed t Place





7. Bonding Procedures

A 3/0 sable brush (Belle de St. Claire, Chatsworth, CA) was used to apply the silane coupler through the Teflon™ tubes (Plate 6A). Once applied, the silane was allowed to air dry for at least 2 minutes. The composite resin luting agent was then mixed equal parts base to catalyst and loaded into a composite syringe (Mark III, Centix Corp., Cleavland, Ohio). The composite resin was injected near the coupon surface from one side of the exposed porcelain surface to the other in order to minimize air entrapment (Plate 6B). In order to standardize the amount of composite resin injected in each Teflon™ tube, the Teflon™ tubes were one third filled. This allowed for a composite resin thickness of approximately 2mm.

Light activation of the composite resin was accomplished using a hand held light (Marathon II light No 3940, Den Mat Corp., Monrovia, Ca.). The light was positioned directly over the open end of the Teflon™ tube and activated for 60 seconds (Plate 7A). Since dual cure resin was used, the specimens were also left to bench set for a minimum of 15 minutes to ensure chemical polymerization was complete. Finally, the Teflon™ tube and tape was removed from the specimen and the specimens were light activated a second time from all four sides for 20 seconds each (Plate 7B). This was done, as an added measure, to ensure completeness of light polymerization at the composite resin-porcelain interface (Diaz-Arnold and Aquilino, 1989; Diaz-Arnold *et al.*, 1989).

Plate 6. Bonding Composite Resin to Porcelain Substrate

A. Silane Coupling Agent Applied to Substrate Surface

B. Composite Resin Injected onto Silanated Substrate Surface

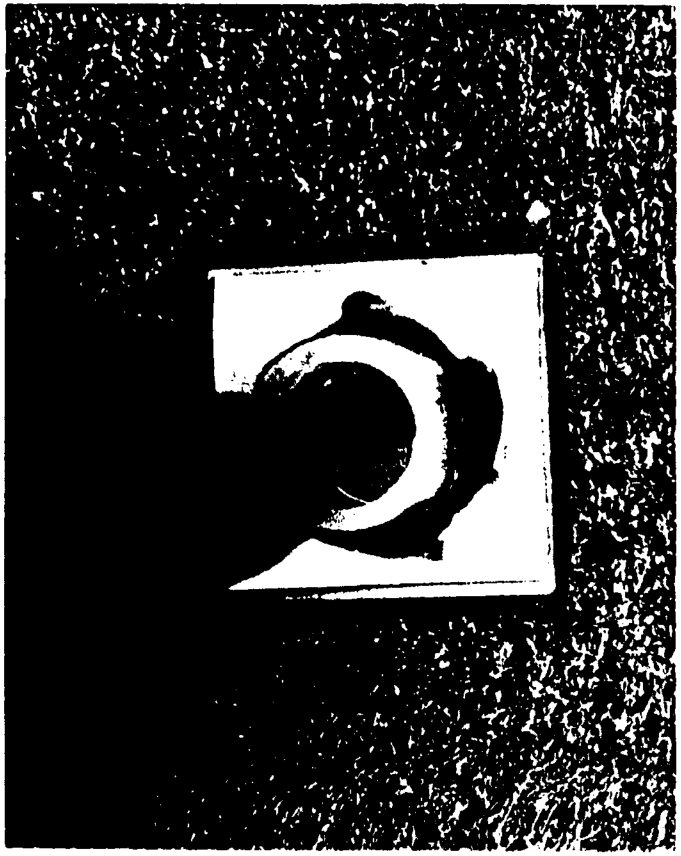
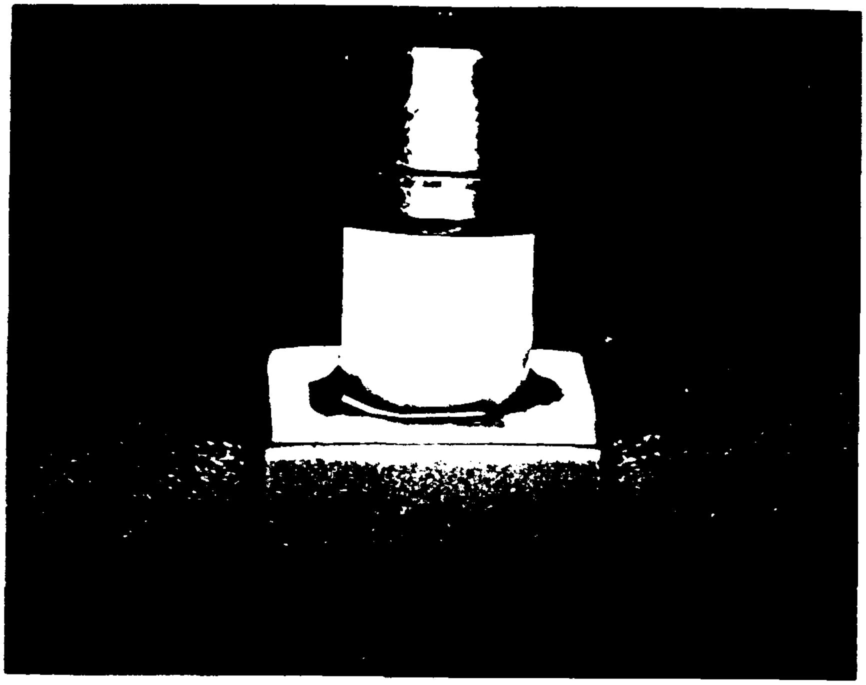
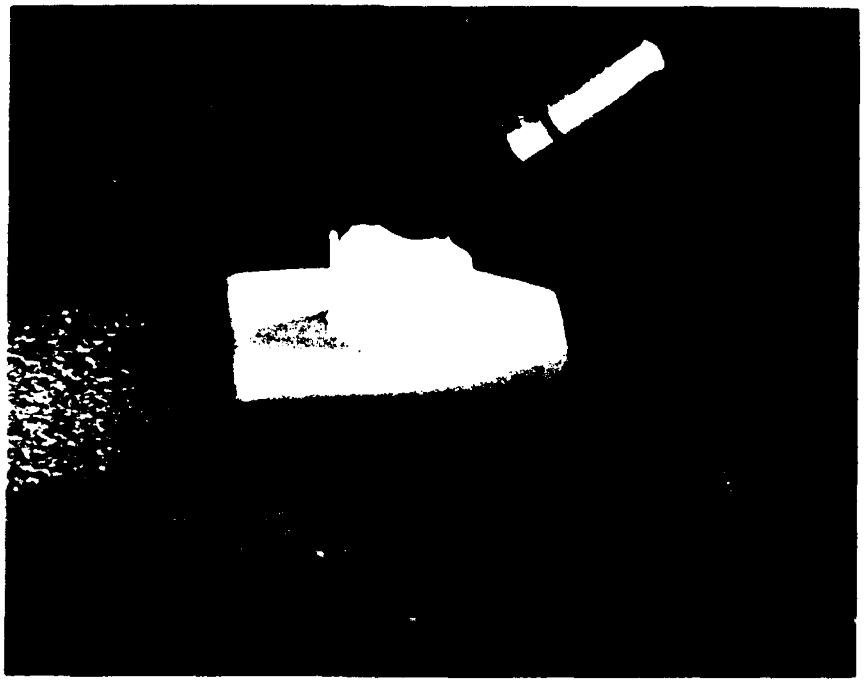


Plate 7. Photoactivating Composite Resin with White Light

A. Photoactivation Through Open End of Teflon™ Tube

B. Photoactivation After Removal of Teflon™ Tube





8. Principal Study Aging of Bonded Specimens

Half of the bonded specimens from each respective subgroup (Fig 1) were stored in 37° C deionized water for 71 days while the other half was stored in 37° C deionized water for 70 days followed by thermocycling for one thousand cycles between 6° C and 60° C using 30 second dwell times (Crim *et al.*, 1985; Thomas *et al.*, 1987; Norling *et al.*, 1988). The water temperature was calibrated and maintained at ± 2° C in each of the baths by means of a thermostat. A custom made thermocycling apparatus built for the University of Texas Health Science Center, San Antonio, was used for this purpose (Plate 8).

9. Shear Bond Testing

Shear bond strengths of all specimens were measured using a universal testing machine (Instron™). A 5 KN load cell was used with a full scale set at 500 N. Each specimen was placed in a specially machined test fixture made to hold the sized specimens used in this study (Plate 9A).

The shear stresses were applied by engaging each specimen at and parallel to the porcelain-resin interface with a monobeveled blade at a crosshead speed of 1 mm/min (Plate 9B). The resulting shear force necessary to fracture the specimens was recorded in newtons (N) by the Instron™ using a chart paper speed of 50 mm/min. and then converted to megapascals (MPa).

Plate 8. Thermocycling Apparatus

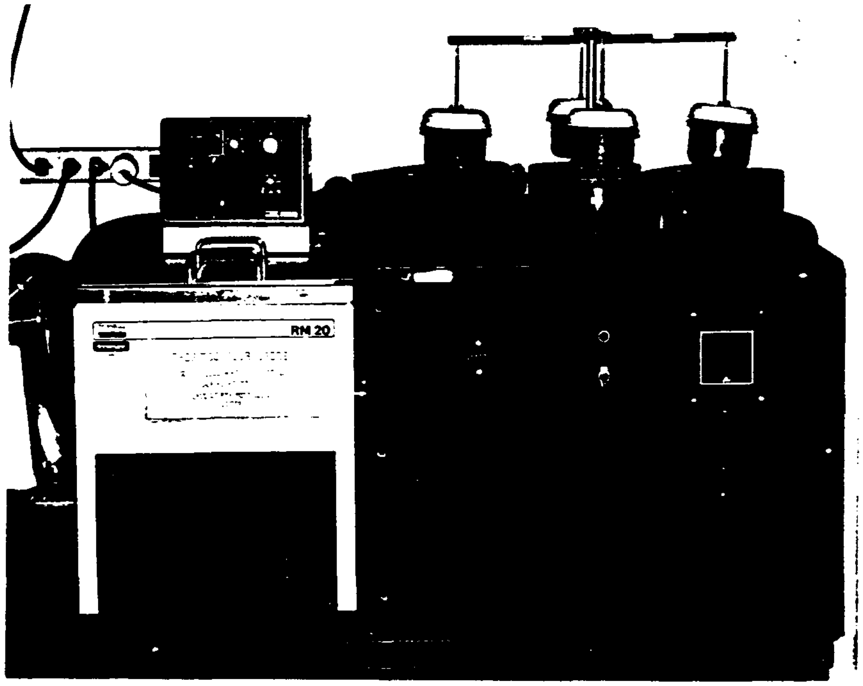
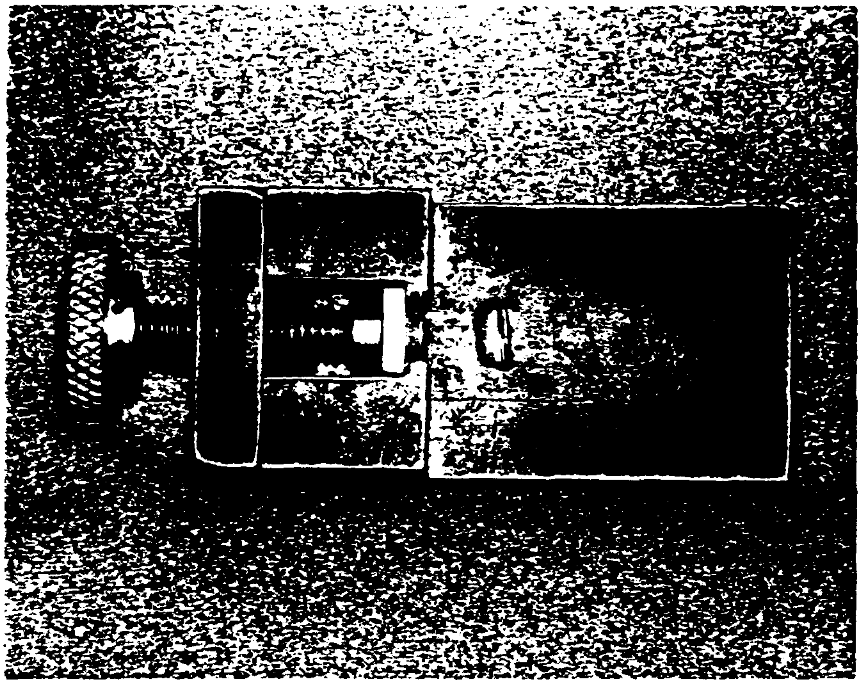
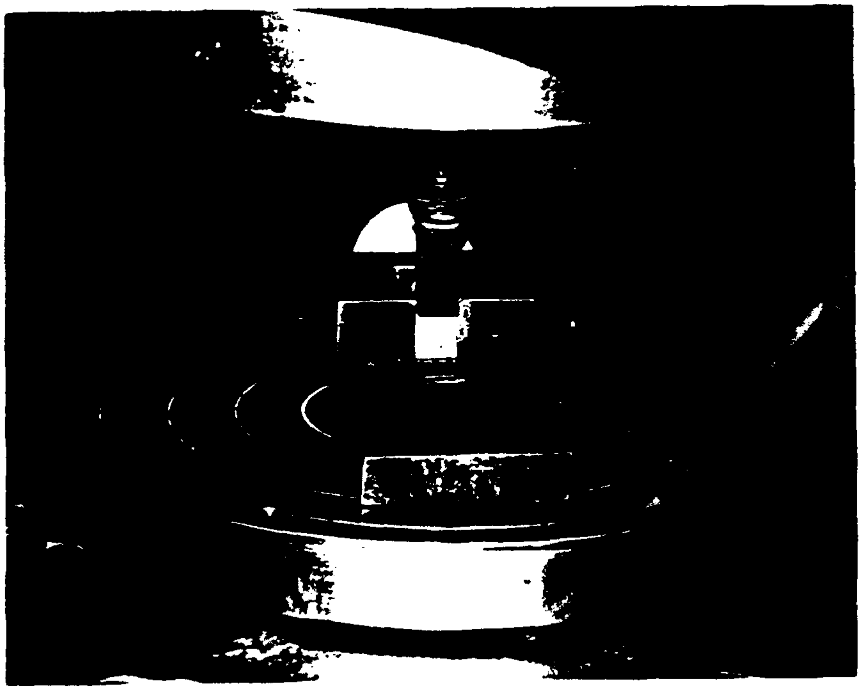

RM 20

Plate 9. Shear Testing of Bonded Specimens

A. Metal Fixture Used to Hold Bonded Specimens During Shear Testing

B. Shear Force Applied to Bonded Specimen in Instron™ Machine





10. Fracture Site Examination

Each of the specimens shear bond tested in the principal study was examined under x30 magnification using a stereomicroscope to determine the mode of failure as occurring adhesively (interfacially), cohesively in porcelain, or cohesively in resin. For specimens that failed in more than one mode (mixed fractures), the failure was recorded by ranking each component mode of failure according to percentage of fracture attributed to each respective component mode of failure. For example, a specimen could fail 75% cohesively in porcelain, 20% cohesively in resin, and 5% adhesively at the interface. The mode of failure was ranked as follow: 1 = Cohesive Porcelain, 2 = Cohesive Resin, and 3 = Adhesive.

Representative specimens of different failure modes were selected, examined, and photographed under SEM after being desiccated and sputter coated with gold-palladium. A Phillips Model 500 Scanning Electron Microscope was used for this purpose.

11. Statistical Analysis

a. Introduction

A three factor (6 X 2 X 2, porcelain surface pretreatment X silane X aging protocol) experimental design was selected for the principal study. The shear bond strength data was analyzed by a three-way analysis of variance (ANOVA): porcelain surface pretreatments (glazing, air-abrasion, air-abrasion/sputter coating, air-abrasion/plasma cleaning, air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating) X silanes

(Silicoup™ and Scotchprime™) X aging protocol (hydration or nonthermocycled and hydration/thermocycling or thermocycled).

b. Surface Pretreatment Comparisons

Individual porcelain surface pretreatment means were compared with the Newman-Keuls test. Although some variances appeared unequal, Cochran's test indicated that they could be considered equal (for the 12 surface pretreatment x silane combinations, $C = 0.1737$, $df = 19$ per group; for the 24 surface pretreatment x silane x thermocycling combinations, $C = 0.1080$, $df = 9$ per group; $P > 0.05$ in both cases).

Power and sample size estimates were based on the smallest sample sizes for a cell by cell comparison with Student's t test. A difference of 50 N between two means was judged to be clinically significant. To detect an effect size of 50 N with a sample size of 10 per group, the power was approximately 0.7 at the 0.05 significance level. To detect a difference of 75 N, the power was approximately 0.9 at the 0.05 significance level. For the two-way interaction cells, sample sizes were 20, and power was 0.9 or greater for any difference of at least 50 N at the 0.05 significance level.

c. Silane Comparisons

The Student t-test was used to compare Silicoup™ to Scotchprime™ means for both specimen aging protocols with and without glazed samples excluded from the analysis as follows: (1) overall Silicoup™ vs. Scotchprime™, (2) nonthermocycled Silicoup™ vs. Scotchprime™, (3) thermocycled Silicoup™ vs. Scotchprime™, (4) nonthermocycled

Silicoup™ vs. Scotchprime™ (glazed samples excluded from analysis), and (5) thermocycled Silicoup™ vs. Scotchprime™ (glazed samples excluded from analysis).

d. Thermocycled Silane Comparisons for Each Surface Pretreatment

Bonferroni t-tests were used to compare Silicoup™ to Scotchprime™ means for each of the six thermocycled surface pretreatments (glazing, air-abrasion, air-abrasion/sputter coating, air-abrasion/plasma cleaning, air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating. Bonferroni t-tests were used to control for Type I errors.

e. Nonthermocycled Silane Comparison for Each Surface Pretreatment

Bonferroni t-tests were also used to compare Silicoup™ to Scotchprime™ means for each of the six nonthermocycled surface pretreatments (glazing, air-abrasion, air-abrasion/sputter coating, air-abrasion/plasma cleaning, air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating.

f. Thermocycling Comparisons

Student t-tests were used to compare hydrated (nonthermocycled) and hydrated/thermocycled (thermocycled) means for overall and silane comparisons, with and without glazed samples excluded in the analyses as follows: (1) overall nonthermocycled vs. thermocycled, (2) nonthermocycled vs. thermocycled Silicoup™, (3) nonthermocycled vs. thermocycled Scotchprime™, (4) overall nonthermocycled vs. thermocycled (glazed samples excluded from analysis), (5) nonthermocycled vs.

thermocycled Silicoup™ (glazed samples excluded from analysis), and (6) nonthermocycled vs. thermocycled Scotchprime™ (glazed samples excluded from analysis).

g. Thermocycling Comparisons for Each Silane-Surface Pretreatment Combination

Bonferroni *t*-tests were used to compare nonthermocycled vs.thermocycled means for each of the twelve silane-porcelain surface pretreatment combinations (Silicoup™-glazed, Scotchprime™-glazed, Silicoup™-air-abraded, Scotchprime™-air-abraded, Silicoup™-air-abraded/sputter coated, Scotchprime™-air-abraded/sputter coated, Silicoup™-air-abraded/plasma cleaned, Scotchprime™-air-abraded/plasma cleaned, Silicoup™-air-abraded/hydrofluoric acid etched, Scotchprime™-air-abraded/hydrofluoric acid etched, Silicoup™-air-abraded/silicoated, and Scotchprime™-air-abraded/silicoated.

h. Thermocycled Silane-Surface Pretreatment Combination Comparisons

A Newman-Keuls multiple comparison test was performed on each silane-porcelain surface pretreatment combination. This was followed by two separate Newman-Keuls multiple comparison tests for each Silicoup™ and Scotchprime™-porcelain surface pretreatment combination subgroup.

V. Results

A. Introduction

Shear bond strength and failure mode raw data are recorded in the Appendix, Table 3. The raw data for shear bond strength, as recorded by the Instron™ machine in Newtons, was used for all statistical analysis. The means and standard deviations of shear strength values along with the corresponding failure modes are listed in Table 3.

To illustrate results in graphic form and to make comparisons easier, all shear strength values in Newtons were converted to Megapascals (MPa) as follows: MPa = Force/Unit Area = MN/m^2 = N x 10^6 / mm^2 x 10^6 = N/mm^2. The porcelain surface area to be bonded was delimited by Teflon™ tape. This resulted in composite resin buttons that had a standardized 4.8 mm diameter at the composite resin-porcelain interface. The bonded area (unit area) was calculated to be 18.1 mm^2. Therefore, MPa = Newtons/18.1 mm^2. The shear strength values are reported with three significant digits. For purposes of discussion, in the text, shear strength values are rounded to two significant digits.

B. Statistical Results

The results of the three-way Analysis of Variance (ANOVA) are summarized in Table 4. The results of the ANOVA showed that each of the independent variables significantly affected shear bond strength. There was a significant surface pretreatment effect ($F_{5,216}$) = 45.45, P = 0.0000), a significant silane effect ($F_{1,216}$ = 15.86, P = 0.0000), a significant aging effect ($F_{1,216}$ = 20.41, P = 0.0000), a significant surface pretreatment by silane interaction ($F_{1,216} = 3.705$, $P = 0.0031$), and a significant surface pretreatment by silane by aging interaction ($F_{5,216} = 2.276$, $P = 0.0477$).

1. Overall Surface Pretreatment Comparisons

To determine the best overall pretreatment, individual means were compared with the Newman-Keuls test (Table 5). The means of the six surface pretreatment groups were compared first. The mean of the glazed only group (5.9 MPa) was significantly lower than the other five means ($p < 0.05$). The means of the air-abraded only (11.9 MPa), air-abraded/sputter coated (11.8 MPa), and air-abraded/plasma cleaned (11.9 MPa) groups were equivalent, but were significantly lower ($p < 0.05$) than the means of the air-abraded/hydrofluoric acid (HF) etched (14.6 MPa) and air-abraded/silicoated (14.0 MPa) groups ; the means of the air-abraded/HF etched and air-abraded/silicoated groups were not significantly different. Figure 4 illustrates these findings graphically.

2. Thermocycled Surface Pretreatment Comparisons

Since hydration/thermocycling (thermocycling) may give a better indication of clinical success, the thermocycled pretreatment means were compared next (Table 6). The mean of the glazed only group (4.9 MPa), was significantly lower than the other five means ($p < 0.05$). The means of the air-abraded only (10.9 MPa), air-abraded/sputter coated (11.1 MPa), and air-abraded/plasma cleaned (10.7 MPa) groups were equivalent, but were significantly lower ($p < 0.05$) than the means of the air-abraded/HF etched (13.7 MPa) and air-abraded/silicoated (13.5 MPa) groups; the means of the air-abraded/HF etched and air-abraded/silicoated groups were statistically equivalent. Figure 5 illustrates these results graphically.

3. Silane Comparisons

To determine if one silane performed better overall, the overall Silicoup™ silane mean was compared to the overall Scotchprime™ silane mean. A t-test showed that the Silicoup™ mean (12.4 MPa) was significantly larger than the Scotchprime™ mean (10.9 MPa), p = 0.0063 (Table 7). To determine if one silane performed better for each aging protocol subgroup, t-tests showed that a significant difference could not be found between the nonthermocycled Silicoup™ (13.0 MPa) and Scotchprime™ (12.0 MPa) means, p = 0.2283 (Table 8); for the thermocycled samples, the Silicoup™ mean (11.9 MPa) was significantly larger than the Scotchprime™ mean (9.8 MPa), p = 0.0064 (Table 9).

4. Silane Comparisons (Glazed Samples Excluded)

Next, the silanes were evaluated with the glazed samples excluded from the analysis. The glazed samples were excluded because they did not receive the additional air-abrasion pretreatment. The two silanes could, therefore, be compared fairly in their ability to effect composite resin-porcelain bonding on air-abraded surfaces. T-tests were used for the comparisons. For the nonthermocycled samples, a significant difference could not be found between the Silicoup™ (13.7 MPa) and Scotchprime™ (14.6 MPa) means (Table 10); for the thermocycled samples, the Silicoup™ mean (12.8 MPa) was once again significantly larger than the Scotchprime™ mean (11.2 MPa), p = 0.0136 (Table 11).

5. Thermocycled Silane Comparison for Each Surface Pretreatment

To identify individual differences, Bonferroni t-tests were used to compare the two silanes for each surface pretreatment. In order to better evaluate the silanes for effectiveness in a simulated oral environment, the thermocycled silane means were compared. A significance level of 0.01 was adopted for the Bonferroni procedure as a control for Type I errors. A summary of these results can be found in Table 12. The results showed Silicoup™ to produce higher shear bond strengths for glazed only (P = 0.0001) and air-abraded/sputter coated (P = 0.0043) pretreatments; significant differences could not be found between the silanes for air-abraded only (P = 0.5326), air-abraded/plasma cleaned (P = 0.1774), air-abraded/HF etched (P = 0.3714), and air-abraded/silicoated (P = 0.5076) surface pretreatments. The comparisons are illustrated in Figure 6.

6. Nonthermocycled Silane Comparison for Each Surface Pretreatment

Nonthermocycled silane comparisons were included as an added measure for comparing the silanes before and after thermocycling. It was also another way of looking at the effects of thermocycling. To identify individual differences, Bonferroni t-tests were used to compare the two silanes for each of the surface pretreatments. A significance level of 0.01 was adopted for the Bonferroni procedure as a control for Type I errors. A summary of these results can be found in Table 13. The results showed Silicoup™ to produce higher shear bond strengths only for the glazed-only pretreatment (P = 0.0001); Significant differences could not be found between the silanes for air-abraded only (P = 0.0276), air-abraded/sputter coated (P = 0.2024), air-abraded/plasma cleaned (P = 0.7939), air-abraded/HF etched (P = 0.6414), and air-abraded/silicoated (P = 0.6060) surface pretreatments. The comparisons are illustrated in Figure 7.

7. Thermocycling Effects

To demonstrate the overall effect of thermocycling, overall hydrated only (nonthermocycled), and overall thermocycled mean shear bond strengths were compared. A t-test showed that the thermocycled mean was significantly lower (p = 0.0019) than the nonthermocycled mean (Table 14). Thermocycling effects were also determined for each silane. T-tests showed that significant differences could not be found between the nonthermocycled and thermocycled Silicoup™ means, p = 0.0970 (Table 15). The thermocycled Scotchprime™ mean was significantly lower than the nonthermocycled Scotchprime™ mean, p = 0.0070 (Table 16).

8. Thermocycling Effects (Glazed Samples Excluded)

To demonstrate the effects of thermocycling on air abraded surfaces, the same t-tests just described were performed after exclusion of the glazed samples from the analysis and showed that overall, the thermocycled sample mean was significantly larger than the nonthermocycled sample mean, p = 0.0005 (Table 17); a significant difference could not be found between the nonthermocycled and thermocycled Silicoup™ means, p = 0.1788

(Table 18); the thermocycled Scotchprime™ mean was significantly lower than the nonthermocycled Scotchprime™ mean, p = 0.0004 (Table 19).

9. Thermocycling Effects for Each Silane-Surface Pretreatment Combination

To identify individual differences, Bonferroni t-tests were used to test effects of thermocycling for each Silicoup™ silane-pretreatment and Scotchprime™ silane-pretreatment combination. These results are summarized in Table 20 and illustrated in Figure 8. Although two of these p values are less than 0.05, a significance level of 0.005 was adopted for the Bonferroni procedure as a control for Type I errors. The results showed that thermocycling was significant only for the Scotchprime™-glazed sample (p = 0.0043); significant thermocycling effects could not be found for the Silicoup™-glazed (p = 0.0975), Silicoup™-air-abraded only (p = 0.0556), Scotchprime™-air-abraded only (p = 0.5179), Silicoup™-air-abraded/sputter coated (p = 0.2717), Scotchprime™-air-abraded/sputter coated (p = 0.0126), Silicoup™-air-abraded/plasma cleaned, Scotchprime™-air-abraded/plasma cleaned (p = 0.0129), Silicoup™-air-abraded HF etched (p = 0.6914), Scotchprime™-air-abraded/HF etched (p = 0.0636), Silicoup™-air-abraded/silicoated (p = 0.9653), and Scotchprime™-air-abraded/silicoated (p = 0.3095) combinations.

10. Thermocycled Silane-Surface Pretreatment Comparisons

To determine the best combinations of silane and porcelain surface pretreatment, the thermocycled pairs were compared. Thermocycled means were compared because these conditions better simulate the oral environment. The twelve cell means were ranked as follows: 2.8 MPa (Scotchprime™-Glazed), 7.1 MPa (Silicoup™-Glazed), 9.5 MPa (Scotchprime™-air-abraded/sputter coated), 10.1 MPa (Scotchprime™-air-abraded/plasma cleaned), 10.4 MPa (Scotchprime™-air-abraded only), 11.3 MPa (Silicoup™-air-abraded/plasma cleaned), 11.4 MPa (Silicoup™-air-abraded only), 12.8 MPa (Silicoup™-air-abraded/sputter coated), 12.9 MPa (Scotchprime™-air-abraded/HF etched), 13.1 MPa (Scotchprime™-air-abraded/silicoated), 14.0 MPa (Silicoup™-air-abraded/silicoated), 14.6 MPa (Silicoup™-air-abraded/HF etched). These means were compared using the Newman-Keuls test (The error degrees of freedom were reduced to 119 for these comparisons). The means, standard deviations, and comparisons are shown in Table 21. The results are illustrated graphically in Figure 9. The lowest mean, from the Scotchprime™-glazed combination (2.8 MPa), was significantly lower ($p< .05$) than all other means. Means of 9.5 MPa or lower were significantly lower than means of 10.5 MPa or higher ($p< 0.05$). No significant differences could be found between means of 11.3 MPa or greater ($p< 0.05$). Again, comparisons showed that the highest bond strengths were associated with the air-abraded/HF etched and air-abraded/silicoated surface pretreatments, with the four highest means being in these two surface pretreatment levels. However, only the highest mean of 14.6 MPa, for the Silicoup™-air-abraded/HF etched combination, was significantly greater than means of 10.4 MPa or less ($p< 0.05$).

11. Thermocycled Silane-Surface Pretreatment Comparisons for Each Type of Silane

To better evaluate for best surface pretreatment for each type of silane, the best silane-surface pretreatment combinations were determined for each silane separately. Again, the thermocycled pairs were compared, because these conditions better simulate the oral environment. The Silicoup™-surface pretreatments were compared first. The six cell means were ranked as follows: 7.1 MPa (Silicoup™-Glazed), 11.3 MPa (Silicoup™-air-abraded/plasma cleaned), 11.4 MPa (Silicoup™-air-abraded only), 12.8 MPa (Silicoup™-air-abraded/sputter coated), 14.0 MPa (Silicoup™-air-abraded/silicoated), and 14.6 MPa (Silicoup™-air-abraded/HF etched). These means were compared using the Newman-Keuls test (The error degrees of freedom were reduced to 59 for these comparisons). The means, standard deviations, and comparisons are shown in Table 22. The results are illustrated graphically in Figure 10. The lowest mean, from the Scotchprime™-glazed combination (2.8 MPa), was significantly lower ($p < .05$) than all other five means. A significant difference ($p > 0.05$) could not be detected among the last five means as listed above and in Table 22.

The Scotchprime™-surface pretreatments were compared next. The six cell means were ranked as follows: 2.8 MPa (Scotchprime™-Glazed), 9.5 MPa (Scotchprime™-air-abraded/sputter coated), 10.1 MPa (Scotchprime™-air-abraded/plasma cleaned), 10.4 MPa (Scotchprime™-air-abraded only), 12.9 MPa (Scotchprime™-air-abraded/HF etched), and 13.1 MPa (Scotchprime™-air-abraded/silicoated). These means were compared using the Newman-Keuls test (The error degrees of freedom were reduced to 59 for these comparisons). The means, standard deviations, and comparisons are shown in Table 23. The results are illustrated graphically in Figure 11. The lowest mean, from the Scotchprime™-glazed combination (2.8 MPa), was significantly lower ($p < 0.05$) than all other five means. The means of the Scotchprime™-air-abraded/sputter coated (9.5 MPa), Scotchprime™-air-abraded/plasma cleaned (10.1 MPa), and Scotchprime™-air-abraded only (10.4 MPa) groups were equivalent, but were significantly lower ($p < 0.05$) than the means of the, Scotchprime™-air-abraded/HF etched (12.9 MPa) and Scotchprime™-air-abraded/silicoated (13.1 MPa) groups; the means of the Scotchprime™-air-abraded/HF etched and Scotchprime™-air-abraded/silicoated groups were not significantly different.

Table 3. Shear Bond Strengths and Failure Modes, Principal Study

				MEAN (SD)		Failure Mode, #		
Pretreatment	Silane[1]	Aging[2]	n	Newtons	MPa	C[3]	P[4]	A[5]
Glazed	1	1	10	171.7 (63.2)	9.49 (3.49)	-	6	4
Glazed	1	2	10	128.3 (46.5)	7.09 (2.57)	-	-	10
Glazed	2	1	10	77.2 (18.1)	4.26 (1.00)	-	-	10
Glazed	2	2	10	50.4 (18.5)	2.78 (1.02)	-	-	10
Air Abraded	1	1	10	264.8 (57.0)	14.62 (3.15)	5	5	-
Air Abraded	1	2	10	205.9 (71.0)	11.37 (3.92)	6	4	-
Air Abraded	2	1	10	204.0 (56.4)	11.27 (3.12)	8	2	-
Air Abraded	2	2	10	189.2 (43.0)	10.45 (2.38)	5	5	-
Sputter Coated◆	1	1	10	204.0 (61.5)	11.27 (3.40)	3	5	2
Sputter Coated	1	2	10	231.6 (46.3)	12.79 (2.56)	4	4	2
Sputter Coated	2	1	10	244.8 (75.7)	13.52 (4.18)	3	4	3
Sputter Coated	2	2	10	171.8 (34.8)	9.49 (1.92)	1	7	2
Plasma Cleaned	1	1	10	239.2 (50.5)	13.21 (2.79)	9	1	-
Plasma Cleaned	1	2	10	205.0 (37.5)	11.32 (2.07)	8	2	-
Plasma Cleaned	2	1	10	233.4 (47.3)	12.89 (2.61)	7	3	-
Plasma Cleaned	2	2	10	182.5 (34.1)	10.08 (1.88)	7	3	-
HF Etched	1	1	10	274.5 (24.0)	15.16 (1.33)	9	1	-
HF Etched	1	2	10	263.4 (83.6)	14.55 (4.62)	10	-	-
HF Etched	2	1	10	283.4 (54.3)	15.66 (3.00)	8	2	-
HF Etched	2	2	10	234.0 (57.4)	12.92 (3.17)	10	-	-
Silicoated	1	1	10	254.1 (34.9)	14.04 (1.93)	9	1	-
Silicoated	1	2	10	253.3 (45.6)	13.99 (2.52)	10	-	-
Silicoated	2	1	10	266.3 (64.7)	14.71 (3.57)	10	-	-
Silicoated	2	2	10	237.4 (58.8)	13.12 (3.25)	10	-	-

[1] Silane 1=Silicoup (Kulzer), Silane 2=Scotchprime (3M)

[2] Aging 1 = Storage in 37° deionized water for 71 days.
Aging 2 = Storage in 37° deionized water for 70 days, followed by 1000 thermocycles between 6 and 60° C with a dwell time of 30 sec.

[3] Totally cohesive [4] Partial cohesive/adhesive [5] Adhesive

◆ All pretreatments below symbol were preceded by air abrasion using 50μm aluminum oxide.

Table 4. Three Way Analysis of Variance Summary
(Principal Study)

Source	df	SS	MSS	F	P
Between Subjects	239	1393829.88			
Surface Pretreatment (P)	5	616687.75	123337.55	45.45	0.0000
Silane (S)	1	43040.81	43040.81	15.86	0.0001
Aging (A)	1	55388.81	55388.81	20.41	0.0000
P × S	5	50268.78	10053.75	3.71	0.0031
P × A	5	5124.28	1024.86	0.38	0.8649
S × A	1	6303.75	6303.75	2.32	0.1289
P × S × A	5	30886.55	6177.31	2.28	0.0477
Subjects within Groups	216	586129.19	2713.56		

Table 5. Results of Newman Keuls Multiple Comparison Test and Failure Mode Examination for Nonthermocycled & Thermocycled Samples

	MEAN (SD)				Failure Mode, %		
Pretreatment	n	Newtons	MPa	NK[1]	C[2]	P[3]	A[4]
Glazed	40	106.9 (76.4)	5.9 (3.4)	A	0	15	85
Air-abraded	40	216.0 (62.7)	11.9 (3.5)	B	60	40	0
Sputter Coated*	40	213.0 (61.4)	11.8 (3.4)	B	27.5	50	22.5
Plasma Cleaned*	40	215.0 (47.2)	11.9 (2.6)	B	77.5	22.5	0
HF Etched*	40	263.8 (59.5)	14.6 (3.3)	C	92.5	7.5	0
Silicoated*	40	252.8 (51.3)	14.0 (2.8)	C	97.5	2.5	0

[1] Newman-Keuls Grouping; A < B < C (P< 0.05)

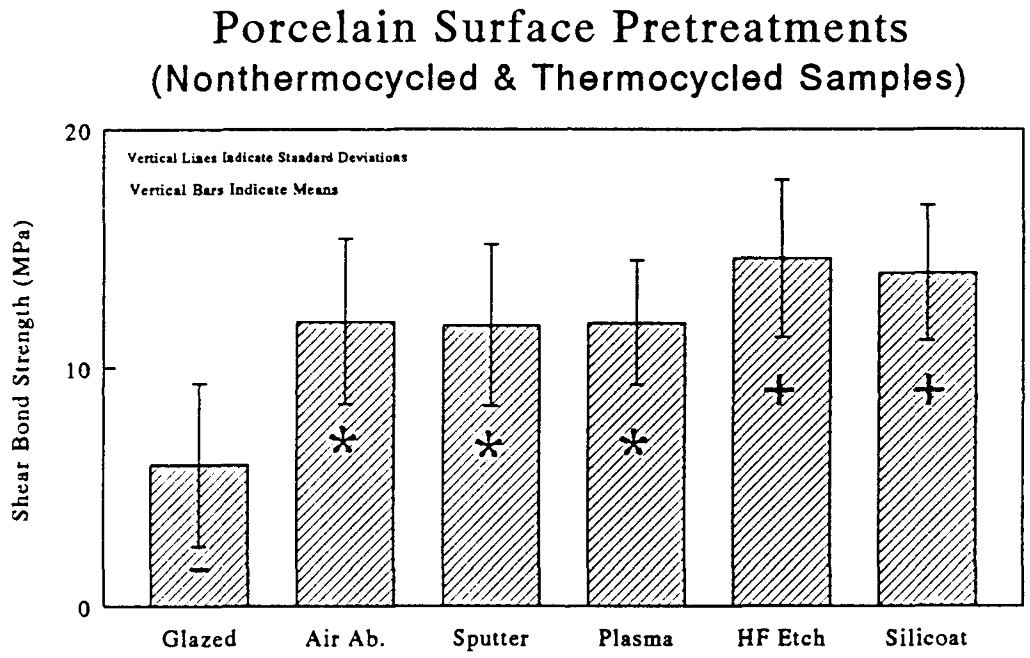
[2] Totally cohesive failure (cohesive porcelain; cohesive porcelain/cohesive resin)

[3] Partially cohesive/adhesive failure (cohesive porcelain/adhesive; cohesive porcelain/cohesive resin/adhesive)

[4] Totally adhesive failure

* Surfaces indicated were preceded by air-abrasion using 50µm aluminum oxide.

Figure 4. Bar Graph Illustrating Newman Keuls Multiple Comparison Test of Nonthermocycled & Thermocycled Porcelain Surface Pretreatments



Significant Difference Between Means With Different Symbols ($p < 0.05$)

Table 6. Results of Newman Keuls Multiple Comparison Test and Failure Mode Examination for Thermocycled Samples

	MEAN (SD)				Failure Mode, %		
Pretreatment	n	Newtons	MPa	NK[1]	C[2]	P[3]	A[4]
Glazed	20	89.3 (52.7)	4.9 (2.9)	A	0	0	100
Air-abraded	20	197.5 (57.7)	10.9 (3.2)	B	55	45	0
Sputter Coated*	20	201.7 (50.3)	11.1 (2.8)	B	25	55	20
Plasma Cleaned*	20	193.7 (36.7)	10.7 (2.0)	B	75	25	0
HF Etched*	20	248.7 (71.4)	13.7 (3.9)	C	100	0	0
Silicoated*	20	245.3 (51.8)	13.5 (2.9)	C	100	0	0

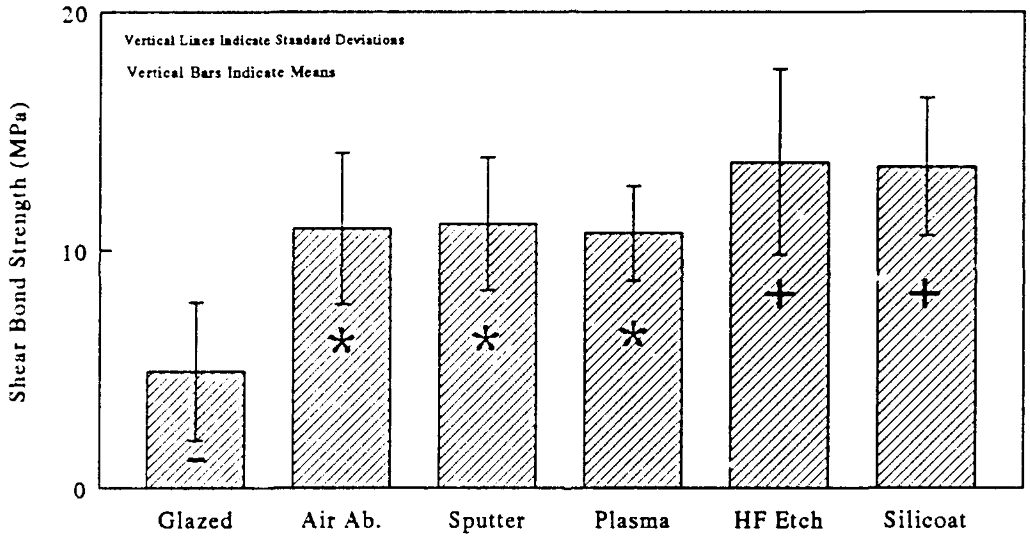
[1] Newman-Keuls Groupings; A < B < C ($p < 0.05$)

[2] Totally cohesive failure (cohesive porcelain; cohesive porcelain/cohesive resin)
[3] Partially cohesive/adhesive failure (cohesive porcelain/adhesive; cohesive porcelain/cohesive resin/adhesive)
[4] Totally adhesive failure

* Surfaces indicated were preceded by air-abrasion using 50µm aluminum oxide.

Figure 5. Bar Graph Illustrating Newman Keuls Multiple Comparison Test of Thermocycled Porcelain Surface Pretreatments

Porcelain Surface Pretreatments
(Thermocycled Samples)



Significant Difference Between Means With Different Symbols ($p < 0.05$)

Table 7. T-Test Comparing Overall Silicoup vs. Scotchprime Means

		MEAN (SD)			
Silane	n	Newtons	MPa	t	p
Silicoup	120	224.6 (66.4)	12.41 (3.67)	2.75	0.0063
Scotchprime	120	197.9 (83.3)	10.93 (4.60)		

Significant difference between means ($p < 0.05$)

Table 8. T-Test Comparing Nonthermocycled Silicoup vs. Scotchprime Means

		MEAN (SD)			
Silane	n	Newtons	MPa	t	p
Silicoup	60	234.7 (60.6)	12.97 (3.34)	1.21	0.2283
Scotchprime	60	218.2 (86.7)	12.05 (4.79)		

No significant difference between means

Table 9. T-Test Comparing Thermocycled Silicoup vs. Scotchprime Means

		MEAN (SD)			
Silane	n	Newtons	MPa	t	p
Silicoup	60	214.6 (70.9)	11.86 (3.91)	2.78	0.0064
Scotchprime	60	177.6 (75.1)	9.81 (4.15)		

Significant difference between means ($p < 0.05$).

Table 10. T-Test Comparing nonthermocycled Silicoup vs. Scotchprime Means (Glazed Samples Deleted)

		MEAN (SD)			
Silane	n	Newtons	MPa	t	p
Silicoup	50	247.3 (52.0)	13.66 (2.87)	0.08	0.9360
Scotchprime	50	246.4 (64.2)	14.61 (3.55)		

No significant difference between means

Table 11. T-Test Comparing Thermocycled Silicoup vs. Scotchprime Means (Glazed Samples Deleted)

		MEAN (SD)			
Silane	n	Newtons	MPa	t	p
Silicoup	50	231.8 (61.8)	12.81 (3.41)	2.51	0.0136
Scotchprime	50	203.0 (52.7)	11.22 (2.91)		

Significant difference between means ($p < 0.05$).

Table 12. Summary Results of Bonferroni T-Tests Comparing Shear Bond Strengths of Silicoup vs. Scotchprime Samples for Each Thermocycled Porcelain Surface Pretreatment

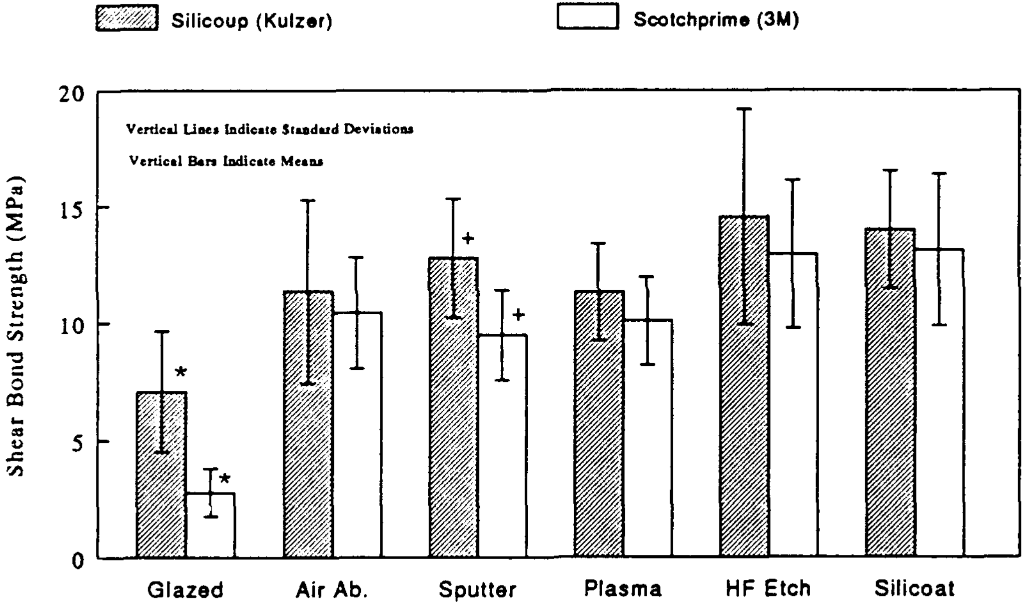
			MEAN (SD)		
Pretreatment	Silicoup vs. Scotchprime	n	Newtons	MPa	P
Glazed	Silicoup	10	128.3 (46.5)	7.09 (2.57)	0.0001*
	Scothcprime	10	50.4 (18.5)	2.78 (1.02)	
Air-abraded	Silicoup	10	205.9 (71.0)	11.37 (3.92)	0.5326
	Scotchprime	10	189.2 (43.0)	10.45 (2.38)	
Sputter Coated[°]	Silicoup	10	231.6 (46.3)	12.79 (2.56)	0.0043*
	Scotchprime	10	171.8 (34.8)	9.49 (1.92)	
Plasma Cleaned	Silicoup	10	205.0 (37.5)	11.32 (2.07)	0.1774
	Scotchprime	10	182.5 (34.1)	10.08 (1.88)	
HF[§] Etched	Silicoup	10	263.4 (83.6)	14.55 (4.62)	0.3714
	Scotchprime	10	234.0 (57.4)	12.93 (3.17)	
Silicoated	Silicoup	10	253.3 (45.6)	13.99 (2.52)	0.5076
	Scotchprime	10	237.4 (58.8)	13.12 (3.25)	

* $P < .01$ indicates significant difference between means.

[°] All pretreatments below symbol were preceded by air-abrasion using 50μm aluminum oxide.

[§] Hydrofluoric acid

Figure 6. Bar Graph Illustrating Summary Results of *Bonferroni T-Tests* Comparing Shear Bond Strengths of Silicoup vs. Scotchprime Samples for Each Thermocycled Porcelain Surface Pretreatment



Porcelain Surface Pretreatments
(Thermocycled Samples)

Significant Difference Between Pair of Means Indicated by Same Symbol ($p < 0.01$)

Table 13. Summary Results of Bonferroni T-Tests Comparing Shear Bond Strengths of Silicoup vs. Scotchprime Samples for Each Nonthermocycled Porcelain Surface Pretreatment

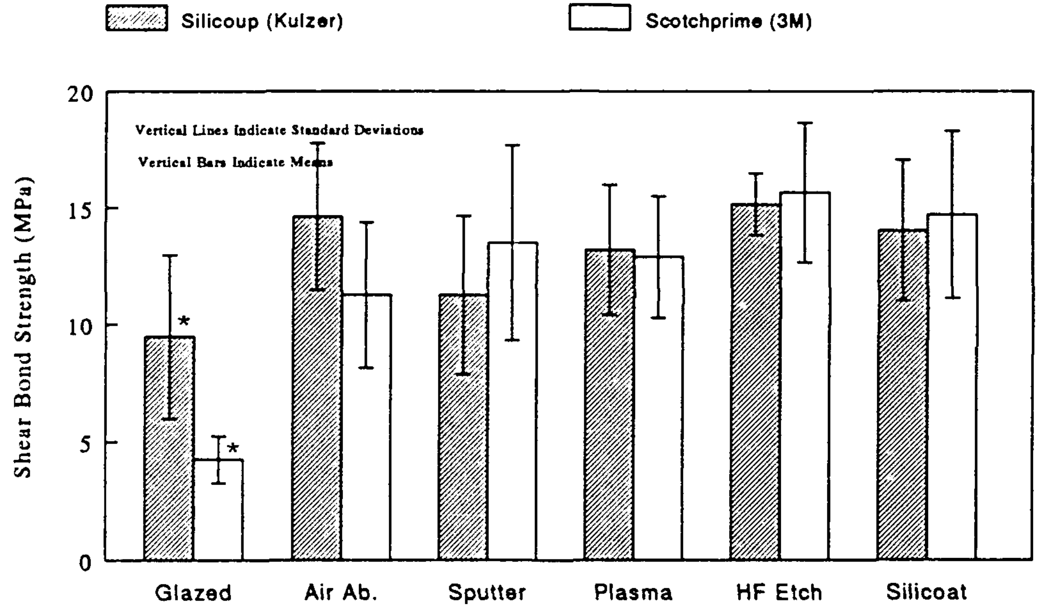
Pretreatment	Silicoup vs. Scotchprime	n	MEAN (SD) Newtons	MEAN (SD) MPa	P
Glazed	Silicoup	10	171.7 (63.2)	9.49 (3.49)	0.0003*
	Scotchprime	10	77.2 (18.1)	4.26 (1.00)	
Air Abraded	Silicoup	10	264.8 (57.0)	14.63 (3.15)	0.0276
	Scotchprime	10	204.0 (61.5)	11.27 (3.12)	
Sputter Coated°	Silicoup	10	204.0 (61.5)	11.27 (3.40)	0.2024
	Scotchprime	10	244.8 (75.7)	13.52 (4.18)	
Plasma Cleaned	Silicoup	10	239.2 (50.5)	13.22 (2.79)	0.7939
	Scotchprime	10	233.4 (47.3)	12.90 (2.61)	
HF$ Etched	Silicoup	10	274.5 (24.0)	15.16 (1.32)	0.6414
	Scotchprime	10	283.4 (54.3)	15.66 (3.00)	
Silicoated	Silicoup	10	254.1 (54.9)	14.04 (3.03)	0.6060
	Scotchprime	10	266.3 (64.7)	14.71 (3.57)	

* P < .01 indicates significant difference between means.

° All pretreatments below symbol were preceded by air abrasion using 50μm aluminum oxide.

$ Hydrofluoric acid

Figure 7. Bar Graph Illustrating Summary Results of Bonferroni T-Tests Comparing Shear Bond Strengths of Silicoup vs. Scotchprime Samples for Each Nonthermocycled Porcelain Surface Pretreatment



Porcelain Surface Pretreatments
(Nonthermocycled Samples)

Significant Difference Between Pair of Means Indicated by Same Symbol ($p < 0.01$)

Table 14. T-test comparing overall Nonthermocycled vs Thermocycled means

		MEAN (SD)			
Nonthermocycled vs. Thermocycled	n	Newtons	MPa	t	p
Nonthermocycled	120	226.4 (74.9)	12.51 (4.12)	3.14	0.0019
Thermocycled	120	196.1 (75.1)	10.83 (4.12)		

Significant difference between means ($p < 0.05$).

Table 15. T-Test Comparing Nonthermocycled vs Thermocycled Silicoup Means

Nonthermocycled vs. Thermocycled	n	MEAN (SD) Newtons	MEAN (SD) MPa	t	p
Nonthermocycled	60	234.7 (60.6)	12.97 (3.34)	1.67	0.0970
Thermocycled	60	214.6 (70.9)	11.86 (3.91)		

No significant difference between means.

Table 16. T-Test Comparing Nonthermocycled vs. Thermocycled Scotchprime Means

		MEAN (SD)			
Nonthermocycled vs. Thermocycled	n	Newtons	MPa	t	p
Nonthermocycled	60	218.2 (86.7)	12.05 (4.79)	2.74	0.0070
Thermocycled	60	177.6 (75.1)	9.81 (4.15)		

Significant difference between means ($p < 0.05$).

Table 17. T-Test Comparing Overall Nonthermocycled vs Thermocycled Means (Glazed Samples Deleted)

Nonthermocycled vs. Thermocycled	n	MEAN (SD) Newtons	MEAN (SD) MPa	t	p
Nonthermocycled	100	246.8 (58.1)	13.64 (3.20)	3.56	0.0005
Thermocycled	100	217.4 (59.0)	12.01 (3.26)		

Significant difference between means ($p < 0.05$).

Table 18. T-Test Comparing Nonthermocycled vs. Thermocycled Silicoup Means (Glazed Samples Deleted)

Nonthermocycled vs. Thermocycled	n	MEAN (SD) Newtons	MEAN (SD) MPa	t	p
Nonthermocycled	50	247.3 (52.0)	13.66 (2.87)	1.35	0.1788
Thermocycled	50	231.8 (61.8)	12.81 (3.41)		

No Significant difference between means.

Table 19. T-Test Comparing Nonthermocycled vs. Thermocycled Scotchprime Means (Glazed Samples Deleted)

		MEAN (SD)			
Nonthermocycled vs. Thermocycled	n	Newtons	MPa	t	p
Nonthermocycled	50	246.4 (64.2)	14.61 (3.55)	3.70	0.0004
Thermocycled	50	203.0 (52.7)	11.22 (2.91)		

Significant difference between means ($p < 0.05$).

Table 20. Summary Results of T-Tests Comparing Shear Bond Strengths of Nonthermocycled vs. Thermocycled Samples for Each Silane-Porcelain Surface Pretreatment Combination

			MEAN (SD)			
Pretreatment	Silane	Nonthermocycled[1] vs. Thermocycled[2]	n	Newtons	MPa	P
Glazed	Silicoup	Nonthermocycled	10	171.7 (63.2)	9.49 (3.49)	0.0975
	Silicoup	Thermocycled	10	128.3 (46.5)	7.09 (2.57)	
Glazed	Scotchprime	Nonthermocycled	10	77.2 (18.1)	4.26 (1.00)	0.0043*
	Scotchprime	Thermocycled	10	50.4 (18.5)	2.78 (1.02)	
Air-abraded	Silicoup	Nonthermocycled	10	264.8 (57.0)	14.62 (3.15)	0.0556
	Silicoup	Thermocycled	10	205.9 (71.0)	11.37 (3.92)	
Air-abraded	Scotchprime	Nonthermocycled	10	204.0 (56.4)	11.27 (3.12)	0.5179
	Scotchprime	Thermocycled	10	189.2 (43.0)	10.45 (3.38)	
Sputter Coated[◆]	Silicoup	Nonthermocycled	10	204.0 (61.5)	11.27 (3.40)	0.2717
	Silicoup	Thermocycled	10	231.6 (46.3)	12.79 (2.56)	
Sputter Coated	Scotchprime	Nonthermocycled	10	244.8 (75.7)	13.52 (4.18)	0.0126
	Scotchprime	Thermocycled	10	171.8 (34.8)	9.49 (1.92)	
Plasma Cleaned	Silicoup	Nonthermocycled	10	239.2 (50.5)	13.21 (2.79)	0.1026
	Silicoup	Thermocycled	10	205.0 (37.5)	11.32 (2.07)	
Plasma Cleaned	Scotchprime	Nonthermocycled	10	233.4 (47.3)	12.89 (2.61)	0.0129
	Scotchprime	Thermocycled	10	182.5 (34.1)	10.08 (1.88)	
HF Etched	Silicoup	Nonthermocycled	10	274.5 (24.0)	15.16 (1.33)	0.6914
	Silicoup	Thermocycled	10	263.4 (83.6)	14.55 (4.62)	
HF Etched	Scotchprime	Nonthermocycled	10	283.4 (54.3)	15.66 (3.00)	0.0636
	Scotchprime	Thermocycled	10	234.0 (57.4)	12.93 (3.17)	
Silicoated	Silicoup	Nonthermocycled	10	254.1 (34.9)	14.04 (1.93)	0.9653
	Silicoup	Thermocycled	10	253.3 (45.6)	13.99 (2.52)	
Silicoated	Scotchprime	Nonthermocycled	10	266.3 (64.7)	14.71 (3.57)	0.3095
	Scotchprime	Thermocycled	10	237.4 (58.8)	13.12 (3.25)	

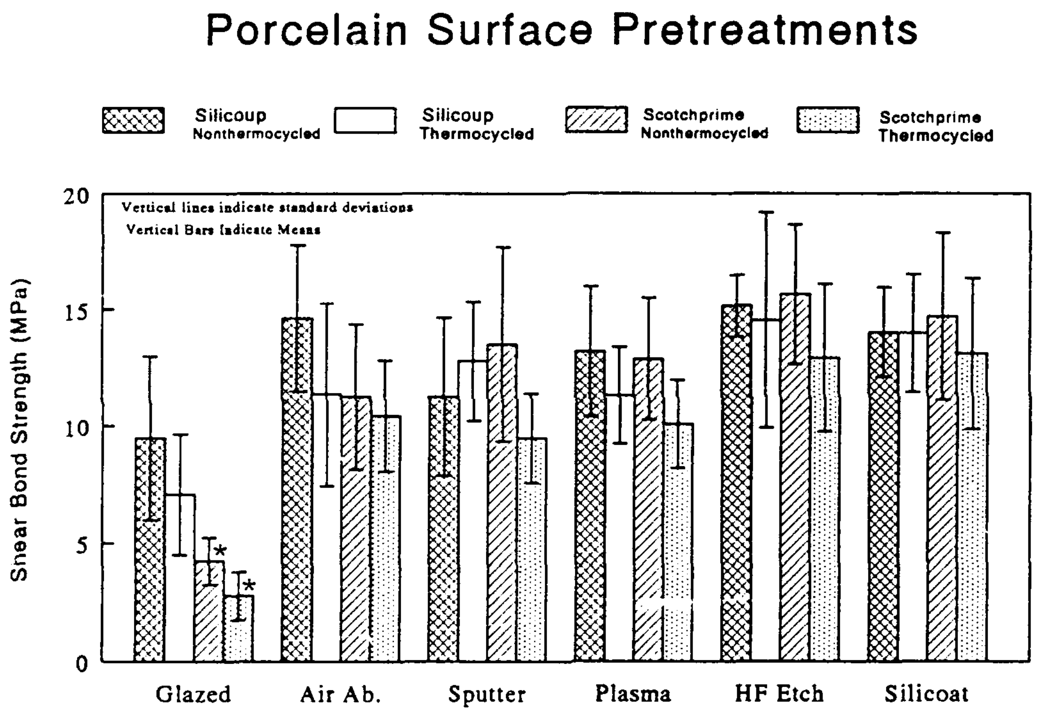
* $P < 0.005$ indicates significant difference between means.

[1] Storage in 37° deionized water for 71 days.

[2] Storage in 37° deionized water for 70 days, followed by 1000 thermocycles between 6 and 60° C with a dwell time of 30 sec.

[◆] All pretreatments below symbol were preceded by air-abrasion using 50μm aluminum oxide.

Figure 8. Bar Graph Illustrating Summary Results of Bonferroni T-Tests Comparing Nonthermocycled vs. Thermocycled Samples for Each Silane-Surface Pretreatment Combination



Porcelain Surface Pretreatments

Significant Difference Between Pair of Means Indicated by Symbols ($p < 0.005$)

Table 21. Summary Results of Newman-Keuls Multiple Comparison Test of Thermocycled Silane-Porcelain Surface Pretreatment Combinations

		MEAN (SD)						
Pretreatment	Silane	n	Newtons	MPa	Subset[1]			
HF§ Etched*	Silicoup	10	263.4 (83.6)	14.55 (4.62)	│			
Silicoated*	Silicoup	10	253.3 (45.6)	13.99 (2.52)	│	│		
Silicoated*	Scotchprime	10	237.4 (58.8)	13.12 (3.25)	│	│	│	
HF Etched*	Scotchprime	10	234.0 (57.4)	12.93 (3.17)	│	│	│	
Sputter Coated*	Silicoup	10	231.6 (46.3)	12.79 (2.56)	│	│	│	
Air Abraded	Silicoup	10	205.9 (71.0)	11.37 (3.92)	│	│	│	
Plasma Cleaned*	Silicoup	10	205.0 (37.5)	11.32 (2.07)	│	│	│	
Air Abraded	Scotchprime	10	189.2 (43.0)	10.45 (2.38)		│	│	
Plasma Cleaned*	Scotchprime	10	182.5 (34.1)	10.08 (1.88)		│	│	│
Sputter Coated*	Scotchprime	10	171.8 (34.8)	9.49 (1.92)			│	│
Glazed	Silicoup	10	128.3 (46.5)	7.09 (2.57)			│	│
Glazed	Scotchprime	10	50.4 (18.5)	2.78 (1.02)				

[1] Subsets connected by vertical bars are not significantly different ($p < 0.05$).

§ Hydrofluoric acid

* *Pretreatments indicated were preceded by air abrasion using 50μm aluminum oxide.*

Table 22. Results of Newman-Keuls Multiple Comparison Test And Failure Mode Analysis for Thermocycled Silicoup-Porcelain Surface Pretreatment Combinations

	MEAN (SD)				Failure Mode, %		
Pretreatment	n	Newtons	MPa	NK[1]	C[2]	P[3]	A[4]
Glazed	10	128.3 (46.5)	7.1 (2.6)	A	0	0	100
Air Abraded	10	205.9 (71.0)	11.4 (3.9)	B	60	40	0
Sputter Coated*	10	231.6 (46.3)	12.8 (2.6)	B	40	40	20
Plasma Cleaned*	10	205.0 (37.5)	11.3 (2.1)	B	80	20	0
HF§ Etched*	10	263.4 (83.6)	14.6 (4.6)	B	100	0	0
Silicoated*	10	253.3 (45.6)	14.0 (2.5)	B	100	0	0

[1] Newman-Keuls Groupings; A < B ($p < 0.05$)

[2] Totally cohesive failure (cohesive porcelain; cohesive porcelain/cohesive resin)

[3] Partially cohesive/adhesive failure (cohesive porcelain/adhesive; cohesive porcelain/cohesive resin/adhesive)

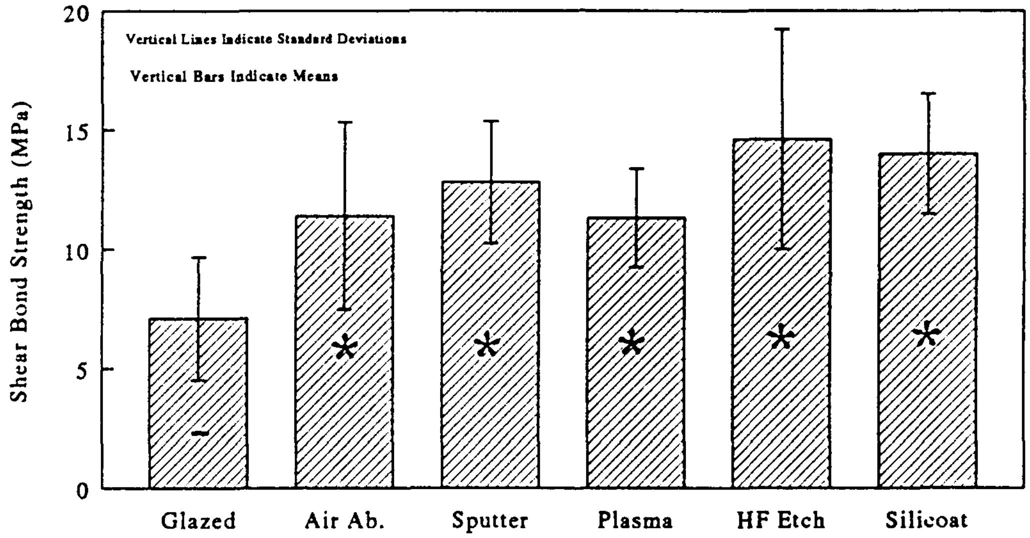
[4] Totally adhesive failure

* Surfaces indicated were preceded by air abrasion using 50μm aluminum oxide.

§ Hydrofluoric acid

Figure 9. Bar Graph Illustrating Newman Keuls Multiple Comparison Test of Thermocycled Silicoup-Porcelain Surface Pretreatment Combinations

Porcelain Surface Pretreatments
(Thermocycled Silicoup Samples)



Significant Difference Between Means With Different Symbols (p< 0.05)

Table 23. Results of Newman-Keuls Multiple Comparison Test And Failure Mode Analysis for Thermocycled Scotchprime-Porcelain Surface Pretreatment Combinations

	MEAN (SD)				Failure Mode, %		
Pretreatment	n	Newtons	MPa	NK[1]	C[2]	P[3]	A[4]
Glazed	10	50.4 (18.5)	2.8 (1.0)	A	0	0	100
Air Abraded	10	189.2 (43.0)	10.4 (3.4)	B	50	50	0
Sputter Coated[*]	10	171.8 (34.7)	9.5 (1.9)	B	10	70	20
Plasma Cleaned[*]	10	182.5 (34.1)	10.1 (1.9)	B	70	30	0
HF[§] Etched[*]	10	234.0 (57.3)	12.9 (3.2)	C	100	0	0
Silicoated[*]	10	237.4 (58.8)	13.1 (3.2)	C	100	0	0

[1] Newman-Keuls Groupings; A < B < C ($p < 0.05$)

[2] Totally cohesive failure (cohesive porcelain; cohesive porcelain/cohesive resin)

[3] Partially cohesive/adhesive failure (cohesive porcelain/adhesive; cohesive porcelain/cohesive resin/adhesive)

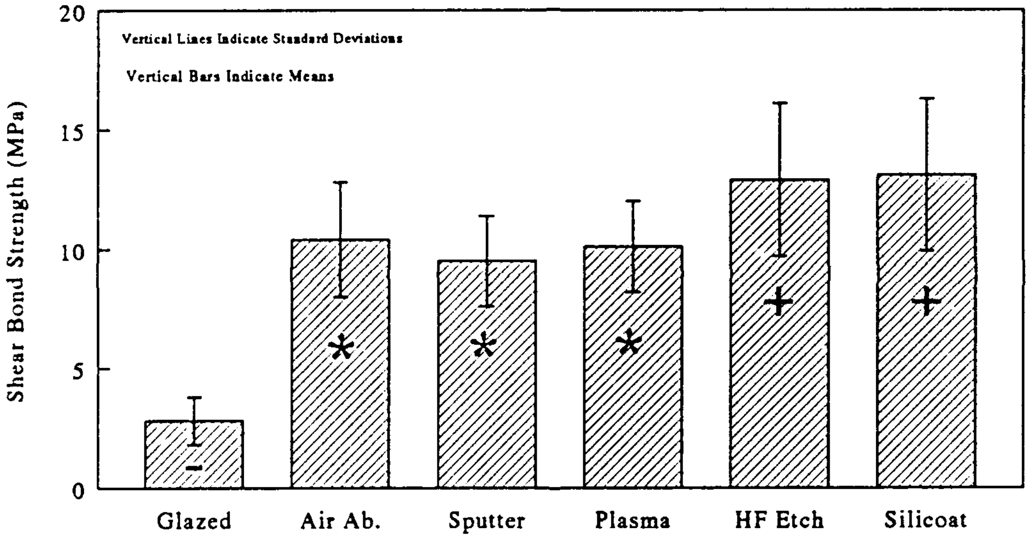
[4] Totally adhesive failure

[*] Surfaces indicated were preceded by air abrasion using 50μm aluminum oxide.

[§] Hydrofluoric acid

Figure 10. Bar Graph Illustrating Newman Keuls Multiple Comparison Test of Thermocycled Scotchprime-Porcelain Surface Pretreatment Combinations

Porcelain Surface Pretreatments
(Thermocycled Scotchprime Samples)



Significant Difference Between Means With Different Symbols ($p < 0.05$)

C. Fracture Site Examination Results

Each of the specimens shear bond tested was examined under x30 magnification to determine modes and sites of failure using a stereomicroscope. Additionally, a representative specimen of each different failure mode was selected and examined under scanning electron microscopy (SEM).

1. Stereomicroscopic Examination

To report results of the stereomicroscopic examination, the modes of failure were categorized and ranked according to approximate percentage of cohesive porcelain, cohesive resin, and adhesive failure observed. Stated in other terms, for each specimen, the primary, secondary, and if needed, tertiary modes of failure were recorded. This system of categorization was considered necessary because there were a number of different kinds of failures observed. As a result, both halfs of the fractured specimens were examined individually. In many cases where the fracture occurred cohesively in porcelain and adhesively, the composite button half of the specimen exhibited fractured off pieces of composite resin. When the porcelain coupon half of the same specimen was examined, no evidence of composite resin remains could be found on the porcelain. It was, therefore, assumed that the composite resin fragmented during shear testing immediately after specimen failure and the mode of failure was considered cohesive porcelain/adhesive.

The raw data of the ranked failure modes can be found in the Appendix (Table 3). Since different kinds of cohesive and mixed failures were observed, for purposes of data analysis, the raw data were transformed into numbers of failures occurring in each group as follows: totally cohesive (cohesive in porcelain or cohesive in porcelain/cohesive in resin), partial cohesive/adhesive (cohesive in porcelain/adhesive or cohesive in porcelain/cohesive in resin/adhesive), and totally adhesive. This transformed data can be found in Table 3. For purposes of discussion, the transformed data were expressed as percentages of each failure mode and can be found in Tables 5 and 6 for pooled silane/aging pretreatments and pooled thermocycled pretreatments, respectively.

Of interest are the following observations on mode of failure for the thermocycled specimens (Table 6). Specimens which were pretreated by either air-abrasion-silicoating or air-abrasion-HF etching failed in a totally cohesive mode 100% of the time. The air-abraded-only specimens did not exhibit any totally adhesive failures and had an approximately equal distribution of cohesive and partial cohesive/adhesive failures, 55% and 45% respectively. The air-abraded-sputter coated specimens experienced all possible modes of failure described above. Only 25% of the air-abraded-sputter coated specimens failed totally cohesively and 75% had some component of adhesive failure, 20% of which failed totally adhesively. The air-abraded-plasma cleaned specimens resulted in 75% totally cohesive failures and 20% partial adhesive failures. The glazed specimens exhibited the highest adhesive failure rate (100%) with the hydrated-only Silicoup™ subgroup having the only specimens exhibiting another mode of failure (6 partially cohesive/adhesive failures), accounting for the remaining 15% of the glazed specimens failures.

In general, other than the hydrated-only Silicoup™ subgroup, there did not seem to be any trends or differences in failure modes between silane and aging protocol subgroups within each major pretreatment category (compare Tables 5, 6, 7 and 8).

2. Scanning Electron Microscopic Examination

Fractured surfaces representative of the different failure modes, as viewed under the scanning electron microscope (SEM), are shown in Plates 10 through 16. Examination of the representative fracture sites under the SEM verified the stereomicroscopic results for those specimens. Total cohesive failure in porcelain is displayed in Plates 10A and 10B. Plates 11A and 11B are representative of mixed cohesive porcelain/cohesive resin failure without evidence of any failure along the bonded interface. Plates 12A, 12B, 13A, 13B, 14A, and 14B are photomicrographs of the same specimen showing evidence of mixed cohesive porcelain/adhesive failure. Even though Plate 12A shows that a portion of composite resin fractured off of the composite button during shear testing, Plate 12B exhibits a cohesive porcelain/adhesive failure mode with respect to the porcelain coupon surface. The failure mode of the bond was therefore considered cohesive porcelain/adhesive. Plates 13A and 13B, demonstrating cohesive porcelain/adhesive failure, are photomicrographs of the same specimen as shown in Plate 12B. Plates 14A and 14B are photomicrographs of the same specimen as shown in Plate 12A. The top of Plate 14A is representative of cohesive porcelain/adhesive failure. The top of plate 14A is the same specimen as shown in Plate 14B, but at higher magnification, which exhibits the zone of interface fracture between the porcelain and composite resin. At this magnification, composite resin can be seen in the porcelain porosities at the fracture zone interface. Plates 15A and 15B are representative of a mixed cohesive porcelain/cohesive resin/adhesive failure mode. The totally adhesive failures, as seen only in the glazed specimens, is shown in Plates 16A and 16B.

Plate 10. Totally Cohesive Failure in Porcelain

A. 16x

Fractured Porcelain Adhering to Composite Resin Button

(Marker = 1 mm)

B. 500x

Cohesive Porcelain Failure

(Marker = .1 mm)

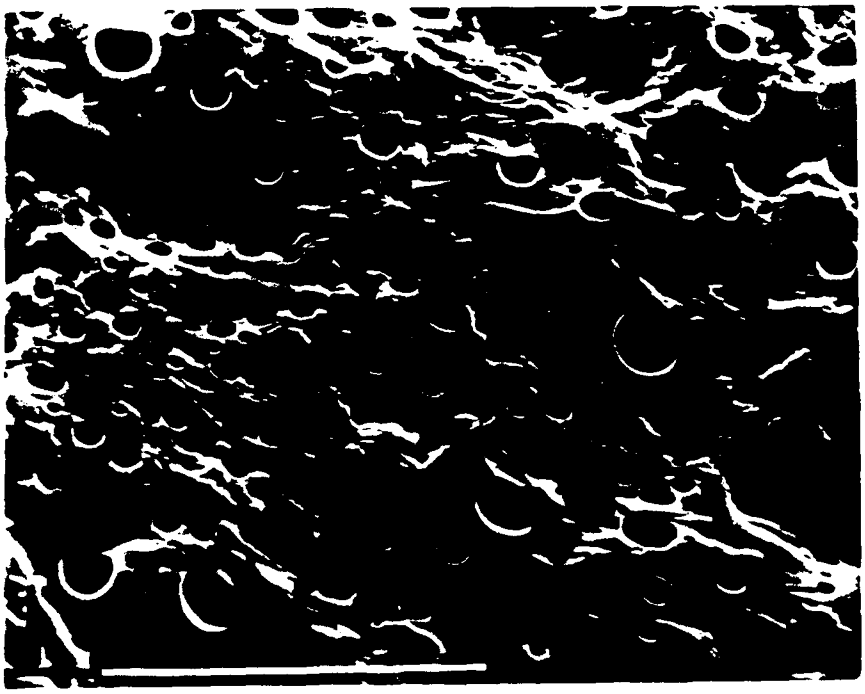


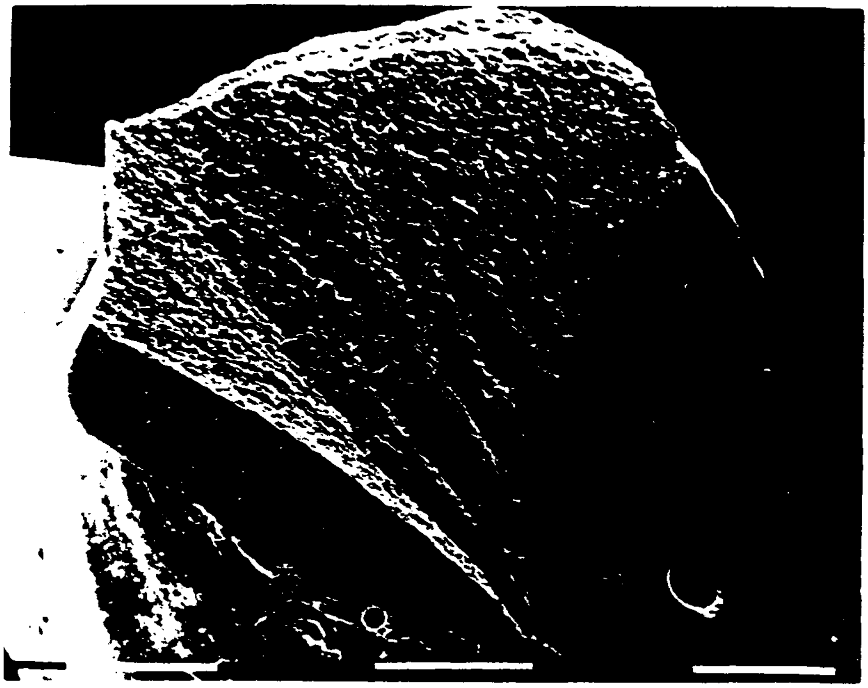
Plate 11. Cohesive Porcelain/Cohesive Resin Failure

A. 20x

Cohesive Porcelain Failure on Left Side of Photomicrograph;
Cohesive Resin Failure on Right Side of Photomicrograph
(Marker = 1 mm)

B. 50x

Cohesive Porcelain Failure on Left Side of Photomicrograph;
Cohesive Resin Failure on Right Side of Photomicrograph
(Marker = 1 mm)



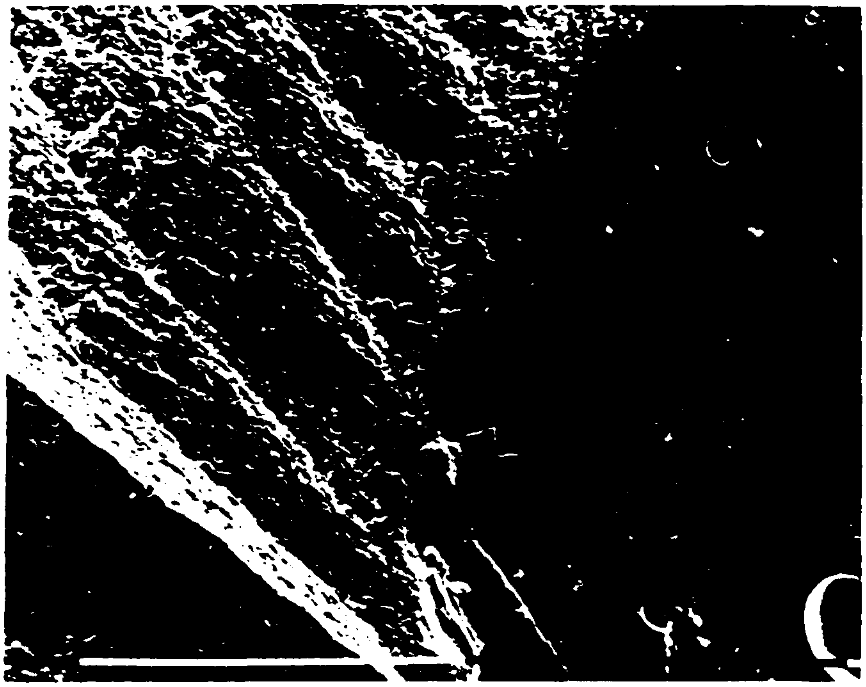


Plate 12. Cohesive Porcelain/Adhesive Failure

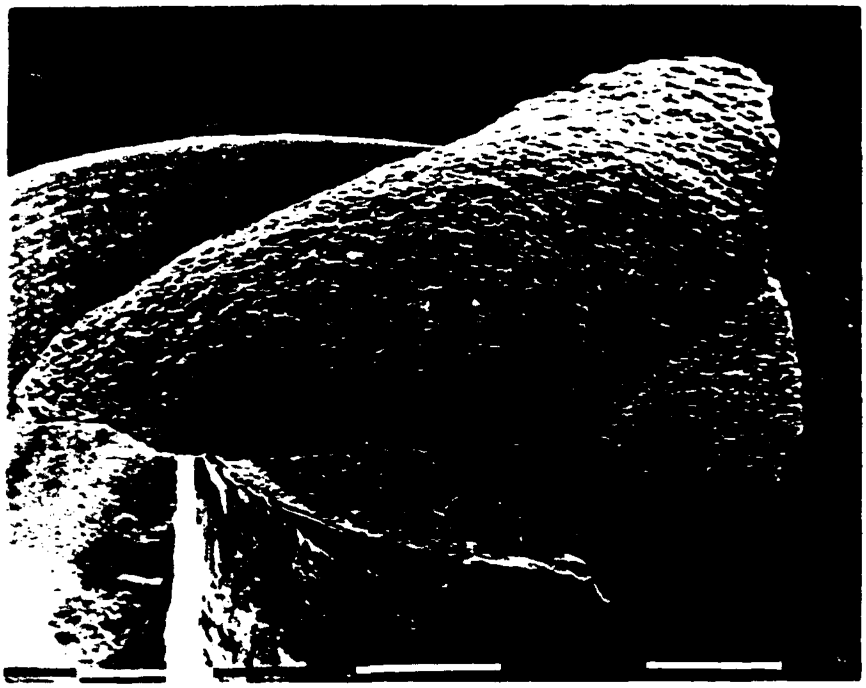
A. 19x

Cohesive porcelain/adhesive failure of composite button away from porcelain coupon. Portion of composite resin fractured cohesively away from composite resin button during shear testing.

(Marker = 1 mm)

B. 10x

Other half of specimen shown in plate 12A above. This shows that failure occurred cohesively in porcelain and adhesively at composite resin-porcelain interface.



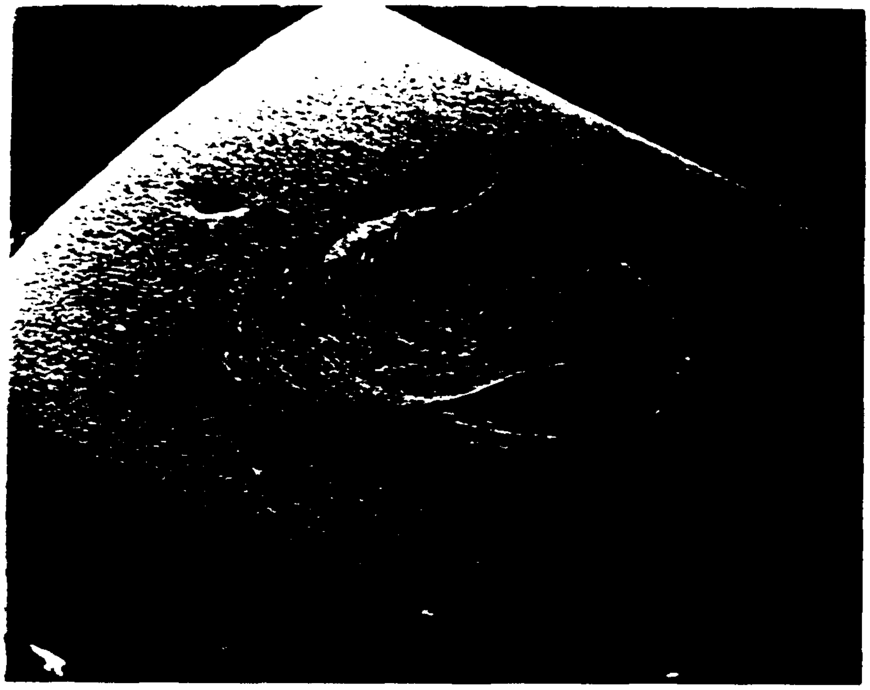


Plate 13. Cohesive Porcelain/Adhesive Failure (Cont.)

A. 30x

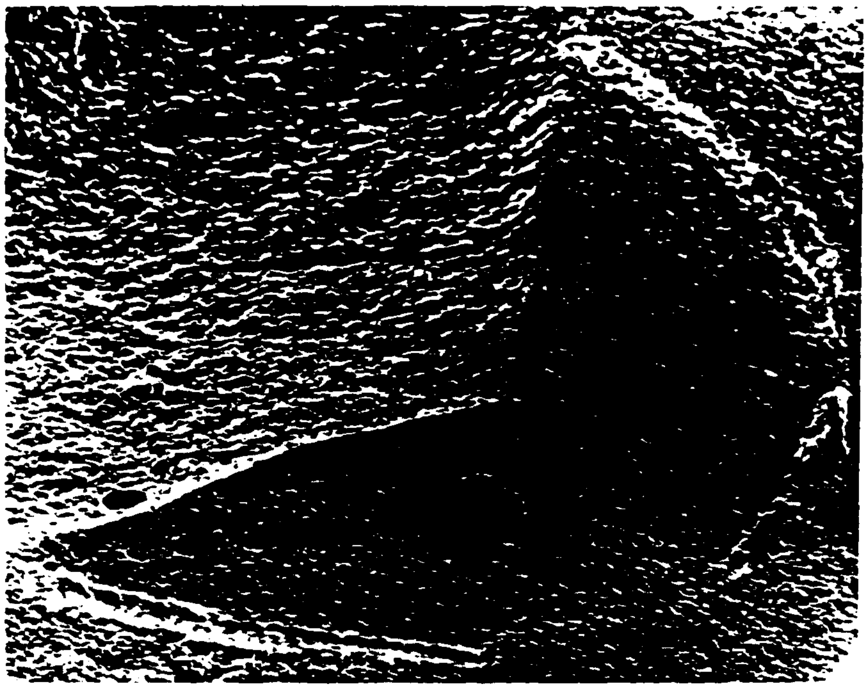
Same specimen as shown in Plate 12B.

Cohesive Porcelain/Adhesive Failure

B. 250x

Same specimen as shown in Plate 12B. Cohesive porcelain failure shown on left side of photomicrograph. Right side of photomicrograph displays porcelain surface from which composite resin fractured adhesively.

(Marker = .1 mm)



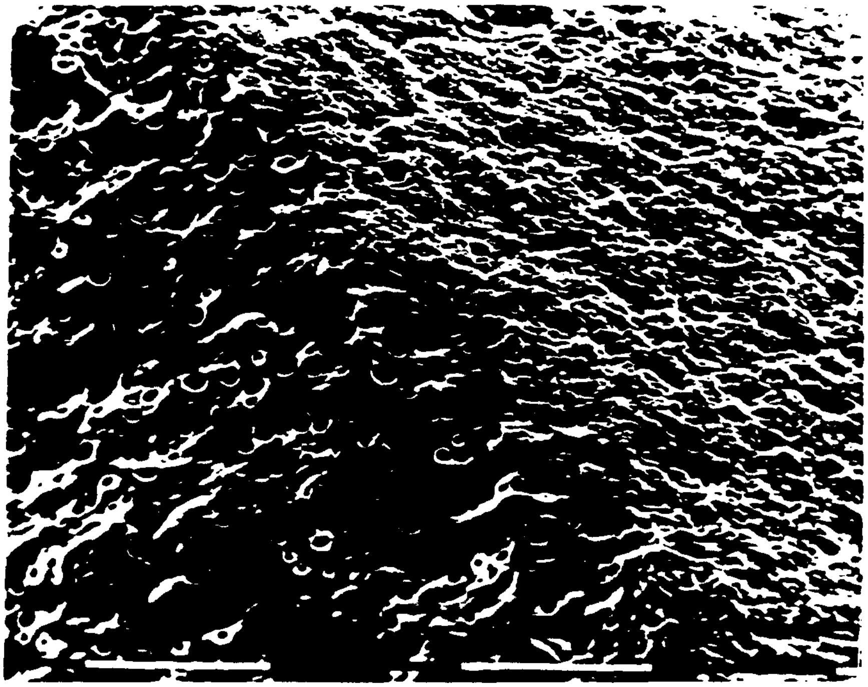


Plate 14. Cohesive Porcelain/Adhesive Failure (Cont.)

A. 140x

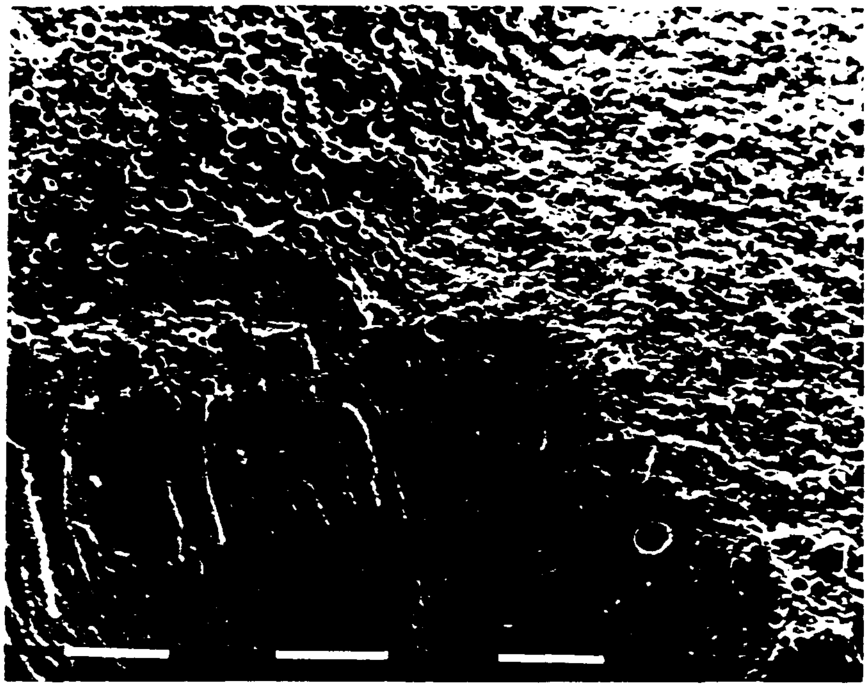
Same specimen as shown in Plate 12A. Top left of photomicrograph shows cohesive porcelain failure. Top right of photomicrograph shows composite resin surface reflecting adhesive failure.

(Marker = .1 mm)

B. 500x

Same specimen as shown in Plate 12A. Left side of photomicrograph shows cohesive porcelain failure. Right side of photomicrograph shows composite resin surface from which porcelain fractured adhesively. The zone of fracture interface can be seen running from bottom left corner of photomicrograph to top right corner. Note the composite resin at the interface which flowed into the porcelain porosity.

(Marker = .1 mm)



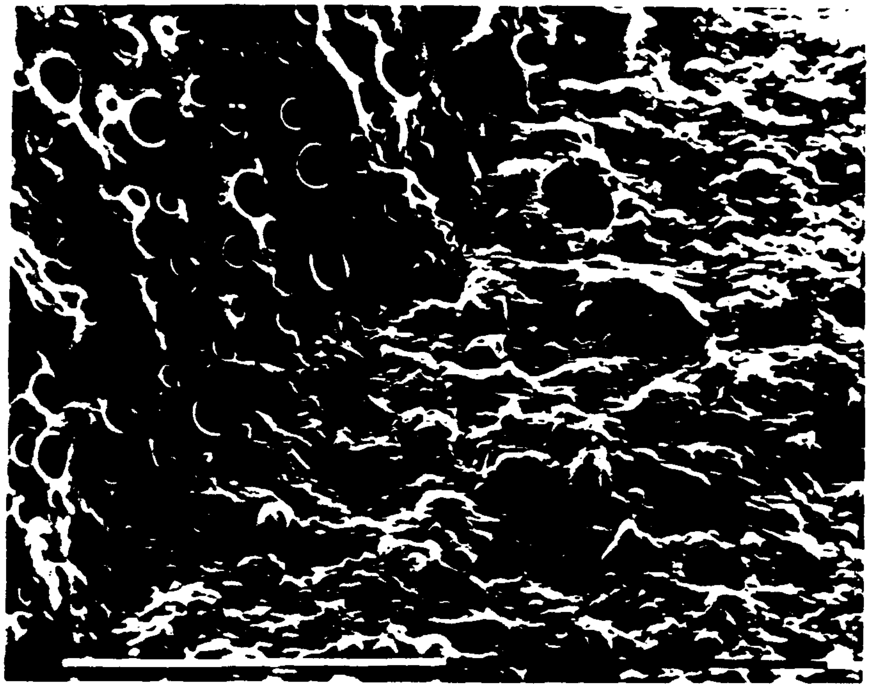


Plate 15. Cohesive Porcelain/Cohesive Resin/Adhesive Failure

A. 18x

Fractured specimen surface from left to right shows cohesive porcelain, adhesive, and cohesive resin failures.

(Marker = 1 mm)

B. 140x

Left side of photomicrograph shows cohesive porcelain failure with adhesive failure above and below it. Right side of photomicrograph shows cohesive resin failure.

(Marker = .1 mm)

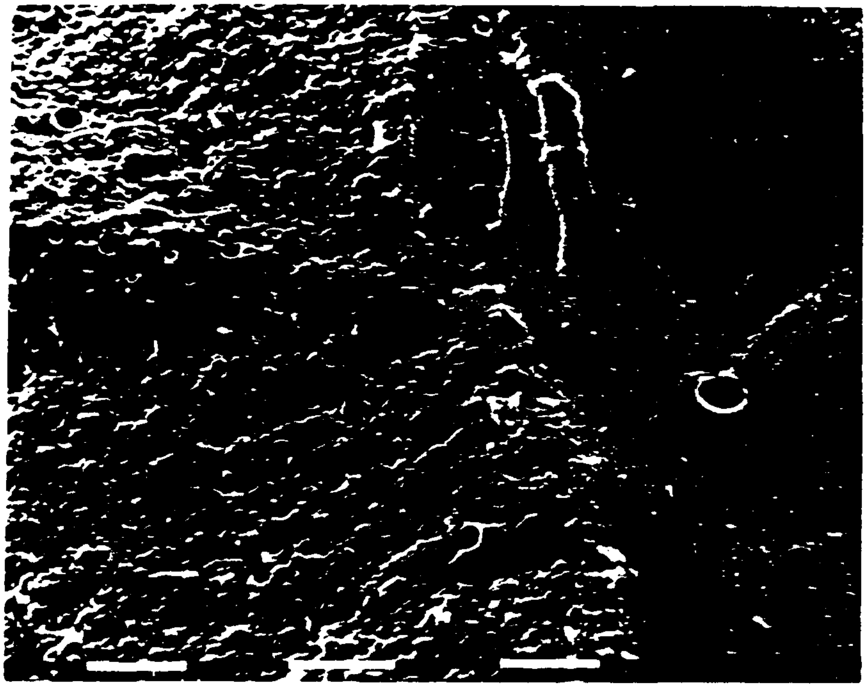


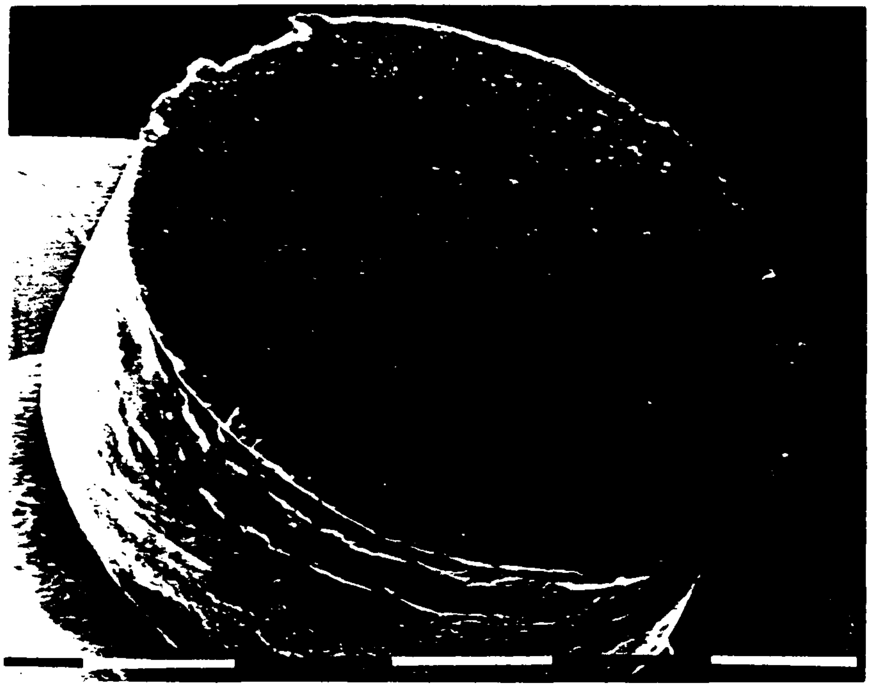
Plate 16. Adhesive Failure (Glazed Specimen)

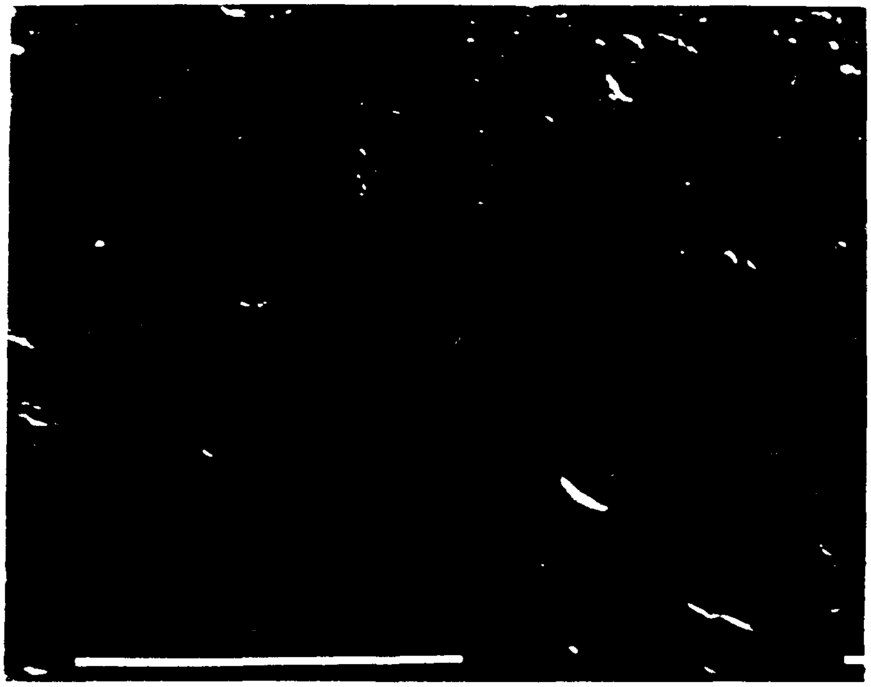
A. 20X

(Marker = 1 mm)

B. 500X

(Marker= .1 mm)





VI. DISCUSSION

The objectives of this study were to compare the effects of six porcelain surface pretreatments, two silanes, and thermocycling on the shear bond strength of composite resin bonded to dental porcelain. In order to accomplish these objectives, it was necessary to perform a pilot and a preliminary study as well as a principal study. The pilot study will be discussed first, followed by discussions on the preliminary and principal studies.

A. Pilot Study

The pilot study was intended to assess overall project feasibility, refine the experimental protocol, and determine sample size for the principal study. The feasibility of this project was particularly important with respect to plasma cleaning and sputter coating porcelain, because apparently these two porcelain surface pretreatments had not been compared previously. A study on the effects of silicoating porcelain had only been reported after the data gathering phase of this investigation. The results of the pilot study indicated that plasma cleaning, sputter coating, and silicoating all produced initial composite resin-porcelain bond strengths comparable to those obtained from hydrofluoric acid etching. This outcome demonstrated that plasma cleaning, sputter coating, and silicoating all had the potential of being viable porcelain surface pretreatments. They were, therefore, tested further in the principal study.

B. Preliminary Study

Upon completion of the pilot study, the preliminary study was begun with the intention to determine the hydrofluoric acid etching time and concentration for the Vita VMK 68™ porcelain used in the principal study. This was accomplished based upon the recommendation of Calamia *et al.* (1985) who concluded that to maximize etched porcelain veneer bond strengths, different etchant concentrations and etching times are needed for different porcelains. Because an optimal HF etchant concentration and etch time for Vita VMK 68™ had not been definitively established, the preliminary study became a prerequisite for the principal study. This was especially important because hydrofluoric acid etching is a common porcelain surface pretreatment used presently which the other porcelain surface pretreatments, investigated in the principal were compared.

The hydrofluoric acid etchant concentration and etch times compared in the preliminary study were based on the findings of Calamia *et al.* (1985). In that study, the hydrofluoric acid concentration was not found to be significant for vita VMK 68™ porcelain while etch time was significant for all etchant concentrations evaluated.. The two etch times used in the Calamia *et al.*, (1985) study were 2.5 and 20 minutes. The hydrofluoric acid etchant concentrations evaluated were 5%, 7.5%, and 10%. The shear bond strengths obtained from the 2.5 min etch were twice as strong as the bond strengths obtained from the 20 min etch for all hydrofluoric acid concentrations evaluated. The authors concluded that longer etching times produced weaker bond strengths. Because only two etch times were included in the Calamia *et al.* (1985) study, it was deemed necessary to compare additional etch times so a definitive hydrofluoric acid etch time and concentration could be used for the principal study. Based on Calamia's conclusion that longer etch times produced weaker bond strengths, 1 min, 2.5 min, and 5 min etch times were evaluated in the preliminary study using 5%, 10%, and 15% hydrofluoric acid concentrations. The results of the preliminary study support Calamia's findings in that hydrofluoric acid etchant concentration was not significant but the length of the time was significant. The 1 minute etching time produced the weakest shear bond strengths while for 5% and 10% HF acid concentrations, there was not a significant difference between the 2.5 and 5 minute etch times. The 2.5 min/10% HF acid etch time and concentration combination was determined to be optimal for two reason. First of all, the 2.5 min etch, being shorter, is more time efficient. Secondly, the 2.5 min/10% HF acid etch time and concentration combination resulted in the highest numerical composite resin-porcelain shear bond strength mean (15.5 MPa).

It is important to note, and should be obvious, that if proper etching times and hydrofluoric acid concentrations are not used, less than optimal bond strengths will result. This was, in fact, demonstrated in the preliminary study. When the air-abraded porcelain was etched for only one minute, significantly lower composite resin-porcelain mean shear bond strengths were produced regardless of the hydrofluoric acid concentration used. This finding coupled with Calamia's conclusion that longer etch times produce weaker bond strengths serves to point out that etching porcelain is analogous to etching enamel. In both cases, too short or too long of an etching period can actually weaken the bond bond of composite resin bonded to porcelain or enamel respectively.

The preliminary study supports findings of other investigators that it is imperative that etching times and etchant concentrations for each type of porcelain used be closely followed (Calamia *et al.*, 1985; Stangel *et al.*, 1987) . Hydrofluoric acid etching, as a porcelain surface pretreatment, is therefore porcelain protocol specific. This factor, coupled with the fact that the use of hydrofluoric acid is a potential hazard, are two reasons why an alternative to hydrofluoric acid etching as a porcelain surface pretreatment was pursued in the principal study the samples were aged for one day in 37° C deionized water. The bond strengths measured were initial hydrated shear bond strengths. The bond strength values, therefore, served as measurements of relative bond strengths for the purpose of selecting an optimal hydrofluoric acid etch time and etchant concentration and should not be used as comparisons to the bond strengths obtained in the principal study from samples hydrated for 3 months.

C. Principal Study

Six porcelain surface pretreatments were evaluated in the principal study. Because silane coupling agents play such important roles in the production of strong composite resin-porcelain bonds, both hydrolized and prehydrolized forms of silane were used and compared as well. In an attempt to help clear up conflicts in the literature on thermocycling's effect on composite resin-porcelain bond strength, hydrated specimens were compared to hydrated/thermocycled specimens.

1. Aging Protocols

To better simulate intraoral conditions, specimens tested in the principal study were hydrated in 37° C deionized water (closed mouth temperature) for 71 days. To determine the effect of thermocycling on composite resin-porcelain shear bond strength, half of the samples were thermocycled 1000 thermocycles on the 71st day between 6 and 60° C with a dwell time of 30 seconds. In addition to simulating oral conditions, hydration and thermocycling were considered especially important in this study because the silane promoted composite resin-porcelain bond is subject to hydrolysis

(Plueddemann, 1982). The hydration time used in the principal study was selected based on the recommendation of Pratt *et al.* (1989) who found that hydration for three months followed by thermocycling gave a better indication of long-term bond strength than did two day hydration followed by thermocycling. Due to the differences in coefficients of thermal expansion between composite resin and porcelain, it is thought that thermocycling accelerates the hydrolysis induced degradation of the composite resin-porcelain bond. Hydration coupled with thermocycling is the aging protocol of choice when evaluating composite resin-porcelain bond strength. (Pleuddemann, 1982; Diaz-Arnold and Aquilino, 1989; Pratt *et al.*, 1989). Therefore, any conclusions drawn from this study, comparing the six porcelain surface pretreatments to each other and the two silanes to each other, were primarily based on the hydrated/thermocycled (thermocycled) mean shear bond strength data and not the hydrated only (nonthermocycled) data.

2. Bonding Resins

An intermediary bonding resin between the silane coupling agent and composite resin was not used. Lee (1973) stated that in order to have good wetting by an adhesive, regardless of adhesion mechanism, certain conditions must exist. One must have a clean surface, a low enough viscosity in the adhesive to allow it to flow in and around surface irregularities, and lastly, a chemical compatibility between the adhesive and adherend so that the molecules of the two substances can come in closer contact. Because the porcelain surfaces bonded to were clean, a low viscosity luting resin was used, and the silane modified porcelain surface was chemically compatible with the composite luting resin, an unfilled intermediary bonding resin between the silane and composite resin was not used in this study. Another reason for not using an unfilled resin was that previous studies have shown that unfilled resins can actually cause a decrease in composite resin-porcelain bond strengths when used with a silane coupler (Diaz-Arnold and Aquilino, 1989; Ross *et al.*, (1990). This was sufficient justification not to include an unfilled resin.

3. Porcelain Surface Pretreatment Comparisons

To reiterate, the six thermocycled porcelain surface pretreatments compared were glazing, air-abrasion only, air-abrasion/sputter coating, air-abrasion/plasma cleaning, air-abrasion/hydrofluoric acid (HF) etching and air-abrasion/silicoating pretreatments. After being oven fired, the glazed only specimens were not given an additional surface pretreatment. The specimens were only cleaned prior to the application of one of the two silane coupling agents. Any bonding between composite resin and porcelain was due principally to chemical bonding provided by the silane coupling agent. In a sense, this group controlled for any treatment effects which might be due to mechanical bonding. The results of this study showed that the bond strengths of the samples pretreated by the other five methods were significantly higher than the bond strengths of the glazed samples. For the thermocycled samples, 100% of the glazed specimens (Table 6) fractured adhesively at the composite resin-porcelain interface. These findings are consistent with those of Newburg and Pameijer (1978).

The air-abraded only group controlled for treatment effects to ensure that any additional mean shear bond strength was due to the pretreatment unique to the sputter coated, plasma cleaned, HF etched, and silicoated specimens. As might be expected, the air-abraded only group had significantly higher mean shear bond strengths than the glazed group (Table 6). These results lend further support to Newburg and Pameijer's (1978) contention that removal of the porcelain glaze is essential for successful composite resin-porcelain bonding. The greater bond strengths can be attributed to the increased surface area for both mechanical and chemical bonding (Sarkar *et al.*, 1984).

The air-abraded-only (10.9 MPa), air-abraded/plasma cleaned (10.7 MPa), and air-abraded/silica sputter coated (11.1 MPa) groups resulted in statistically equivalent mean shear bond strengths (Table 6). It was somewhat surprising that air-abraded/plasma cleaning did not promote better composite resin-porcelain bonding than air-abrasion-alone. Theoretically, plasma cleaning should enhance composite resin-porcelain bonding by increasing the porcelain surface free energy. This is effected by a molecular cleansing of the exposed porcelain surface which results from plasma volatilization of organic residues through chemical reactions with dissociated oxygen and impurity desorption from low energy ion, neutral-particle and/or electron bombardment of the substrate surface (Brown, 1970). An immaculate surface should result in optimal wetting of the porcelain substrate by the silane and consequently better composite resin-porcelain bonding. These results do not challenge this hypothesis, but merely show air-abrasion to be just as effective in achieving the same ends. In an analogous fashion, the air-abrasion exposes a pure and immaculate porcelain surface which for all practical purposes, according to these results, does not get any cleaner. Air-abrasion/silica sputter coating (11.8 MPa) was no more effective in producing high composite resin-porcelain mean shear bond strengths than air-abrasion-alone (11.9 MPa). In retrospect, this outcome was also surprising because air-abrasion/silicoating (14.0 MPa) did produce significantly higher composite resin-porcelain shear bond strengths. One might think that because sputter coating silica is essentially a purer form of silicoating, the results of these two surface pretreatments might be equivalent, but they were not. The silicoating process was more effective than sputter coating. The reason for this result cannot be accounted for by this research. It is interesting to point out that, although stainless steel crowns were used as the substrates, Norling *et al.* (1988) also found that the shear bond strengths of thermocycled substrates bonded to composite resin via silicoating were significantly higher than those produced by sputter coating silica.

When looking at mode of fracture, 75% of the sputter coated specimens had some component of adhesive failure, 20% of which were totally adhesive failure (Table 6). The silicoated specimens, however, exhibited only total cohesive failures. These findings could indicate either ineffective silane coupling to the sputter coated silica or ineffective adhesion of the sputtered silica to the porcelain substrate. Again, due to the limitations of this study, it cannot be said exactly which of these instances, if either, occurred.

The thermocycled air-abrasion/silicoating (13.5 MPa) and air-abrasion/HF etching (13.7 MPa) pretreatments produced the highest composite resin-porcelain mean shear bond strengths which were significantly greater than the mean shear bond strengths resulting from the other four porcelain surface pretreatment groups. Furthermore, there was no significant difference between the shear bond strength of air-abrasion/silicoated (13.5 MPa) and air-abrasion/HF etched (13.7 MPa) specimens. These high mean shear bond strengths obtained from the air-abrasion/HF etched sample groups were anticipated.

Calamia and Simonsen (1984) reported HF etching as producing approximately the same nonthermocycled composite resin-porcelain mean shear bond strength (14.3 MPa) as reported in the present study for nonthermocycled air-abraded/HF etched porcelain (14.6 MPa)(Table 5).

Several past studies have shown that HF etching combined with silane coupling is a porcelain surface treatment combination which consistently produces the highest composite resin-porcelain bond strengths: 14.3 MPa (Calamia and Simonson, 1984); 24.0 MPa (Hsu *et al.*, 1985); 15.1 MPa (Lacy *et al.*, 1988); 29.8 MPa (Sheth *et al.*, 1988); 20.1 MPa (Sorenson *et al.*, 1991). The bonding promoted by HF etching is a product of both mechanical and chemical bonding. HF etching preferentially degrades the silica component of porcelain (Timokhin and Komarova, 1985) thus creating surface microporosities into which the silane and composite resin adhesives can flow. The composite resin becomes mechanically interlocked to the porcelain. Lee (1973) attributed mechanical bonding or mechanical adhesion to geometrical effects and rheological effects. Geometrical effects are characterized by adhesives becoming hooked onto or wedged into the microscopic porosity or roughness of a surface. Rheological effects are characterized by the flow of an adhesive around a mechanical projection in the liquid phase followed by flow of the adhesive in the solid phase due to polymerization and/or cooling shrinkage which causes a mechanical lock on the mechanical projection. Another name for this is a "shrink fit" (Lee, 1983). Chemical bonding or "specific adhesion" (Lee, 1973) of the composite resin to the porcelain is facilitated by silane coupling agents. Silanes are bifunctional organosilane molecules having one end that bonds to the composite resin and the other end that bonds to the dental porcelain (Stangel *et al.*, 1987; Diaz-Arnold, 1989). Etching the porcelain surface improves the silane's effectiveness by increasing the bonding surface area and leaving the porcelain surface in a high energy surface state (Sheth *et al.*, 1988). In short, HF etching and silane act synergistically and result in a strong micromechanical chemical composite resin-porcelain bond.

Overall, air-abrasion/silicoating also produced a strong composite resin-porcelain bond and produced mean shear bond strengths equivalent to bond strengths of air-abrasion/HF etching. Even though the outcomes of these two porcelain surface pretreatments are the same, the adhesive bonding mechanisms are quite different. In fact, the adhesive-porcelain bonded interface is different. In viewing the porcelain-composite resin structure as a laminated system, one can see that silicoated porcelain is a four component system consisting of porcelain, SiOx-C, silane, and composite resin. The HF etched porcelain combination is a three component system comprised of porcelain, silane, and composite resin. This difference, along with variations in the porcelain surface topography, affects both the mechanical and chemical bonding. The mechanical bond resultant from silicoating, unlike etching, does not rely on microscopic porosities for bonding. Silicoating achieves strong mechanical interlocking to porcelain due to an intimate association of the SiOx-C constituents to the air-abraded porcelain surface. According to Musil and Tiller (1984), because the SiOx-C molecules are only 10 to 20 Angstroms in size, they can cover 100% of a roughened substrates' surface to optimize both mechanical and chemical adhesion. One can even speculate that microscopic porosities could reduce shear bond strengths, because Caeg *et al.* (1990) discovered that air-abraded, etched, and silicoated composite resin-metal bond strengths were significantly lower than bond strengths achieved from air-abrasion and silicoating alone. Using SEM, they concluded that silicoating was ineffective in coating the shielded portions of the subsurface microstructures created by the etching process.

The chemical bonding of composite resin to air-abraded/HF etched and air-abraded/silicoated porcelain surfaces differs in terms of the number of silica constituents available for bonding. Since silicoating adds an outer shell of solid silica to the porcelain surface, theoretically 100% of this surface can serve as a substrate for bonding to a silane coupling agent with the end product being composite resin bonded completely across the entire available porcelain surface area. It is safe to conclude that the porcelain surface left after hydrofluoric acid etching has considerably fewer silica molecules available for chemical bonding as compared to the silicoated surface. This is primarily due to the fact that unaltered feldspathic porcelain contains between 57%-68% silica (Phillips, 1982; Jones, 1985; Craig,1989). Once hydrofluoric acid has etched away enough silica to create the needed microporosities for mechanical bonding, the surface silica percentage is reduced even further. The available silica for bonding is, therefore, considerably less in this situation than in the one just described for silicoating. Even so, the bond strengths of the air-abraded/HF etched samples, apparently, were not dependent on chemical bonding but on mechanical bonding. According to many studies (Calamia and Simonsen, 1984; Tjan and Nemetz, 1988; Sorenson *et al.*, 1989; Ross *et al.*, 1990), mechanical bonding is the most important factor for bonding when using etching as a pretreatment.

The findings of this study indicate that although porcelain surface irregularities, caused by air-abrasion, promote mechanical bonding (unless silicoated), these irregularities are significantly less effective in promoting higher bond strengths than the microporosities caused by air-abrasion and etching. This conclusion is based on the fact that air-abrasion-alone produced thermocycled composite resin-porcelain mean shear bond strengths (10.9 MPa) which were significantly lower than the thermocycled mean shear bond strengths produced by air-abrasion followed by HF etching (13.7 MPa)(Table 6).

Previous studies have shown that to get optimal composite resin-porcelain bond strengths from air-abrasion/HF etching, a specific etching protocol must be established (Calamia *et al.*, 1985 and Stangel *et al.*, 1987). This makes HF etching somewhat protocol specific or dependent. In addition, it is necessary to modify the HF etching protocols to match the type of porcelain used (Kanchanatwewat and Stannard, 1989; Sorenson *et al.*, 1991). This makes HF etching material specific as well. Unlike air-abrasion/HF etching, air-abrasion/silicoating is not material and protocol specific. In fact, air-abrasion/silicoating is not influenced by the type of surface, because silicoating optimizes both mechanical and chemical bonding. Theoretically, silicoating makes use of 100% of both the mechanical and chemical bonding sites. If the porcelain surface is roughened in some fashion, silicoating should work. Certainly, further study in this area is warranted to support or refute this hypothesis.

Fractured specimens which were pretreated by either air-abrasion/silicoating or air-abrasion/HF etching failed in a totally cohesive mode 100% of the time (Table 6). Totally cohesive failures consisted of failures either occurring solely in porcelain or failures occurring in composite resin as well as porcelain. It should be pointed out that when cohesive failures occur, the strength test actually measures the strength of the adhesive or the adherend. The interfacial bond strength is, therefore, maximized when its strength exceeds the strength of either the adhesive of adherend. This was the case for both the air-abraded/HF etched and the air-abraded/silicoated groups. Evidently, the composite resin-dental porcelain bond promoted by air-abrasion/HF etching and air-abrasion/silicoating should result in restorations as strong as the porcelain from which they are made or the resin luting agent they are cemented with. Clinical studies are indicated to investigate this supposition.

Failures in dental porcelain invariably originate from surface microcracks which act as stress concentrators (McLean, 1979). These microcracks are termed Griffith's flaws. There are many reasons why Griffith's flaws arise in a dental porcelain surface, to include grinding, thermal stressing, and abrasion to name a few (McLean, 1979). Once initiated, the crack extension is ensured by the applied stress and the proportionally increased stress-concentration factor of the propagating crack (Southan, 1975). This accounts for the sudden fracture of porcelain under failure loads. In a study by Baez and

Blackman (1988), etched Dicor specimens weakened by etching regained some strength once bonded with a luting resin. They concluded that the strengthening was most likely due to the composite resin sealing and containing the Griffith's flaws. It should be pointed out however that clinically, the enhanced strength would only be of benefit after cementation and complete curing of the luting resin intraorally. Another potential advantage of silicoating over HF etching as a porcelain surface pretreatment is that much of the strengthening effect of the porcelain surface may occur immediately after the silicoating process and before try in of the restoration. This would occur if silicoating filled in the surface microcracks (Griffith's flaws). Because porcelain laminate veneer restorations are very fragile, the majority of their fractures occur during cementation (Horn, 1983b; Jordan, 1985). Silicoating could potentially decrease the number of these fractures occurring during cementation. The design of this study did not include any evaluation of any prestrengthening of air-abraded porcelain, but this may prove to be a fruitful area for future research.

4. Silane Comparisons

Silanes play an important role in composite resin-porcelain bonding by supplying the chemical bonding mechanism which links the composite resin to the porcelain through primary bonding. Silanes can perform this linkage because they are bifunctional molecules having one end (inorganic end) that bonds to the porcelain and an opposite end (organic end) that bonds to the composite resin (Diaz-Arnold *et al.*, 1989). The organic end bonds to composite resin through an alkene polymerization reaction which results in a stable hydrolysis resistant covalent bond. The inorganic end supplies methoxy (OCH_3) groups which first must be hydrolized to form reactive silanol (SiOH) groups which can bond to the silica matrix in the porcelain. The silanols bond to silica by first forming hydrogen bonds with hydroxyl groups on the silica surface and then ultimately condense to siloxane (Si-O-Si) bonds across the silica silane interface (Pleuddeman, 1982). It is this siloxane bond that is subject to hydrolysis which in turn causes a degradation of the composite resin-porcelain bond strength.

The results of the data analysis showed that, overall, Silicoup™ produced higher composite resin-porcelain mean shear bond strengths than Scotchprime™ (Table 7). The silanes were then compared to each other for each aging protocol subgroup. It was interesting to find that for the nonthermocycled subgroup (Table 8), Silicoup™ and Scotchprime™ were not statistically different. However, when the two samples were thermocycled, Silicoup™ promoted significantly higher composite resin-porcelain shear bond strengths than Scotchprime™ did (Table 9). This finding leads one to suspect that under conditions better simulating the oral environment Silicoup™ works better. To determine whether or not the glazed specimens were influencing the final outcome of the overall and aging protocol silane comparisons, the two silanes were compared with the glazed samples excluded from the statistical analysis (Tables 10 and 11). Again, Silicoup™ had higher mean shear bond strengths than Scotchprime™ in the overall and thermocycled sample comparisons. The conclusion which might be drawn from this finding is that overall and under conditions better simulating the oral environment, Silicoup™ is more effective in promoting durable composite resin-porcelain bonding on air-abraded specimens. However, it is not safe to assume this because when comparisons between the silanes were made for each individual thermocycled porcelain surface pretreatment (Table 12), significant differences between the silanes could only be found for the glazed and sputter coated pretreatments. Nonetheless, it should be pointed out that, regardless of surface pretreatment, Silicoup™ promoted higher numerical thermocycled bond strengths than Scotchprime™ (Fig 6). This is especially noteworthy because in general, before thermocycling, the Scotchprime™ bond strengths were numerically similar to Silicoup's™ bond strengths for one pretreatment and greater than Silicoup's™ bond strengths for three pretreatments (Fig 7). Stated in other terms, in relation to before and after thermocycling, there was an inversion in most of the Silicoup™ and Scotchprime™ mean shear bond strengths (compare Fig 6 to Fig 7). This was somewhat surprising because previous studies had shown Scotchprime™ prehydrolized silane to be superior to other non-prehydrolized silanes when both types of silane are tested with thermocycling (Diaz-Arnold and Aquilino, 1989; and Pratt *et al.*, 1989). However, none of the previous studies included Silicoup™ silane. This is the first study to directly compare Silicoup™ silane to Scotchprime™ silane. Furthermore, the finding that Silicoup™ silane was more effective than Scotchprime™ on glazed surfaces was noteworthy. As mentioned previously, the glazed samples were included in this study to specifically control for mechanical bonding, which might otherwise mask the effectiveness of the silanes to chemically bond to dental porcelain. It was apparent that Silicoup™ was more effective than Scotchprime™ at promoting chemical composite resin-porcelain bonding. Culler *et al.* (1986) discovered a strong correlation between the degree of hydrolysis of silane and shear bond strength of composite resin bonded to silane primed porcelain teeth. They reported that the silanes with the highest degree of hydrolysis produced the highest bond strengths. Thus it would appear that Silicoup™ silane produced composite resin-porcelain shear bond strengths that were not significantly different than those produced by Scotchprime™ silane because it was just as well hydrolyzed. Because Scotchprime™ is prehydrolyzed, the manufacturer contends that it is resistant to deterioration and has an extended shelf life. The findings of this research place suspicion on this claim at least when Scotchprime™ is compared to

Silicoup™ silane. This study also shows that further research comparing Silicoup™ to Scotchprime™ is clearly indicated.

The suggestion that Silicoup™ is better than Scotchprime™ at promoting chemical bonding is further supported by the microscopic evaluation of the fracture sites. Of the glazed specimens, the only specimens to fracture cohesively in porcelain were from the nonthermocycled Silicoup™ subgroup (Table 3). Specimens from the nonthermocycled Scotchprime™ subgroup, on the other hand, all fractured 100% adhesively. This differs from findings of Diaz-Arnold *et al.* (1989) who reported cohesive VMK 68™ porcelain fractures for nonthermocycled glazed specimens bonded with Scotchprime™ silane. It should be pointed out that the hydration time used in the Diaz-Arnold study was 1 month as compared to a 3 month hydration period in this study. The extended hydration time could account for differences in results. The longer hydration time provides a greater opportunity for hydrolysis induced degradation of the silane-porcelain bond. Apparently, studies on the effects of varying hydration time on the porcelain surface pretreatments and silanes evaluated are needed.

5. Thermocycling Effects

Overall, thermocycling caused a significant decrease in composite resin-porcelain bond strength (Table 14). This finding was anticipated, because previous studies have shown that when silanes are used in the bonding of composite resin to dental porcelain, they are subject to hydrolysis induced by thermocycling (Newburg and Pameijer, 1978; Nowlin *et al.*, 1981; Thomas *et al.*, 1987; Diaz-Arnold and Aquilino, 1989; and Pratt *et al.*, 1990). What was not expected were the effects thermocycling had on the composite resin-porcelain mean shear bond strength when both silanes were analyzed separately (Tables 15 and 16). Thermocycling caused an overall significant decrease in mean shear bond strengths produced by Scotchprime™ silane but did not have a statistically significant effect on the mean shear bond strengths produced by Silicoup™ silane. In order to compare the silanes for air-abraded surfaces, the effects of thermocycling were reevaluated after eliminating the glazed samples from the analysis. The outcome remained unchanged when the effects of thermocycling were reanalyzed.

In general, the effects of thermocycling seem to correlate well with the results, previously discussed, in the Silane Comparisons results section, showing Silicoup™ as consistently producing higher numerical bond strengths than Scotchprime™ after thermocycling (Fig 6). However, when looking at significant differences, only the mean shear bond strength produced by Scotchprime™ for specimens with the glazed surface pretreatment were statistically lower than those produced by Silicoup™. Significant decreases in bond strengths could not be detected for the other individual Scotchprime™-surface pretreatments. Because thermocycling significantly decreased the mean shear bond strength produced by Scotchprime™ for the glazed surface pretreatments, it may be safely assumed that Scotchprime™'s chemical bond was less resistant to hydrolysis. Conversely, the chemical bond produced by Silicoup™ silane was more resistant to hydrolysis with no significant ill effects from thermocycling. Further evaluation of the relative effects of thermocycling on Scotchprime™ silane versus Silicoup™ silane is warranted.

6. Best Silane-Porcelain Surface Pretreatment Combinations

A discussion of the results of the comparison of the different thermocycled silane-porcelain surface pretreatment combinations in many ways serves to summarize the overall results of this study. When a ranking of the mean shear bond strengths of the different combinations was performed, air-abrasion/HF etching for both silanes and air-abrasion/silicoating for both silanes were the four silane-surface pretreatment combinations resulting in the highest numerical composite resin-porcelain mean shear bond strengths. This reinforces the overall findings that air-abrasion/HF etching and air-abrasion/silicoating are the best and equivalent surface pretreatments.

The overall results showing Silicoup™ silane as being significantly more effective in producing hydrolysis resistant bond strengths is born out in the individual silane-surface pretreatment comparisons as well. As long as Silicoup™ silane was used in combination with a surface pretreatment having a component of air-abrasion, a significant difference between their means could not be found regardless of the surface pretreatment used (Table 21). As long as Silicoup™ silane is used on an air-abraded porcelain surface, no significant differences in bond strengths should result regardless of the porcelain surface pretreatment. This finding has important clinical significance in regards to porcelain repairs intraorally and surface pretreatments extraorally for bonded porcelain restorations.

The current method used for repairing fractured porcelain restorations involves roughening the fractured porcelain with a diamond bur or silicon carbide disk followed by placement of a silane coupling agent and composite resin (Pratt *et al.*, 1989; Diaz Arnold and Aquilino, 1989; Diaz-Arnold *et al.*, 1989). This research shows that intraoral air-abrasion is potentially a better alternative to disking or roughening with a diamond bur as long as Silicoup™ silane is used. Further study is needed comparing these different mechanical methods of pretreating porcelain using Silicoup™ silane as the silane coupling agent.

Clinical investigation of porcelain repair is needed to definitively determine the effectiveness of air-abrasion as a surface pretreatment for porcelain repairs. Again, this research shows that air-abrasion and Silicoup™ silane used together has the potential to work clinically in an oral environment. The resulting thermocycled composite resin-porcelain bond strength (11.4 MPa) was statistically comparable to the strength obtained from HF etching (14.6 MPa) and was resistant to hydrolysis induced by thermocycling. Since HF etching appears to be working clinically as a porcelain surface pretreatment for bonding porcelain laminate veneers (Calamia *et al.*, 1987), perhaps the air-abrasion-Silicoup™ combination could be clinically as effective for porcelain repairs.

Pratt *et al.* (1989) evaluated porcelain repair materials under conditions similar to those in this study. Because of the decreases in composite resin-porcelain shear bond strengths caused by 3 month hydration and thermocycling (500 cycles, 6 to 60° C), they concluded that porcelain repairs should be considered an interim procedure. It should be pointed out that Pratt *et al.*, (1989) roughened the porcelain with a coarse diamond, whereas this study air-abraded the porcelain surface to be bonded. This research suggests that if Silicoup™ silane is used as the coupling agent, porcelain repairs could potentially become more effective. In vivo research is needed to prove or disprove this suggestion.

With respect to bonding porcelain restorations, ideally, composite resin-porcelain bond strengths which match the bond strength of composite resin bonded to enamel are desired. Because a significant difference could not be found in composite resin-porcelain mean shear bond strengths between the porcelain surface pretreatments as long as Silicoup™ silane was used, technically any of these methods could be used. However, based on the results of this study it is recommended that either air-abrasion/HF etching or air-abrasion/silicoating be used as the porcelain surface pretreatment. Preferentially, Silicoup™-air-abrasion/HF etching or Silicoup™-air-abrasion/silicoating could be used because in this study, composite resin-porcelain mean thermocycled shear bond strengths obtained by Silicoup™-air-abrasion/HF etching (14.6 MPa) and Silicoup™-air-abrasion/silicoating (14.0 MPa) (Table 21) were the best silane-surface pretreatment combinations to approach estimated composite resin-enamel bond strengths, 18.9 MPa (Bowen and Cobb, 1983). Additionally, unlike air-abrasion-alone, air-abrasion/plasma cleaning and air-abrasion/sputter coating, air-abrasion/HF etching and air-abrasion/silicoating did not appear to be silane dependent. The air-abrasion/HF etching or air-abrasion/silicoating silane-surface pretreatment combinations are therefore recommended. With respect to the laboratory pretreatment of porcelain restorations, in preparation for cementation, air-abrasion/silicoating should be considered a safe alternative to air-abrasion/HF etching and unlike HF etching, does not appear to be protocol and material specific. Research on the effects of silicoating on different types of porcelain are clearly indicated.

7. Best Silane-Porcelain Surface Pretreatment Combinations for Each Type of Silane

The silane-porcelain surface pretreatment combinations were compared separately for Silicoup™ and Scotchprime™ silanes (Tables 22 and 23 respectively). This seemed apropos since most dental clinicians and laboratory technicians probably keep one type of silane in stock. In addition, because there were significant differences in the two silanes in their ability to promote primarily chemical composite resin-porcelain bonding, a comparison of the six porcelain surface pretreatments for each silane was in order.

The results of the two separate analyses clearly showed that the effectiveness of the air-abrasion-alone, air-abrasion/sputter coating, and air-abrasion/plasma cleaning surface pretreatments in producing high composite resin-porcelain shear bond strengths was dependent on the type of silane used. To lend statistical support to the conclusions drawn from the comparison of all twelve silane-surface pretreatment combinations (discussed previously)(Table 21), it was shown that a significant difference between air-abrasion-alone (11.4 MPa), air-abrasion/sputter coating (12.8 MPa), air-abrasion/plasma cleaning (11.3 MPa), air-abrasion/HF acid etching (14.6 MPa), and air-abrasion/silicoating (14.0 MPa) surface pretreatments could not be found as long as Silicoup™ silane was used (Fig 9). If Scotchprime™ silane was used (Fig 10), air-abrasion-alone (10.4 MPa), air-abrasion/sputter coating (9.5 MPa), and air-abrasion/plasma cleaning (10.1) surface pretreatments produced significantly lower shear bond strengths than those produced by the air-abrasion/HF acid etching (12.9 MPa) and air-abrasion/silicoating (13.1 MPa) surface pretreatments. It could therefore be concluded that if Silicoup™ silane is used, any pretreatment other than glazing could be used for the pretreatment of porcelain restorations. However, for reasons previously discussed, Silicoup™-air-abrasion/HF etching or Silicoup™-air-abrasion/silicoating are recommended. In the same respects, Silicoup™-air-abrasion-alone should be considered for intraoral porcelain repairs.

If Scotchprime™ silane is used, the choice of porcelain surface pretreatment to be used becomes important. For bonding porcelain restorations, of the porcelain surface pretreatments evaluated in this study, Scotchprime™-air-abrasion/HF etching and Scotchprime™-air-abrasion/silicoating are the only two Scotchprime-porcelain surface pretreatments recommended.

In closing the discussion, it should be stressed that all of the conclusions and recommendations concerning the clinical application of the porcelain surface pretreatments and silanes evaluated in this research can not stand alone. Clinical research on effects of porcelain surface pretreatments and silanes on composite resin-porcelain bond strengths is needed.

VII. SUMMARY

This objectives of this investigation were to determine the effects that six porcelain surface pretreatments, two types of silane, and thermocycling had on composite resin-dental porcelain shear bond strength. The study was conducted in three parts; a pilot, preliminary, and principal study. The pilot study examined overall project feasibility, refined experimental protocol, and determined the sample size to be used for the principal study. The preliminary study determined the optimal hydrofluoric acid etch time and etchant concentration that were used in the principal study.

The principal study compared six porcelain surface pretreatments, two silanes, and two specimen aging protocols. The six porcelain surface pretreatments compared were glazing, air-abrasion, air-abrasion/plasma cleaning, air-abrasion/sputter coating silica, air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating. The two types of silanes evaluated were Scotchprime™ prehydrolyzed silane and Silicoup™ nonprehydrolyzed silane. The two aging protocols consisted of hydration for 71 days in 37° C deionized water and hydration for 70 days in 37° C deionized water followed by 1000 thermocycles between 6 and 60° C. Shear bond strengths were quantitatively measured on an Instron™ Universal Testing Machine. Resulting fracture sites were examined under a stereomicroscope to determine mode of failure. Specimens representative of the different failure modes were further examined under a scanning electron microscope.

In comparing the porcelain surface pretreatments and silanes, statistical analyses were performed for nonthermocycled/thermocycled pooled data and thermocycled data. Because thermocycling better simulates the oral environment, conclusions were based on the thermocycled samples. The nonthermocycled data was used to determine the effects of thermocycling.

Based on the results of this study, the following conclusions are offered:

1. The optimal hydrofluoric acid etching time and etchant concentration for the porcelain evaluated in this study, VMK 68™, was a 2.5 minute etch time with a 10% solution of hydrofluoric acid.

2. All of the porcelain surface pretreatments having a component of air-abrasion resulted in significantly higher composite resin-porcelain mean shear bond strengths than those produce by glazing alone, with all of the thermocycled glazed specimens failing totally adhesively. These findings were significant because they demonstrated that removal of the glazed porcelain surface layer is essential for successful composite resin-porcelain bonding.

3. Across both silanes, air-abrasion/hydrofluoric acid (HF) etching and air-abrasion/silicoating produced the statistically highest mean composite resin-porcelain mean shear bond strengths which were not statistically different from each other. Following air-abrasion/HF etching and air-abrasion/silicoating, the next best porcelain surface pretreatments were air-abrasion/sputter coating, air abrasion alone, and air-abrasion/plasma cleaning.

4. All of the thermocycled air-abrasion/HF etched and air-abrasion/silicoated specimens failed totally cohesively in porcelain or in porcelain/resin. This demonstrated

that the composite resin-porcelain bond produced by these two surface pretreatments was stronger than the cohesive strength of the porcelain or the porcelain and resin. It is anticipated that restorations bonded using air-abrasion/hydrofluoric acid etching, and air-abrasion/silicoating might be as strong as the porcelain from which they are made or the composite resin they are cemented with.

5. A majority of the thermocycled air-abraded/plasma cleaned (75%), and air-abraded-alone (55%) specimens failed totally cohesively in porcelain or porcelain/resin. The rest of these specimens failed in a mixed mode.

6. The majority of thermocycled air-abrasion/sputter coated specimens resulted in mixed fractures (55%) with 25% failing cohesively in porcelain or resin and 20% failing adhesively at the composite resin-porcelain interface.

7. There were no significant differences between Silicoup™ and Scotchprime™ silanes in their ability to effect composite resin-porcelain bonding for air-abraded only, air-abraded/plasma cleaned, air-abraded/hydrofluoric acid etched, and air-abraded/silicoated samples. Silicoup™ was significantly more effective for glazed and sputter coated samples. A trend could be seen, in that, regardless of the porcelain surface pretreatment used, Silicoup™ produced higher numerical composite resin-porcelain shear bond strengths than did Scotchprime™ after thermocycling.

8. In general, thermocycling decreased the composite resin-porcelain bond strengths more for the Scotchprime™ samples than for the Silicoup™ samples. Furthermore, prior to thermocycling, for three of the six individual surface pretreatments, Scotchprime™

samples were numerically stronger than Silicoup™ samples. After thermocycling, this trend was reversed with Silicoup™ having higher mean shear bond strength values for four of the six surface pretreatments.

9. Thermocycling did not significantly affect the composite resin-porcelain shear bond strengths produced by both Silicoup™ and Scotchprime™ silanes, except for the Scotchprime-glazed sample. The finding that thermocycling significantly decreased the mean shear bond strength of the Scotchprime™-glazed sample but had no significant affect on the Silicoup™-glazed sample showed that the chemical bond promoted by Silicoup™ was more resistant to hydrolysis and thermocycling than the chemical bond promoted by Scotchprime™.

10. When comparing the different thermocycled silane-porcelain surface pretreatment combinations, Silicoup™-air-abrasion/hydrofluoric acid etching, Silicoup™-air-abrasion/silicoating, Scotchprime™-air-abrasion/silicoating, Scotchprime™-air-abrasion/hydrofluoric acid etching, Silicoup™-air-abrasion/sputter coating, Silicoup™-air-abrasion-alone, and Silicoup™-air-abrasion/plasma cleaning all produced statistically equivalent composite resin-porcelain mean shear bond strengths. As long as Silicoup™ silane was used on a once air-abraded porcelain surface, a significant difference between their means could not be found. Regardless of the type of silane used, air-abrasion/hydrofluoric acid etching and air-abrasion/silicoating produced the highest four numerical thermocycled composite resin-porcelain shear bond strength means.

11. When comparing the silane-porcelain surface pretreatment combinations separately for Silicoup™ and Scotchprime™ silanes, for Silicoup, other than the glazed sample, a

significant difference between the surface pretreatments could not be detected. For the Scotchprime™ sample, the best surface pretreatments were air-abrasion/HF acid etching, and air-abrasion/silicoating which were not significantly different from each other, but produced significantly higher bond strengths than did glazing, air-abrasion-alone, air-abrasion/sputter coating , and air-abrasion/plasma cleaning. Clinically these findings suggest that if Silicoup™ were used as the silane coupling agent, air-abrasion-alone may be as effective as hydrofluoric acid etching when it comes to repairing porcelain restorations clinically. With respect to the laboratory pretreatment of porcelain restorations, in preparation for cementation, air-abrasion/silicoating appears to be just as effective in producing high bond strengths as air-abrasion/hydrofluoric acid etching and both would not be dependent on the type of silane used.

12. Because the use of hydrofluoric acid is fraught with potential medical hazards, the findings of this research suggest that Silicoup™-air-abrasion-alone be considered for repairing defective porcelain restorations intraorally. Extraorally, air-abrasion/silicoating should be considered a safe alternative to air-abrasion/hydrofluoric acid etching and is recommended over air-abrasion-alone, air-abrasion plasma/cleaning, and air-abrasion/sputter coating because it does not appear to be silane dependent.

13. Several follow-up studies from this research are indicated. First, in vitro studies evaluating the various surface pretreatments and silanes used this investigation are needed to define their clinical uses. The effects silicoating itself has on porcelain surface strength needs to be investigated. This would have implications for prestrengthening porcelain restorations prior to cementation. Further research comparing Silicoup™ to Scotchprime™ silane is also warranted. Studies comparing silicoating to other relatively

new porcelain surface pretreatments, such as APF, are needed. The effects silicoating has on bond strength of composite resin bonded to other types of porcelain (such as aluminous porcelains) and other ceramic materials (such as castable ceramics) needs to be determined. Lastly, the effects that the new MD Silicoater system has on composite resin-porcelain bond strength needs to be investigated, because this would be easier to apply to fragile porcelain restorations.

APPENDIX

RAW DATA FOR TEST SPECIMENS

Table I. Raw Data, Pilot Study

PRETREATMENT	NEWTONS	MPa
Air Abraded	345	19.06
Air Abraded	310	17.13
Air Abraded	270	14.92
Air Abraded	350	19.34
Sputter Coated[°]	370	20.44
Sputter Coated	212	11.73
Sputter Coated	254	14.03
Plasma Cleaned	280	15.47
Plasma Cleaned	207	11.44
Plasma Cleaned	395	21.82
Plasma Cleaned	143	7.90
HF[§] Etched	212	11.71
HF Etched	265	14.64
HF Etched	355	19.61
HF Etched	390	21.55
Silicoated	390	21.55
Silicoated	345	19.06
Silicoated	380	20.99
Silicoated	425	23.48

[°] All pretreatments below symbol were preceded by air abrasion using 50 μm aluminum oxide.

[§] Hydrofluoric Acid

TABLE II. RAW DATA, PRELIMINARY STUDY OF ETCH TIME[1], [HF][2]

[HF]	TIME	NEWTONS	MPa	[HF]	TIME	NEWTONS	MPa	[HF]	TIME	NEWTONS	MPa
5	1	190	10.50	5	2.5	216	11.93	5	5	140	7.73
5	1	175	9.67	5	2.5	229	12.65	5	5	203	11.21
5	1	163	9.00	5	2.5	261	14.42	5	5	258	14.25
5	1	342	18.89	5	2.5	328	18.12	5	5	312	17.24
5	1	280	15.47	5	2.5	237	13.09	5	5	298	16.46
5	1	159	8.78	5	2.5	274	15.14	5	5	197	10.88
5	1	135	7.46	5	2.5	243	13.42	5	5	297	16.41
10	1	203	11.21	10	2.5	207	11.44	10	5	293	16.19
10	1	220	12.15	10	2.5	352	19.45	10	5	215	11.88
10	1	198	10.94	10	2.5	318	17.57	10	5	175	9.67
10	1	190	10.50	10	2.5	331	18.29	10	5	250	13.81
10	1	245	13.53	10	2.5	309	17.07	10	5	265	14.64
10	1	175	9.67	10	2.5	147	8.12	10	5	315	17.40
10	1	231	12.76	10	2.5	300	16.57	10	5	294	16.24
15	1	157	8.67	15	2.5	210	11.60	15	5	370	20.44
15	1	200	11.05	15	2.5	171	9.45	15	5	174	9.61
15	1	188	10.39	15	2.5	209	11.55	15	5	282	15.58
15	1	145	8.01	15	2.5	145	8.01	15	5	205	11.33
15	1	169	9.34	15	2.5	225	12.43	15	5	195	10.77
15	1	247	13.65	15	2.5	161	8.89	15	5	205	11.33
15	1	132	7.29	15	2.5	200	11.05	15	5	391	21.60

[1] Hydrofluoric Acid Etch Time in Minutes

[2] Concentration of Hydrofluoric Acid in Weight Percent

TABLE III. RAW DATA, PRINCIPAL STUDY
(Shear Bond Strength and Mode of Failure)

PRETREATMENT	SILANE[1]	AGING[2]	NEWTONS	MPa	CP[3]	CR[4]	A[5]
Glazed	1	1	277	15.30	1[6]	-	2[7]
Glazed	1	1	170	9.39	1	1	2
Glazed	1	1	108	5.97	-	-	1
Glazed	1	1	200	11.05	-	-	1
Glazed	1	1	158	8.73	-	-	1
Glazed	1	1	158	8.73	1	-	2
Glazed	1	1	280	15.47	1	2	3[8]
Glazed	1	1	130	7.18	1	-	2
Glazed	1	1	103	5.69	1	-	2
Glazed	1	1	133	7.35	-	-	1
Air Abraded	1	1	362	20.00	1	2	-
Air Abraded	1	1	240	13.26	1	-	2
Air Abraded	1	1	217	11.99	1	-	2
Air Abraded	1	1	335	18.51	1	-	-
Air Abraded	1	1	216	11.93	2	1	3
Air Abraded	1	1	285	15.75	1	2	-
Air Abraded	1	1	227	12.54	1	-	-
Air Abraded	1	1	322	17.79	1	2	-
Air Abraded	1	1	202	11.16	1	-	2
Air Abraded	1	1	242	13.37	1	2	2
Sputter Coated[9]	1	1	266	14.70	1	-	-
Sputter Coated	1	1	211	11.66	1	-	2
Sputter Coated	1	1	240	13.26	1	-	2
Sputter Coated	1	1	273	15.08	1	-	-
Sputter Coated	1	1	126	6.96	-	-	1
Sputter Coated	1	1	190	10.50	-	-	1
Sputter Coated	1	1	163	9.01	1	-	1
Sputter Coated	1	1	126	6.96	-	-	1
Sputter Coated	1	1	291	16.08	1	-	-
Sputter Coated	1	1	154	8.51	1	-	2
Plasma Cleaned	1	1	310	17.13	1	-	-
Plasma Cleaned	1	1	316	17.46	1	2	-
Plasma Cleaned	1	1	180	9.94	1	-	-
Plasma Cleaned	1	1	253	13.98	1	-	2
Plasma Cleaned	1	1	282	15.58	1	2	-
Plasma Cleaned	1	1	249	13.76	1	-	-
Plasma Cleaned	1	1	200	11.05	1	-	-
Plasma Cleaned	1	1	196	10.83	1	-	-
Plasma Cleaned	1	1	189	10.44	1	-	-

PRETREATMENT	SILANE	AGEING	NEWTONS	MPa	CP	CR	A
Plasma Cleaned	1	1	217	11.99	1	-	-
HF Etched	1	1	287	15.86	1	-	-
HF Etched	1	1	278	15.36	1	-	-
HF Etched	1	1	330	18.23	1	-	-
HF Etched	1	1	248	13.70	1	-	-
HF Etched	1	1	283	15.64	1	-	-
HF Etched	1	1	273	15.08	1	2	-
HF Etched	1	1	252	13.92	1	2	2
HF Etched	1	1	267	14.75	1	-	-
HF Etched	1	1	277	15.30	1	2	-
HF Etched	1	1	250	13.81	1	-	-
Silicoated	1	1	217	11.99	1	-	-
Silicoated	1	1	213	11.77	1	-	-
Silicoated	1	1	229	12.65	1	-	-
Silicoated	1	1	235	12.98	1	-	-
Silicoated	1	1	232	12.82	1	-	2
Silicoated	1	1	275	15.19	1	-	-
Silicoated	1	1	294	16.24	1	1	-
Silicoated	1	1	250	13.81	1	-	-
Silicoated	1	1	282	15.58	1	-	-
Silicoated	1	1	314	17.35	1	-	-
Glazed	2	1	53	2.93	-	-	1
Glazed	2	1	103	5.69	-	-	1
Glazed	2	1	68	3.76	-	-	1
Glazed	2	1	83	4.59	-	-	1
Glazed	2	1	69	3.81	-	-	1
Glazed	2	1	96	5.30	-	-	1
Glazed	2	1	69	3.81	-	-	1
Glazed	2	1	93	5.14	-	-	1
Glazed	2	1	50	2.76	-	-	1
Glazed	2	1	88	4.86	-	-	1
Air Abraded	2	1	188	10.39	1	-	2
Air Abraded	2	1	260	14.36	1	-	-
Air Abraded	2	1	166	9.17	1	-	2
Air Abraded	2	1	146	8.07	1	-	-
Air Abraded	2	1	107	5.91	1	-	2
Air Abraded	2	1	253	13.98	1	2	-
Air Abraded	2	1	195	10.77	1	-	-
Air Abraded	2	1	199	10.99	1	-	2
Air Abraded	2	1	291	16.08	1	2	-
Air Abraded	2	1	235	12.98	1	2	-
Sputter Coated	2	1	148	8.18	-	-	1
Sputter Coated	2	1	284	15.69	1	-	-

PRETREATMENT	SILANE	AGEING	NEWTONS	MPa	CP	CR	A
Sputter Coated	2	1	250	13.81	1	-	-
Sputter Coated	2	1	235	12.98	1	3	2
Sputter Coated	2	1	239	13.20	1	-	2
Sputter Coated	2	1	149	8.23	2	2	1
Sputter Coated	2	1	372	20.55	1	-	-
Sputter Coated	2	1	289	15.97	1	-	2
Sputter Coated	2	1	160	8.84	-	-	1
Sputter Coated	2	1	322	17.79	2	1	-
Plasma Cleaned	2	1	184	10.17	1	-	-
Plasma Cleaned	2	1	198	10.94	1	-	-
Plasma Cleaned	2	1	268	14.81	1	2	-
Plasma Cleaned	2	1	210	11.60	1	-	-
Plasma Cleaned	2	1	233	12.87	1	-	-
Plasma Cleaned	2	1	222	12.27	2	1	3
Plasma Cleaned	2	1	288	15.91	1	-	-
Plasma Cleaned	2	1	319	17.62	1	2	-
Plasma Cleaned	2	1	243	13.43	1	-	-
Plasma Cleaned	2	1	169	9.34	1	-	2
HF Etched	2	1	354	19.56	1	-	-
HF Etched	2	1	271	14.97	1	2	-
HF Etched	2	1	316	17.46	1	-	-
HF Etched	2	1	372	20.55	1	1	-
HF Etched	2	1	279	15.41	1	-	-
HF Etched	2	1	228	12.60	1	2	-
HF Etched	2	1	318	17.57	1	2	-
HF Etched	2	1	220	12.15	1	-	-
HF Etched	2	1	231	12.76	1	2	-
HF Etched	2	1	245	13.54	1	-	-
Silicoated	2	1	227	12.54	1	-	-
Silicoated	2	1	345	19.06	1	-	-
Silicoated	2	1	377	20.83	1	-	-
Silicoated	2	1	303	16.74	1	2	-
Silicoated	2	1	169	9.34	1	-	-
Silicoated	2	1	250	13.81	1	-	-
Silicoated	2	1	305	16.85	1	-	-
Silicoated	2	1	236	13.04	1	-	-
Silicoated	2	1	246	13.59	1	2	-
Silicoated	2	1	205	11.33	1	-	-
Glazed	1	2	72	3.98	-	-	1
Glazed	1	2	61	3.37	-	-	1
Glazed	1	2	173	9.56	-	-	1
Glazed	1	2	174	9.61	-	-	1
Glazed	1	2	76	4.20	-	-	1

PRETREATMENT	SILANE	AGEING	NEWTONS	MPa	CP	CR	A
Glazed	1	2	148	8.18	-	-	1
Glazed	1	2	143	7.90	-	-	1
Glazed	1	2	99	5.47	-	-	1
Glazed	1	2	157	8.67	-	-	1
Glazed	1	2	180	9.94	-	-	1
Air Abraded	1	2	180	9.94	1	-	-
Air Abraded	1	2	159	8.78	1	2	-
Air Abraded	1	2	197	10.88	1	-	-
Air Abraded	1	2	238	13.15	1	-	2
Air Abraded	1	2	195	10.77	1	-	-
Air Abraded	1	2	273	15.08	1	2	-
Air Abraded	1	2	155	8.56	1	-	-
Air Abraded	1	2	150	8.29	1	-	2
Air Abraded	1	2	370	20.44	1	-	-
Air Abraded	1	2	142	7.85	1	-	-
Sputter Coated	1	2	175	9.67	-	-	1
Sputter Coated	1	2	275	15.19	1	2	2
Sputter Coated	1	2	197	10.88	1	-	1
Sputter Coated	1	2	248	13.70	1	-	2
Sputter Coated	1	2	150	8.29	-	-	1
Sputter Coated	1	2	284	15.69	1	-	-
Sputter Coated	1	2	251	13.87	1	1	2
Sputter Coated	1	2	206	11.38	1	-	-
Sputter Coated	1	2	260	14.36	-	-	1
Sputter Coated	1	2	270	14.92	1	-	-
Plasma Cleaned	1	2	216	11.93	1	-	-
Plasma Cleaned	1	2	166	9.17	1	-	-
Plasma Cleaned	1	2	197	10.88	1	2	-
Plasma Cleaned	1	2	257	14.20	1	-	-
Plasma Cleaned	1	2	209	11.55	1	-	
Plasma Cleaned	1	2	241	13.31	1	2	2
Plasma Cleaned	1	2	254	14.03	1	-	-
Plasma Cleaned	1	2	177	9.78	1	-	-
Plasma Cleaned	1	2	147	8.12	1	-	-
Plasma Cleaned	1	2	186	10.28	1	-	2
HF Etched	1	2	146	8.07	1	-	-
HF Etched	1	2	241	13.31	1	-	-
HF Etched	1	2	224	12.38	1	-	2
HF Etched	1	2	423	23.37	1	2	-
HF Etched	1	2	240	13.26	1	-	-
HF Etched	1	2	335	18.51	1	-	-
HF Etched	1	2	242	13.37	1	-	-
HF Etched	1	2	186	10.28	1	-	-

PRETREATMENT	SILANE	AGEING	NEWTONS	MPa	CP	CR	A
HF Etched	1	2	239	13.20	1	-	2
HF Etched	1	2	358	19.78	1	-	-
Silicoated	1	2	255	14.09	1	2	-
Silicoated	1	2	305	16.85	2	1	-
Silicoated	1	2	294	16.24	1	-	-
Silicoated	1	2	172	9.50	1	-	-
Silicoated	1	2	199	10.99	1	-	-
Silicoated	1	2	261	14.42	1	-	-
Silicoated	1	2	234	12.93	1	-	-
Silicoated	1	2	297	16.41	1	-	-
Silicoated	1	2	293	16.19	1	-	-
Silicoated	1	2	223	12.32	1	2	-
Glazed	2	2	28	1.55	-	-	1
Glazed	2	2	36	1.99	-	-	1
Glazed	2	2	64	3.54	-	-	1
Glazed	2	2	35	1.93	-	-	1
Glazed	2	2	25	1.38	-	-	1
Glazed	2	2	58	3.20	-	-	1
Glazed	2	2	80	4.42	-	-	1
Glazed	2	2	53	2.93	-	-	1
Glazed	2	2	56	3.09	-	-	1
Glazed	2	2	69	3.81	-	-	1
Air Abraded	2	2	218	12.04	1	2	-
Air Abraded	2	2	137	7.57	1	-	-
Air Abraded	2	2	175	9.67	1	2	3
Air Abraded	2	2	132	7.29	1	-	2
Air Abraded	2	2	210	11.60	1	-	2
Air Abraded	2	2	175	9.67	1	-	2
Air Abraded	2	2	271	14.97	1	-	-
Air Abraded	2	2	225	12.43	1	1	-
Air Abraded	2	2	192	10.61	1	-	-
Air Abraded	2	2	157	8.67	1	-	2
Sputter Coated	2	2	175	9.67	1	-	-
Sputter Coated	2	2	165	9.12	1	3	2
Sputter Coated	2	2	235	12.98	1	-	2
Sputter Coated	2	2	167	9.23	1	-	2
Sputter Coated	2	2	214	11.82	1	-	2
Sputter Coated	2	2	104	5.75	-	-	1
Sputter Coated	2	2	168	9.28	1	-	2
Sputter Coated	2	2	168	9.28	1	-	2
Sputter Coated	2	2	170	9.39	-	-	1
Sputter Coated	2	2	152	8.40	1	-	2
Plasma Cleaned	2	2	147	8.12	1	-	-

PRETREATMENT	SILANE	AGEING	NEWTONS	MPa	CP	CR	A
Plasma Cleaned	2	2	186	10.28	1	-	-
Plasma Cleaned	2	2	193	10.66	1	-	2
Plasma Cleaned	2	2	170	9.39	1	-	-
Plasma Cleaned	2	2	222	12.27	1	1	-
Plasma Cleaned	2	2	196	10.83	1	-	-
Plasma Cleaned	2	2	144	7.96	1	-	2
Plasma Cleaned	2	2	128	7.07	1	-	-
Plasma Cleaned	2	2	217	11.99	1	-	2
Plasma Cleaned	2	2	222	12.27	1	-	-
HF Etched	2	2	208	11.49	1	-	-
HF Etched	2	2	287	15.86	1	-	-
HF Etched	2	2	200	11.05	1	2	-
HF Etched	2	2	337	18.62	1	-	-
HF Etched	2	2	267	14.75	2	1	-
HF Etched	2	2	149	8.23	1	-	-
HF Etched	2	2	223	12.32	1	-	-
HF Etched	2	2	236	13.04	1	2	-
HF Etched	2	2	165	9.12	1	-	-
HF Etched	2	2	268	14.81	1	-	-
Silicoated	2	2	182	10.06	1	-	-
Silicoated	2	2	220	12.15	1	-	-
Silicoated	2	2	249	13.76	1	-	-
Silicoated	2	2	217	11.99	1	-	-
Silicoated	2	2	192	10.61	1	-	-
Silicoated	2	2	188	10.39	1	-	-
Silicoated	2	2	273	15.08	1	-	-
Silicoated	2	2	375	20.72	1	-	-
Silicoated	2	2	204	11.27	1	-	-
Silicoated	2	2	274	15.14	1	2	-

[1] Silane 1 = Silicoup (Kulzer)
Silane 2 = Scotchprime (3M)

[2] Aging 1 = Storage in 37° deionized water for 71 days.
Aging 2 = Storage in 37° deionized water for 70 days, followed by 1000 thermocycles between 6 and 60° C with a dwell time of 30 sec.

[3] CP = Cohesive failure in porcelain
[4] CR = Cohesive failure in composite resin
[5] A = Adhesive failure at composite resin-porcelain interface
[6] Primary failure mode
[7] Secondary failure mode
[8] Tirtiary failure mode

• Except for "glazed and air abraded" specimens, all surface pretreatments after symbol were preceded by air abrasion using 50 μm aluminum oxide.

LITERATURE CITED

Abassi, J.; Bertolotti, R. L.; Lacy, A. M.; and Watanabe, L. G. (1988): Bond Strengths of Porcelain Repair Monomers, J Dent Res 67:880, Abst No. 886.

Annusavice, K. J.; Shen, C.; Hickey, T.; and Ban, S. (1989): Shear Strength and Fracture Characteristics of Repaired Metal-Ceramic Substrates, J Dent Res 68:271, Abst No. 722.

Arkles, B. (1977): Tailoring Surfaces with Silanes, Chemtech 7: 766-778.

Baez, R.; and Blackman, R. (1988): Glazing Inside Surfaces of Castable Ceramic Crown Segments to Improve Strength, J Dent Res 67:378, Abst No. 2120.

Bailey, J. H. (1989): Porcelain-to-Composite Bond Strengths Using Four Organosilane Materials, J Prosthet Dent 61:174-177.

Barzilay, I.; Myers, M. I.; Cooper, L. B.; and Graser, G. N. (1988): Mechanical and Chemical Retention of Laboratory Cured Composite to Metal Surfaces, J Prosthet Dent 59:131-137.

Beck, D. A.; Janus, C. E.; and Douglas, H. B. (1990): Shear Bond Strength of Composite Resin Porcelain Repair Materials Bonded to Metal and Porcelain, J Prosthet Dent 64:529-533.

Bello, J. A.; Myers, M.; Graser, G.; and Jarvis, R. (1985): Bond Strength and Microleakage of Porcelain Repair Materials, J Prosthet Dent 54:788-791.

Barreto and Bottaro (1982): A Practical Approach to Porcelain Repair Systems, J Prosthet Dent 48: 349-351.

Blanco, L. J. (1988): Comparison of Microleakage of Composite Resin Veneering Systems at the Alloy Interface, Thesis: University of Texas Health Science Center, San Antonio, Texas.

Boenig, H. V. (1982): Plasma Science and Technology, Ithaca, New York: Cornell University Press, pp. 260-288.

Bowen, R. L. (1963): Properties of a Silica-Reinforced Polymer for Dental Restorations, J Amer Dent Assoc 66:57-64.

Bowen, R. L. and Cobb, E. N. (1983): A Method for Bonding to Dentin and Enamel, J Am Dent Assoc 107: 734-736.

Brown, R. (1970): In: Handbook of Thin Film Technology, L.I. Maissel and R. Glang, Co-Ed., McGraw-Hill Book Co., New York, NY.

Brown, T. P.; and Norling, B.K. (1990): Comparison of Three Bonding Systems for Veneering Stainless Steel Crowns, J Dent Res 69:208, Abst No. 799.

Brownd, C. L. (1982): An Investigation of Shear Bond Strengths of Dental Porcelain Repair Systems and Silane Coupling Agents, Thesis: University of Texas Health Science Center, San Antonio, Texas.

Burgar, C. G.; Barghi, N. I.; Nowlin, T. P.; and Norling, B. K. (1980): Evaluation of Three Composite Resin Systems, J Dent Res 59:433, Abst No. 663.

Caeg, C.; Leinfelder, K. F.; Lacefield, W. R.; and Bell, W. (1990): Effectiveness of a Method Used in Bonding Resins to Metal, J Prosthet Dent 64:37-41.

Calamia, J. R. (1983): Etched Porcelain Facial Veneers: A New Treatment Modality Based on Scientific and Clinical Evidence, NYJ Dent 53:255-259.

Calamia, J. R.; and Simonsen, R. J. (1984): Effect of Coupling Agents on Bond Strength of Etched Porcelain, J Dent Res 63:179, Abst No. 79.

Calamia, J. R. (1985): Etched Porcelain Veneers: The Current State of the Art, Quintessence Int 16:5-12.

Calamia, J. R.; Vaidyanathan, J.; Vaidyanathan, T. K.; and Hirsch, S. M. (1985): Shear Bond Strength of Etched Porcelains, J Dent Res 64:296, Abst No. 1096.

Calamia, J. R.; Calamia, S.; Lemler, J.; Hamburg, M.; and Scherer, W. (1987): Clinical Evaluation of Etched Porcelain Laminate Veneers: Results at 6 Months-3 Years, J Dent Res 66:245, Abst No. 1110.

Calamia, J. R. (1987): Rationale for Etched Porcelain Restorations. In: Perspectives in Dental Ceramics, J.D. Preston, Ed., Chicago: Quintessence Publishing Co., Inc., pp. 317-329.

Campbell, D. S. (1970): Mechanical Properties of Thin Films. In: Handbook of Thin Film Technology, L.I. Maissel and R. Glang, Co-Ed., McGraw-Hill Book Co., New York, NY, pp. 12.6-12.35.

Chan, D. C. N.; Jensen, M. E.; Sheth, J.; and Sigler, T. (1987): Shear-bond Strengths of Etched Porcelain Bonded with Resin to Enamel, J Dent Res 66:245, Abst No. 1109.

Copps, D.; Lacy, A.; Curtis, T.; and Carman, J. E. (1984): Effects of Topical Fluorides on Five Low-Fusing Dental Porcelains, J Prosthet Dent 52:340-343.

Craig, R. G. (1989): Polymers and Polymerization. In: Restorative Dental Materials, St. Louis: C.V. Mosby Co., pp. 139-143.

Crim, G. A.; Swartz, M. L.; and Phillips, R. W. (1985): Comparison of Four Thermocycling Techniques, J Prosthet Dent 53:50-53.

Culler, S. R.; Krueger, D. D.; and Joos, R. W. (1986): Investigations of Silane Priming Solutions to Repair Fractured Porcelain Crowns, J Dent Res 65:191, Abst No. 193.

Dahlquist, C. A. (1969): The Significance of Surface Energy in Adhesion. In: Aspects of Adhesion, D.J. Alner, Ed., London: University of London Press Ltd., pp. 183-201.

Dent, R. J. (1979): Repair of Porcelain-Fused-To-Metal Restorations, J Prosthet Dent 41:661-664.

Diaz-Arnold, A. M.; Schneider, R. L.; and Aquilino, S. A. (1989): Porcelain Repairs: An Evaluation of the Shear Strength of Three Porcelain Repair Systems, J Dent Res 66:207, Abst No. 806.

Diaz-Arnold, A. M.; and Aquilino, S. A. (1989): An Evaluation of the Bond Strength of Four Organosilane Materials in Response to Thermal Stress, J Prosthet Dent 62:257-260.

Eames, W. B.; Rogers, L. B.; Feller, P. R.; and Price, W. R. (1977): Bonding Agents for Repairing Porcelain and Gold - An Evaluation, Oper Dent 2:118-124.

Eames, W.; and Rogers, L. (1979): Porcelain Repairs - Retention After One Year, Oper Dent 4:75-77.

Edris, A. A.; Jabr, A. A.; Cooley, R. L.; and Barghi, N. (1990): SEM Evaluation of Etch Patterns by Three Etchants on Three Porcelains, J Prosthet Dent 64:734-739.

Ferrando, J. M.; Graser, G. N.; Tallents, R. H.; and Jarvis, R. H. (1983): Tensile Strength and Microleakage of Porcelain Repair Materials, J Prosthet Dent 50:44-50.

Flood, S. (1988): Hydrofluoric Acid Burns, American Family Physician 37:175-182.

Hansson, O. (1989): The Silicoater Technique for Resin-Bonded Prostheses: Clinical and Laboratory Procedures, Quintessence International 20:85-98.

Harbert G.; and Dudek, R. P. (1985): Ceramic Facings-Refractory Cast Technique. In: Perspectives in Dental Ceramics, Proceedings of the Fourth International Symposium on Ceramics, J. D. Preston, Ed., Chicago: Quintessence Publishing Co., Inc., pp 389-393.

Hero, H.; Ruyter, I. E.; Waarli, M. L.; and Hultquist, G. (1987): Adhesion of Resins to Ag-Pd Alloys by Means of the Silicoating Technique, J Dent Res 66:1380-1385.

Highton, R. M.; Caputo, A. A.; Matyas, J. (1979): Effectiveness of Porcelain Repair Systems, J Prosthet Dent 42:292-294.

Hinson, D. C. (1982): Basics of Plasmas. In: The Book of Basics, 3rd ed., W.H. Class Materials Research Corporation, Orangeburg, NY, Sections 1-1 to 1-5.

Hollahan, J. R.; and Bell, A. T. (1974): Techniques and Applications of Plasma Chemistry, John Wiley and Sons, Inc., p. 327.

Horn, H. H. (1983a): A New Lamination - Porcelain Bonded to Enamel, NY State Dent J 49:401-403.

Horn, H. H. (1983b): Porcelain Laminate Veneers Bonded to Etched Enamel, Dental Clinics of North America 27:671-684.

Horsley, G. M. (1989): The Repairability of Laboratory Cured Composite Resins, Thesis: University of Texas Health Science Center, San Antonio, Texas.

Hsu, C. S.; Stangel, I.; and Nathanson, D. (1985): Shear Bond Strength of Resin to Etched Porcelain, J Dent Res 64:296, Abst No. 1095.

Jenkins, C. B. G. (1981): Coupling Agents: Their Effectiveness and Possible Role in Conservation, J Dent Res 60(B):1081, Abst No. 16.

Jochen, D. G. (1973): Repair of Fractured Porcelain Denture Teeth, J Prosthet Dent 29:228-230.

Jochen, D. G.; and Caputo, A. A. (1977): Composite Resin Repair of Porcelain Denture Teeth, J Prosthet Dent 38:673-679.

Johnson, R. G. (1980): A New Method for Direct Bonding Orthodontic Attachments to Porcelain Teeth Using a Silane Coupling Agent, Am J Orthod 77: 233.

Jones, D. W. (1985): Low Fusing Porcelains. In: Perspectives in Dental Ceramics, Proceedings of the Fourth International Symposium on Ceramics, J.D. Preston, Ed., Chicago: Quintessence Publishing Co., Inc., p. 34.

Jordan, R. E. (1986): Esthetic Composite Bonding-Techniques and Materials, St. Louis: C. V. Mosby Co., p. 126.

Kanchanatawewat, K. and Stannard, J. G. (1989): Bond Strength of Porcelain for Laminate Veneer Restorations, J Dent Res 68:270, Abst No. 713.

Kulzer Product Information: Silicoater, Kulzer, Inc., 10005 Muirlands Blvd., Unit G., Irvine, CA 92718.

Lacy, A. M.; LaLuz, J.; Watanabe, L. G.; and Dellinges, M. (1988): Effect of Porcelain Surface Treatment on the Bond to Composite, J Prosthet Dent 60, 288-291.

Land, C. H. (1903): Porcelain Dental Art, Dental Cosmos XLV:437-441.

Laufer, B. Z.; and Nicholls, J. I. (1987): Time Delay Effects on the Tensile Bond Strength Developed by the Silicoater, Quintessence Dent Technol 11:199-203.

Laufer, B. Z.; Nicholls, J. I.; and Townsend, J. D. (1988): SiOx - C Coating: A Composite-to-Metal Bonding Mechanism, J Prosthet Dent 60:320-327.

Lee, H. (1973): Adhesion of Polymeric Materials to Tooth Structure. In: Dental Adhesive Materials, NIDR Workshop, U.S. Public Health Service Publication, pp. 132-179.

Maissel, L. (1970): Application of Sputtering to the Deposition of Films. In: Handbook of Thin Film Technology, L. J. Maissel and R. Glang, Co-Ed., McGraw-Hill Book Co., New York, NY, pp. 4.1-4.42.

Matsumra, H.; Kawahara, M.; Tanaka, T.; and Atsuta, M. (1989): A New Porcelain Repair System, J Dent Res 68:670, Abst No. 36.

McLaughlin, G. (1984): Porcelain Fused to Tooth - A New Esthetic and Reconstructive Modality, Compend Contin Educ Dent 5:430-435.

McLean, J. W. (1979): The Science and Art of Dental Ceramics, Vol. I: The Nature of Dental Ceramics and Their Clinical Use, Chicago: Quintessence Publishing Co., p. 55.

Moffa, J. P.; Jenkins, W. A.; and Weaver, R. G. (1975): Silane Bonding of Porcelain Denture Teeth to Acrylic Resin Denture Bases, J Prosthet Dent 33: 620-627.

Musil, R.; Petschauer, R.; and Welker, D. (1982): Werkstoffkundlich-vergleichende Untersuchungen an zahnfarbenen Plastensowie am Plast-Metall-Verbund bei unterschiedlicher Polymerisations- und Retentionsart, Stomatol DDR 32: 274-283.

Musil, R.; and Tiller, H-J. (1984): The Adhesion of Dental Resins to Metal Surfaces. The Kulzer Silicoater Technique, Wehreheim FRG: Kulzer & Co., GmBH:18-34.

Myerson, R. L. (1969): Effects of Silane Bonding of Acrylic Resins to Porcelain on Porcelain Structure, J Amer Dent Assoc 78: 113-119.

Naegeli, D. G.; Duke, E. S.; Schwartz, R.; and Norling, B. K. (1988): Adhesive Bonding of Composite to a Casting Alloy, J Prosthet Dent 60: 279-283.

Nathanson, D. (1988): Dental Porcelain Technology. In Porcelain Laminate Veneers, D. A. Garber, Ed., Chicago: Quintessence Publishing Co., Inc., p 25.

Nayyar, A.; Wenner, K.; and Kincaid, J. (1985): Bond Strength of Four Porcelain Repair Systems, J Dent Res 64:296, Abst No. 1094.

Nelson, E.; and Barghi, N. (1989): Effect of APF Etching Time on Resin Bonded Porcelain, J Dent Res 68, Abst No. 716.

Newburg, R.; and Pameijer, C. H. (1978): Composite Resins Bonded to Porcelain with Silane Solution, J Amer Dent Assoc 96:288-291.

Nicholls, J. I. (1988): Tensile Bond of Resin Cements to Porcelain Veneers, J Prosthet Dent 60:443-447.

Norling, B. K.; and Bugg, J. L. (1980): Bonding Composite Resins to Stainless Steel Substrates, J Dent Res 59:425, Abst No. 631.

Norling, B. K.; Murrey, A. J.; and Dal Santo, F. B. (1988): Comparison of Bonding Methods for Veneering Stainless Steel Crowns, J Dent Res 67:224, Abst No. 888.

Norris, R. A.; Norling, B. K.; and McCourt, J. W. (1990): Bond Strengths of Mesh Backed vs. Silica Coated Orthodontic Brackets, J Dent Res 69:209, Abst No. 802.

Nowlin, T. P.; Barghi, N.; and Norling, B. K. (1981): Evaluation of the Bonding of Three Porcelain Repair Systems, J Prosthet Dent 46:516-518.

O'Kray, K.; Suchak, A. J.; and Stanford, J. W. (1987): Shear Strength of Porcelain Repair Materials, J Dent Res 66:207, Abst No. 805.

Paffenbarger, G. C.; Sweeney, W. T.; and Bowen, R. L. (1967): Bonding Porcelain Teeth to Acrylic Resin Denture Bases, J Amer Dent Assoc 74:1018-1023.

Pleuddemann, E. P. (1982): Silane Coupling Agents, New York: Plenum Press, pp. 16-121.

Phillips, R.W. (1982): Skinners Science of Dental Materials, 8th Ed., Philadelphia: W.B. Saunders Co., pp. 502-504.

Pratt, R. C.; Burgess, J. O.; Schwartz, R. S.; and Smith, J. H. (1989): Evaluation of Bond Strength of Six Porcelain Repair Systems, J Prosthet Dent 62:11-13.

Reagan, S.; Brackett, W.; DePrater, W.; and Duncanson, M. (1990): An Evaluation of the Effects of Two Porcelains, Two Etchants and Two Luting Agents on Shear Bond Strength, J Dent Res 69:363, Abst No. 2040.

Ross, J. A.; Gilpatrick, R. O.; and McBride, M.A. (1990): Comparison of Porcelain to Enamel Luting Methods Using G-Cera, J Dent Res 69:209, Abst No. 805.

Sarkar, N. W.; Rawls, R. H.; Ledoux, P. M. (1984): Surface Phenomena. In: Dental Materials Science, Syllabus, LSU Dental School, pp. 43-59.

Saunders, W. P.; and Adamson, M. (1988): The Influence of Surface Treatment Upon the Retention of Porcelain Veneers, J Dent Res 67:661, Abst No. 170.

Semmelman, J. D.; and Kulp, P. R. (1968): Silane Bonding Porcelain Teeth to Acrylic, J Amer Dent Assoc 76:69-73.

Sheth, J.; Jensen, M.; and Tolliver, D. (1988): Effect of Surface Treatment on Etched Porcelain Bond Strength to Enamel, Dental Materials 4:328-337.

Simonsen, R. J.; and Calamia, J. R. (1983): Tensile Bond Strength of Etched Porcelain, J Dent Res 62:297, Abst No. 1154.

Solomans, T. W. G. (1976): Functional Groups and Families of Organic Compounds: The Major Reaction Types. In: Organic Chemistry, New York: John Wiley and Sons, Inc., pp. 60-61.

Sorenson, J. A.; Engelman, M. J.; Torres, T. J.; and Avera, S. A. (1991): Shear Bond Strength of Composite Resin to Porcelain Surface Treatments, Int J Proshodont 4: 17-23.

Southan, D. E. (1975): Dental Porcelain. In: Scientific Aspects of Dental Materials, J. A. von Fraunhofer, Ed., Boston: Butterworth, pp 298-305.

Sposetti, V.; Shen, C.; and Levin, A. (1986): The Effect of Topical Fluoride Application on Porcelain Restorations, J Prosthet Dent 55:677-682.

Stangel, I.; Nathanson, D.; and Hsu, C. S. (1987): Shear Strength of the Composite Bond to Etched Porcelain, J Dent Res 66:1460-1465.

Stannard, J. G.; and Kanchanatawewat, K. (1990): SiOx C-Coating of Porcelain for Enhanced Bond Strength, J Dent Res 69:209, Abst No. 804.

Sterman, S.; and Marsden, J.G. (1963): Silane Coupling Agents as Integral Blends in Resin-Filler Systems, Mod Plast 39:135.
Stuart, R. V. (1983): Vacuum Technology, Thin Films, and Sputtering: An Introduction, Academic Press, New York, NY, p. 87-96.

Thomas, C. A.; Hartsock, T. E.; Dossett, J.; and Mitchell, R. J. (1987): Thermocycling, Silanization, and Tensile Bond Strength of Resin to Porcelain, J Dent Res 66:207, Abst No. 808.

Thomas, C. A.; Hartsock, T. E.; Richards, N. D.; and Mitchell, R. J. (1988): Effects of Silanization Treatments on Resin-Porcelain Bond Strength, J Dent Res 67:880, Abst No. 882.

Timokhiv, A. R.; and Komarova, C. A. (1985): Chemical Reaction of Ammonium Bifluoride with Quartz Glass, Glass and Ceramics 42:267-269.

Tjan, A. H.; and Nemetz, H. (1988): A Comparison of the Shear Bond Strength Between Two Composite Resins and Two Etched Ceramic Materials, Int J Prosthodont 1:73-79.

Tomasovic, B. A.; and Glace, W. R. (1989): Testing of New Low-Flouride In Vivo Porcelain Etchant, J Dent Res 68:892, Abst No. 202.

Vanderbilt, B. M.; and Simko, J. P. (1960): Silane Coupling Agents in Glass Reinforced Plastics, Mod Plastics 38:135.

Watanabe, L. G.; Lacy, A. M.; and Davis, D. R. (1988): Shear Bond Strength, Single Plane vs. Conventional Lap Shear, J Dent Res 67: 383, Abst No. 2159.

Wehner, G. K.; and Anderson, G. S. (1970): The Nature of Physical Sputtering. In: Handbook of Thin Film Technology, L. I. Maissel and R. Glang, Co-Ed., McGraw-Hill Book Co., New York, NY, pp. 3.1-3.9.

Wunderlich, R. C.; and Yaman, P. (1986): In Vitro Effect of Topical Fluoride on Dental Porcelain, J Prosthet Dent 55:385-388.