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Preparation and testing of novel blocked isocyanate dental adhesives based upon hydroxyhexylmethacrylate

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ABSTRACT

Title of Thesis: Preparation and Testing of Novel Blocked Isocyanate Dental Adhesives Based upon Hydroxyhexylmethacrylates.

Yunwen Ye, Master of Science in Chemical Engineering, NJIT, 1989.

Thesis directed by: Professor David Kristol &
Doctor James Stackhouse Jr.

A new kind of dental adhesive, O-Chlorophenol-TDI-HEMA-Pentaerythritol (TDI), was studied under long term conditions. The test was done in human third molar teeth which had been extracted 7 days to 6 months. Both citric acid and non citric acid pre-treatments were used on dentin surfaces. Based on Causton's[9] mineralizing solution pre-treatment method, we have used 3 kinds of mineralizing solutions, ITS, 0.5% $CaCl_2$, NaF, as pre-treatment solutions. There were no significant differences between the citric acid and non citric acid pre-treatment. The ITS mineralizing solution pre-treatment caused a large increase in bond strength. The average bond strength of 1791 psi after 24 hrs in 0.9% saline solution fell to 625 psi after 6 month in the saline solution. When compared with five commercial dentin bonding agents under the same conditions, the TDI produced the highest bond strengths.

PREPARATION AND TESTING OF NOVEL BLOCKED ISOCYANATE DENTAL ADHESIVES BASED UPON HYDROXYHEXYLMETHACRYLATE

By

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Thesis submitted to the Faculty of the Graduate School of
The New Jersey Institute of Technology in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering.

1989

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I. Introduction.

Currently-used dental restorative materials generally do not adhere to dentin,[2] so some type of intervening adhesive must be used.

Adhesion between dentin and composite restorations has two potential benefits. First, marginal leakage may be reduced, and second, if sufficient bond strength could be achieved, the need to cut retentive cavities would cease. In both cases, the loss of healthy tooth substance would be expected[3].

A successful dental adhesive should satisfy the following requirements: (1) should be easy to munipulate; (2) its bond strength should be equivalent to that of the surrounding dentin tissues; (3) it should attach itself to a wet dentin surface at approximately body temperature; (4) it must be non-toxic of toxicity; and (5) should maintain long term high bond strength.

Dentin is a wet, heterogeneous, highly permeable, very complex living tissue. It is a composite of inorganic crystals and organic matrix containing 60% hydroxyapatite, 20% organic matter ,and 20% water by weight[4,5]. Organic matter called collagen[6,7] is a triply

stranded protein molecule which contains a large number of polar groups with active hydrogen such as -NH_2, -OH, -COOH. These highly polar groups make it possible for one or more reactions with the intermediates as well. This thesis deals with the novel method of bonding via the use of blocked isocynates with most attention on o-Chlorophenol-TDI-HEMA-Pentaerythritol(TDI). Dentin pre-treatment or no pre-treatment with citric acid or other materials has been a subject of controversy with reports for and against pre-treatment. This research was done to test the efficiency of TDI as a long term bonding agent when using several dentin pre-treatments

Adhesive bonding to dentin is accomplished by the following sequence of events: (1) a liquid adhesive, (2) intimately bonding surfaces, (3) formation of a strong solid, and (4) attraction to dentin surface.

According to the molecular theory[8], adhesion is a result of intermolecular forces, and the bond strength depends on where it is created. The creation of a strong bond between dental materials and hard tooth tissues as a result of van der Waals forces is very difficult. This is due to the presence of water, the shrinkage of materials, and internal forces. The stability of the bond may be markedly increased, however, by acid conditioning of the enamel. This is explained by "tag" formation[9]. This bond was explained using McBain's mechanical theory, which is applicable to rough and porous materials.

The well-known reactions of organic isocyanates with active

hydrogen compounds[1][10], and the potential availability of a large number of such active hydrogen sites in collagen suggested the synthesis of monomers with isocyanate groups as potential adhesion promoting agents for collagenous substrates.

One anticipated problem in this study was the presence of the smear layer, which forms on the surface of dentin[11] or enamel[12] when they have been cut or mechanically disturbed.

Other problems which affect bonding are uncut dentin and cementum surfaces that have been uncovered by gingival recession or afflicted by cervical erosion, abrasion, or decalcification. These have a microscopic covering of a salivary pellicle[13]. Such influences reduce or prevent durable adhesive bond. Hydrated organic films (e.g., salivary pelivary pellicle) and surface layers that have been mechanically disturbed (smear layers) must be removed, or transformated into a surface layer with adequate mechanical tenacity and suitable chemical characteristics. The smear layer can be removed by acidic solution, but a strong acidic solution is clearly an undesirable material to dentin in a clinical setting since the acid may etch through the tubules of dentin and kill the pulp. As mentioned by Causton[1,14], application of certain kinds of mineralizing solutions to acid-treated dentin surface before adhesive application may form crystals which would block the open tubules and pretect the pulp. In addition, such solutions would prevent degradation of the adhesive from attacks by water from the pulp. The mineralizing solutions suggested by Causton are 1M $CaCl_2$, 1%NaF, and ITS[14] solution.

It is very difficult to find the efficiency of a dentin bonding agent, One way to do that is to use a Scanning Electron Micrographs machine (SEM) to study the interface between adhesive and dentin.

The focus of this thesis was on the utilization of acidic solutions, dimethoxy ethane (DME), mineralizing solution pre-treatments, long-term post-treatment, a comparison of our dental adhesive with five other most commonly-used commercial dentin bonding agents and, interface study between our adhesive and dentin by SEM.

II. MATERIAL AND METHOD.

A. BLOCKED ISOCYANATES IN DENTIN BONDING.

The fact that dentin consists of 20% organic matter and 20% water by weight has encouraged many investigators to search for a suitable bonding agent. The highly polars -COOH, -OH, $-NH_2$ present in dentin are also extremely useful in the search for a suitable bonding agent. Isocyanates are known to react effectively with these given polar groups. The collagen content which is the home of active H^+ sites make more available sites for the isocyanates to react. Our work concentrated on making use of these available polar groups, because isocyanates make bonding easier to occur, although in the oral environment they are reactive towards water. The hydrolysis of isocyanates takes place in two stages:

$RNCO + H_2O$ ------> $RNHCO_2H$

$RNHCO_2H$ ------> $RNH_2 + CO_2$

Dependind on the conditions, there can also be some

reaction of the product amine with the reactant:

$$RNCO + RNH_2 \text{ ------> } RNHCONHR$$

The end product is urea.

The most common reaction of isocyanates is the one involving the active H^+ sites:

$$RNCO + HX \text{ ------> } RN{=}C{-}X \text{ ------> } RNHCOX$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

This reaction proceeds at room temperature in the absence of catalysts[15].

Compounds containing active H^+ atoms attached to oxygen also react with isocyanates:

$$RNCO + R'OH \text{ ------> } RNHCOOR'$$

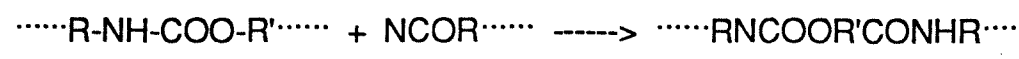
This end product is a carbanate.

With a carboxylic acid group an amide is produced:

$$RNCO + HOOC{-}R' \text{ ------> } RNHCOOR' + CO_2$$

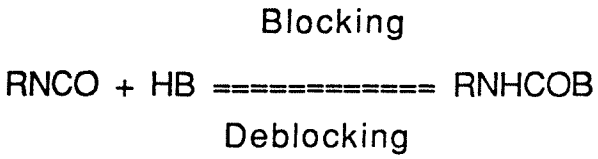
The advantage of choosing a diisocyanate is associated with the fact that the polyureas, and to a lesser extent

polyamides and polyurethanes form cross-linked chains because the -CONH groups in the polymer chain react futher with the isocyanate groups:



B. BLOCKED ISOCYANATES.

Polyureas react with the free isocyanates to form an equilibrium mixture. The concept of "blocking" and "deblocking" could be attributed to this: A blocked isocyanate can be described as one which has the capability to be stable at room temperature by virtue of its having already undergone a reaction with a substance which inhibits its further reaction with traditional groups such as $-NH_2$, -COOH, and -OH. The exception to this is that it is not valid at higher temperature. The reaction could be depited as:



The donor molecule could be either of amine, phenol, or an

alcohol. Hence the extent of blocking or deblocking is coupled with the choice of the donor molecule. If BH represents an amine or alcohol deblocking at room temperature ranges from about 0 to 5% or less, whereas when BH represents a phenol, there is produced a higher percentage of deblocking. Since dentin consists of a number of reactive groups with an active H^+, the blocking agent could be released chemically via a "blocked" polymer an example being HOR':

RNHCOOR' ------> RNCO + HOR'

RNCO + NH_2--Dentin ------> RNHCONH--Dentin

Hence the choice of the blocking agent alters the extent to which the reaction goes to completion; in other words the efficiency of the reaction is affected by this choice. The choice of eugenol, o-methoxyphenol, p-cresol, and o-chlorophenol, in our studies could be attributed to the sustained efforts of the previous investigators of this thesis[16,17,18]. The investigators of this research advocated the use of toluene diisocyanate (TDI) because aromatic isocyanates deblock more readily than aliphatic isocyanates. The TDI is reacted with a space group, hydroxy-ethyl-methacrylate (HEMA). Previous investigations on HEMA had yielded the best bond strengths for o-chlorophenol[17]. Since there is no universal test method for

dentin tensile strength, it is difficult to make a comparason of our adhesive material with other dentin bonding agents, so we have to use our test method to test 5 other most common used dentin bonding commercial products such as Gluma, Scotch Bond, Vivident, Prisma, and J&J dentin bonding agent, then compare with our novel dentin bonding material, O-Chlorophenol-TDI-HEMA- Petaerythritol.

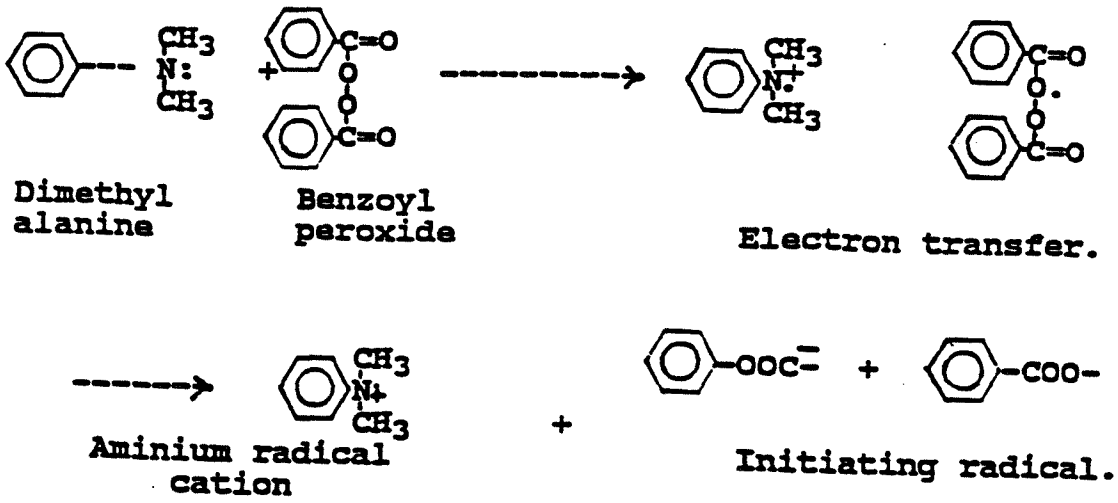
Chemical bonding to dentin alone would not suffice since bonding to a filling material also has to be taken care of. The process through which this is accomplished is best visualised via vinyl radical polymerization. The interface of the adhesive material layer is a copolymer, and the restorative material itself is a homopolymer. The homopolymerization and copolymerization reactions could best be explained incorporating the initiation and accelaration mechanisms as described in the succeeding paragraphs.

1. Initiation.

Peroxides and aliphatic azocompounds are well known initiators in radical polymerisation. The decomposition of peroxides was stated by Hey and waters[19] to be ofthe type:

R-COOOOC-R' ------> R-COO- + R'-COO-

in which either or both of the radicals produced may loose CO_2 to yield the corresponding alkyl or aromatic free radical. Usually this decomposition involves a higher order of complexity. The mechanism could be depicted as follows[20]:



This involves a one-electron transfer mechanism. The amine transfers one of its unshared electrons to the peroxide, thereby activating its decomposition to the initiating radical and the aminium radical cation, which could undergo a series of complex secondary reactions. Benzoyl peroxide is a good initiator due to the fact that it has the least ten-hour half-life temperature of 73°C compared to 87°C of t-butyl-peroxymaleic acid, 105°C of t-butyl perbenzoate, etc. This was extensively studied by Antonucci et.al.[20] and inference could be drawn that benzoyl peroxide is widely used as an initiator because it decomposes at relatively low temperatures to release free radicals.

The free radical homopolymerization reaction is initiated

in the presence of benzoyl peroxide when the initiator decomposes into free radical. When a monomer unit is added, a chain radical is formed (e.g., MMA monomer). Since the restorative material as described (vide infra) in 'Polymerization reactions' is a bifunctional monomer of PMMA-$(MMA)_r$, a chain reaction is initiated. This reaction terminates when an alkane or an alkene reacts with it.

2. Polymerization reaction.

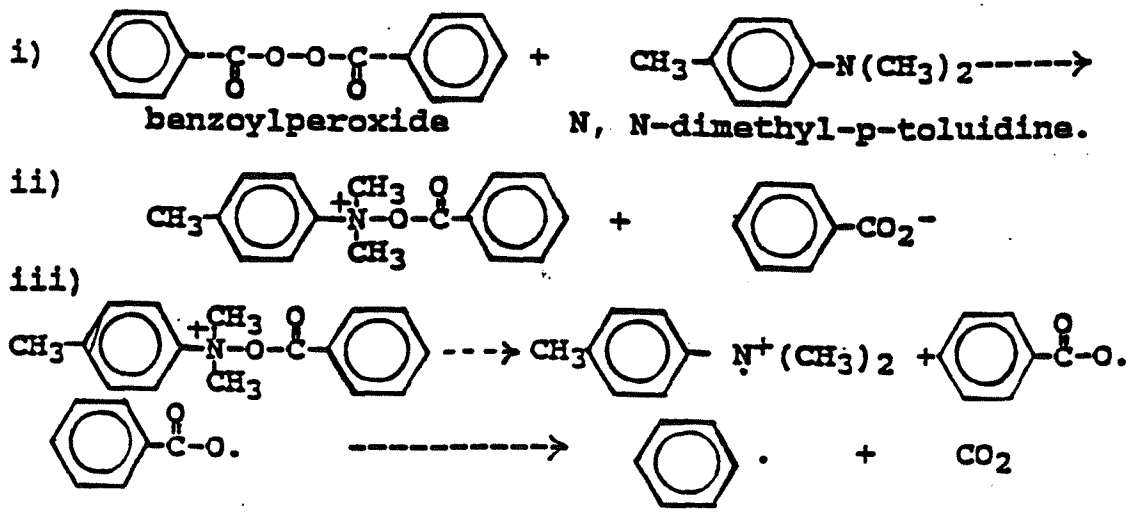
Peroxide catalysed polymerization reactions of MMA, proceed faster in the presence of tertiary amines[21]. This is because rapid decomposition of the peroxides takes place in the presence of amines, thereby increasing the rate of polymerization. A bifunctional monomer which could bind to the surface of dentin and also polymerize with a restorative material is ideal as demonstrated by Bowen[22]. Of later in medical as well as in dental applications, the most widely used restorative material is poly-methyl-methacrylate (PMMA). In dental applications however, PMMA is not used by itself. Instead it is used in conjunction with a fixed ratio of the liquid monomer methyl-methacrylate (MMA), for example 25 to 75 percent or 30 to 70 percent by weight. When the MMA-PMMA mixture is mixed with the adhesive material, a polymerization reaction occurs not

between MMA monomers themselves but also between MMA and hydroxy-hexyl-methacrylate monomers. This could be pictured by the following reactions:

NH-CO-NH·····R-TDI-HEMA·····$(MMA)_r$-MMA·····

Isocyanate material	Adhesive material	Restorative material

Polymerisation[2] reactions require an optimal concentration of benzoyl peroxide to proceed faster. An optimum concentration of benzoyl peroxide initiator is 2.0% as reported by Rose et.al[23]. Apart from increasing the concentration of monomer, a substance which could accelarate the decomposition of the initiator into free radicals faster could be used. The use of accelarator increases the efficiency of the radical without altering the initiator concentration. A suitable accelarator that could be used and is widely used in polymerisation reactions is N,N-dimethyl-p-toluidine. A study of the free radical and accelarator coupling reaction could be depicted as follows:



According to the above reaction the substitution of electron repelling groups in the para position of dimethylaniline increases decomposition rate efficiency, whereas a methyl group substitution in the ortho position of dimethylianiline reduces the decomposition rate of benzoyl peroxide and polymerization would not take place readily[21]. The copolymerization of MMA and HEMA takes place by the same mechanism of initiation and termination as described above with the exception that the monomers of types M_1 and M_2 lead to freeradicals of types $M_1\cdot$ and $M_2\cdot$. The nature of the end group on the radical chain is important[24]. An alternating copolymer, or a blocked copolymer is used with the monomers M_1 or M_2 [25]. In an ideal copolymer, the end group on a growing chain does not affect the rate of addition of monomer. A random distribution of the units takes place depending on the concentration of the monomers. Very rarely a blocked copolymer is produced and thus copolymerization systems are either alternating on ideal systems or lie in between the two.

III. EXPERIMENTAL.

A. DENTIN COLLECTION.

We arranged with oral surgeons at the University of Medicine and Dentistry of New Jersey for the collection of freshly extracted third molars. The time of extraction, the age and sex of the patient were recorded for each collected tooth. The storage medium for the extracted teeth was 0.9% physiological saline. These extracted teeth were obtained from patients of all age groups and both sexes.

B. PREPARATION OF DENTIN SLICES.

We prepared dentin slices approximately 400μm thick aided by an Isomet Diamond - saw cutting machine. The slowly turning diamond blade was constantly bathed in water to prevent calcium decomposition and overheating of the tooth specimens. The tooth slices were cut in order with the one near the occlusal (the crown) stored as 1st, the next slice which is the middle one was the 2nd, and the one closest to the pulp (the last) was the

3rd (Figure 1). Slices having enamel remnants, or pulp chamber voids were discarded. The intact slices were stored in separate glass containers refrigerated in 0.9% physiological saline with appropriate labels until used. The stored specimens were bonded within 2 hours of cutting. No more than three slices were obtained from a tooth specimen.

C. PRE-TREATMENT OF DENTIN.

1. Effect of citric acid pre-treatment.

5% citric acid, was suggested by investigators[26] to be used to remove the smear layer but not hurt the pulp. In this thesis, we tried dentin slices pre-treated with or without 5% citric acid to determine the optimum characteristics of our novel dental adhesive, o-Chlorophenol-TDI-HEMA-Pentaerythritol.

2. Effect of mineralizing solutions pre-treatment.

As mentioned by Causton[1,14], application of certain kinds of mineralizing solution to the acid treated dentin surface before adhesion may form crystals which would block the open tubules,

hence protect the pulp and also prevent degradation of adhesive by attack of water from the pulp. Our attention to pre-treatment mineralizing solution was confined to 3 kinds of mineralizing solutions, 1M $CaCl_2$ at pH 7.0, 1% NaF at pH 7.0, and ITS[14] solution at pH 7.4 (for composition of ITS, see table VI).

D. SYNTHESIS OF ADHESIVE.

Details of the synthesis process of our novel adhesive, o-Chlorophenol-TDI-HEMA-Pentaerythritol, was described in[16].

E. SYNTHESIS OF PMMA-MMA MIXTURE.

The PMMA-MMA mixture used in our experiments was synthesized using a ratio of 25% PMMA and 75% MMA by weight. The synthesis was performed in an inert nitrogen atmosphere. The equipment set-up for the systhesis is shown in Figure 2. 936g of MMA monomer was transferred into the reaction flask. 312g of PMMA was slowly added to the MMA in the flask until all of it was added. The stirrer speed had to be increased as time passed by, because the viscosity of the reaction mixture

increased. The white specks of PMMA required about 5-6 hours for completing dissolution. Nitrogen was maintained during reaction, otherwise the reaction mixture would have polymerized. The flask used for the experiment had to be cleaned throughly because any specks of dirt or loose particles could be an initiator of polymerization within the flask. When all of the PMMA had dissolved in the MMA, as indicated by a clear solution, the reaction is stopped. The mixture was carefully transferred into a container and purged with nitrogen.

F. COUPON.

1. Description of coupon.

With a view of subjecting our samples to a "tensile test" to measure adhesion, aluminium alloy rods were chosen as "coupons" for bonding because of their high surface energy. These "coupons" had a hole in one end and a flattened face at the other (Figure 6). They were manufactured in the Mechanical Engineering Shop in NJIT. The "rod-polymer" assembly had been tested before for dentin adhesion with a number of monomers[18]. With a view to minimizing the adhesive leakage during the application of the adhesive to the pre-treated dentin slices, rubber sleeves were used to cover the tops of the coupons. This also ensured a

standardized, constant bond area of 0.4908 $inch^2$.

2. Preparation of coupon.

The flattened face of the coupon was sanded with a 320 grit sandpaper in a machine on which four coupons could be sanded in one batch. These sanded coupons were then "Sand-blasted" with an "A1-silica" sand (manufactured by KIN-IEK Lab. Inc.) to reduce the surface tension and to enhance adhesion.

After the coupons were subjected to sandblasting, they were "etched" in a solution which had a composition by weight of 1 : 15 : 30 of Na_2CrO_7, H_2SO_4, and H_2O, in an oven maintained at 35^oC. for period of 8 minutes. The purpose of the sandblasting and etching was to ensure that the bond failure always occured at the adhesive/dentin interface. The etched coupons were washed with distilled water and dried using a paper towel taking precaution not to contaminate the base of the coupons, since this would be detrimental to bonding.

G. PREPARATION OF SAMPLE DENTIN SLICES.

The subsequent step in our study was to adhere the dentin slices to the A1 rod assembly with the adhesive. The procedure

incorporated the following:

The cut dentin slices, which were labelled appropriately as described (vida supra), were dried with a paper towel and transferred onto watch glasses which had inscriptions 11, 12, 13, and 21, 22, 23 to prevent the dentin slices from two different tooth specimens from being interchanged. The surfaces of the dentin slices were pre-treated with 5% citric acid for 2 minutes. This was advocated by investigators[26] in order to open the tubules of the dentin surface sufficiently enough for the adhesive to penetrate the dentin. The treated slices were then washed with distilled water for approximately 30 seconds. The washed slices were then dipped in distilled dimethoxyethane for a period of 2 minutes in order to remove water present on the dentin surface. 1.5g of appropriate o-Chlorophenol-TDI-Pentaerythritol blocked monomer was weighed and transferred to a dry test tube. 3.5ml of distilled dimethoxyethane was mixed with the weighed monomer and the test tube was gently shaken to ensure complete dissolution. After 2 minutes treatment with DME the dentin slices were dipped for 5 minutes in the monomer-DME mixture. The dentin slices were dried in air with the appropriate ordering of the slices being maintained. 2.0g of mixture of 75-25% PMMA-MMA was weighed in a watchglass and 12 drops (0.2g) of the accelerator N,N-DMPT mixed throughly with the PMMA-MMA. The initiator benzoyl peroxide weighed previously (0.02g) was added to this to initiate polymerization. As referred to in the section on "initiation", 0.02g of benzoyl

peroxide was found to be an optimum quantity. A puff of smoke evolves when benzoyl peroxide is stirred with the PMMA-MMA, N,N-DMPT mixture owing to the exothermic nature of the reaction. The dentin slices set to dry in air were dipped in this "polymer mixture". The PMMA-MMA and DME containers were purged with nitrogen to ensure that polymerization is not initiated in the containers in which they are stored, and then the sample were store in a refrigirator at about 0-5^{o}C.

H. PRESS FOR BONDING.

A method was developed to apply a moderate force to our (Aluminium coupon-adhesive-dentin-adhesive-aluminium coupon) system[27]. The press unit was fabricated in the engineering facility in the Mechanical Engineering Shop at NJIT (Figure 3-6). Six dentin slices were adhered simultaneously and the stabilized system supporting the six slices is shown in Figure 7. The metal base supported the A1 coupons with a firm base and allowed uniform distribution of the stresses in the adhesive layer[28] of the six coupon pairs.

The press was arranged with rubber sleeves (Figure 8) at the bonding edge of each coupon and perfect alignment of each coupon pair was ensured for all of the six pairs. An initial

coating of the "copolymer mixture" is applied over the coupon surfaces on which the dentin slices would be subjected to bonding. After the slices are aligned in order, the top portion of the press is brought in contact with the bottom and a 2 kg mass is placed on the press with the help of a mount (Figure 7). This is set to rest for 1 hour and then removed from the press. The rubber sleeves are carefully removed and the coupon-adhesive-dentin assembly (see Figure 8) is stored in 0.9% physiological saline for a period of time (normally 24 hours, or up to 6 months). After this time elapses, the assemblies are tested in tension in a Scott CRE tensile-tester and the bond strength reported in psi for each of the tooth slices.

I. EFFECT OF POST-TREATMENT TIME ON BONDING.

At typical oral temperatures, dental adhesives tend to biodegrade because of the presence of water. The most common commercial dental adhesive products last only 5 to 10 years in the environment of the mouth. So it is very important to determine the life of the dental materials under wet conditions. To determine the correlation between post-treatment time and bond strength in our novel adhesive, we stored our

coupon-adhesive-dentin assemblies in 0.9% physiological saline at room temperature at periods from 24 hours to 6 months (4380 hours), then pulled the assemblies to failure by the Scott CRE tensile-tester.

J. COMPARISON OF COMMERCIAL DENTIN ADHESIVE WITH OUR ADHESIVE BY USING OUR TEST METHOD.

Since there is no universal test method for the dentin tensile test, it is difficult to make a comparison between the various dentin bonding agents, so we have to use our test method to test other most common used dentin bonding commercial products. The commercial products we chose were Gluma, Scotch Bond, J&J Dentin Bonding Agent, Prisma Universal Bond and, Dentin-Adhesit. The manufacturers of these dentin bonding agents are listed in Table X. Since the drying agent, dimethoxy ethane (DME), which was used in our test method, may reduce the bond strengths of the other dentin bonding agents, we had dentin slices pre-treated with or without DME in order to determine the effect of DME.

1. Comparison of five commercial dentin bonding agents by using our test method without DME treatment.

Except for the TDI specimens, the dentin slices were pre-treated in all cases according to the manufacturer's instructions. TDI samples were pre-treated as our test method but without using DME.

2. Comparison of five commercial dentin bonding agents by using our test method with DME treatment.

All of the dentin slices used in this test were pre-treated according to our test method.

K. CALCULATIONS OF TENSILE STRENGTH AND CORRELATION ANALYSIS.

The full load scale of the Scott tester is equivalent to 500 lbs. We operated at a load of 50 percent of the full load which is equivalent to 250 lbs. The cross-head speed of the tester was calibrated at 1mm per minute. A digital output corresponding to the breaking strength of the adhesive samples was obtained and was also plotted on a chart interfaced with the tester. The conversion to psi was accomplished vis a vis:

The area of the coupons which were used for the tensile tests was constant (diameter 0.25 inch):

$\Pi/4 * (0.25)^2 = 0.045$ inch^2

250 lbs (our operation load which was half of the full load

scale), and 0.700mv were used in our calibrations.

250 lbs/0.700mv = Y lbs/ X mv

where X is the observed voltage and Y the equivalent load for the observed voltage.

Therefore,

Y lbs = 250 lbs * X mv / 0.700 mv

Y lbs / 0.045 $inch^2$ = Z psi

where 0.045 is the area of the coupon.

All bond strengths of the coupon-dentin-coupon assemblies were obtained by this method. The results were analysed using a 2 by 3 factorial Analysis of Variance (ANOVA) for each of the monomers studied to delineate any differences between the bond strengths. The results are reported in the section on Results and Discussion.

L. INTERFACE STUDY.

SEM 4500 was used in the study of the interface between adhesive and dentin in order to determine the breakage areas.

IV. RESULTS AND DISCUSSIONS.

The bond strengths of three levels of dentin (level 1: the highest, closest to the crown; level 2: middle; and level 3: the lowest, closest to the pulp) were considered in this analysis.

The experimental results obtained were analyzed by a 2 by 3 factorial design technique as described by Winner[29,30,31]. A program written in EXCEL on a Macintosh computer was utilized to calculate the results.

A. CITRIC ACID AND NON-CITRIC ACID PRE-TREATMENT AND POST-TREATMENT EFFECT.

1. 24 hours post-treatment in 0.9% saline.

The bond strength values along with the mean and

standard deviation for each level are reported in Table I.

The grand mean of bond strength for 5% citric acid pre-treated dentin slices with 24 hours post-treatment time was 1698 psi with 378 psi standard deviation, and the grand mean of bond strength for non-citric acid pre-treated dentin slices with 24 hours post-treatment time was 1810 psi with 441 psi standard deviation.

A two-sample t-test[31] shows $t = 1.630 < 1.645$ at the level of significance $\alpha = 0.05$ in comparing the two categories, so the dentin slices pre-treated with or without 5% citric acid had no significant difference in bond stregth after 24 hours post-treatment in 0.9% saline.

2. 48 hours (2 days) post-treatment in 0.9% saline.

The bond strength values along with the mean and standard deviation for each level are reported in Table II.

The grand mean of bond strength for 5% citric acid

pre-treated dentin slices with 48 hours post-treatment time was 1627 psi with 465 psi standard deviation, and the grand mean of bond strength for non-citric acid pre-treated dentin slices with 48 hours post-treatment time was 1616 psi with 261 psi standard deviation.

A two-sample t-test shows $t = 0.360 < 1.645$ at the level of significance $\alpha = 0.05$ in comparing the two categories, so the dentin slices pre-treated with or without 5% citric acid had no significant difference in bond stregth after 48 hours post-treatment in 0.9% saline.

3. 720 hours (30 days) post-treatment in 0.9% saline.

The bond strength values along with the mean and standard deviation for each level are reported in Table III.

The grand mean of bond strength for 5% citric acid pre-treated dentin slices with 720 hours post-treatment time was 1223 psi with 209 psi standard deviation, and the grand mean of bond strength for non-citric acid pre-treated

dentin slices with 720 hours post-treatment time was 1231 psi with 234 psi standard deviation.

A two-sample t-test shows $t = 0.186 < 1.645$ at the level of significance $\alpha = 0.05$ in comparing the two categories, so the dentin slices pre-treated with or without 5% citric acid had no significant difference in bond stregth after 720 hours post-treatment in 0.9% saline.

4. 1440 hours (60 days) post-treatment in 0.9% saline.

The bond strength values along with the mean and standard deviation for each level are reported in Table IV.

The grand mean of bond strength for 5% citric acid pre-treated dentin slices with 1440 hours post-treatment time was 1176 psi with 195 psi standard deviation, and the grand mean of bond strength for non-citric acid pre-treated dentin slices with 1440 hours post-treatment time was 1184 psi with 191 psi standard deviation.

A two-sample t-test shows $t = 0.268 < 1.645$ at the

level of significance α = 0.05 in comparing the two categories, so the dentin slices pre-treated with or without 5% citric acid had no significant difference in bond stregth after 1440 hours post-treatment in 0.9% saline.

5. 4380 hours (one-half year) post-treatment in 0.9% saline.

The bond strength values along with the mean and standard deviation for each level are reported in Table V.

The grand mean of bond strength for 5% citric acid pre-treated dentin slices with 4380 hours post-treatment time was 637 psi with 102 psi standard deviation, and the grand mean of bond strength for non-citric acid pre-treated dentin slices with 4380 hours post-treatment time was 625 psi with 110 psi standard deviation.

A two-sample t-test shows $t = 0.390 < 1.645$ at the level of significance α = 0.05 in comparing the two categories, so the dentin slices pre-treated with or without 5% citric acid had no significant difference in bond stregth after 4380 hours post-treatment in 0.9% saline.

6. Discussion.

It can be concluded that the bond strength of our dental adhesive material, o-Chlorophenol-TDI-HEMA-Pentarythritol, drops rapidly when post-treatment time increases as is the case for other commonly used commercial dentin bonding materials.

No significant differences have been found in the citric acid and non-citric acid pre-treatment. This is different from Lee's[26] results because of our novel adhesive material.

After long term post-treatment in 0.9% physiological saline, the average bond strength fell from 1791 psi after 24 hours in 0.9% saline solution, to 625 psi after one half year post-treatment in o.9% saline solution at room temperature. The effect of long term immersion on adhesive bond strength is shown in the computer generated graphs shown in Figure 9 and Figure 10. The general trend of decreasing bond strength is quite apparent in these graphs.

B. EFFECT OF MINERALIZING SOLUTIONS PRE-TREATMENT.

1. ITS mineralizing solution pre-treatment.

The bond strength values along with the mean and standard deviation for different post-treatment time are reported in table VII.

The grand mean of bond strength for ITS mineralizing pre-treated dentin slices with one day post-treatment time in saline was 3013 psi with 336 psi standard deviation.

The grand mean of bond strength for ITS mineralizing pre-treated dentin slices with seven days post-treatment time in saline was 2484 psi with 351 psi standard deviation.

A two-sample t-test shows $t = 4.870 > 1.645$ at the level of significance $\alpha = 0.05$ in comparing the two categories, so we can say that there is a significant difference in bond strengths of ITS solution pre-treatment between the post-treatment times of 1 day and 7 days in saline.

2. 1M $CaCl_2$ mineralizing solution pre-treatment.

The bond strength values along with the mean and standard deviation for different post-treatment time are reported in table VIII.

The grand mean of bond strength for $CaCl_2$ mineralizing pre-treated dentin slices with one day post-treatment time in saline was 1621 psi with 198 psi standard deviation.

The grand mean of bond strength for $CaCl_2$ mineralizing pre-treated dentin slices with seven days post-treatment time in saline was 1281 psi with 185 psi standard deviation.

A two-sample t-test shows $t = 5.610 > 1.645$ at the level of significance $\alpha = 0.05$ in comparing the two categories, so we can say that there is a significant difference in bond strengths of $CaCl_2$ solution pre-treatment between the post-treatment times of 1 day and 7 days in saline.

3. 1% NaF mineralizing solution pre-treatment.

The bond strength values along with the mean and standard deviation for different post-treatment time are reported in table IX.

The grand mean of bond strength for NaF mineralizing pre-treated dentin slices with one day post-treatment time in saline was 1664 psi with 178 psi standard deviation.

The grand mean of bond strength for NaF mineralizing pre-treated dentin slices with seven days post-treatment time in saline was 1188 psi with 140 psi standard deviation.

A two-sample t-test shows $t = 9.400 > 1.645$ at the level of significance $\alpha = 0.05$ in comparing the two categories, so we can say that there is a significant difference in bond strengths of NaF solution pre-treatment between the post-treatment times of 1 day and 7 days in saline.

4. Discussion.

From several hundred previous tests, we can normally anticipate average bond strengths of about 1200 to 1400 psi

for most samples bonding with TDI. In the tests with mineralizing solutions, the ITS solution pre-treatment approximately doubled the anticipated bond strengths. The $CaCl_2$ and NaF had little effect over "normal expected values". As one can see, in all cases the bond strength fell when the specimens had been immersed in 0.9% physiological saline for one week before the tensile tests were done. A long term post-treatment study on the samples pre-treated with mineralizing solutions needs to be done.

Figure 11 is a graph which shows the effect on o-Chlorophenol-TDI-HEMA-Pentaerythritol of pre-treating dentin with mineralizing solutions. Dentin pre-treated with ITS is the highest in bond strength.

C. COMPARASON OF COMMERCIAL DENTIN ADHESIVES WITH OUR ADHESIVE BY USING OUR TEST METHOD.

1. Dentin slices pre-treated without DME.

Table XI shows the bond strengths of TDI compared with Scotch Bond, Gluma, Vivadent, Prisma Universal Bond, Johnson and Johnson Dentin Bonding Agent.

The mean bond strength obtained from Scotch Bond was 391 psi with 155 psi standard deviation. Gluma had a mean bond strength of 972 psi with 340 psi standard deviation. Vivadent had a mean bond strength of 500 psi with 222 psi standard deviation. Prisma Universal Bond had a mean bond strength of 333 psi with 123 psi standard deviation. Johnson and Johnson Dentin Bonding Agent had a mean bond strength of 413 psi with 154 psi standard deviation. TDI had a very constant bond strength of 637 psi in mean with 171 psi in standard deviation.

2. Dentin slices pre-treated with DME.

In contrast to the preceding Table XI, Table XII shows the bond strengths of TDI compared with Scotch Bond, Gluma,

Vivadent, Prisma Universal Bond, Johnson and Johnson Dentin Bonding Agent when dimethoxyethane (DME) was used.

The mean bond strength obtained from Scotch Bond was 630 psi with 160 psi standard deviation. Gluma had a mean bond strength of 1566 psi with 230 psi standard deviation. Vivadent had a mean bond strength of 282 psi with 97 psi standard deviation. Prisma Universal Bond had a mean bond strength of 465 psi with 207 psi standard deviation. Johnson and Johnson Dentin Bonding Agent had a mean bond strength of 475 psi with 156 psi standard deviation. TDI had a mean bond strength of 1714 psi and 471 psi in standard deviation.

3. Discussion.

Figure 12 is a graph of TDI bonding agent compared to 5 commercial dentin bonding agents for dentin slices treated with and without DME. Statistically significant improvement in bond strength when using DME can be seen for TDI, Gluma,

and Scotch Bond. There was no improvements for the J&J Dentin Bonding Agent and Prisma, and a worsening for the Vivadent Dentin adhesive.

D. SEM STUDY ON SEPARATED DENTIN-COUPON INTERFACE.

With the help from Dr. S. Berenson of New Jersey Medical School, we were able to use SEM to analyze the separated dentin-coupon interface of our TDI dentin bonding agent. Examination of the end of a separated dentin-coupon shows (Figure 13) that a small area of fracture occured at the metal-adhesive interface (about 5% adhesive failure), a larger area occured at the dentin interface (about 30% adhesive failure), and an even larger area occured through the body of the adhesive (about 65% cohesive failure). This large area of cohesive failure is encouraging because it means our TDI adhesive is bonding well to the dentin.

V. CONCLUSIONS.

Several important facts can be concluded as follows from this research:

1. Pre-treatment of the dentin substrate with 5% citric acid had no significant effect upon dentin-adhesive bond strength.
2. Pre-treatment of dentin with ITS mineralizing solution was definitely advantageous and doubled the bond strength. The $CaCl_2$ and NaF pre-treatments were not different from each other and did not cause an increase in bond strength. The bond strengths of all specimens tended to fall with time of immersion in saline.
3. Dentin pre-treatment with dimethoxy ethane was advantageous to the TDI, Gluma, and Scotch Bond adhesives. It was not advantageous to the J&J Dentin Bonding Agent, Prisma Universal Bond, and Dentin Adhesit adhesives.
4. The bond strength of TDI steadily declined in an almost linear pattern over a six month's time period which were not treated with mineralizing solutions.

VI. RECOMMENDATIONS.

1. Long term testing of the TDI bond strengths after treatment with ITS mineralizing solution to determine what level bond strength falls.
2. Combine the bonding agent with a bacteriocide.
3. Develop a combination dentin-enamel bonding agent by incorporating phosphate esters into bonding mixture.

TABLE I

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

POST-TREATMENT: 24 HOURS IN 0.9% SALINE IN ROOM TEMPERATURE.

PRE-TREATMENT: TREAT WITH DME AND,

	WITH CITRIC ACID			WITHOUT CITRIC ACID		
LEVELS:	1	2	3	1	2	3
	1513	553	1426	1979	2197	2561
	1244	1382	1099	2081	1644	1863
	1783	1812	517	1135	953	851
	1790	1492	1884	895	1200	1579
	2285	1899	2044	1310	1215	1717
	1884	2132	2125	1281	1477	1652
	1579	1921	1666	1921	2088	2081
	1462	1855	1695	1666	1775	2139
	2161	1542	1920	2175	1877	1943
	1688	1986	1593	2030	2125	1994
	1790	2015	1564	2560	2791	1871
	1928	1870	1877	1658	2082	2349
	2161	1448	1994	1788	1604	2104
	1200	1535	1994	2081	1579	2131
Quantity :		42			42	
Mean :		1698 psi			1810 psi	
Std. Dev. :		378 psi			441 psi	

TABLE II

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

POST-TREATMENT: 48 HOURS IN 0.9% SALINE IN ROOM TEMPERATURE.

PRE-TREATMENT: TREAT WITH DME AND,

	WITH CITRIC ACID			WITHOUT CITRIC ACID		
LEVELS:	1	2	3	1	2	3
	1659	1266	1870	1893	1540	1569
	1492	1499	1150	1237	1654	1137
	1703	1521	1535	1079	1750	1438
	1593	1753	1644	1612	1671	1935
	2859	1775	1128	1793	1670	1843
	2568	1921	953	2078	1710	1479
Quantity :		18			18	
Mean :		1627 psi			1616 psi	
Std. Dev. :		465 psi			261 psi	

TABLE III

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

POST-TREATMENT: 720 HOURS IN 0.9% SALINE IN ROOM TEMPERATURE.

PRE-TREATMENT: TREAT WITH DME AND,

	WITH CITRIC ACID			WITHOUT CITRIC ACID		
LEVELS:	1	2	3	1	2	3
	1588	1186	985	981	1136	1277
	1608	1441	1222	1034	710	895
	1775	1288	953	1329	1014	1514
	1313	1221	1127	1237	1096	1418
	918	1131	1028	1571	1494	1231
	1316	1517	978	1655	1139	1314
	1492	917	1172	1104	1488	1717
	1459	1031	1128	1020	1598	1214
	1420	974	1045	1575	1058	1207
	1250	1247	1298	1132	1076	1398
	897	1077	1137	1286	1121	1070
	1131	1316	1011	966	1450	978
	1240	1302	1135	836	1230	1159
	1328	1418	1510	1450	1533	1007
Quantity :		42			42	
Mean :		1223 psi			1232 psi	
Std. Dev. :		209 psi			234 psi	

TABLE IV

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

POST-TREATMENT: 1440 HOURS IN 0.9% SALINE IN ROOM TEMPERATURE.

PRE-TREATMENT: TREAT WITH DME AND,

	WITH CITRIC ACID			WITHOUT CITRIC ACID		
LEVELS:	1	2	3	1	2	3
	1057	1476	1448	1279	1774	1062
	1101	924	1358	1185	1095	989
	1174	1150	1505	1261	1246	1291
	1153	1125	1241	1649	1277	1360
	1247	1289	1458	1089	1115	1365
	1435	1129	1237	1428	1587	1277
	1032	980	1238	1304	991	1105
	908	959	1203	1094	988	974
	1120	1214	911	1318	998	1016
	980	1231	1033	988	1285	1119
	1301	1100	1707	1053	1123	962
	908	924	1066	1311	1017	980
	1160	1387	1078	1287	1018	990
	902	1510	1031	1326	1031	1126
Quantity :		42			42	
Mean :		1176 psi			1184 psi	
Std. Dev. :		195 psi			191 psi	

TABLE V

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

POST-TREATMENT: 4380 HOURS IN 0.9% SALINE IN ROOM TEMPERATURE.

PRE-TREATMENT: TREAT WITH DME AND,

	WITH CITRIC ACID			WITHOUT CITRIC ACID		
LEVELS:	1	2	3	1	2	3
	833	514	754	745	492	577
	589	580	784	677	745	440
	625	759	622	814	624	736
	793	680	524	646	591	752
	622	592	610	657	749	577
	704	459	502	489	524	629
	699	604	745	743	701	437
	480	578	624	580	625	439
Quantity :		24			24	
Mean :		637 psi			625 psi	
Std. Dev. :		102 psi			110 psi	

TABLE VI

COMPOSITION OF ITS MINERALIZING SOLUTION

COMPONENT	g/Li
$CaCl_2$	0.200
KCl	0.200
$MgCl_2 \cdot 6H_2O$	0.050
NaCl	8.000
$NaHCO_3$	1.000
NaH_2PO_4	0.050
Glucose	1.000

TABLE VII

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

PRE-TREATMENT: TREAT WITH CITRIC ACID, ITS SOLUTION, AND DME.

POST-TREATMENT: IMMERSED IN 0.9% PHYSIOLOGICAL SALINE FOR:

1 DAY	7 DAYS
3129	2299
2350	2117
3289	2597
2219	2263
2289	2095
3107	2750
2576	1739
2879	2299
3165	2248
2961	2576
3391	2496
3165	2270
3427	3019
3296	2568
2685	2321
2932	3114
3238	2343
3398	3187
2852	2743
3303	2627
Quantity: 20	20
Mean: 3013 psi	2484 psi
Std. dev.: 336 psi	351 psi

TABLE VIII

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

PRE-TREATMENT: TREAT WITH CITRIC ACID, 1M $CaCl_2$ SOLUTION, AND DME.

POST-TREATMENT: IMMERSED IN 0.9% PHYSIOLOGICAL SALINE FOR:

	1 DAY	7 DAYS
	1654	1543
	1431	1232
	1714	1454
	1217	1214
	1514	1074
	1711	1324
	1315	1752
	1417	1033
	1903	1140
	1560	1270
	1607	1426
	1794	1129
	1938	1021
	1654	1543
	1717	1301
	1540	1299
	1414	1303
	1584	1055
	1755	1254
	1980	1259
Quantity:	20	20
Mean:	1621 psi	1281 psi
Std. dev.:	198 psi	185 psi

TABLE IX

BOND STRENGTH OF O-CHLOROPHENOL-TDI-HEMA-PENTA

PRE-TREATMENT: TREAT WITH CITRIC ACID, 1% NaF SOLUTION, AND DME.

POST-TREATMENT: IMMERSED IN 0.9% PHYSIOLOGICAL SALINE FOR:

	1 DAY	7 DAYS
	1656	1234
	1297	1136
	1751	1204
	1811	1155
	1531	1099
	1715	1104
	1533	1034
	1754	1155
	1435	1238
	1699	1089
	1977	1155
	1780	1634
	1938	1204
	1564	1315
	1831	1154
	1325	1054
	1533	1165
	1738	1157
	1655	1024
	1760	1454
Quantity:	20	20
Mean:	1664 psi	1188 psi
Std. dev.:	178 psi	140 psi

TABLE X. COMPARISON OF TDI AND 5 COMMERCIAL DENTIN BONDING AGENTS.

MATERIAL	COMPANY	CODE	BATCH #
TDI/o-CHLOROPHENOL	- -	TDI	- -
GLUMA	CUTTER	GLM	4166B
SCOTCH BOND	3M	SBD	O30985
J&J DENTIN BONDING AGENT	J&J	J/J	Lot 2301
PRISMA UNIVERSAL BOND	CAULK	PRS	O21386
DENTIN-ADHESIT	VIVADENT	VIV	B6153

Table XI. Effect of DME on 5 Commercial DBA's-No DME

Obs	SB	GL	VIV	PR	JJ	TDI
1	257	1456	329	126	309	598
2	500	530	466	354	415	320
3	422	924	826	368	718	617
4	280	1201	350	448	281	798
5	382	622	416	201	365	626
6	270	996	654	339	400	577
7	436	459	217	268	466	742
8	401	1245	731	367	488	866
9	395	1047	794	222	553	679
10	702	825	218	633	702	521
11	460	1103	754	471	502	767
12	348	487	666	275	575	499
13	195	1336	403	453	130	575
14	538	1026	182	395	357	976
15	268	851	529	200	446	399
16	372	942	164	310	287	876
17	771	1230	854	215	435	566
18	167	397	425	280	230	768
19	422	1186	496	477	195	547
20	240	1586	530	252	407	424
Quant.	20	20	20	20	20	20
Mean	391	973	500	333	413	637
Std Dev	155	340	222	123	154	171

1-Way Analysis of Variance with Duncan's Multiple Range Test.

Table XII. Effect of DME on 5 Commercial DBA's-With DME

Obs	SB	GL	VIV	PR	JJ	TDI
1	766	1754	254	458	204	1779
2	820	1487	126	327	379	2197
3	454	1353	425	199	356	2561
4	516	1368	136	755	433	2081
5	854	1845	294	540	422	1135
6	630	1514	327	421	349	851
7	859	1920	250	325	567	895
8	490	1405	331	450	389	1310
9	533	1821	143	689	533	1215
10	482	1464	396	219	693	1477
11	928	1260	295	606	240	1652
12	430	1985	318	925	325	1921
13	729	1455	126	314	702	2081
14	801	1591	301	319	479	2161
15	517	1851	437	616	768	1775
16	702	1213	279	170	639	2030
17	536	1701	425	525	440	2125
18	540	1541	239	221	639	1994
19	547	1342	264	679	409	1291
20	466	1455	276	365	532	1754
Quant.	20	20	20	20	20	20
Mean	630	1566	282	465	475	1714
Std Dev	160	230	97	207	156	471

1-Way Analysis of Variance with Duncan's Multiple Range Test.

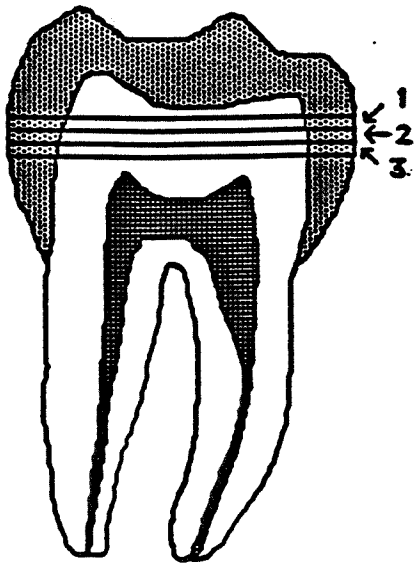


Figure 1. Diagram of tooth with location of cuts.

THE EQUIPMENT SET-UP FOR PMMA-MMA SYNTHESIS.

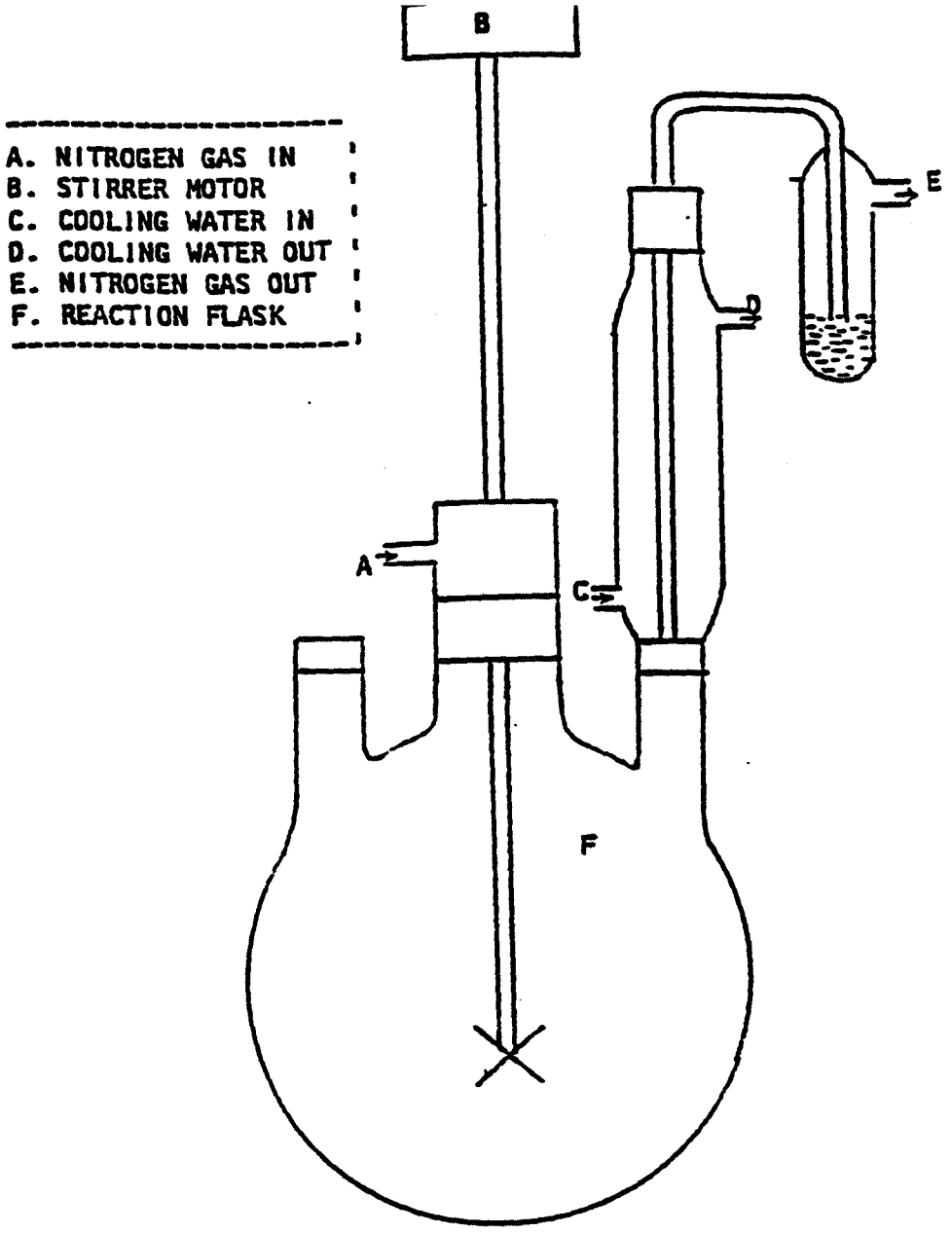


Figure 2

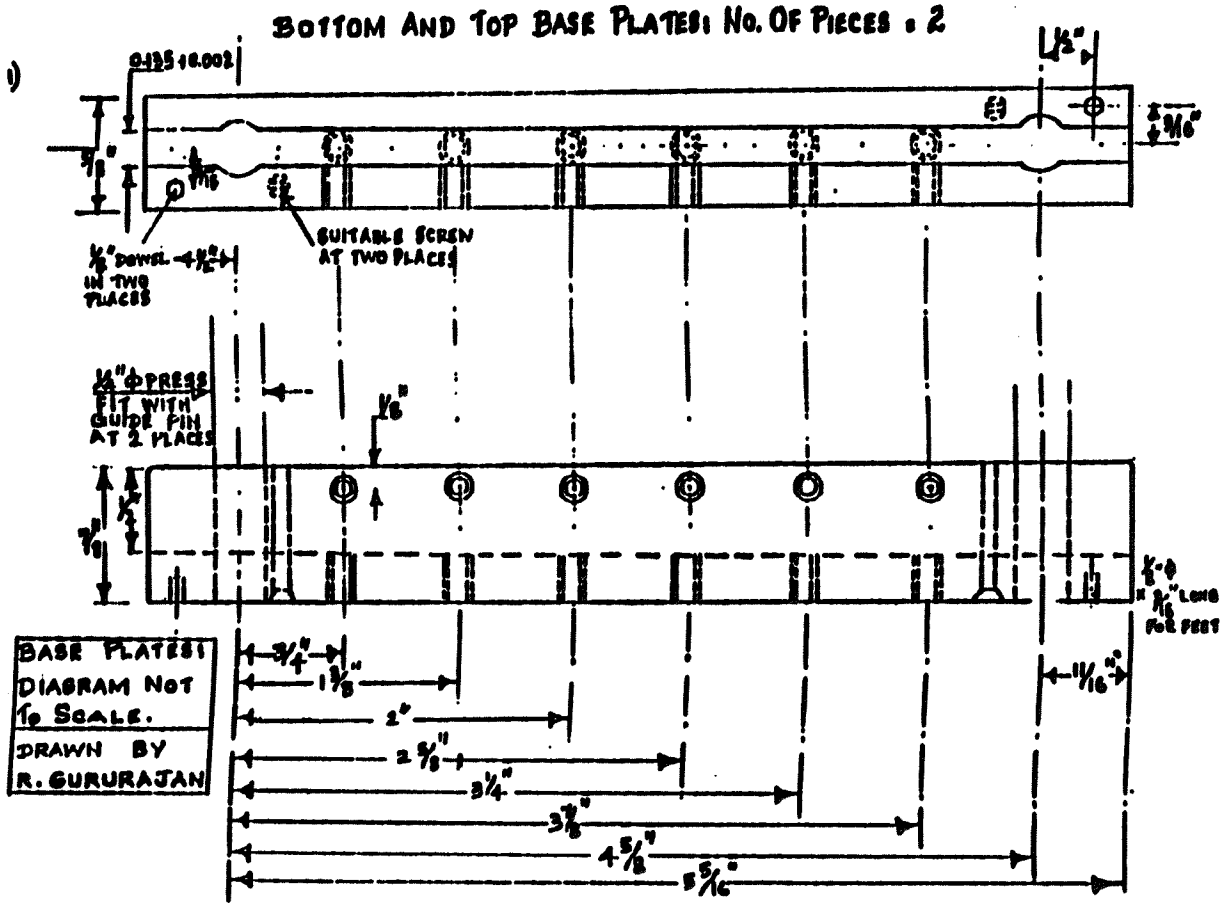


Figure 3. Sectional Elevation of base plates of bonding press.

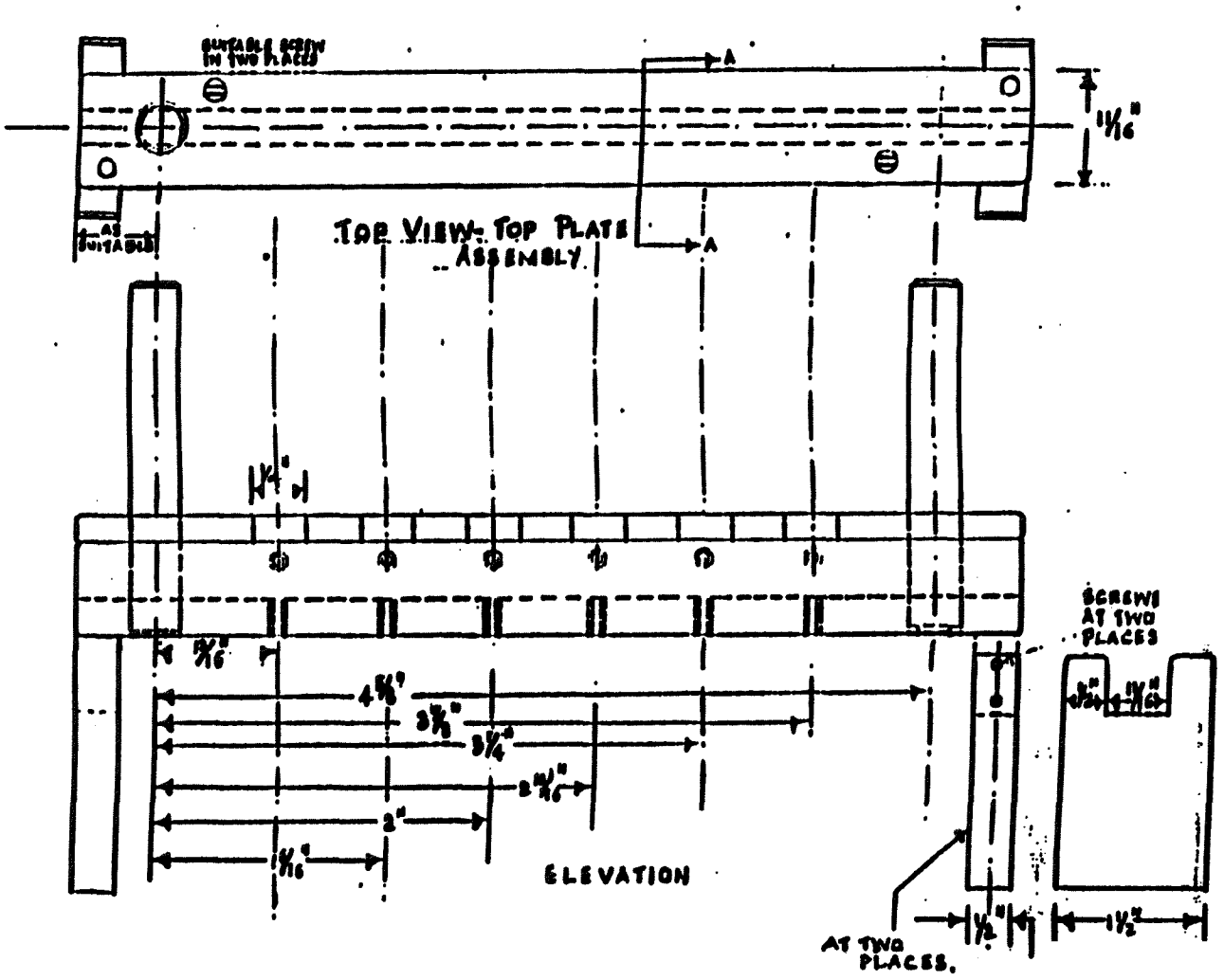


Figure 4. Sectional Elevation of bonding press.

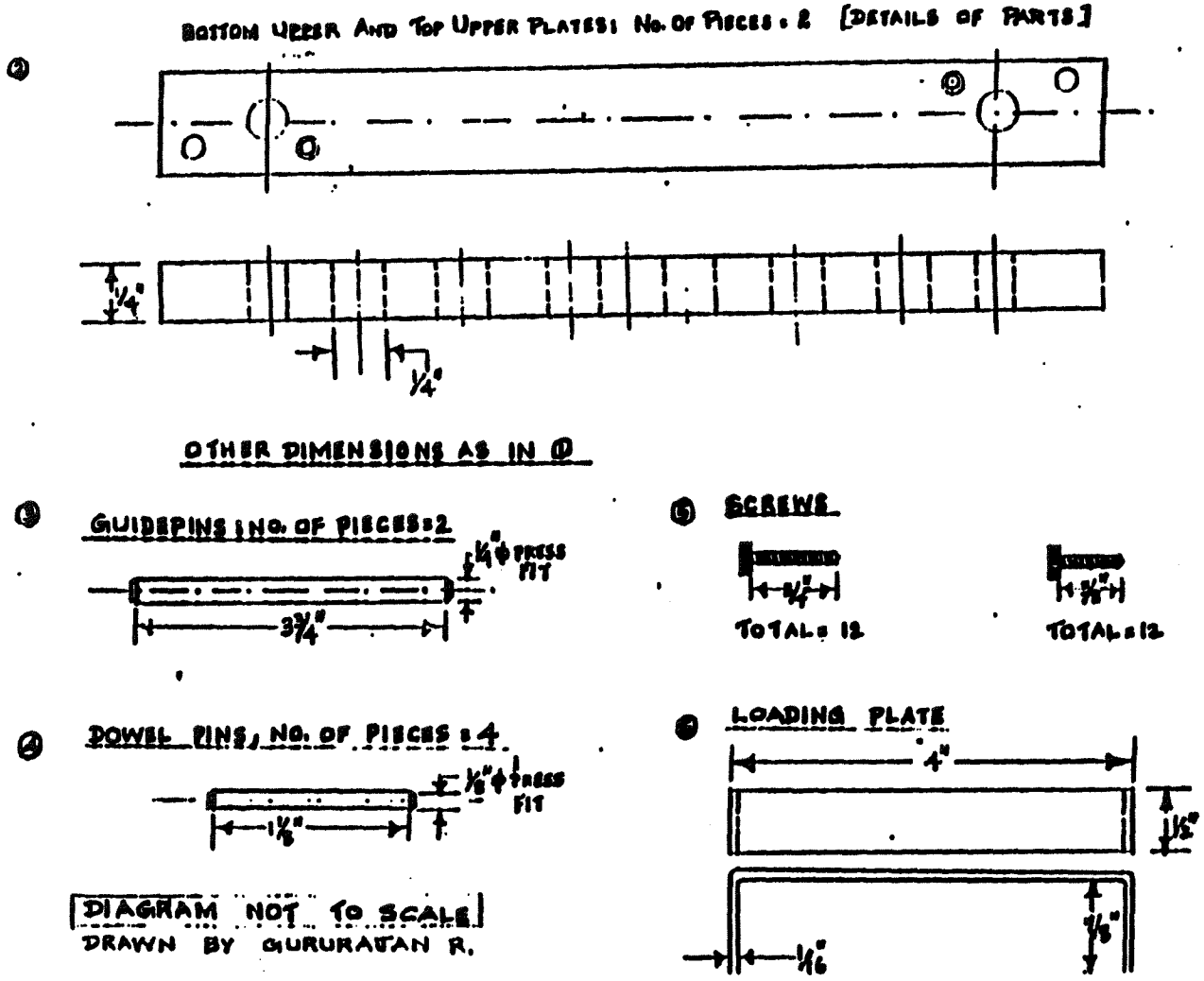


Figure 5. Details of parts of bonding press.

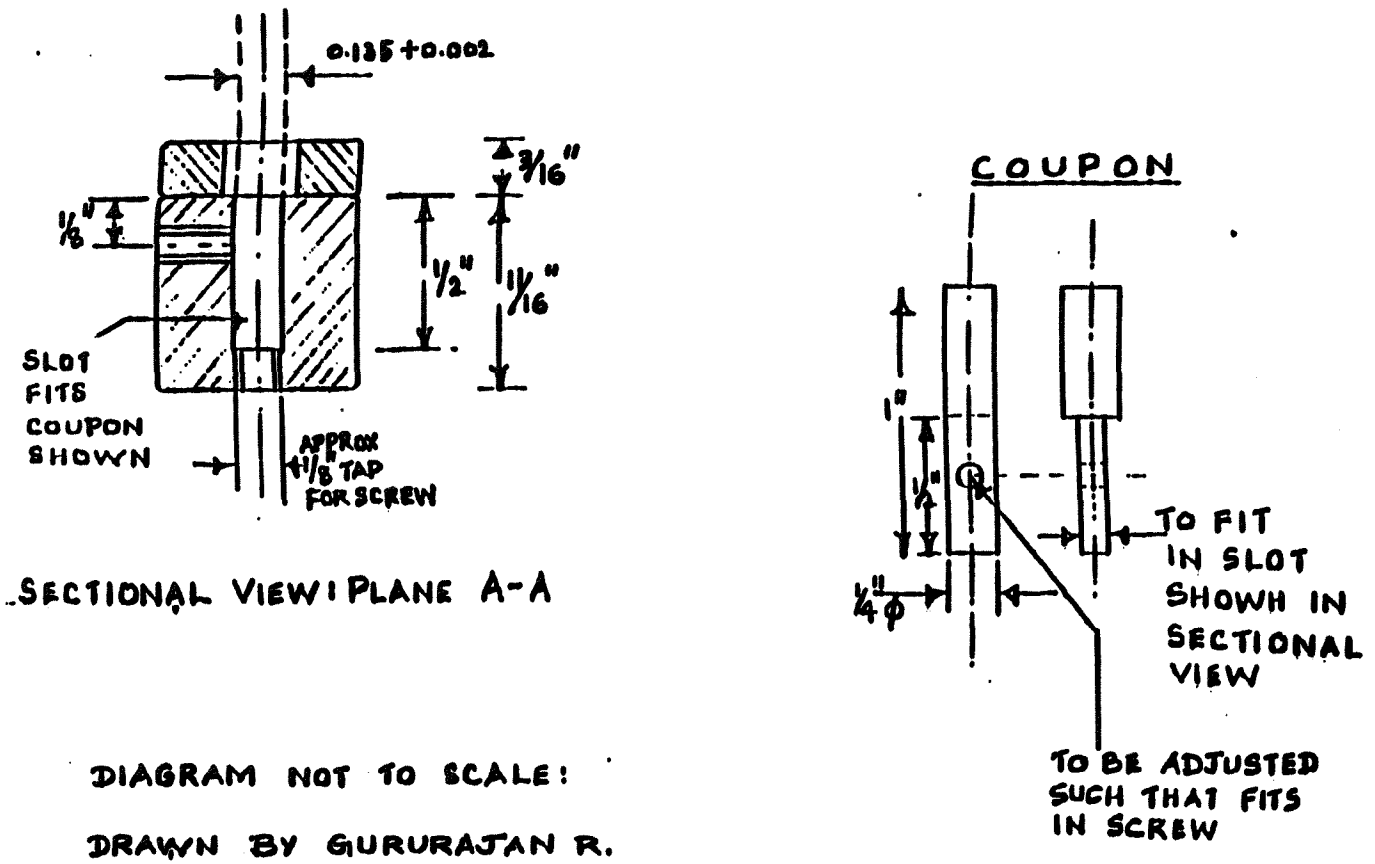


Figure 6. Details of 'coupon' of bonding press.

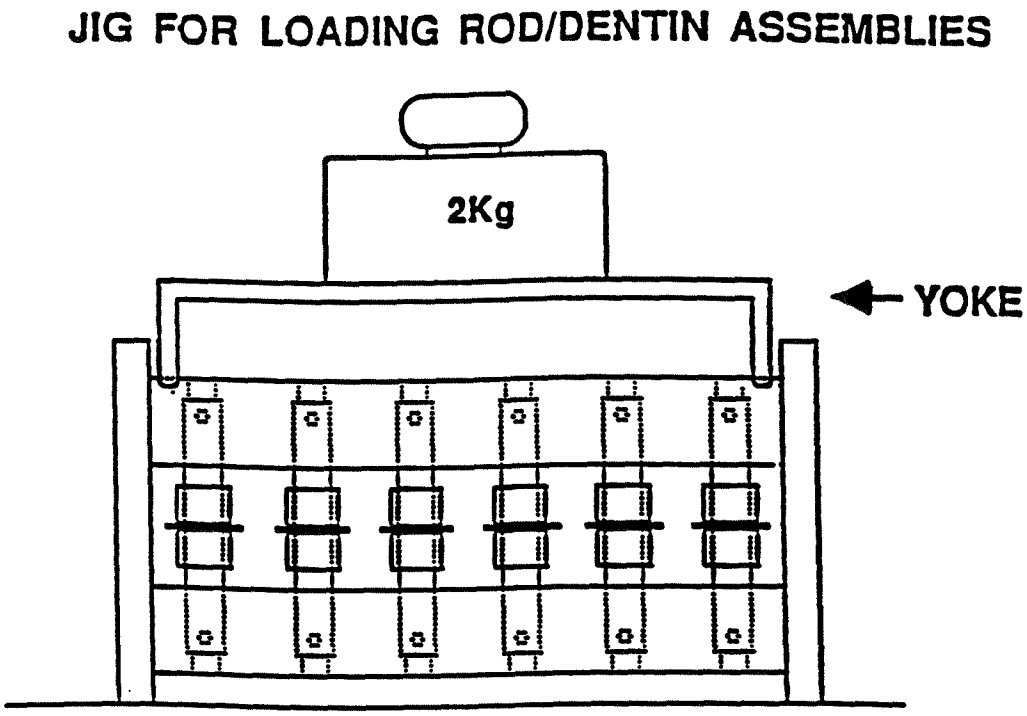


Figure 7.

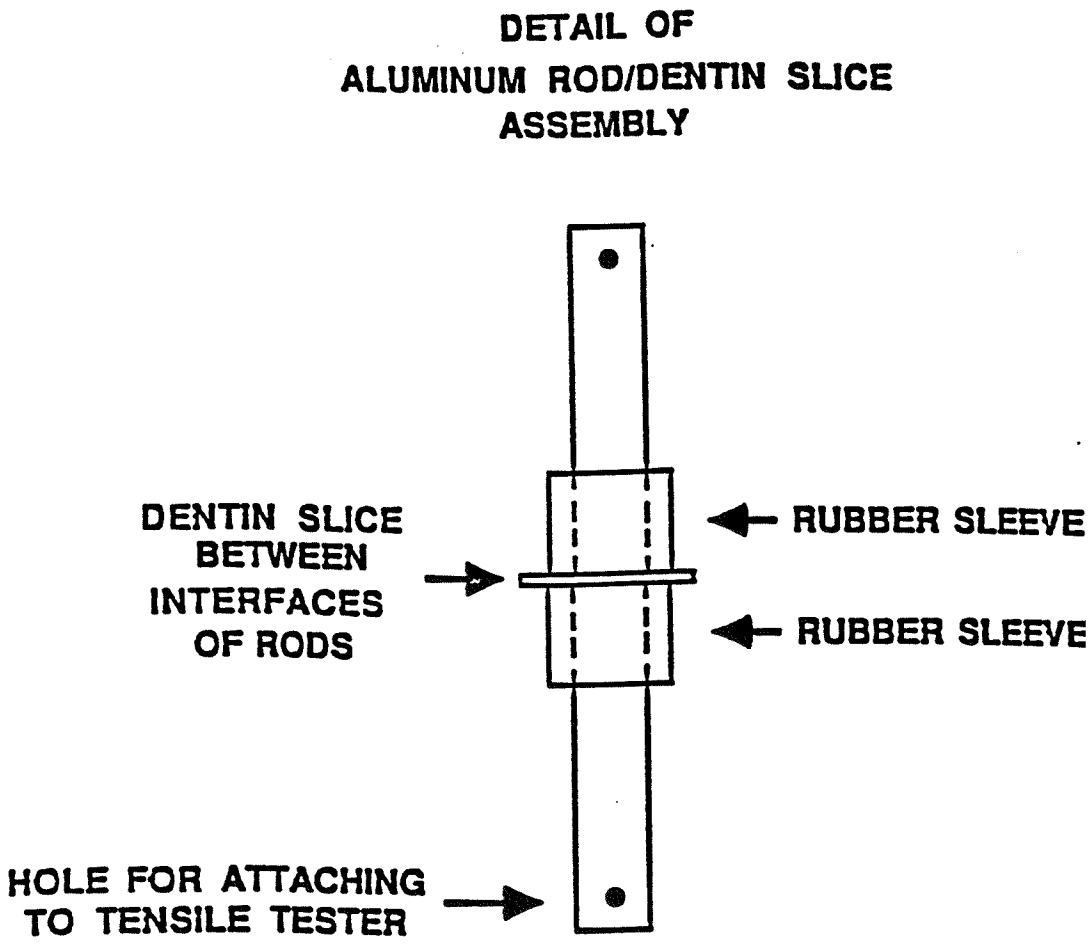
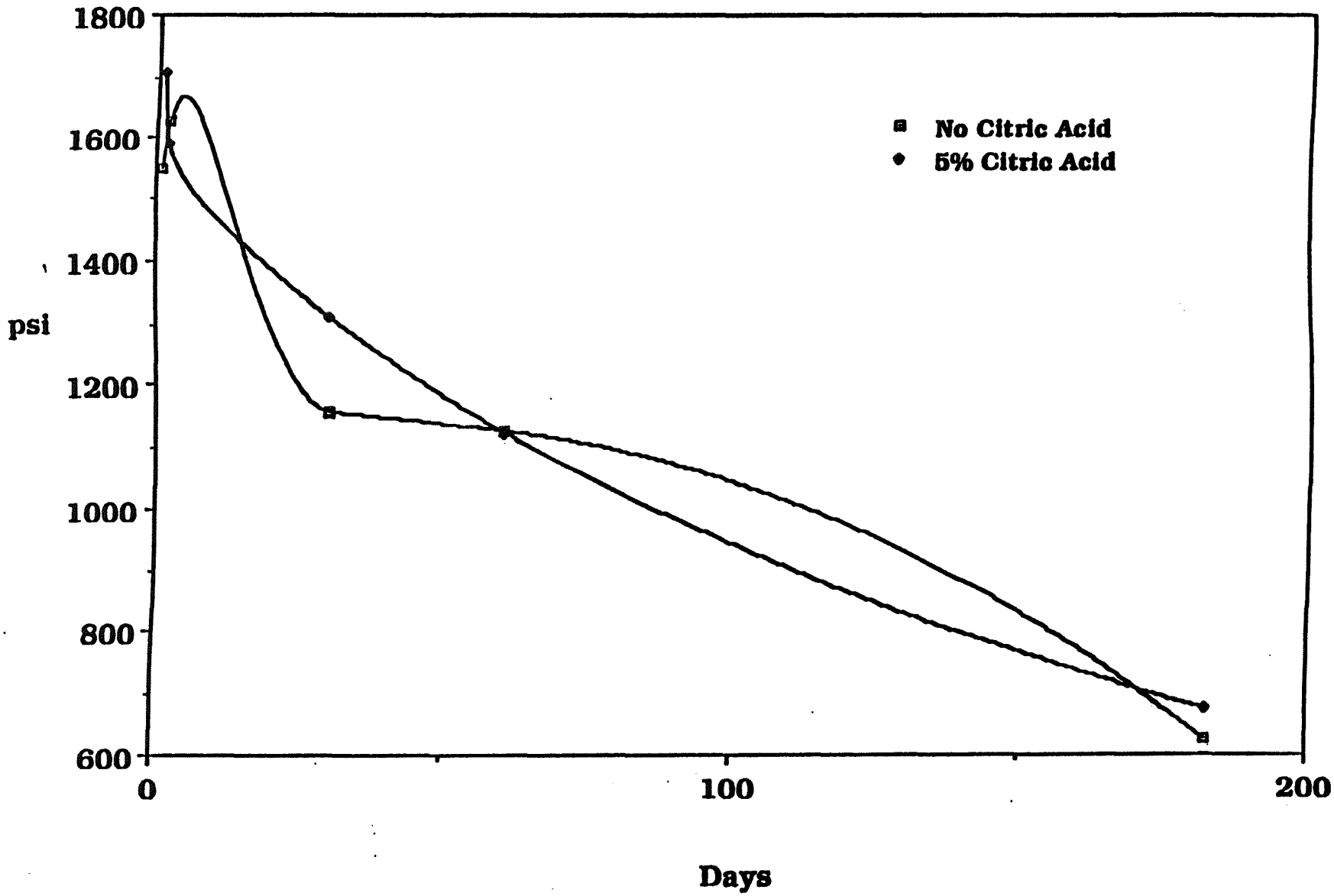
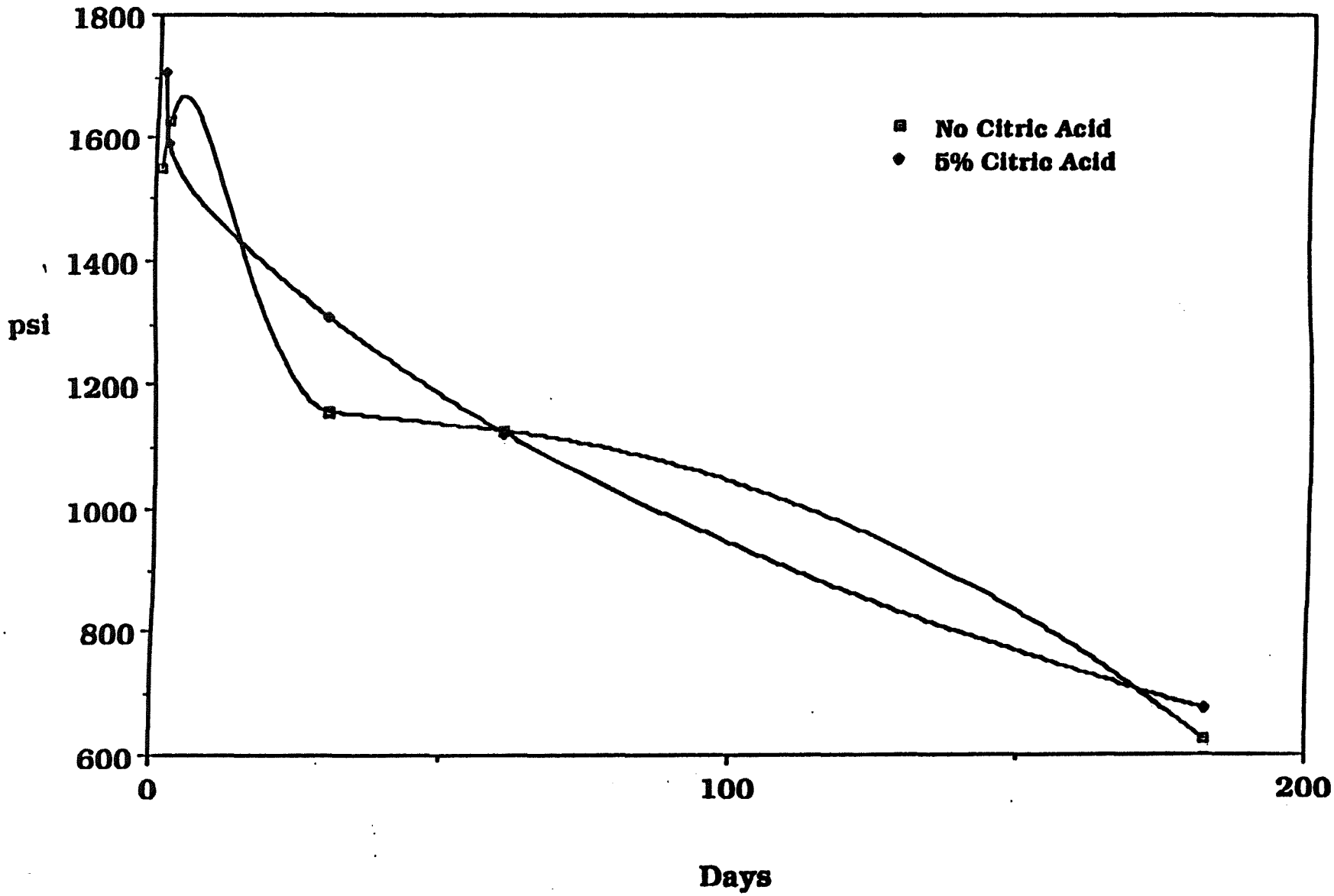

DETAIL OF
ALUMINUM ROD/DENTIN SLICE
ASSEMBLY
DENTIN SLICE
BETWEEN
INTERFACES
OF RODS
RUBBER SLEEVE
RUBBER SLEEVE
HOLE FOR ATTACHING
TO TENSILE TESTER

Figure 8.

EFFECT OF LONG TERM IMMERSION ON TDI/DENTIN BOND STRENGTH



EFFECT OF LONG TERM IMMERSION ON TDI/DENTIN BOND STRENGTH



EFFECT ON TDI/DENTIN BOND STRENGTH OF PRE-TREATING DENTIN WITH MINERALIZING SOLUTIONS

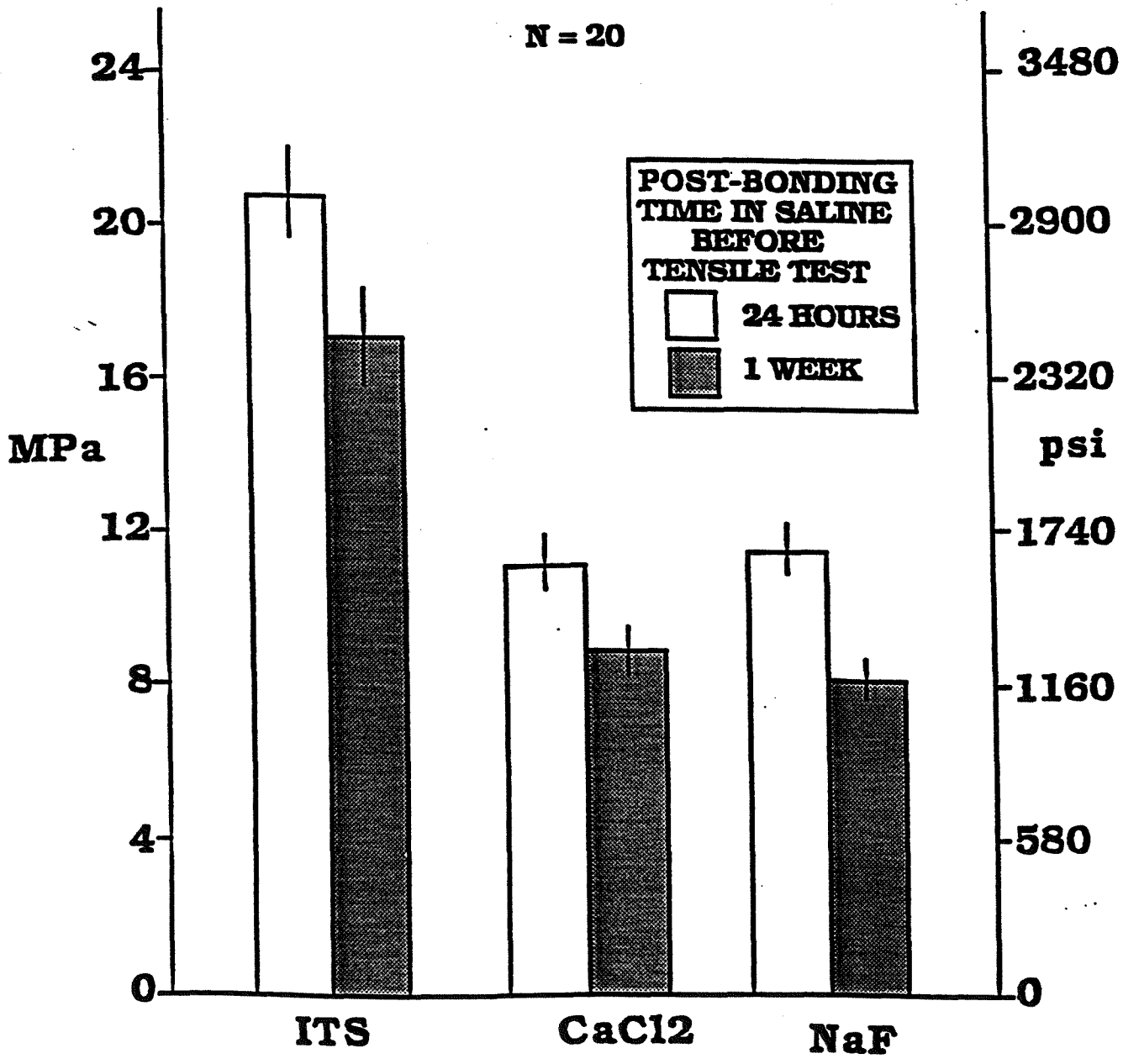


Figure 11.

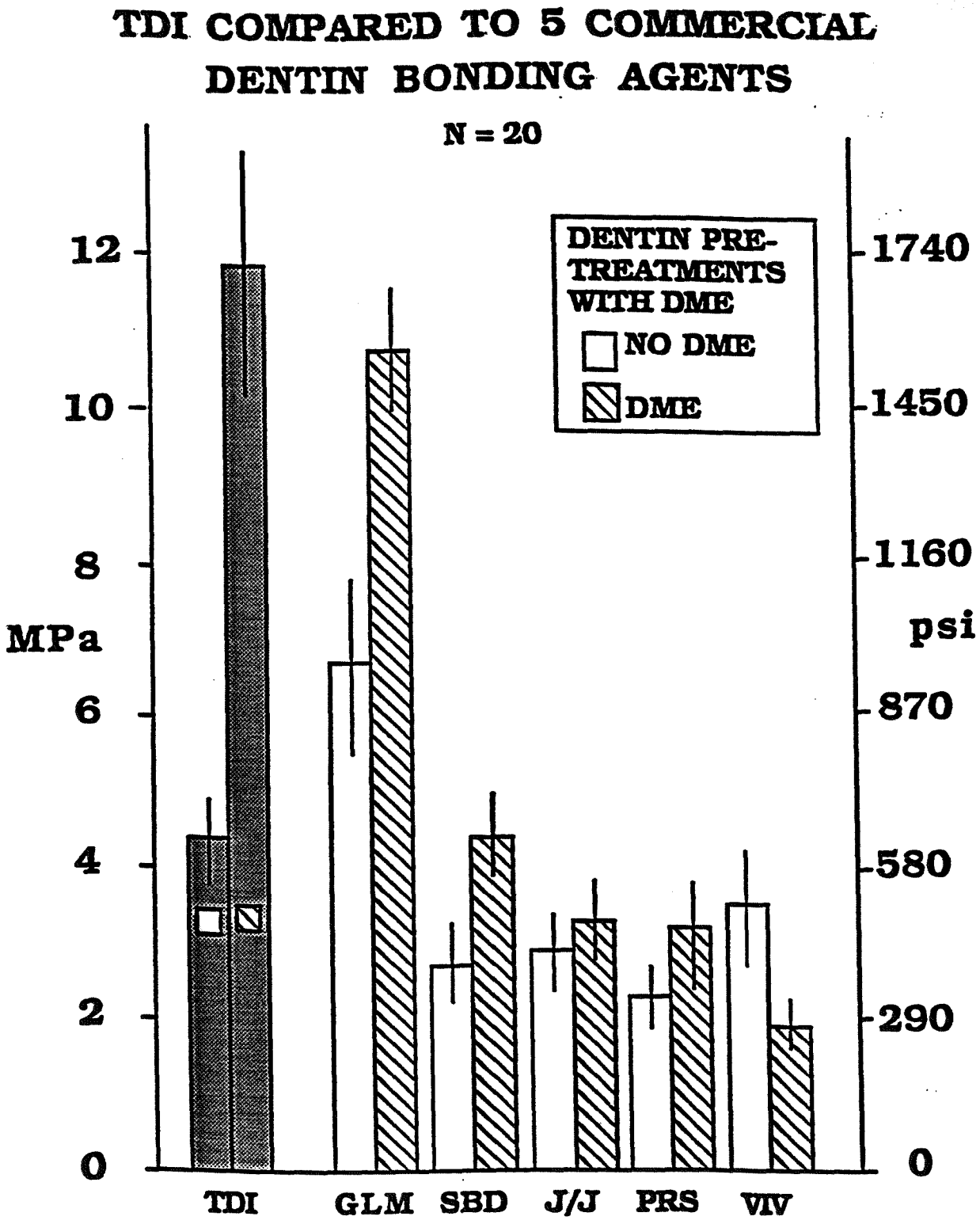

TDI COMPARED TO 5 COMMERCIAL DENTIN BONDING AGENTS
N = 20
DENTIN PRE-TREATMENTS WITH DME
NO DME
DME
MPa
psi
12
10
8
6
4
2
0
1740
1450
1160
870
580
290
0
TDI
GLM
SBD
J/J
PRS
VIV

Fig. 12

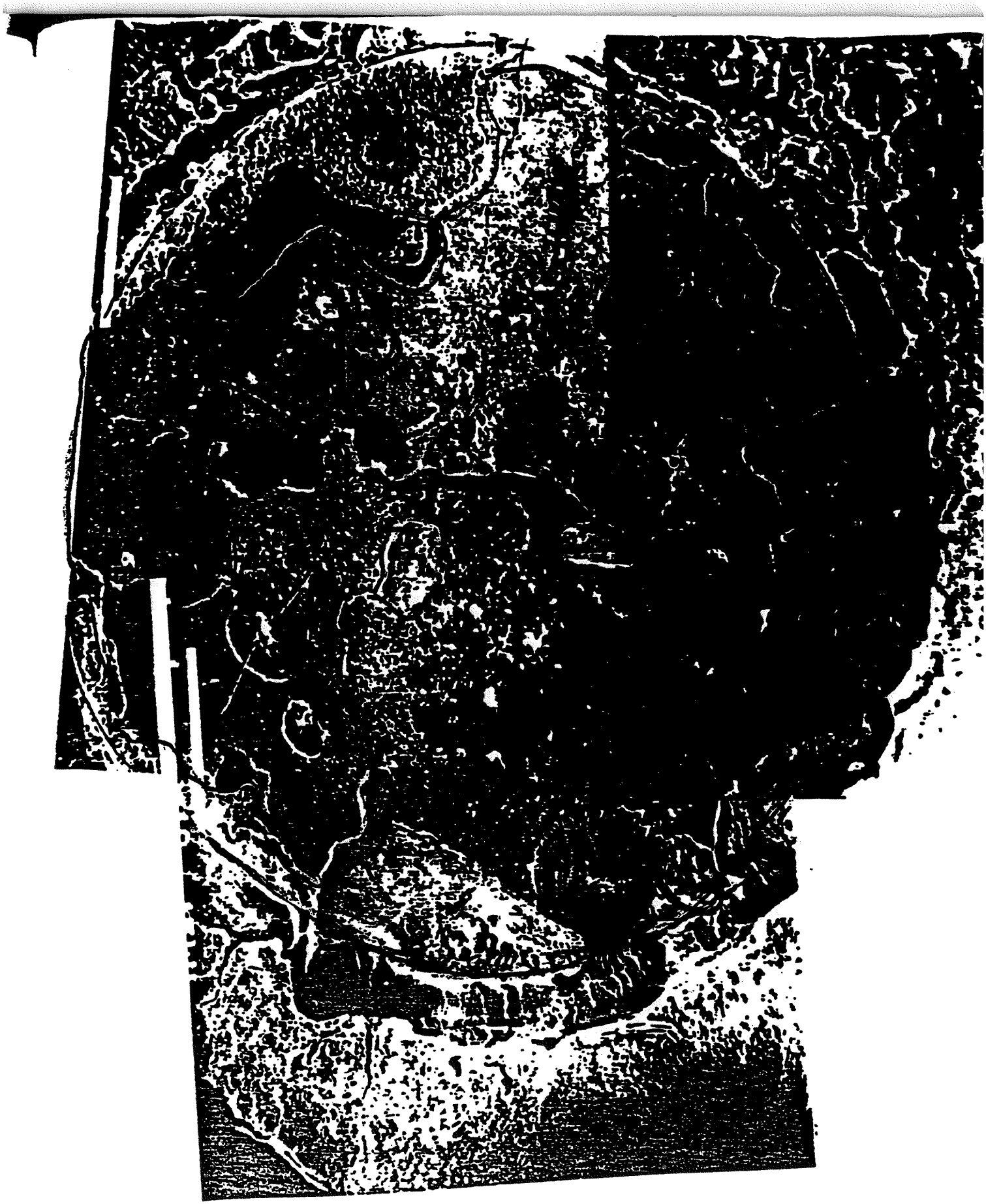


Figure 13.

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