THE BONDING OF RESINS TO DENTAL TISSUES

by

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Abstract

The bonding of resins to dental tissues is reviewed and a model is described for the mechanisms involved. A method of bonding resins to dentine by means of a novel coupling agent is proposed.

The preparation and characterisation of the coupling agent is described.

The reaction of the coupling agent with dentine is demonstrated and dentine thus treated is shown to interact with dental resin in an altered manner.

Experimental work to measure the tensile strength and specific adhesive fracture energy of adhesive joints between dental resin and dentine, made with and without the use of the coupling agent, is described. The results obtained are discussed.

Scanning electron micrographs are presented in an attempt to show alteration of the physical characteristics of the adhesive interface produced by the use of the coupling agent.

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1.0 BONDING RESINS TO DENTAL TISSUES

1.001 INTRODUCTION

The restoration of decayed and broken teeth has been practised for over two thousand years, and in this time a wide assortment of materials has been used for the replacement of lost dental tissue. Archigenes of Syria (98 - 117 AD) used a mixture of red nitre, pounded peach kernels, and resin as a restorative material, whilst in the fourteenth century Guy de Chauliac, in a list of restorative materials then in current use, mentions gallia, mastich, myrrh, sulphur, camphor, wax, ammoniacum and asafetida (LUFKIN, 1948). Gold was first used as a dental restorative material during the fifteenth century, and a stable, long lasting, silver-tin amalgam was described by BLACK (1895) in the nineteenth century. Both of these last two materials are still in widespread use in modern dentistry, and continue to form the majority of restorations.

Dental restorations of metal tend to be conspicious, and the demands of cosmetically conscious patients have led to a search for durable, tooth coloured restorative materials. Various cements have been formulated, but none has proved capable of combining the required appearance with the ability to withstand the dissolving effects of the oral fluids, and the abrasion produced by mastication. The production in the 1930s of acrylic resins which were translucent, and which could be easily coloured, appeared to offer the dental profession an opportunity to provide an ideal, tooth coloured, non soluble restorative material. The major problem to be solved was that of polymerisation initiation. Current methods required the application of heat to initiate the polymerisation reaction, and this was not easily done in the oral environment, without endangering the vitality of the tooth being restored. The discovery by German chemists, in the early 1940s, (U.S.A. PUBLICATION BOARD REPORT, 1946) of chemical means of polymerisation initiation, removed the obstacles to safe and easy use of acrylic resins as dental restorative materials.

The new materials were quickly adopted by the dental profession, as aesthetically they were a considerable improvement upon the best of the then available silicate cements. Later developments have enabled resins to be used for other dental purposes, such as splinting anterior teeth, bonding orthodontic brackets to teeth, and sealing pits and fissures in posterior teeth.

These further uses for dental resins have been actively investigated, despite the recognition in the early 1950s of problems caused by the dimensional instability of resins, as compared with other restorative materials (NELSEN, WOLCOTT and PAFFENBARGER, 1952). It was soon generally recognised that if the dental resin were to adhere firmly, or to bond, to the dental tissue it was placed against, the majority of the problems associated with the use of dental resins would be solved (CUTLER, 1952; McLEAN and KRAMER , 1952).

This thesis is an investigation into the problem of bonding of resins to dental tissues.

1.1 RESIN DENTAL RESTORATIONS

1.101 DENTAL RESINS

The resins commonly used for dental restorative work can be divided into two main groups. Firstly the unfilled acrylic resins, based upon poly(methymethacrylate); and secondly the more modern filled, aromatic diacrylate resins, commonly known as 'composite resins'. There are, or have been, a few dental restorative resins that fall outside or between these two categories, but they constitute only a tiny proportion of the materials used. The resins can be made to resemble the natural dental tissue in appearance, being more translucent than the older silicate dental cements. As dental resins are usually used to restore teeth in parts of the mouth which are easily seen, their ability to produce a restoration of high aesthetic quality meant that they became widely used by dental surgeons in a very short time.

1.102 EARLY USE OF DENTAL RESINS

Soon after widespread usage of resins had started, disadvantages became apparent. Restorations made with the resins suffered much staining around their margins and secondary dental caries was noted in many instances. NELSEN, WOLCOTT and PAFFENBARGER (1972) reported that resin restorations demonstrated marginal percolation, whose cause they attributed to the shrinkage of the resin upon polymerisation, and its subsequent thermal contraction and expansion. The coefficient of thermal expansion of the resin differs from that of the surrounding tooth by a factor of 8. Thus if a tooth and its restoration are cooled, any gap between them will enlarge, and the surrounding oral fluids will be able to flow into the space. Subsequent recovery to the original temperature will close the gap again, and the fluid will be expressed.

1.103 EARLY ADHESION SYSTEMS

It was generally recognised at this time that adhesion of the resin to the walls of the cavity would improve the restorations and prevent the marginal percolation.
CUTLER (1952) describes "a marked degree of adhesiveness or 'stiction' "when one dental resin was used, but it was quickly pointed out by McLEAN (1952) that the "adhesiveness ... is only apparent when these resins are applied to a dry tooth."

However, methods of actively obtaining adhesion to the dental tissues in vivo were being investigated. KRAMER and McLEAN (1952) and McLEAN and KRAMER 1952) reported on the use of glycerophosphoric acid dimethacrylate as a cavity adhesive. They also mention the use by NORDIN (1951) of an amine catalyst to promote polymerisation against the dentine of the cavity walls, and thus hopefully to improve adhesion of the resin to the dentine.

A new technique of using acrylic resin was suggested by NEALON (1952), which he claimed gave a perfect marginal finish.

None of these attempts were shown to be successful in producing a long lasting adhesion between a resin and dental tissue in vivo.

1.104 ACID ETCHING

In 1955 BUONOCORE demonstrated that adhesion of acrylic resin to dental enamel was considerably improved by etching the enamel with an acid, and gave examples of suitable acids.

At about the same time BOWEN (1956), (1958), (1962), was investigating alternative resins for dental use, including epoxy type resins, and also studied the effects of incorporating an inert siliceous filler in the resin. He produced a dental resin with mechanical properties superior to the plain acrylic resins that were then in use. By incorporating a high molecular weight backbone chain into the monomer, he increased the hardness and strength of the final polymerised resin, and reduced the polymerisation shrinkage. The incorporation of two "acrylic" groups into the monomer allows polymerisation to take place in a similar fashion to methylmethacrylate polymerisation, but with a high degree of cross linking, which again improves the strength of the resin. The fillers import an increased compressive strength to the resin, and by virtue of their low coefficient of thermal expansion, reduce the overall thermal expansion of the polymerised resin.

BOWEN (1965) also proposed the use of a surface active comonomer as a means of promoting adhesion between the inorganic dental tissue and the diacrylate resin.

Both Buonocore's and Bowen's work were accepted by the dental profession and today Bowen's resin forms the basis for most of the resins available commercially. Etching fluids are sold in a package with the dental resins, so that restorations may be produced, which are bonded to the enamel that forms the outer margin of the restoration.

Investigations of Buonocore's method by other workers have suggested the acids and their concentrations that give optimum etching of the enamel (GWINNETT and BUONOCORE, 1965; RETIEF and DRYER, 1967; BUONOCORE et al, 1968; MulHOLLAND and deSHAZER, 1968), and resins have been produced that have the optimum viscosity and setting time for maximum adhesion. Today many restorations are made that are bonded in this way to etched dental enamel. These restorations have a high resistance to marginal breakdown and marginal percolation. In many restorations, the adhesive bond between the dental enamel and the resin is the sole means of retention of the resin.

There is, however, a very large number of restorations placed where enamel does not form the border around the whole of the margin, and an even larger number where there is insufficient thickness of enamel to provide a means of adhesive retention of the restoration. As the resins do not adhere to the dentine, which forms the greater part of each tooth, these restorations are subject to marginal percolation where there is no enamel.

If the resins could be made to adhere to dentine as well as to enamel, then nearly all resin restorations would be free of marginal percolation. At the same time, it is possible to envisage that true adhesion to dentine will allow less preparation of the dental cavity to be performed, as undercutting of the cavity walls to provide retention would become unnecessary.

Adhesion of acrylic and diacrylate dental resins to dentine would be most advantageous in improving resin restorations, as performed at present. Together with present methods of adhesion to enamel, the restoration would be able to withstand the oral environment for longer periods of time, and with less trouble.

1.2 ADHESION

1.201 DEFINITION

Adhesion has been defined as a "mechanism by which mechanical force or work is transferred from one solid body to another, in tension or in shear, without interfacial slip or inelastic displacement of one body with respect to the other" (GOOD, 1971). This definition allows the adhesive force to be ascribed to almost any physical phenomenon or phenomena, and does not specify any particular molecular interaction between the adhering bodies. As long as there is a mechanism for transmission of mechanical effects across the joint, adhesion is present.

1.202 ADHESIVE FORCES

In the absence of covalent and ionic bonding of two adherands, there are several physical forces which are capable of providing adhesive bonds which are as strong as the cohesive bonds of the adhering phases. In all adhesive joints it is interactions between molecules of the adherands that provide the adhesive forces. The interactions that normally occur between an adhesive and the surface to which it is to adhere have been classified by KRUPP (1967).

1. Long Range Attractive Interactions
   including:
   - (a) electrostatic forces
   - (b) van der Waals - dispersion forces
2. Short Range Attractive Interactions
   including:
   - (a) various types of chemical bond
   - (b) intermediate bonds such as hydrogen bonds
3. Interfacial Reactions
   including:
   - (a) sintering effects such as diffusion and condensation
   - (b) diffusive mixing
   - (c) mutual dissolution and alloying

A possible order of events can be envisaged for the interaction of a fluid adhesive with a non specific surface. The fluid will be attracted to and drawn across the surface by the long range forces. As the molecules of the fluid adhesive approach the outermost molecules of the surface, polar forces between them are able to exert an influence, and add to the total of attractive forces. Finally when close atomic contact is made there may be some form of covalent or ionic reaction able to occur, and thus introduce an element of thermodynamically irreversible change into the system. If the fluid now undergoes a change of phase, to become a solid, the two solids will be adhering with molecular interaction providing the same attractive forces as before the phase change. By this reasoning two solids if brought closely together should also adhere to each other. In practice the surfaces are not generally smooth enough or clean enough to allow sufficiently close contact between the surface molecules over the whole surface area. If the surfaces were smooth to one atomic dimension then uniform contact would be possible. This phenomenon can be demonstrated with freshly cleaved mica in vacuum.

1.203 WORK OF ADHESION

FOWKES (1971) states that the work of adhesion W_A is equal to the sum of the work of the attractive interactions viz:-

$$W_A = W_A{}^d + W_A{}^h + W_A{}^{ab} + W_A{}^p + W_A{}^i + \dots$$

where the superscripts are d for dispersion forces, h for hydrogen bonding, ab for acid base interactions, p for dipole-dipole interactions and i for induced dipole-dipole interactions. These are all thermodynamically reversible effects. To the sum may be added the work of any further reaction of covalent, ionic or diffusive type. These will only occur in special cases where there is an inherent reactivity between the two components.

1.204 BREAKDOWN OF ADHESION

If there is a mechanical force between the two adhering phases, there may be physical separation if the adhesive interactions are insufficiently strong. The short range forces require close contact to have an appreciable effect, and under stress the adhering components may separate to such an extent that some of the polar interactions break down. When the stress is relieved, the polar interactions are able to re-establish themselves. The dispersion forces act over a large range, and decrease according to the sixth power of separation distance. If there is a liquid present at the interface the dispersion forces are decreased considerably (GLANTZ, 1969). If there is a polar liquid present then it will compete for the polar sites of attraction on both components. Thus it can be seen that if a joint is stressed in the presence of a polar liquid, there may be an opportunity for the site of the attractive interactions to become occupied by the polar liquid, and the adhesion between the two components diminished. Although only a few sites may be lost to the competing liquid when the stress is applied, repetition of the process will mean that more and more points of adhesion are lost. An adhered layer of liquid molecules will slowly form between the two components, and the dispersion forces will thus decrease as well. Eventually the adhesion may fail completely.

1.205 MECHANICS OF ADHESIVE JOINT FRACTURE

Adhesive fracture has been studied extensively in many different situations in attempts to improve adhesion. The theory advanced by BIKERMAN (1947), that adhesive joints fail only when there is a weak boundary layer in the joint, appeared an attractive theory to many. The theory requires that in the absence of a weak boundary layer, cohesive failure results in the weaker of the two adhering components. However in many cases of apparent interfacial fracture there does not appear to be any weak boundary layer as such.

GOOD (1971) shows that given correct statistical weighting of probabilities, it can be predicted that an interfacial crack will be utterly unable to depart from the interface in growth, if the forces across the interface are only one order of magnitude less than those within the bulk components. He puts forward a more general argument of adhesive failure which shows that under conditions where the interfacial forces are weak, failure will probably commence at the interface. He goes on to suggest that to design a system in which the interfacial region is not the most important source of weakness one should

(a) Provide perfect wetting (of the surface), to eliminate interfacial flows.

(b) Provide strong interfacial forces, by covalent bonding or chemisorption. (If this latter measure is not possible, components having high group dipole, or hydrogen bonding groups should be incorporated.)

(c) Surface treatment such as etching, particle bombardment etc. may be employed to improve the characteristics indicated in (a) and (b) when there is not the freedom to adjust these properties by design of the bulk phases.

This more general treatment does not preclude the concept of a weak boundary layer, but does allow for it to be absent in cases of interfacial fracture. Yet at the same time, one must guard against the formation of a weak boundary layer at the time of joint formation.

Clearly though, in order to obtain the optimum strength of an adhesive joint, the attractive forces must be at a maximum, and any reduction in effect of any one of the forces will serve to weaken the adhesive joint.

1.206 ADHESIVE FAILURE DURING WATER IMMERSION

It has been known for many years that adhesive joints, which are initially quite firm, may fail upon immersion in, or prolonged soaking with water. WAKE (1973) gives a general review of the phenomenon, and derives an expression for the spreading pressure of water between two adhering polymers, with no interfacial covalent linkage. He states that to his knowledge "there is no theoretical analysis of why the continued application of stress in the presence of moisture should be so much more deleterious to an adhesive joint that either effect separately". The analysis of adhesive mechanisms presented earlier in this chapter does suggest though that water will be a very active competitor for the sites of polar adhesion. This mechanism will also stand up to the fact that adhesive breakdown under moisture attack can in some circumstances be reversible, (MacDONALD, 1969), but if interfacial slip or displacement, or further chemical contamination of the surfaces occurs, the opportunity for reversibility will disappear. If the polar water molecules are merely competing for adhesive sites, removal of the water will release the sites for readhesion, if the close molecular contact can be re-established. Interfacial displacement or contamination will prevent this.

If there are covalent or ionic linkages across the interface, breakdown of adhesion by moisture will be greatly reduced. WAKE (1973) describes one such instance where the use of a vinyl silioxane coupling agent prevented adhesion breakdown between glass fibres and a resin in moist conditions. This is in accordance with the recommendations made by GOOD (1973).

1.3 ADHESION TO ENAMEL AND DENTINE

1.301 INTRODUCTION

Using this analysis of general adhesive mechanisms, the bonding of resins to dental tissues can be considered. As mentioned earlier there are two different components of dental tissue, enamel and dentine. Although they are superficially similar, both being hard calcium phosphate based materials, they have differences in composition and structure which account for their different adhesive behaviours.

1.302 ENAMEL

Enamel consists mainly of crystals of calcium hydroxy-apatite. ($Ca_{10}(OH)_2(PO_4)_6$). (JENKINS, 1966). The crystals are formed in an organic matrix, which in mature enamel forms 1.3% by weight or 4% by volume. Water makes up 4% by weight, the balance being crystals of apatite. The crystals are organised into prisms which run an undulating course in a general direction perpendicular to the outer surface. The prisms are a self-supporting structure, the organic matrix itself is composed of protein, and appears to be concentrated in interprismatic regions, and around each enamel crystal (SILNESS, HEGDAHL, and GUSTAVSEN, 1973; ORAMS, 1976).

1.303 DENTINE

Dentine, like enamel, is in the major portion hydroxapatite, but only to the extent of 70% by weight - 48% by volume. 18% by weight, 25% by volume consists or organic material. Water makes up the balance. (JENKINS, 1966). Dentine has a structure different from enamel. Throughout the dentine run tubules, containing long processes of living cells. The cells called odontoblants, are responsible for the formation of dentine. Fibres of collages are laid down, and form the sites for crystallisation of the apatite of dentine. The fibres remain embedded in the apatite and provide much of the strength of dentine.

1.304 RESIN - DENTAL SURFACE INTERACTIONS

It would be expected that when a fluid resin is placed upon a surface of dentine or enamel, there should be many sites where adhesive interactions will occur, and that true adhesion of the resin should take place. The apatite crystals should have many polar sites, and the proteins of the matrix many groups where hydrogen bonds can be formed. It is found though that any adhesion that does form, is very soon reduced or lost, and the analysis of the mechanisms of general adhesion must be used to explain the breakdown of adhesion.

1.305 DENTAL SURFACE CONTAMINATION

If the surface of enamel or dentine after mechanical preparation is examined, it is found that it is contaminated with low surface energy phases (GLANTZ, 1969). By means of contact angle, and wettability experiments, established that the apatitic phases are not present at the surface, but are covered with an adsorbed layer. This is of low surface energy, and most probably of organic origin. It seems that there is always a smeared layer of organic protein adsorbed by the hydroxyapatite crystals. This is in keeping with the second law of thermodynamics. Any short range interactions that can be established between the resin and the protein will tend to be less strong than those obtained between tbe resin and the higher energy surface of the apatite crystals. In effect this contamination appears to be a form of weak boundary layer.

1.306 DENTAL ADHESION AND WATER

The effect of water upon the joint must also be considered. If the dental surface is dried before adhesion is attempted, it has been established that a bond may be formed (SWARTZ and PHILLIPS, 1955). Water surrounding the joint very rapidly produces failure, by means of the mechanism described previously. In vivo, water can reach the adhesive interface by three routes, by interfacial seepage from the margins, by seepage from the dentinal tubules, and by diffusion through the resin. Thus any adhesive bonds are progressively hydrolised by the water molecules, which acgively compete for the sites of attraction.

This model of dental adhesion is also proposed by SMITH (1975) who points to further supporting evidence.

1.307 ENAMEL ETCHING

As mentioned previously, BUONOCORE (1955) demonstrated that etching of enamel with an acid produced an improvement in the adhesion of resins to enamel. The bond produced by this process has been shown by many workers to be resistent to prolonged wetting, and of high mechanical strength. Many studies have been made of the phenomenon and its clinical usage.

The mechanism of adhesion appears to be one of mechanical interlocking of the resin to the roughened etched enamel surface. Several studies have been made of the surface patterns displayed by enamel that has undergone etching (TYLER, 1976; SILVERSTONE et al, 1975; RETIEF, 1973). The enamel surface is etched at different rates in different places, and, according to the technique used for etching, the centres of the prisms, or the margins of the prisms are etched preferentially. It has been shown that resin is able to penetrate the gaps and spaces produced by the etching, often to a depth of up to 50 μm. (RETIEF, 1975; DOGON, 1975; SILVERSTONE, 1975). Fracture of a resin enamel joint produced in this manner often leaves resin still attached to the enamel surface in the form of tags trapped within the crevices and pits in the enamel. (SILVERSTONE, 1975). Etching of dentine does not produce the same increase in adhesion, and no roughening can be demonstrated. (BRANNSTROM and JOHNSON, 1974).

The evidence therefore points to the mechanical interlocking being the retentive feature of the joint between enamel and resin. This view is further supported by assertions that "the development of this surface (enamel) porosity is of vital importance from the point of view of the successful use of the (acid etch) technique. Since teeth vary appreciably in their resistance to etching treatments, routine checking is essential". (TRANTER, 1975).

If the etching produced a change in the type of molecular interaction between resin and enamel, one would expect it to produce a similar effect with dentine. The lack of this effect with dentine suggests that no fundamental alteration of adhesive mechanism is produced.

1.308 ADHESION OF RESINS TO DENTINE

The problem of bonding resins to dentine has been shown to be one of preventing hydrolysis of the sites of the normal attractive forces between dentine and resin. SMITH (1967) suggests that chemical bonds between resin and both mineral and organic phases should be investigated. This would introduce an element of irreversible change into the formation of the adhesive joint, and,as shown by COOVER (1968), shows chemical bonds may resist the progressive desorption of an adhesive at an interface due to moisture infiltration.

This line has been investigated by several workers in attempts to produce dentine adhesion. Most attempts have involved coupling agents, which are molecules capable of reacting in more than one way. The use of a coupling agent would modify the chemical properties of the dentine surface to make them suitable for reaction with the applied resin.

Polar coupling agents have been used by several people viz: KRAMER and McLEAN (1952) (glycero phosphoric acid dimethacrylate), BOWEN (1975), and CHANDLER (1974) (N(2-hydroxy-3-methacryloxpropyl)-N-phenylglycine) and ANBAR and FARLEY (1974) organic polyphosphonates. None of these has proved effective in preventing breakdown of adhesion. As these coupling agents do not promote true covalent or ionic bonding, but merely accentuate the polar interactive forces, this is further confirmation that the mechanism of adhesive breakdown by hydrolysis is correct.

MASUHARA et al. (1968) have investigated the use of polymerisable calcium chelating agents. These have given a small improvement in adhesion, but again this disappeared after storage in water.

In attempts to make the inorganic apatite more readily available for polar interactions, proteolytic enzymes have been used to remove the organic matrix. (LEE, 1969; FOOKSON, 1970; ELLISON and FOOKSON, 1969). Again these methods did not produce material improvements after water storage.

It appears that the inorganic phase of dentine is not amenable to improved polar bonding, or forming chemical bonds with resins or chelating agents. Chemical bonding to the alternative organic phase must be considered.

1.309 ADHESION BY REACTION TO THE ORGANIC PHASE OF DENTINE

Comparatively little work has been done in this field. To date, two methods have been described which use conventional dental resins. BRAUER (1975) describes work by RAO, JOSEPH and NAYDAMMA (1968, 1970, 1971) and by BRAUER and TERMINA (1971, 1973, 1974) using cerium compounds as initiators, to react vinyl monomers with collagen. Although this technique does produce a reaction between the resin and the organic material, and can be used to bond monomers to bone, the conditions for reaction are not suitable for dental use in vivo.

The other described method is the use of tri-n-butyl borane as a polymerisation initiator with poly(methylmethacrylate), to produce a grafting of the polymer to collagen (MASUHARA, 1964). SANJO (1971) has reported on the clinical use of this resin, and it does appear to produce adhesion to dentine, which stands up to prolonged wetting, but further information is required.

It would seem from the limited evidence available that chemical bonding to the organic phase of dentine does promise to be a successful method of preventing breakdown of adhesion. A successful technique must produce the chemical union in a way compatible with the oral environment, and ideally should be able to be used with commercially available resins.

1.310 DESIGN OF A RESIN - DENTINE BONDING SYSTEMS

A reaction between present resins and the dentine organic phase could be achieved with a coupling agent with ability to react with both components. The agent must be capable of reacting with the collagen at or near body temperature (37°C), in a moist environment, and then capable of taking part in the subequent polymerisation reaction.

A search of the literature was made for references to compounds that might fulfil the first part of the double reaction, i.e. react with dental proteins at body temperature. A paper by GOLAND et al. (1965) describes the use of some reactive halogen compounds as fixatives for preserving enamel protein during decalcification. Various compounds were used and shown to react with the organic phase of enamel in such a manner as to strengthen the tissue and allow complete decalcification. They obtained the best results with water soluble reactive dyes, based upon a triazine ring. Further investigation suggested that here was a type of compound that would form the basis of a suitable reactive coupling agent.

Reactive dyes are dichloro-s-triazine compounds. Dichloro-s-triazines are capable of reacting with many organic materials, with the formation of covalent bonds. (DAWSON et al. 1960; VIRNK et al., 1962; MULLEN, 1962). The reaction is usually a condensation reaction with amine or hydroxyl groups of the organic tissue. Collagen, by virtue of its amino acid formation, (JENKINS, 1966), has many free amine and hydroxyl groups. These would be available in dentine to react with a coupling agent containing a dichloro-s-triazine group. The work of GOLAND et al. (1965) also suggests that the enamel proteins would also be able to react with such a reactive coupling agent.

The parent of the dichloro-s-triazines is trichloro-s-triazine, and to this can be attached many different compounds. In the case of the reactive dyes, a "chroma" molecule is linked to the triazine, which in turn binds it to the cloth it is being used to dye. A reactive coupling agent would use the triazine group in a similar manner, to bond a resin polymerisable molecule to the collagenous protein of dentine.

1.311 HYPOTHESIS OF A METHOD OF BONDING RESINS TO DENTINE

The hypothesis is put forward that a dichloro-s-triazine coupling agent, containing a polymerisable group, would react with a dentine surface, and a dental resin, at body temperature, to produce an adhesive bond between the dentine and the resin that would be resistent to deterioration during immersion in water.

1.312 EXPERIMENTAL WORK TO TEST HYPOTHESIS

The work to be described in this thesis tests this hypothesis, and presents the conclusions that can be made. The work undertaken to test the hypothesis falls into the following sections:

(1) Production of a coupling agent from the parent trichloro-s-triazine, its characterisation, and identification.

(2) Confirming the ability of the coupling agent to react with the dentine surface, and the dental resin.

(3) Showing that the bond produced by use of the coupling agent resists deterioration during immersion in a simulated oral environment.

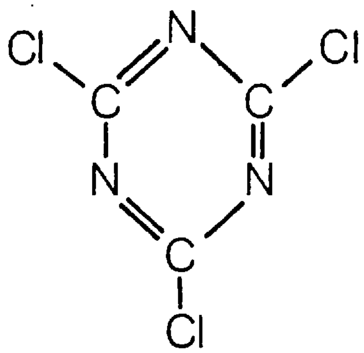
2.0 PREPARATION OF A COUPLING AGENT

2.001 INTRODUCTION

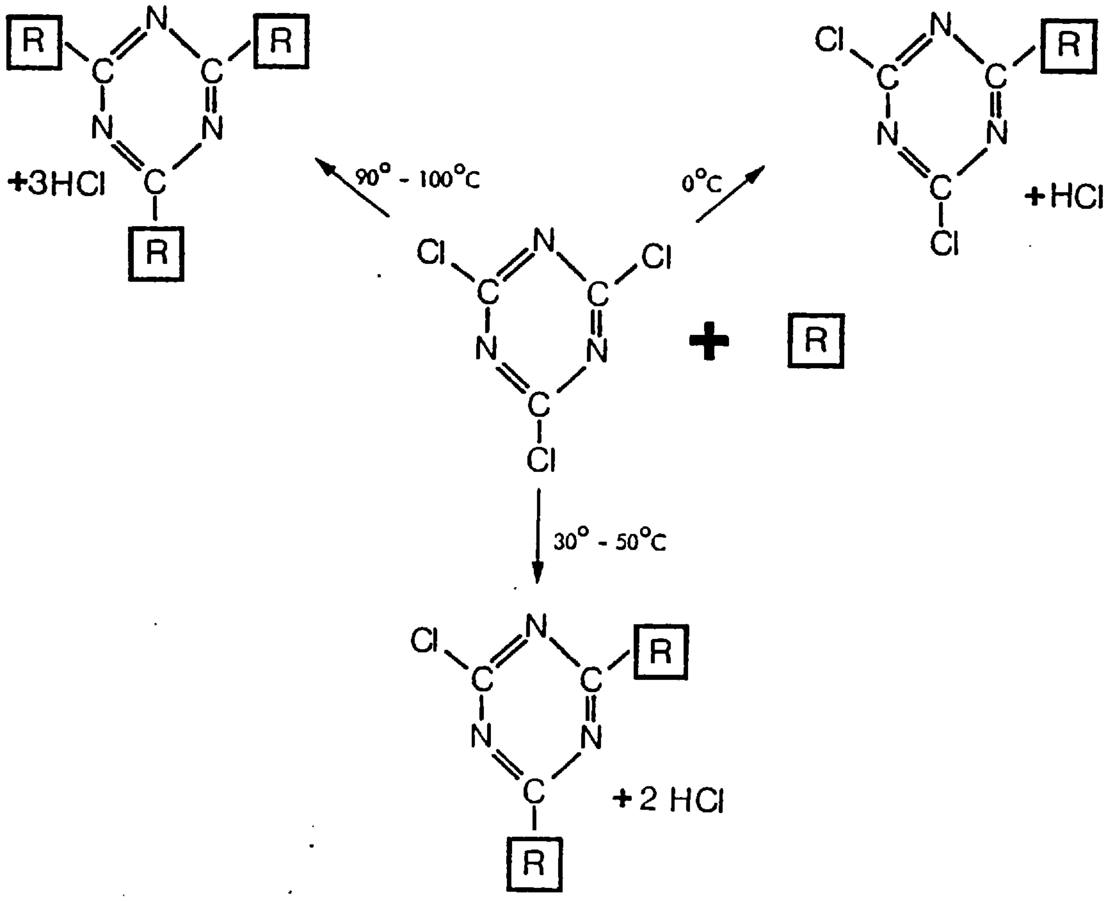
Trichloro - s - triazine was first prepared by SERULLAS in 1828. Since then it has been used as a starting point for the synthesis of many compounds containing the triazine ring. In 1937 FIERZ - DAVID and MATTER published a review of reactions between dyes and trichloro - s - triazine, which was further added to by a series of papers originating from the American Cyanamid Company (THURSTAN et al., 1957). These writers provide much information about the preparation of triazine derivatives.

Trichloro - s - triazine is a white crystalline material with an unpleasant pungent odour. It is a reactive molecule, the most common reactive sites being the three chlorine atoms (Fig. 2:1). These are very reactive, but as substitution of the chlorine atoms occurs, the reactivity declines. By controlling the physical conditions of reaction, mono -, di -, or tri - substituted products may be easily produced (ELDERFIELD, 1962). To produce a molecule of the type proposed in chapter 1 (1.311) capable of acting as a coupling agent, it is necessary to attach to the trichloro - s - triazine a 'vinyl' containing molecule, yet leave the triazine as reactive as possible. This suggests that the coupling agent will be a chloro - triazine of a monosustituted nature, thus leaving two unreacted sites available to take part in reactions with suitable sites in the dental protein (Fig. 2:2).

FIGURE 2:1



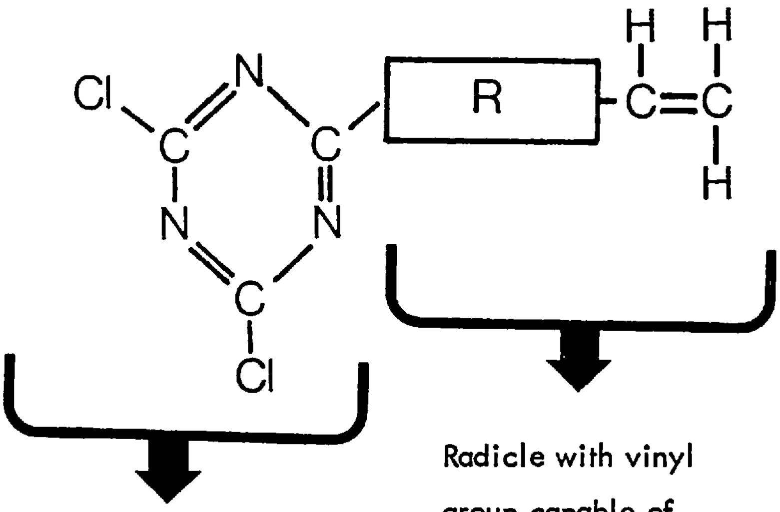
TRICHLORO - S - TRIAZINE AND ITS REACTIONS.



Reactions of Trichloro - s - triazine where $\boxed{R}$ is a molecule with a group having an active hydrogen:-
e.g.:- -OH , $-NH_2$, -SH etc.

FIGURE 2:2

MOLECULAR STRUCTURE OF THE PROPOSED COUPLING AGENT.



Monosubstituted triazine ring to react with suitable sites at tooth surface.

Radicle with vinyl group capable of undergoing polymerisation reaction with acrylic or diacrylate resin.

2.002 SUBSTITUTION OF TRIAZINES

The group that appears most convenient to use in the displacement of the chlorine atom is the amino group. FRIES (1886) and DIELS (1889) were the first to use this reaction, and subsequent work has shown that the chlorine atoms are replaced stepwise at temperatures of approximately (i) 0°C, (ii) 30° - 50°C, and (iii) 90° - 100°C. Thus if the temperature of a substitution reaction is held at about 0°C, a preponderance of the monosubstituted triazine is to be expected in the final product.

2.003 DESIGN OF A COUPLING AGENT

The choice of compound to be reacted with the triazine depends upon the reaction pathway that is selected. The product molecule is require to have:-

(i) One or more ethylenic bonds capable of taking part in a polymerisation reaction with an acrylate.

(ii) Two unsubstituted chlorine atoms on a triazine ring.

If it is assumed for the aforementioned reasons, that the bridge between the two halves of the molecule will be an amino group, then:-

(iii) One amino group will be present within the final product.

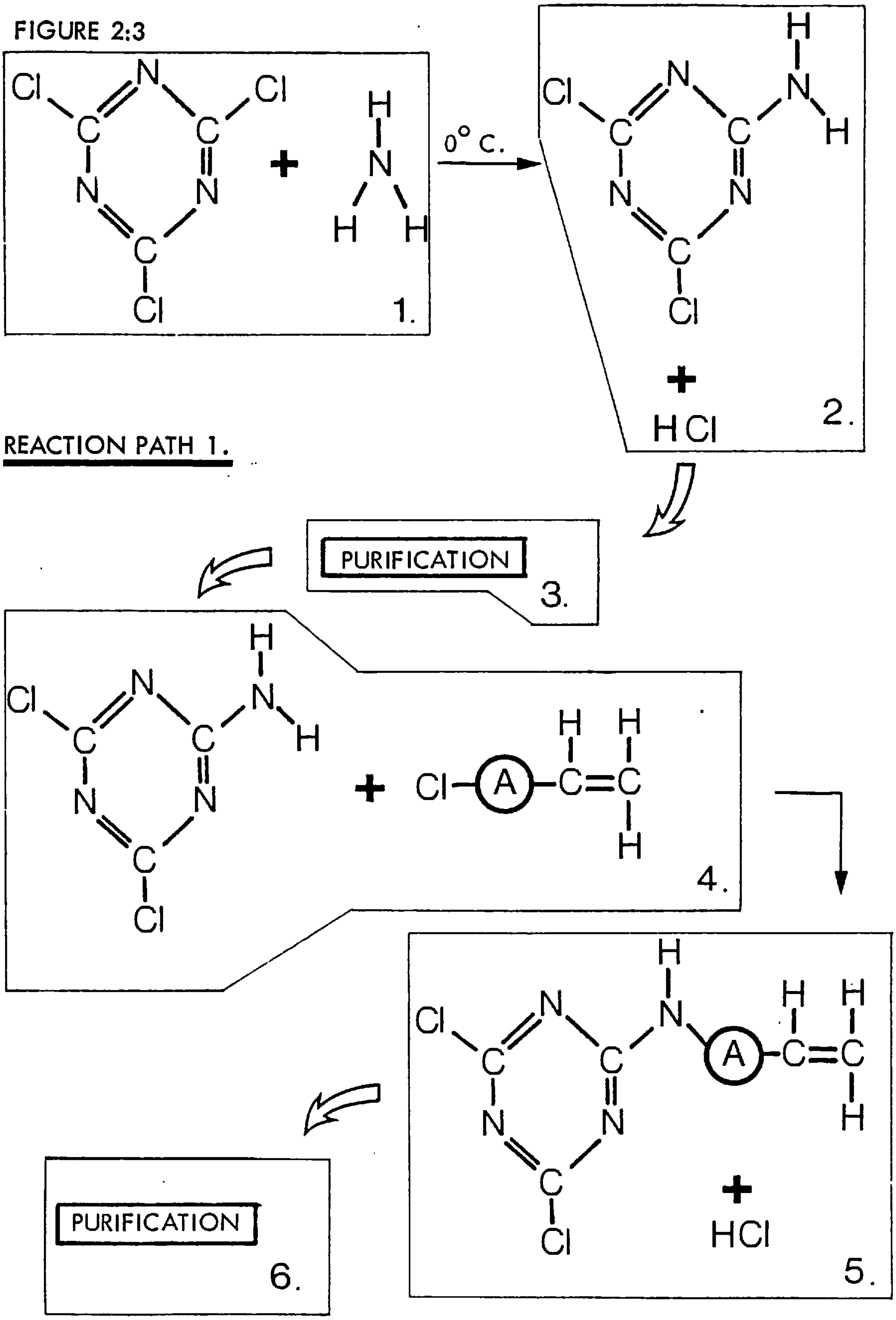
The third premise can, however, be qualified, as THURSTAN et al. (1957) showed that 2 amino, 4,6, dichloro triazines prepared by substitution with secondary amines were considerably less reactive than those prepared by substitution with primary amines. The reason for this is probably the presence of the hydrogen atom of a primary amine group drawing the electron cloud of the triazine towards itself, with a net effect resembling that formerly produced by the now displaced chlorine atom. When a secondary amine is used in the substitution, there is no polar hydrogen atom to attract the electron cloud, and the two remaining chlorine atoms are able to interact with the electron cloud more strongly, and thus become more firmly bound to the triazine ring.

2.004 REACTION PATH 1

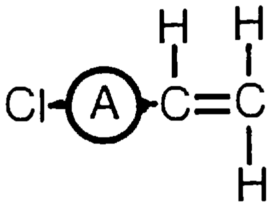
The compound that fits all three requirements can be produced by one of two reaction paths. The first (Fig. 2:3) involves amination of the triazine to give simple 2 amino, 4,6, dichloro - s - triazine, and subsequently reacting this intermediate product with a suitable alkenyl chloride. The first step can be carried out by passing ammonia gas through a solution of trichloro - s - triazine, with the temperature very closely controlled to 0^oC, and with careful measurement of the total quantity of ammonia passed. Any excess will produce the di- and tri- substituted triazines very easily.

The product must be purified twice, firstly after the amination, and then after the reaction with the alkenyl chloride.

FIGURE 2:3



REACTION PATH 1.



$\mathrm{Cl}-\text{Ⓐ}-\mathrm{CH{=}CH_2}$ is an alkenyl chloride.

2.005 REACTION PATH 2

The second reaction path (Fig. 2:4) involves reaction of trichloro - s - triazine directly with an alkenyl amine, followed by purification. Again this reaction must be carried out under conditions of controlled temperature, and with accurately measured quantities of reactants, but it is easier to measure a quantity of liquid or solid than an equivalent quantity of a gas.

Of the two reaction paths, the second appears to be the more sensible to use as only one reaction step is necessary, and thus only one purification stage is required.

SCHAEFFER et al. (1951) have prepared some vinylamino - s - triazines but did not attempt to retain ubsubstituted chlorine atoms. None of their results or preparative methods are applicable here, as their investigations were directed towards rather different ends.

2.006 CHOICE OF REACTANTS

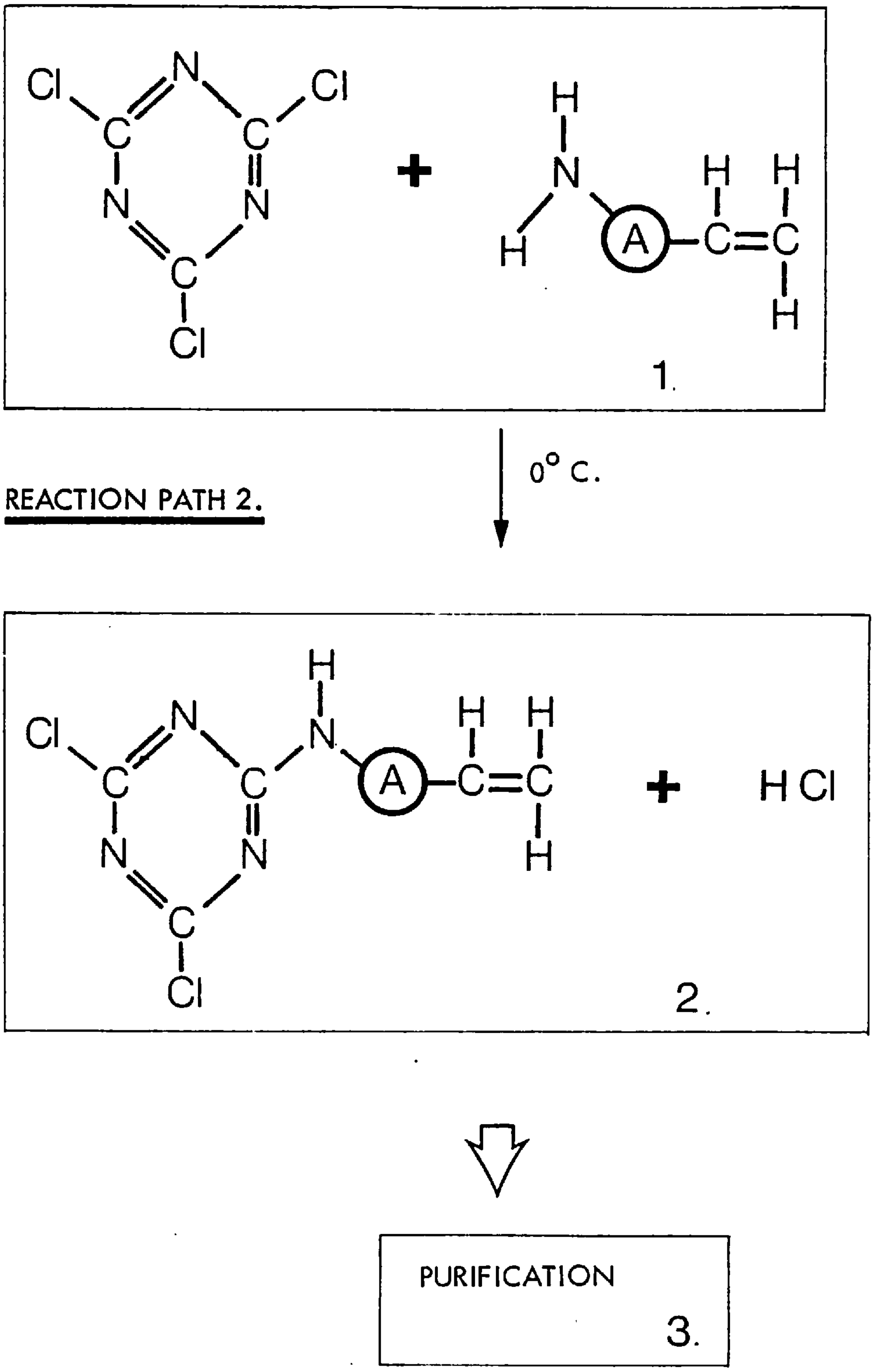
Having made the choice of the one stage reaction, the reactant must be selected. As stated this will be an alkenylamine, of which the simplest available is allylamine (Fig. 2:5). Vinylamine is unknown in its monomeric form, and is thus unsuitable. It was therefore decided to use allylamine.

2.1 METHODS OF PREPARATION

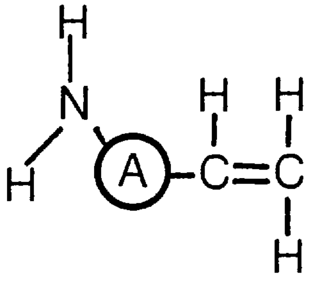
2.101 INTRODUCTION

THURSTAN et al. (1957) describe a method for preparation of monosubstituted amino - chloro - s - triazines which is a modification of a method used by DIELS (1889).

FIGURE 2:4

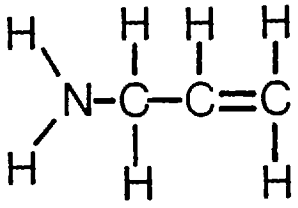


REACTION PATH 2.



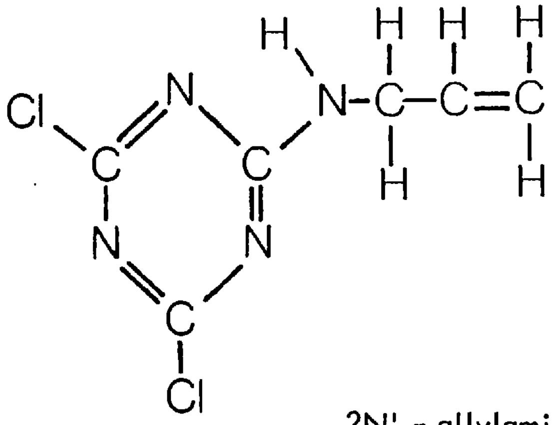
is an alkenyl amine.

FIGURE 2:5



ALLYLAMINE

THE ALKENYL AMINE USED IN THE PREPARATION OF THE COUPLING AGENT AND THE STRUCTURE OF THE PROPOSED REACTION PRODUCT.



2N' - allylamino 4,6, dichloro - s - triazine

The method enables the reaction to take place in an aqueous medium, which allows easy isolation of the end products. The triazine must be in a finely divided state, and this is done by pouring a hot solution of the triazine in dioxane, acetone or similar, into ice water. The reaction is controlled by temperature. The HCl that is produced as a by-product can be neutralised by the addition of a weak base, such as sodium carbonate or bicarbonate. This remains in solution, whilst the wanted reaction product is insoluble in water.

2.102 METHOD OF SYNTHESIS

The preparation of the triazine coupling agent was carried out as follows:-

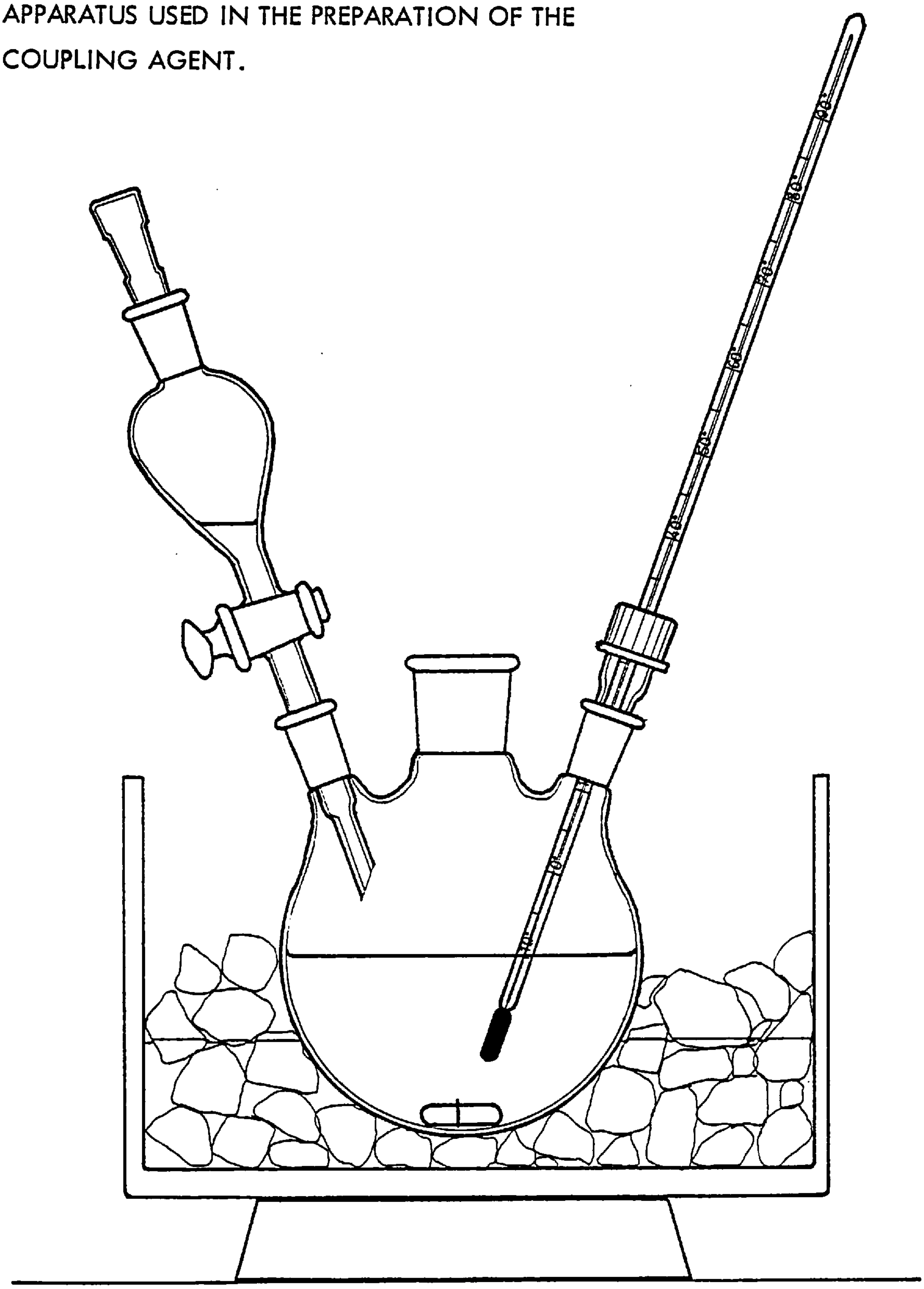
1.85 grams of trichloro - s - triazine were weighed out and dissolved in 6 ml. of hot acetone. This solution was then poured into a triple necked flask containing 10 ml. of distilled water at 0°C. The flask was buried up to the neck in a freezing mixture of ice and common salt, contained in a glass trough. The whole assembly was standing on the platform of a magnetic stirrer, and a magnetic paddle was placed in the flask, to agitate and mix the contents (Fig. 2:6).

Pouring the hot triazine solution into the cold water produced a very fine white suspension of the triazine. The temperature of the contents of the flask was measured with a thermometer that passed into the flask via one of the side necks.

When the temperature of the slurry had decreased to 0°C, a dropper funnel containing 0.6 gm of allylamine

FIGURE 2:6

APPARATUS USED IN THE PREPARATION OF THE COUPLING AGENT.



(0.81 ml) was inserted into the other side neck of the flask, and the allylamine added to the slurry drop by drop. Each addition of the allylamine produced a temperature rise of the flask contents, but by careful control of the addition of the amine, the temperature could be kept below 5°C, and usually below 3°C. The temperature was allowed to return to 0°C before each addition of the amine. About half an hour was required for the addition of the whole of the amine, and then 0.9 gm of sodium hydrogen carbonate was added to the mixture in powder form, to take up the H^+ ions produced during the reaction. This produced a foaming of the vessel contents, as CO_2 in gaseous form was liberated, but this subsided over a period of another twenty minutes, during which the reaction was allowed to go to completion.

2.103 METHOD OF PURIFICATION

The reaction products were then poured into a Buchner funnel containing a paper filter disc, and which was connected to a vacuum pump via a flask. The unwanted filtrate was thus drawn into the flask leaving the solid substituted triazine upon the filter paper. The solid product was then washed thoroughly with distilled water to carry away the un wanted NaCl by-product, plus any other unwanted water soluble by-products. The white powder was then transferred from the filter paper to a glass vessel, and dried overnight under vacuum.

Next day the dried powder was further purified by dissolving it in a minimum of hot 40/60 petrol ether, and allowing the solution to cool. The triazine after a period of time crystallized from the solution, giving an apparently very pure product, and a solute containing the unwanted by-products. The solute was disposed of, and the triazine again transferred to a glass vessel and dried overnight under vacuum.

2.2 CHARACTERISATION OF COUPLING AGENT

2.201 DESCRIPTION OF COUPLING AGENT

The reaction product 2 - N' - allylamino - 4,6 - dichloro - 1,3,5 - triazine, is a white crystalline powder, with needle shape crystals. It has an odour resembling that of its parent unsubstituted triazine, through of lesser intensity. This is to be expected, as the available reactive groups are of similar type, though fewer in number. It is to be expected that the ubsubstituted triazine hydrolizes in contact with the moist nasal membranes, to produce small quantitites do produce small quantities of HCl. At body temperature there are theoretically two potential reaction sites per molecule. With the substituted triazine this number is reduced to one. This will reduce the amount of HCl produced and thus reduce the effects caused by its presence on the nasal lining.

2.202 DETERMINATION OF MELTING POINT

The melting point of the crystals was observed by placing some of the crystals on a glass slide with a cover glass, on a heated microscope stage designed for such purposes. The temperature of the stage and slide was increased slowly and was monitored by means of a thermometer in contact with the stage. The crystals were observed to melt completely at a temperature between 63.5°C and 65°C.

This fairly well defined melting point serves to suggest that the product obtained is indeed of a fairly pure nature.

2.3 CHEMICAL IDENTIFICATION BY INFRA RED SPECTROSCOPY

2.301 INTRODUCTION

To confirm that the chemical produced was in fact 2 - N' - allylamino 4,6 - dichloro - s - triazine, a portion of the sample was examined by means of infra red spectroscopy. In order to identify the chemical correctly it was deemed necessary to search for evidence of molecular features which are peculiar to this molecule, and to no other. The two features which one would first seek to identify are the dichloro substituted triazine ring, and the ethylenic double bond. If these are present then the molecule will most likely be able to fulfil the role for which it was designed. It is important, however, to look for evidence that the amine has in fact reacted with the triazine in the manner intended, and that a bridge has been formed by means of the amino group.

2.302 METHOD

A small quantity of the triazine bonding agent was mixed to a mull with liquid paraffin (Nujol) in the standard manner, and placed in a standard sodium chloride cell. The cell was then placed in a Perkin Elmer double beam infra red spectrometer, and the spectrum,reproduced in Fig. 2:7, was traced.

2.303 INFRA RED SPECTRA OF TRIAZINES

The main features of the spectra of chloro triazines have been reported by REIMSCHUESSEL and McDEVITT (1960). They show that trichloro - s - triazine has strong absorption bands with wave-numbers of 1504 cm^{-1}, 1266 cm^{-1}, 855 cm^{-1} and 798 cm^{-1}.

The 855 cm^{-1} band is allocated to the carbon- chlorine stretch vibration, and is present also in dichloro triazines, but appears to move slightly to lower wave-numbers according to the substituting group. PADGET and HAMNER (1958) make no mention of this absorption peak, yet they present spectra for 8 chlorotriazines, of which all the dichloro triazines show a very strong peak at this point. Monochloro triazines do not show the 855 cm^{-1} band at all, and thus presence or absence of this band allows differentiation between mono and dichloro triazines to be made.

The other three bands, 1504 cm^{-1}, 1266 cm^{-1} and 798 cm^{-1} are all associated with vibration modes of the ring structure itself (REIMSCHUESSEL and McDEVITT, 1960; PADGET and HAMNER,1958). The 1504 cm^{-1} and 1266 cm^{-1} bands have been established as being in plane ring vibrations (GOUBEAU et al., 1954) and are particularly susceptible to alteration when the chlorine atoms are substituted. Substitution appears to split both bands, moving the 1504 cm^{-1} band to slightly higher wave-numbers, whilst the 1266 cm^{-1} band appears to move the other way. The movement of the latter band appears to be dependent upon the substituting group, a butylamino group moving the band further than a simple amino group.

The 1504 cm^{-1} band splits to give 3 identifiable bands at approximately 1563 cm^{-1}, 1504 cm^{-1} and 1450 cm^{-1}, (REIMSCHUESSEL and McDEVITT, 1960), the last usually being weaker than the other two.

The 798 cm^{-1} band is produced by the out-of-plane vibration of the triazine ring, (PADGET and HAMNER, 1958) and is moved very slightly to lower wave-numbers by substitution of the chlorine atoms. Neither PADGETT and HAMNER, nor REIMSCHUESSEL and McDEVITT mention the appearance of a small peak at about 760 cm^{-1} when substitution is performed, but this is apparent on many of the spectra of mono and dichloro - s - triazines that they both present.

2.304 IDENTIFICATION OF TRIAZINE GROUP

On examining the spectrum given in Fig. 2:7, it is possible to identify all of the features described for a dichloro - s - triazine.

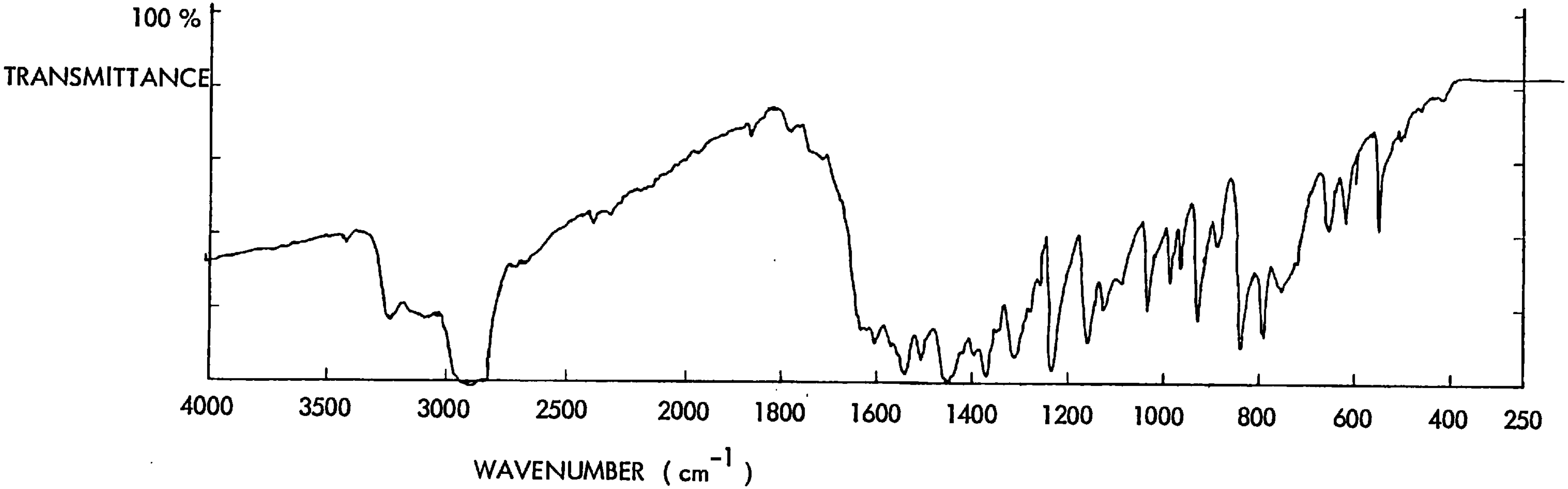
The strong peaks at 1455 cm^{-1} and 1380 cm^{-1}, and the wide band from 2980 to 2820 cm^{-1} can be immediately assigned to the Nujol dispersant used in the mull.

The short-wave, in-plane vibrations of the triazine ring show up at 1553 cm^{-1} and 1513 cm^{-1}, plus the weaker band at 1427 cm^{-1}. The long-wave, in-plane vibration is present, but split and shifted to 1240 cm^{-1} and 1168 cm^{-1}. This fairly large shift can possibly be attributed to the large size of the allylamino substitution molecule.

The out-of-plane triazine ring vibration is also present with a strong band at 796 cm^{-1}, and there is also a small peak at 756 cm^{-1} which may possibly be identified with the 760 cm^{-1} peak mentioned previously.

FIGURE 2:7

INFRA -RED SPECTROGRAM OF THE PRODUCT OF REACTION BETWEEN TRICHLORO - S - TRIAZINE AND ALLYLAMINE.



The 855 cm^{-1} carbon-chlorine stretch band can be identified with the strong peak at 844 cm^{-1}. The presence of this strong band would seem to be substantive evidence that this is the spectrum of a dichloro - s - triazine.

2.305 IDENTIFICATION OF C-H STRETCH VIBRATIONS

The next molecular group to be identified is the vinyl group, present as $R-CH = CH_2$. This group may produce as many as eight identifiable absorption peaks (CROSS and ALAN JONES, 1969). The vibrations producing these peaks may be produced by vibrations of C=C bonds, or C-H bonds, the C-H vibrations being further divided into stretch or deformation vibrations. The C-H vibrations also depend upon the position of the C-H bond within the molecule, those of the $= CH_2$ group vibrating at a different rate to those of the -CH = group.

The vibration frequency for the C=C bond, in the grouping $R-CH=CH_2$, is usually 1645 to 1640 cm^{-1}. A fairly strong peak is present in Fig. 2:7 at 1635 cm^{-1}.

The C-H stretch mode vibrations are normally found at 3095 to 3075 cm^{-1} for the $=CH_2$ group, and at 3040 to 3010 cm^{-1} for the -CH=group. This area of the spectrum in Fig. is partially obscured by the Nujol absorption peak, but it is possible to discern a peak at 3080 cm^{-1}, representing the C-H stretch vibration of the $=CH_2$ group, and a small shoulder appears on the side of the Nujol peak at 3020 cm^{-1} which may represent the C-H stretch vibration of the -CH=group.

2.306 IDENTIFICATION OF C-H DEFORMATION VIBRATIONS

It is possible to be much more definite when the deformation vibrations of the C-H bonds are considered. For the $=CH_2$ group an in-plane vibration frequency is normally found at 1420 to 1410 cm^{-1}, and Fig. 2:7 displays a peak at 1404 cm^{-1}. An out-of-plane vibration peak is normally found at 915 to 905 cm^{-1}, and very often an overtone of this vibration is found at twice this frequency in the range 1850 to 1800 cm^{-1}. Fig. 2:7 displays a peak at 936 cm^{-1}, but the presence of an overtone at double this frequency, 1872 cm^{-1}, must surely confirm its representing the out-of-plane deformation vibration of C-H bonds in the $=CH_2$ group.

There is a possibility that the in-plane vibration of the C-H bonds could be identified with the peak at 1427 cm^{-1} rather than the peak at 1404 cm^{-1}, but this would mean that the short-wave, in-plane vibration of the triazine ring would then have to be assigned to the peak at 1404 cm^{-1}. On balance it is more likely that it is the ring vibration at 1427 cm^{-1}.

The deformation vibrations of the C-H bond of the -CH=group are given as 1300 to 1296 cm^{-1}, for the in-plane vibration, and 995 to 985 cm^{-1} for the out-of-plane vibration. Peaks for these are found in Fig. 2:7 at 1326 cm^{-1} and 994 cm^{-1} respectively.

Although these frequencies individually vary a little from the most usual reported positions, the evidence of their combined presence is sufficiently strong to suggest that there is present in the chemical under investigation, a chemical group of the configuration $R-CH=CH_2$.

2.307 IDENTIFICATION OF N-H STRETCH VIBRATIONS

The last part of the bonding agent molecule that is required to be identified, is the amine 'bridge'. The reaction between the allylamine and the trichloro - s - triazine changes the amine from a primary to a secondary amine. Thus if the amine present in the prepared chemical is a secondary amine, it may be assumed to be acting correctly as a bridge. There are two types of vibrating bond in anine; N-H bonds and N-C bonds. The N-H bonds may vibrate in stretching and deformation modes, whereas the N-C bond stretches only (CROSS and ALAN JONES, 1969).

N-H stretch vibration of a secondary amine occurs at a frequency of 3500 to 3300 cm^{-1}, whilst that for a primary amine occurs at 3450 to 3250 cm^{-1}. Fig. 2:7 shows a peak at 3255 cm^{-1} which probably represents N-H stretch vibration but is a fairly wide peak and alone it cannot be used to differentiate between a primary and a secondary amine.

2.308 IDENTIFICATION OF N-H DEFORMATION VIBRATIONS

In the case of N-H deformation mode vibration, primary amines show a strong peak at 1650 to 1580 cm^{-1}, whilst secondary amines show only a weak peak at circa 1500 cm^{-1}. A shoulder at 1653 cm^{-1} may be distinguished in Fig. 2:7 but it is very small, and is thus more likely to be associated with a secondary amine than a primary amine.

It is to be expected that the hydrogen atom of the amine group in the proposed triazine molecule, will be involved in an interaction with the electron clouds associated with the dichloro substituted ring. This form of hydrogen bonding would be expected to alter significantly the vibrational frequencies of N-H bond.

2.309 IDENTIFICATION OF C-N VIBRATIONS

When the evidence for the presence of the C-N bond is examined, identification is more conclusive. The C-N bond of a primary amine has an absorption peak at 1090 to 1070 cm^{-1}, whilst that of a secondary amine falls at 1190 to 1130 cm^{-1}. In Fig. 2:7 is a peak at 1138 cm^{-1} which may be assigned to a secondary amine.

Once again it is the combined evidence which seems to point to the presence of a secondary amine, rather than the evidence for individual bonds.

2.310 CONCLUSIONS DRAWN FROM INFRA RED SPECTRUM

From the facts presented, it is possible to say that the chemical whose infra red spectrum is shown in Fig. 2:7 can be identified as a dichloro - s - triazine, the substituting group of which contains a secondary amine, and a vinyl group of the form $R-CH=CH_2$. It is known that the chemical is the reaction product of a reaction between trichloro - s - triazine, and allylamine, and it is postulated that it is 2 allylamino - 4,6, dichloro - s - triazine. All of the features displayed in the infra red absorption spectrum by the prepared chemical are those that one would expect to find upon examining the required chemical in a similar way. From the knowledge of the mode of preparation, the well-defined melting point, and the purification procedures undertaken, it is apparent that the chemical is not a mixture of components displaying these features, but a true compound. It is thus claimed that the chemical produced as a coupling agent is in fact 2-N'-allylamino - 4,6, dichloro - s - triazine.

3.0 REACTIONS OF THE COUPLING AGENT

3.001 INTRODUCTION

The use of the reactive coupling agent requires that two reactions must occur if the hypothesis set out in chapter 1 is to be fulfilled. The coupling agent must react with suitable sites on the dental tissue surface and must then react with the polymerising dental resin placed upon it. Demonstration of these reactions is a difficult problem, as it is a surface only that is taking part in the reaction, and the quantity of material involved is very small. Any investigation which requires removal of the surface will destroy the physical distribution of the reaction products, and any evidence of their availability for further reaction. It must surely be best to investigate the surface in situ, and to look for properties that have been changed by the occurrence of the chemical reaction, and which can be attributed to the reactions alone.

As two reactions are involved, two experiments were designed; one to demonstrate the occurrence of each reaction. For the purposes of the experiments, and all subsequent experiments involved in the testing of the hypothesis, standards for methods of preparation, conditions of reaction and reactants were established. These are described as each is first used and reasons given for their choice.

3.1 REACTION OF THE COUPLING AGENT WITH DENTINE

3.101 INTRODUCTION

If a specific chemical reaction has occurred on the dentine surface during the application of the coupling agent, specific chemical sites will be involved and thus become unavailable for further reaction in a similar fashion. If it can be demonstrated that these specific sites are present before treatment of the dentine with the coupling agent, but are either absent, or greatly decreased in number after treatment, then it would be fair to assume that the coupling agent has in some way used up and thus made unavailable, these sites.

This proposal requires a method of showing the presence or absence of the specific sites, and one way of doing this would be to use a chemical analogue of the coupling agent, but an analogue with a readily detectable presence. It is suggested that a triazine type reactive dye will act in a manner sufficiently similar to the required mode of reaction of the coupling agent, that it may be usefully employed as a chemical analogue of the coupling agent.

A dye has the useful property of displaying its presence by colouring the material it is attached to. Thus if the bonding agent is capable of involving the specific reactive sites on the dentine surface, in this case the amine and hydroxyl groups of the collagen of the dentine organic matrix, then a reactive dye will be unable to colour the dental surface after treatment of the surface with the coupling agent.

3.102 EXPERIMENTAL DESIGN

An experiment was designed whereby the colouration of a smooth dried dentine surface could be measured, that is its reflectance could be measured in relation to the wavelength of the illuminant across the whole of the visible light spectrum. This would be done after preparation of a standard surface, to provide a reference for all further measurements.

The surface would then be treated with a standard solution of the reactive dye for a standard period of time and, having removed all surplus dye by washing with water, the surface could then be reassessed for colouration. These two measurements would provide the extremes of the range of colouration to be expected. If immersion of a standard dentine surface in a solution of the coupling agent meant that all of the reactive sites were occupied by the coupling agent, then subsequent immersion in the standard dye solution would produce no change of colouration and the surface would give a colouration measure similar to the untreated standard surface. Conversely, no reaction between the coupling agent and dentine would allow the dye to occupy the reactive sites, and produce a colouration change similar to that produced upon dyeing the untreated standard surface. Partial reaction of the coupling agent would allow partial change of colouration, producing a colour measurement between the two extremes.

3.2 MATERIALS AND METHOD

3.201 PREPARATION OF STANDARD DENTINE SURFACE

Extracted human molar teeth, which had been stored in distilled water, were prepared in the following manner to give a plane dentine surface. A tooth was first ground, plane to the occlused surface, with a rotating disc of 400 mesh silicon carbide paper. Water was sprayed onto the grinding disc to cool the dentine surface and to wash away the debris. The grinding was continued until as large an area as possible of dentine free from fissures or other defects had been obtained. The dentine surface was then washed with water to remove any silicon carbide and debris, and the tooth returned to water storage.

The ground surface was then polished, in order to remove as many surface irregularities as possible that might mechanically retain a dye. It was found that polishing the dentine surface with a water slurry of 600 mesh silicon carbide powder on a flat glass plate produced a dentine surface with a polished sheen. This was tested by immersing the surface in a dye solution: no regular surface pattern of grinding marks picked out by retained dye solution could be seen. After the polishing procedure the tooth was washed with running distilled water, to remove all traces of the abrasive from the dentine surface.

3.202 PREPARATION OF STANDARD REACTIVE DYE SOLUTION

The reactive dye used was a solution of a proprietry dye product, its composition being as shown in table 3:1. This was made up in accordance with the manufacturers' directions by dissolving the dye in hot distilled water, and adding sodium bicarbonate. The dye solution was then kept at a temperature of 37°C by standing it in a water bath. The dye colour was a rich red, and when applied to a dentine surface, gave it a crimson pink hue.

3.203 PREPARATION OF STANDARD COUPLING AGENT SOLUTION

A standard solution of the coupling agent was made up in the following manner. The solubility of the coupling agent, 2-N'-allylamino - 4,6, dichloro - s - triazine, in acetone was determined by experiment. A saturated acetone solution of the triazine was made up at a temperature of 25°C. 10 ml portions of the solution were pipetted into pre-weighed glass beakers. The acetone was then evaporated off, and the vessels with the dry triazine were reweighed. The solubility of the triazine was thus calculated to be 165 grams per litre at 25°C.

It was decided that for the purposes of the experiments a solution of 50 grams per litre concentration should be used. This was regarded as a compromise between the need to provide the highest concentration of triazine at the dentine surface, thus enabling the reaction to proceed quickly, and the need to prevent precipitation of excess triazine upon the surface as the solvent evaporated.

A solution of 2-N'-allylamino - 4,6 dichloro - s - triazine in acetone was made up to 50 grams per litre

TABLE 3:1

CONSTITUENTS OF REACTIVE DYE - MEXICAN RED *
REACTIVE RED 2
REACTIVE RED 6
REACTIVE RED 8
GLAUBERS SALT

---

* Dylon Ltd., London.

strength. Before the coupling agent solution was used, an equal quantity of distilled water containing about 10 grams per litre sodium hydrogen carbonate was added to it. It was found that addition of this amount of water did not cause precepitation of the triazine, but did make the solution aqueous, and thus enhance its absorption on the dentine surface. A fine white cloud appears in the aqueous triazine solution after it had stood for a period of time. This is possibly a colloidal suspension of the triazine. This standard aqueous solution was used for all experiments and will henceforth be referred to as the coupling agent solution.

For this experiment the solution was kept at a temperature of 37°C by standing it in a beaker in a water bath.

3.204 MEASUREMENT OF COLOURATION

To measure the solouration of the dentine surfaces, a BECKMAN Model DK-2A double beam spectrophotometer was used. This instrument has an oscillating, monochromatic light beam that alternately illuminates a standard reflecting surface and the surface of the specimen under test. The frequency of the light used is continuously variable, from just infra-red, through the visible light band, to long wave ultra-violet. A pen on a chart recorder is moved across the chart in step with the variation of wavelength of the light beam. The light reflected from each of the two surfaces is collected by a photosensitive cell, and the comparative reflectance is plotted by the pen as a percentage reflectivity, against wavelength. The instrument is calibrated to 100% reflectance before use by means of a second standard white ceramic tile. For the purposes of this experiment, the machine was set to measure the diffuse reflectance of the specimens.

3.205 EXPERIMENTAL METHODS

A tooth with a standard dentine surface was removed from water storage, dried with an air blast, and then mounted in the specimen chamber of the spectrophotometer with the use of black PVC adhesive tape. The tooth was carefully aligned visually, so that the beam of light was centred upon the middle of the dentine surface. Each time the tooth was placed in the spectrophotometer it was aligned in the same manner so that the same area was surveyed each time.

The machine was then set in operation to give a curve showing reflectance of the surface over the wavelength range of 700 nm to 380 nm. This was numbered curve I.

The tooth was then removed from the spectrophotomer and placed in the standard dye solution for 30 seconds. It was then removed, washed with running distilled water, dried in an air blast, and replaced in the specimen chamber of the spectrophotometer. The reflectance was then plotted again, over the same range of light wavelengths. This was numbered curve II.

The tooth again was again removed from the spectrophotometer, and the dentine surface re-prepared by grinding and repolishing to remove all traces of the dyed dentine. When this had been done, the tooth was washed, and then immersed in the coupling agent solution for one minute. It was then washed again, dried and remounted in the spectrophotometer. Another reflectance curve was plotted, and numbered curve III.

After re-preparing the surface again, the tooth was placed in the coupling agent solution for 30 seconds, washed, and placed in the dye for 30 seconds. It was then washed, dried and replaced in the spectrophotometer. Another reflectance curve was plotted and numbered curve IV.

The final procedure was a repeat of the steps leading to the production of curve IV, but after preparing the surface, the tooth was placed in the coupling agent for a period of 1 minute. The curve obtained this time was numbered curve V.

Families of curves were plotted in a similar fashion for several teeth.

3.3 RESULTS

3.301 DESCRIPTION OF RESULTS

The sets of curves plotted for each of the teeth were compared with each other. In all cases the sets of curves were almost identical. All followed similar patterns, and the relationship of each curve to the others in its family were similar from tooth to tooth. Tracings of the curves produced by one tooth are presented in this thesis, but the description of the curves applies equally well to all of the sets produced.

Curve I (Fig. 3:1) represents the reflectance of the plane dentine surface. It falls in a gentle curve from a reflectance of approximately 60% at 700 nm, to over 25% at 380 nm. Amongst the sets of curves there was greatest variability of intensity of reflectance at the long wavelength, or red, end of the trace. This could be explained by the variability of the colour of dentine. An increase of red reflectance would appear to the eye as a variation in the yellow to "orangeness" of the dentine. At the shorter wavelengths below 450 nm, there was less variation between each set of curves.

Curve II represents the reflectance of dentine after being immersed in the standard dye for 30 seconds. It will be seen that the reflectivity is lower than Curve I over the whole of the range, but at very long wavelengths - 600-700 nm the difference between Curves I and II is slight. The reflectance drops rapidly from 600 nm to 550 nm, and thereafter is much less than that of the undyed dentine surface. At 380 nm Curve II in all of the sets of curves lies between 15 and 17% reflectance. This is to be expected as the crimson dyed tooth will reflect blue light to a lesser extent than the undyed tooth.

Curve III is the plot of the reflectivity of a dentine surface treated with the coupling agent for 1 minute. The reflectivity is almost identical with that of the untreated tooth.

Curve IV is the plot of the reflectivity of a dentine surface treated with the coupling agent for 30 seconds and then with the dye solution for 30 seconds. As can be seen the reflectance falls between Curves I and II.

REFLECTANCE OF DENTINE SURFACES

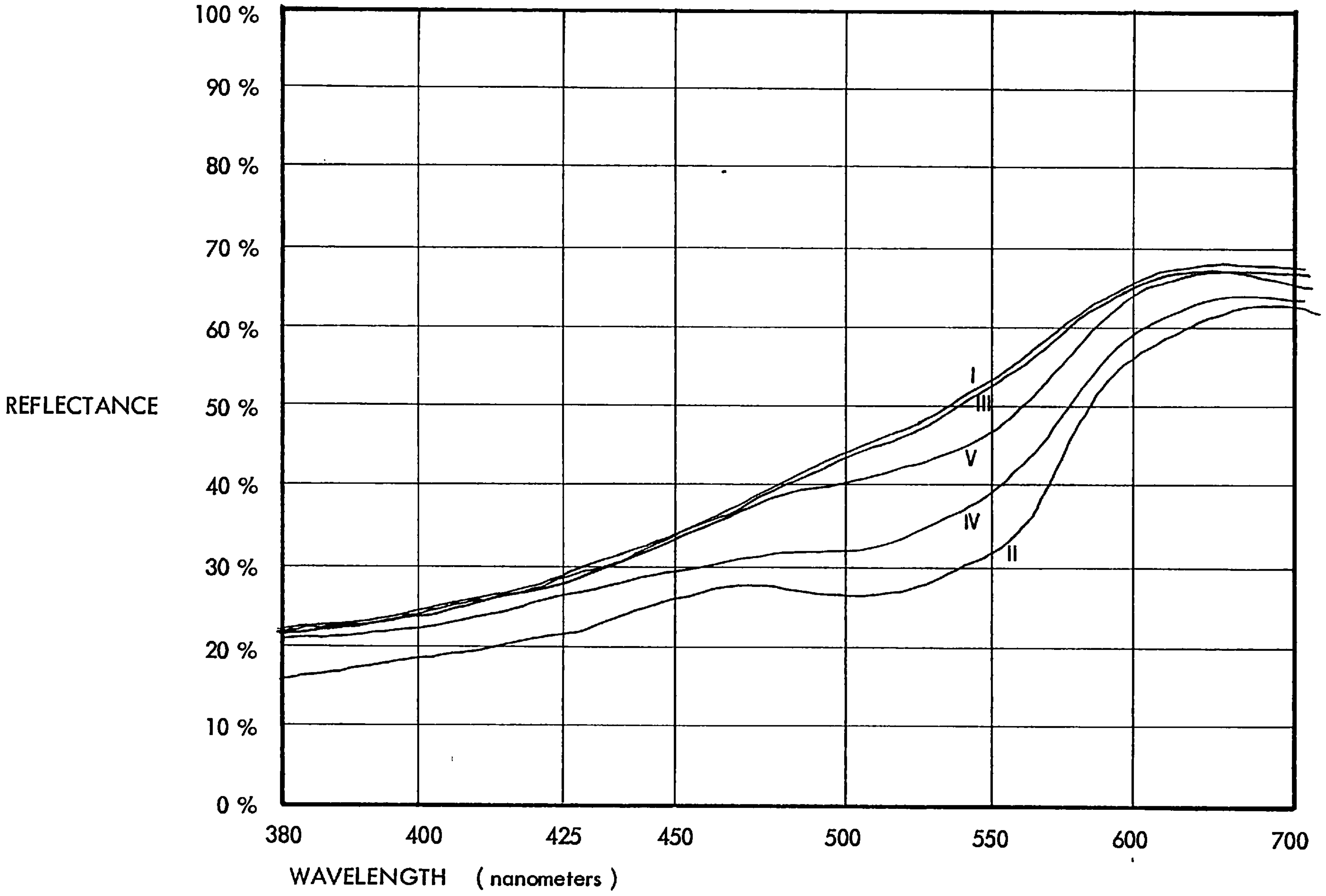


FIGURE 3:1

Curve V is the plot of the reflectivity of a dentine surface treated with the coupling agent for one minute, and then with the dye solution for 30 seconds. The curve is very similar to Curve I below 500 nm, but there is a slight deviation from Curve I between 600 and 500 nm. At 380 nm the reflectance is above 22%.

3.302 DISCUSSION OF RESULTS

From the evidence of the presented results, it is possible to make several conclusions. Immersion of a clean dentine surface in the dye solution alters the reflectance in accordance with the apparent visual change in colour. Immersion at a clean dentine surface in the coupling agent produces little change in the reflectance of the surface, and this too would appear to be in agreement with the visual evidence of no change in appearance.

Immersion of a clean dentine surface in the coupling agent for 30 seconds before immersion in the dye solution for 30 seconds reduces the alteration in colouration of the dentine surface that the dye can produce.

Immersion of a clean dentine surface in the coupling agent for 1 minute almost entirely prevents alteration of the colouration of the dentine surface by the dye solution.

It would appear that one minute's immersion in the coupling agent at 37°C allows sufficient time for the triazine to react with the available sites on the dentine surface, and thus prevent the reactive dye from occupying these sites.

The slight alteration in colouration as shown in Curve V can be explained by a few sites being left available, and by the small amount of dye that will be absorbed on the dentine surface by other mechanisms. Interpretation of Curve IV would suggest that 30 seconds immersion in the coupling agent at $37^{o}C$ is insufficient time to allow the majority of reaction sites to be occupied with the triazine. Instead many are left available for reaction with the subsequently applied dye.

This experiment is offered as evidence that 2-N'-allylamino - 4,6 dichloro - s - triazine in the standard solution, prepared as described, is capable of reacting with dentine under simulated oral conditions, within a time of one minute.

3.4 REACTION OF THE DENTAL RESIN WITH THE TREATED DENTAL SURFACE

3.401 INTRODUCTION

Demonstrating the occurrence of a reaction between the applied dental resin and the reacted dentine surface is more difficult than in the case of the coupling agent to dentine reaction. After the dental resin has been placed upon the surface, the surface is then covered and unavailable for examination. Removal of the resin will not necessarily re-expose the original surface, as, if reaction has taken place, the resin may be firmly bound and failure might not occur interfacially. Instead it was decided to observe the interaction of the surface with the fluid dental resin, and from this to show whether a reaction is occurring.

3.402 WORK OF ADHESION

In chapter 1 it was mentioned how the work of adhesion is equal to the sum of the attractive interactions (FOWKES, 1973). If a covalent reaction occurs at the adhesive interface the work of adhesion W_a will be increased.

3.403 DUPRÉ'S RELATIONSHIP

In 1860 Dupré showed that the work of adhesion between a liquid and a surface was directly related to the free energies of the components of the system in the following fashion

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

where γ_{SV} is the free energy of the surface of the solid in the saturated vapour of the liquid

γ_{LV} is the free energy of the interface of the liquid and its saturated vapour

γ_{SL} is the free energy of the interface between the solid and the liquid

This relationship holds for solids and liquids that are not mutually soluble.

3.404 YOUNG'S RELATIONSHIP

It was shown earlier by Young (1805) that there is a relationship between γ_{SV}, γ_{LV} and γ_{SL}, in that

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} (\cos \theta)$$

where θ is the contact angle of a drop of liquid placed upon the surface.

This relationshiop,like that of Dupré, is true only for a smooth, clean surface, when the system is in equilibrium. Thus surface roughness and contamination will lead to errors in the measured value of contact angle. If, however, a standard surface preparation is adopted a correction can be introduced for the variation of the surface from the ideal conditions; which is known as a surface roughness factor R. This does not make correction for surface contamination, and in the absence of extremely strict controls over conditions of preparation the results obtained after correction for surface roughness can strictly be used only for comparative measurements. If there is minimal contamination, the results will, however, approach the true values.

3.405 WORK OF ADHESION TO DENTINE

Treating the dentine surface with the coupling agent would, if the agent were reacting correctly, be expected to increase the work of adhesion, W_a, between the dentine, and a dental resin. If this does in fact occur, the surface treatment must be altering the difference between γ_{SV} and γ_{SL}, and since γ_{LV} of the resin cannot be affected, the contact angle θ must change.

In this instance it cannot be expected that γ_{SV} will change significantly. GLANTZ (1969) gives a figure of 4.51×10^{-2} J m^{-2} as the value of γ_{SV} for dentine and a figure of 4.12×10^{-2} J m^{-2} as the value for solid pdy(methymethacrylate). If the coupling agent is reacting with the dentine and leaving many vinyl type hydrocarbon groups exposed on the surface, the dentine surface will chemically approach the condition of a poly(methylmethacrylate) surface, and γ_{SV} for the treated dentine may perhaps be expected to decrease slightly. Thus for the work of adhesion, W_a, to increase, γ_{SL} must decrease.

If this is applied to Young's equation, a reduction in γ_{SL} means that $\cos\theta$ must increase to balance the equation (assuming that γ_{SV} and γ_{LV} are constant). If γ_{SV} does decrease slightly then the decrease in γ_{SL} must be even greater to produce the same increase in W_a.

In practical terms this means that a dentine surface treated with the coupling agent will, if the work of adhesion is increased by the coupling agent, allow a drop of a fluid dental resin placed upon it to set up a lower contact angle (higher $\cos\theta$) than will an untreated dentine surface. This provides a simple means of comparing the interactions between a dental resin and treated and untreated dentine surfaces. Any increase in W_a upon treatment with the coupling agent will have been produced by a reduction in γ_{SL} which implies a reaction of some type is occurring between the resin and the treated surface.

It must be realised that an increase in the work of adhesion does not, per se, mean an increase in adhesive bond strength. As has been shown earlier, it is possible to attribute much of the lack of adhesion between resin and dentine to the effects of water upon the bond. Nevertheless, demonstration of an increase in the work of adhesion and increased interaction between the resin and the treated dentine will support the hypothesis of chapter 1.

3.406 EXPERIMENTAL DESIGN

An experiment was devised to show whether an increase in the work of adhesion between a dental resin, and a dentine surface occurred upon treatment of the dentine surface with the coupling agent. A standard dentine surface would be produced, and its surface characterised. This is necessary as the surface roughness factor R affects the value of contact angle established. The characterisation would be performed by measuring the contact angle produced on the standard dentine surface by a drop of distilled water. From this it is possible, using the results obtained by GLANTZ (1969), to make a correction for the roughness factor.

Contact angles would then be measured between a dental resin and dental surfaces left untreated; and between dental resin and dentine surfaces treated with the coupling agent. These measurements would provide an indication of the degree of change of work of adhesion between the resin and the dentine that was resultant upon the use of the coupling agent.

3.407 CHOICE OF EXPERIMENTAL MATERIALS

For this, and all subsequent experiments using a dental resin, it was decided to use poly(methylmethacrylate) resin, for reasons of convenience. The resin has been characterised for many properties, and is readily available. Most of the alternative dental resins are not available in an unfilled form, and values for their physical properties are not always available.

Methylmethacrylate monomer is a thin liquid with a surface energy of $2.8 - 2.9 \times 10^{-2}$ J/m^2. It wets and spreads over dentine without forming a contact angle. This is to be expected as the surface energy of dentine is higher. It would be expected that a fluid dental resin would therefore completely wet and spread over a dentine surface. This is confirmed by HOPPENBROWERS et al. (1974) who conclude that all dental resins will satisfactorily wet dentine and enamel. This is in conflict with work by SNYDER et al. (1967) who were able to establish contact angles between dental resin (poly(methylmethacrylate)) and dentine of between 60° and 94°, implying a lack of wettability. This, it is believed, can be explained by the fact that partially-polymerised dental resins with a component of high molecular weight, do not behave as true fluids. SNYDER et al. used for this experiments polymer-monomer mixtures, made using a polymer powder with a molecular weight of about 20,000. This is well within the range normally found for methacrylate polymer powders used for dental purposes (PHILLIPS, 1973). Adding the powder to the monomer produces a viscous liquid, which is in fact a slurry of polymer particles in a liquid matrix of rapidly increasing molecular weight. The liquid matrix will spread rapidly and easly at first, but as soon as the larger particles require to be moved to allow further spreading, the liquid is restrained. Thus if the resin-dentine system is investigated very closely over distances less than the polymer particle size, the fluid matrix will appear to wet a dentine surface perfectly. If the overall slurry is examined, it will appear to act as a liquid of much higher surface tension, and will appear to establish a finite contact angle with the dentine surface. It is this angle that will be measured and used for the experiment. The actual value of the apparent surface tension of the resin will not matter, as it will remain a constant in all cases.

3.5 MATERIALS AND METHOD

3.501 CONTACT ANGLE GONIOMETER

To carry out the experiment it was necessary to construct a contact angle goniometer. The apparatus built was based upon equipment described and used by GLANTZ (1969). It consists of several parts (Fig.3:2): a solid base plate, a light source, a specimen mounting platform, an optical microscope and a viewing system with a measuring protractor.

3.502 GONIOMETER BASE PLATE

The base plate was made from duralumin alloy and consisted of a plate machined to dimensions of 600 x 250 mm x 30 mm thick. The base plate was mounted on three brass supporting feet, each adjustable for height. A bubble water level was mounted on the plate, and the feet could be adjusted to level the base plate.

3.503 GONIOMETER SPECIMEN PLATFORM

The specimen mounting platform (Fig.3:3) was made from a brass plate size 50 x 45 x 13 mm with a hole drilled tapped to ¾" BSP thread passing through it. Three brass screws passed through the platform resting on a brass block size 50 x 45 x 35 mm. The brass screws had their ends machined to a point with a 90^{o} angle and could be used

GENERAL VIEW OF THE CONTACT ANGLE GONIOMETER.

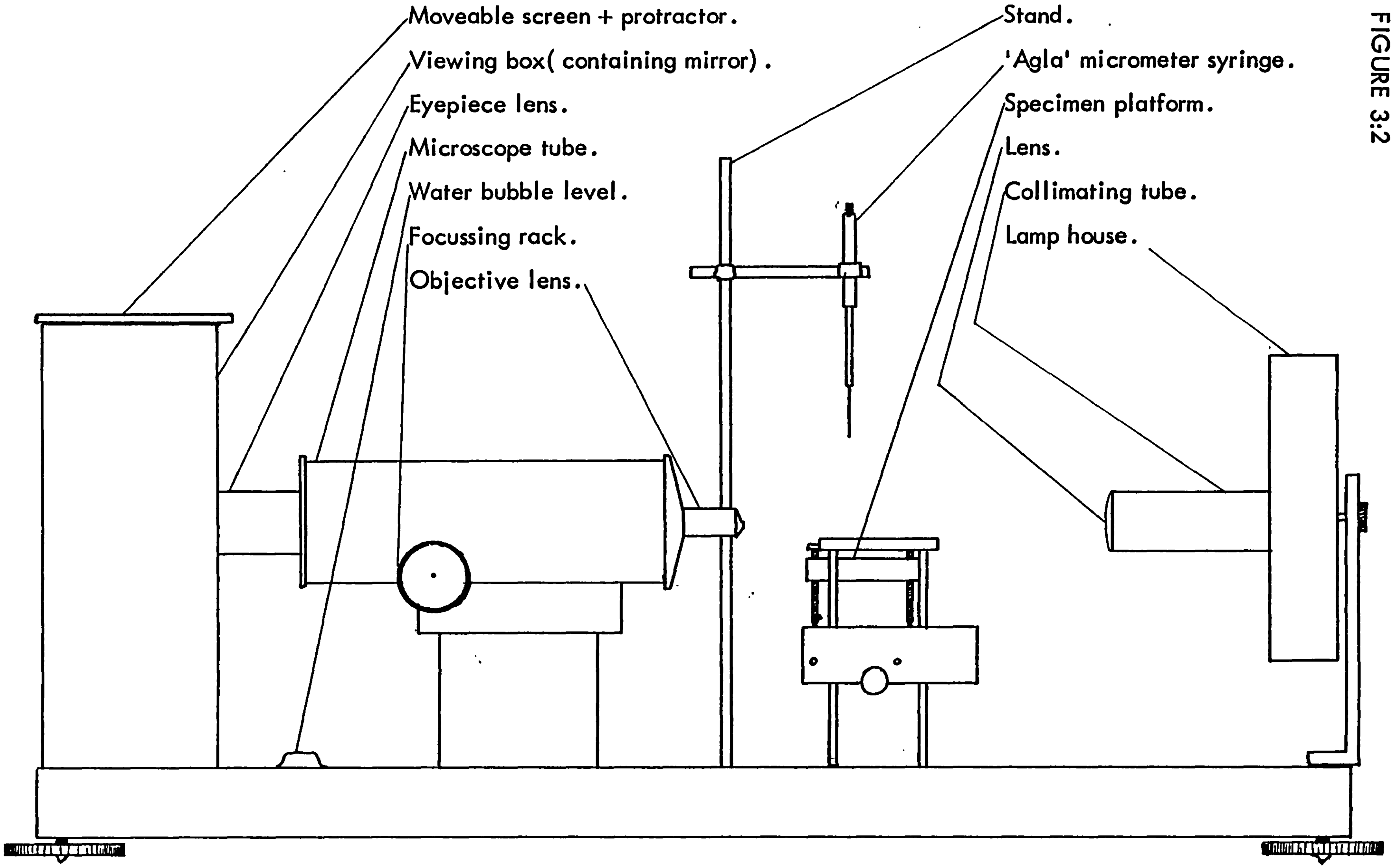
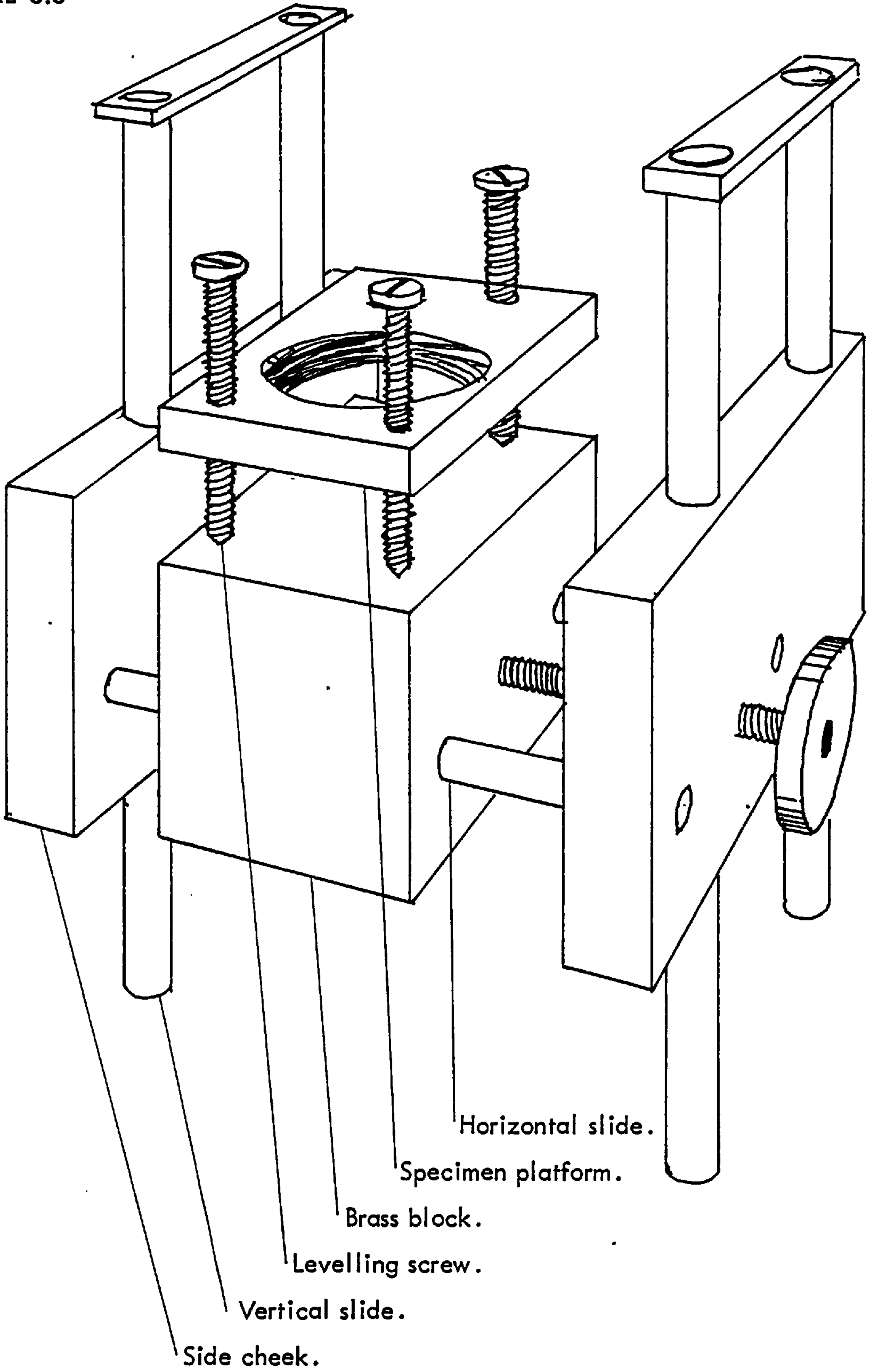


FIGURE 3:2

FIGURE 3:3



THE SPECIMEN MOUNTING PLATFORM OF THE CONTACT ANGLE GONIOMETER.

to adjust the height and to level the platform. The brass block was supported upon two silver steel horizontal rods that were in turn supported by two aluminium cheeks. A threaded rod passed through a threaded hole in one of the cheeks and was attached to the brass block, yet was still able to rotate. A knurled knob was attached to the other end, and upon turning this, the brass block was drawn smoothly along its supporting bars.

The aluminium cheeks were mounted upon four vertical steel pillars which passed through holes in the cheeks, and a set screw enabled the cheeks to be held at any point on the vertical rods.

The platform was mounted on the base plate about 1/3rd of the distance from one end.

3.504 GONIOMETER ILLUMINATION SOURCE

The illumination source consisted of a lamp box containing a 150 watt 12v tungsten halogen projector bulb, with a concave reflector, and light collimating tube. At the end of the tube was mounted a convex lens, to produce an intense parallel beam of light. The lamp box was mounted on a bracket at one end of the base plate.

3.505 GONIOMETER MICROSCOPE

The microscope was mounted with a focussing rack in a horizontal plane. A block of aluminium was mounted upon the base plate and formed a support for the microscope. The objective lens of the microscope could be brought close to an object upon the specimen platform by means of the focussing rack. The eye piece of the microscope projected into the viewing system.

3.506 GONIOMETER VIEWING SYSTEM

The viewing system consisted of an open-ended aluminium box 100 mm x 150 mm x 220 mm. A hole in one side allowed the microscope eye piece to project an image into the box. Inside, a front surface silvered mirror, made from aluminium evaporated onto glass, deflected the image upwards onto a translucent acrylic screen which rested on the top surface of the box.

A scale, made by photographically copying a protractor onto polyester sheet, was bound to the top surface of the screen with P.V.C. tape. A cursor was made from a piece of acrylic sheet 100 mm x 18 mm x 3 mm, by scribing a straight line along the long direction in the centre of the lower face.

3.507 FLUID PLACEMENT SYSTEM

A vertical stand was attached to the base plate at the side of the mounting stage, to which was clamped a horizontal arm carrying an 'Agla' Micrometer Syringe. The syringe could thus be aligned to place drops of liquid upon the surface of specimen mounted upon the brass platform.

3.508 PREPARATION OF DENTINE SPECIMENS

Teeth to be used in the experiment were embedded in brass pipe joints using a self-polymerising acrylic resin. The pipe joints were used as they provided a readily available source of mounting chucks with a pre-machined thread. This enabled the specimens to be firmly attached to the platform of the goniometer, and also to the supporting arm of the grinding machine which was used to produce the flat dentine surface, on the tooth.

The surface was prepared by grinding with a water cooled disc covered with 400 grit silicon carbide paper. This produced a fairly smooth even surface.

The teeth used in the experiment were extracted human molar teeth, and were stored in distilled water before and after mounting.

3.509 PREPARATION OF STANDARD RESIN

The poly(methylmethacrylate) resin used were a proprietry self-polymerising resin supplied by North Hill Plastics Limited, in the form of polymer beads, and liquid monomer. An accelerator and catalyst to induce polymerisation was incorporated in the resin by the manufacturer. The resin was mixed in the following manner. Five drops of monomer were placed in a glass pot. A 0.3 gram of polymer powder, was added to the monomer, stirred, one more drop of monomer added, and the mixture stirred again. The resin was used 30 seconds after the start of mixing. This technique of mixing the resin was used for all experiments using the resin.

3.510 EXPERIMENTAL METHOD - PART 1

The mounted tooth to be used was attached to the specimen platform and a clean glass microscope slide placed upon the flat dentine surface. The light source was turned on, the microscope adjusted and the specimen platform moved until the dentine surface was clearly in focus upon the viewing screen. A water level was placed upon the glass slide, and using the three adjusting screws, the dentine surface was levelled. The level and microscope slide were then removed. The dentine surface was dried by a five second blast of nitrogen gas from a cylinder. Using the micrometer syringe, a drop of distilled water was placed upon the dentine surface. The focussing of the optical system was readjusted so that the side of the water drop was clearly in focus. The drop was allowed time to spread over the surface until an equilibrium was established, at which time the viewing screen could be moved until the origin of the protraction was at the image of the contact point of the water drop. The 0^o axis of the protractor was then aligned with the image of the horizontal axis of the dentine surface and the cursor carefully placed upon the screen tangentially to the image of the contour of the drop, at the contact point. The contact angle could then be read off from the protractor scale.

The dentine was then dried again with another nitrogen blast, and the whole procedure repeated a number of times. The whole experiment was repeated for several different teeth.

3.511 EXPERIMENTAL METHOD - PART 2

In the second part of the experiment the specimens were prepared in the same way, and mounted in the goniometer in a similar fashion. The liquid used to produce the drop was the standard dental resin. A small drop was placed on the surface from a small spatula, and allowed to spread and form a stable contact angle.

After each reading, the surface was re-prepared by grinding, to ensure removal of all of the resin.

These procedures were also repeated, but before the specimen was mounted on the goniometer, the dentine surface was immersed in the standard coupling agent solution at a temperature of 37°C for one minute, then washed with distilled water.

3.6 RESULTS

3.601 RESULTS OF PART 1 TO CALCULATE R FACTOR

The contact angles measured for drops of distilled water on five different dentine surfaces are given in table 3:2. GLANTZ (196) gives a value for the contact angle between water and human dentine as 45.29°.

WENZEL (1936) demonstrated that the roughness of a surface affects the contact angle and he proposed a roughness factor R should be introduced such that

$$R = \frac{R^r}{R^s} = \frac{\text{Cos } \theta^r}{\text{Cos } \theta^s}$$

where R is the true area of the solid surface and superscripts r and s refer to the rough and smooth surfaces respectively. R factors of 1.0 are rare, and ground surfaces usually display R factors of the order 1.5 - 2.0 or more (GLANTZ, 1969).

Taking the mean value of contact angle measured for each of the five surfaces, together with GLANTZ'S figure for the contact angle of water upon dentine, it is possible using WENZEL'S equation to calculate an R factor for each surface. These are shown in table 3:3.

TABLE 3:2

MEASURED VALUES OF CONTACT ANGLES θ OF WATER ON STANDARD DENTINE SURFACES.

SURFACE NO.	I	II	III	IV	V
	27	26	20	29.5	32
	31	20	16.5	25	27
	36	27	19	25	28
	30	24	21	24	28
	20	26	25.5	21	28
	22.5	29	21	20	23.5
	28	22	20	22	24.5
	22	28	24	20	31
	23	20	23	18	31.5
	20	25	23	17	23.5
	32	18	21.5	24	27.5
	29	27	28	28	24
	26	20	21.5	22	21
	24	25	23	22.5	20
	22	23	18	24	26
	28	21	23	21	22
	29.5	17	20	20	28.5
	33	24	24	22	23
	34	24	22	20.5	29.5
	34	23	21	23	23.5
MEAN VALUES	27.6	23.5	21.8	22.4	26.1

TABLE 3:3

R FACTORS CALCULATED FOR STANDARD DENTINE SURFACES FROM MEAN VALUES OF CONTACT ANGLE θ.

Surface No.	Contact angle	Cosine θ	R Factor
I	27.6°	0.8862	1.26
II	23.5°	0.9170	1.30
III	21.8°	0.9284	1.32
IV	22.4°	0.9245	1.31
V	26.1°	0.8980	1.28
MEAN VALUE OF R FACTOR			1,.29

Calculated from Wenzel's equation :- $R = \frac{\cos \theta^{\circ}}{\cos 45.29^{\circ}}$

Value for contact angle of water on polished dentine of 45.29° given by GLANTZ (1969).

3.602 RESULTS OF PART 2 OF EXPERIMENT

The results for seven measurements of the contact angle of resin upon seven different standard dentine surfaces are presented in table 3:4. They are all measurements made using a standard dentine surface, so the mean value of R factor obtained from the previous results has been used to obtain a corrected value of the mean contact angle.

In table 3:5 the results for seven measurements of the contact angle of resin upon seven different standard dentine surfaces treated with the coupling agent, are presented. Again the corrected value of the mean contact angle has been calculated.

It will be seen that all of the values of the contact angle shown in table 3:4 are lower than those shown in table 3:5. This difference is apparent in the values of the mean contact angles corrected for the surface roughness effect.

3.603 DISCUSSION OF RESULTS

From the results presented it is possible to state that treating a dentine surface with the standard coupling agent solution causes a dental resin placed upon that surface to set up a lower contact angle than if the surface were left untreated. From the analysis of the forces involved that was presented earlier in this chapter, it is possible to state that the treatment of the surface probably reduces the interfacial free energy between resin and dentine, and thus increases the work of adhesion.

Because of the limitations of the experiment it is

TABLE 3:4

VALUES OF CONTACT ANGLE θ OF DENTAL RESIN ON STANDARD DENTINE SURFACES.

Measured values of contact angle θ.	36.5° 37° 38° 39° 36° 36° 32°
Mean value of contact angle θ.	36.36°
Cosine of mean value of θ.	0.8053
Cosine of mean value of θ corrected for R factor of standard dentine surface - 1.29	0.6243
Value of contact angle θ corrected for surface roughness.	51.37°

TABLE 3:5

VALUES OF CONTACT ANGLE θ OF DENTAL RESIN ON STANDARD DENTINE SURFACES TREATED WITH COUPLING AGENT.

Measured values of contact angle θ.	31° 24° 23° 20.5° 20° 18° 23°
Mean value of contact angle θ.	22.79°
Cosine of mean value of θ.	0.9222
Cosine of mean value of θ corrected for R factor of standard dentine surface - 1.29	0.7149
Value of contact angle θ corrected for surface roughness.	44.36°

not possible to calculate by how much the interfacial tension is reduced, or by how much the work of adhesion is increased.

It would be fair though to attribute the reduction in interfacial tension to an interaction between the resin and the surface treated with the coupling agent, and these experimental results are offered as evidence to show that this interaction takes place.

4.0 MEASUREMENT OF ADHESIVE STRENGTHS

4.001 INTRODUCTION

The measurement of adhesive bond strengths is a problem that has produced a host of different solutions. The physical nature and geometry of an adhesive system. will affect the form of the measurement procedures that are undertaken and this in turn will affect the results that are obtained. Most methods of measurement involve the application of an increasing stress to an adhesive joint, until fracture of the joint occurs and then relating the stress at the time of fracture to the area of the fractured joint. This apparently gives a measurement of the load that similar joints will bear before fracture occurs, but what is often not stated is that this figure applies only when the joint is stressed in a manner similar to that employed during the test. The dynamic properties of the adhering bodies will affect the stresses that appear at the joint interface and different rates or positions of loading on the bodies may give very different stress levels at the interface.

BIKERMAN (1971) states that "the rupture of a solid almost always starts at one point, namely at the point where the local stress first overcomes the local strength. The accent is on the word local. Consequently, the absolute value of the force F applied, perhaps, several centimetres away from the source of fracture, has no direct relation to the stress σ which really causes the pre-existing flaw or crack to grow and split the solid in two parts". This further states the case that any given figure of measurement of bond strength usually applies only to the situation in which it was obtained. It is therefore very difficult to compare directly results obtained by different methods, for the strengths of a series of similar adhesive joints. It is however valid to compare results obtained for different series of adhesive joints if all are tested in a standard manner. The joints must be of identical geometry to enable the same test method to be used, but differences in the methods of preparing the joints are permissible. These general facts are of course of equal importance in the assessment of dental adhesives, but owing to the difficulties of the size and preparation of samples, no standard test method has yet been adopted.

4.002 MEASUREMENT OF DENTAL ADHESION STRENGTHS

Most measurements of dental adhesive bond strength have been made by measuring the tensile strengths of the joints. All tensile tests involve pulling an adherand away from a prepared surface of dental tissue, but numerous methods have been employed to hold ad align the specimens (SWARTZ and PHILLIPS, 1955; LEE, SWARTZ and CULP, 1969; EDEN, CRAIG and PEYTON, 1970). Various shear strength tests have been described (PATRICK et al., 1968; UY and CHANG, 1965; SNYDER et al., 1967) but they are not as easy to perform as the tensile tests, and appear to give a wider variation of results.

One method of testing has been described that is different from other tests, is that it gives a measure of the energy required to fracture an adhesive joint. This is the 'blister' or 'bubble' method used by

WILLIAMS, De VRIES and DESPAIN (1973).

4.003 EXPERIMENTAL DESIGN

For the purposes of testing the hypothesis it was decided to carry out a simple form of tensile bond strength test to determine whether use of the coupling agent gave any improvement in the strength of adhesion of dental resin to dentine and then to try to measure the bond strengths of resin to dentine, both with and without the use of the coupling agent, by means of the 'blister' test described by WILLIAMS et al.

Accordingly, the first experiment was design whereby two groups of adhesive joints would be compared. Specimens of adhesive joints, between dental resin and dentine, would be prepared, one group with the use of the coupling agent, one group without. All the prepared specimens would be stored in water at a temperature of 37°C for a period of at least 72 hours to allow water induced breakdown of the adhesive joint to occur and then the specimens would be subjected to a simple tensile test. The results of the tests of the two groups of specimens would then be compared, to see whether the coupling agent gave any increase in tensile bond strength to the adhesive joints.

4.1 METHODS AND MATERIALS FOR TENSILE STRENGTH MEASUREMENTS

4.101 MOUNTING OF TEETH

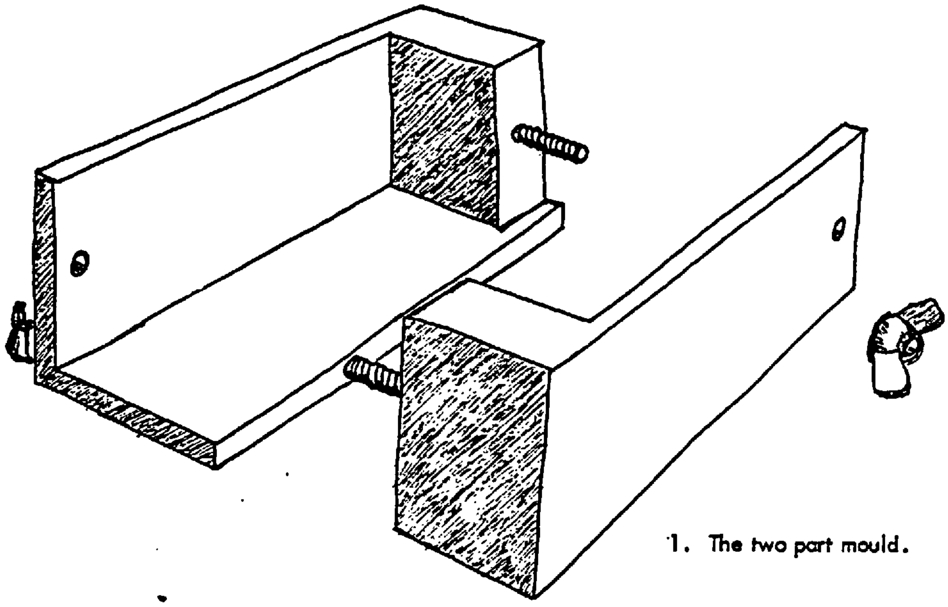
Extracted human teeth, which had been stored in distilled water, were mounted in plaster blocks so that they could be held in the tensile testing machine. To perform the mounting procedure, a two part aluminium mould was constructed, with an oblong cavity of dimensions 50 mm by 25 mm by 25 mm, Fig. 4:1. The interior was carefully machined so that opposite faces were parallel to each other, and perpendicular to adjacent faces. The upper part of the mould was left open so that after greasing the mould with petroleum jelly, Kaffir D plaster could be poured into the mould. The upper outer surface of the mould was machined parallel to the lower interior face, so that the surface of the plaster could be smoothed. This was done by drawing a straight metal blade across the upper surface of the mould, removing the unset plaster that was above the upper level of mould. A tooth was then embedded in the open plaster surface, so that the occlused surface of the mould was uppermost and clear of the plaster surface by about 4 - 10 mm.

When the plaster had set, the mould was dismantled, and the plaster block removed. The block with its tooth was then stored in a water bath at 37°C. Several blocks were prepared in this manner.

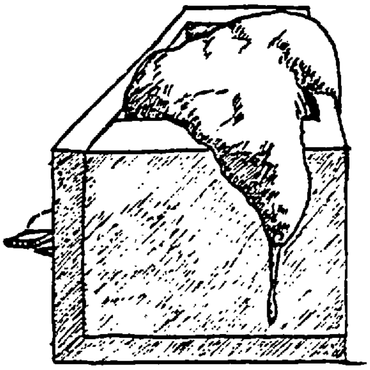
4.102 PREPARATION OF DENTINE SURFACES

The occlusal surfaces of the mounted teeth were ground to provide a flat surface of dentine, parallel to the upper and lower surfaces of the plaster blocks. This was done with a diamond coated metal grinding disc, mounted on a mondrel and held in the cheek of a vertical drill stand. The plaster block was stood on the bedplate of the drill stand and the rotating abrasive disc lowered until it contacted and ground the tooth. Distilled water was sprayed on to the grinding disc to cool the tooth and to

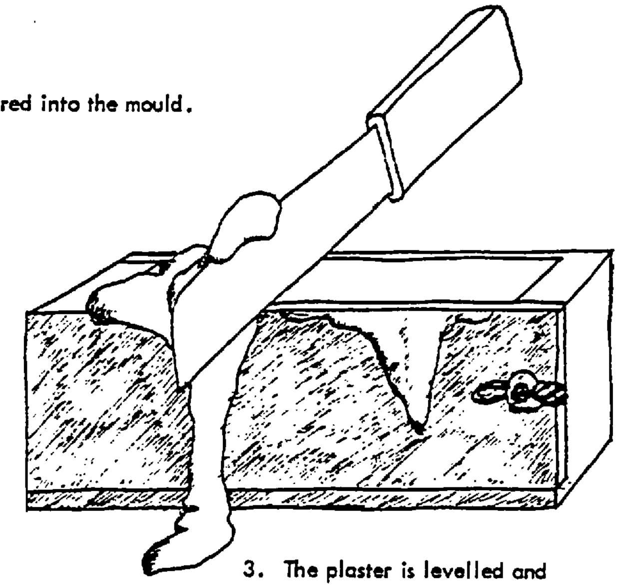
FIGURE 4:1



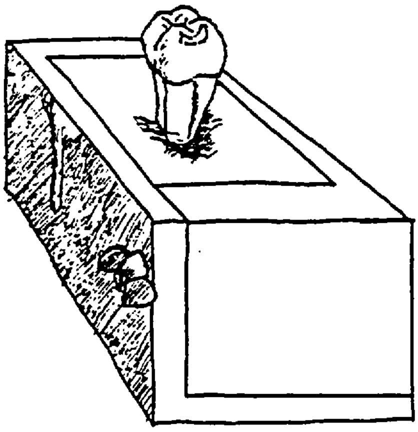
1. The two part mould.



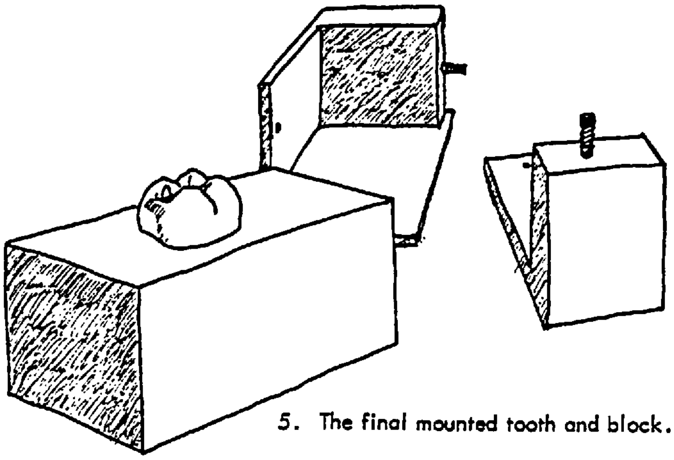
2. Plaster is poured into the mould.



3. The plaster is levelled and the excess removed.



4. The tooth is embedded.



5. The final mounted tooth and block.

clear away the the debris of abrasion.

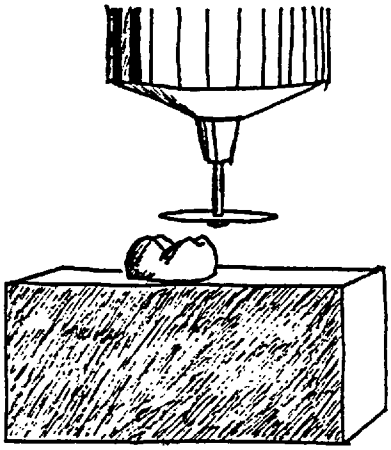
When a flat dentine surface, free from defects, had been formed over the whole cross section of the crown of the tooth with the exception of the enamel at the margins, the grinding was stopped and the tooth and block washed with distilled water. The block was then returned to storage in the water bath.

4.103 PREPARATION OF ADHESIVE JOINTS

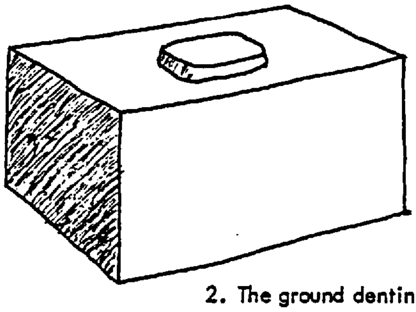
The samples of adhesive joint for testing were prepared individually, so that each received a fresh mix of resin, Fig. 4:2. A plaster block was removed from the water bath, stood on the bench with the tooth uppermost, and then dried with a short blast of gas from a cylinder of nitrogen. At this stage those specimens selected to be treated with the coupling agent were given a one minute application of the standard solution of the triazine coupling agent (3.203). This was kept at a temperature of 37°C, and was applied to the dentine surface by means of a copper wire loop. The dentine surface was then washed with distilled water and dried again.

The resin that was to be used was poly(methylmethacrylate) and this was mixed in the previously adopted standard manner (3.509). A bead of the resin was placed upon the dentine surface and then the head of a steel dressmaker's pin was inserted into the bead of resin. This was held vertical by hand until the resin became thick enough to support the pin, at which stage the block was inverted and stood on a horizontal support, so that the pin hung vertically downwards and perpendicular to the dentine

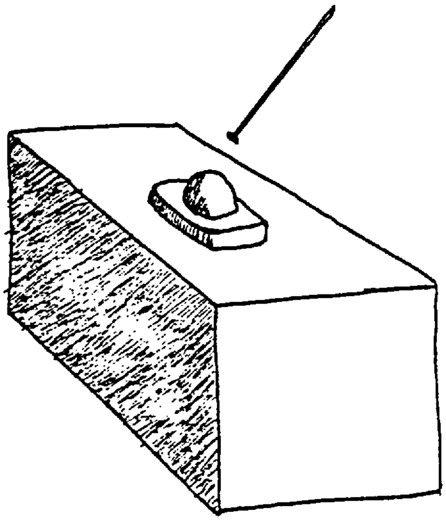
FIGURE 4:2



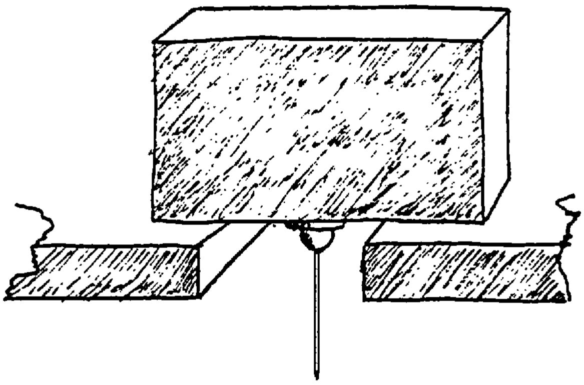
1. The tooth is ground to give a flat dentine surface.



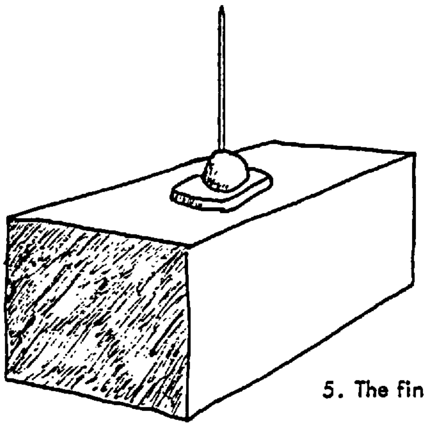
2. The ground dentine surface.



3. A bead of resin is placed on the dentine surface , and a pin is then inserted.



4. The pin is allowed to hang vertically until the resin has set.



5. The finished specimen ready for tensile testing.

surface. The resin was allowed to harden in this position. When the resin was completely cured, in about 20 minutes, the block was turned the right way up again and returned to the water bath for at least 72 hours.

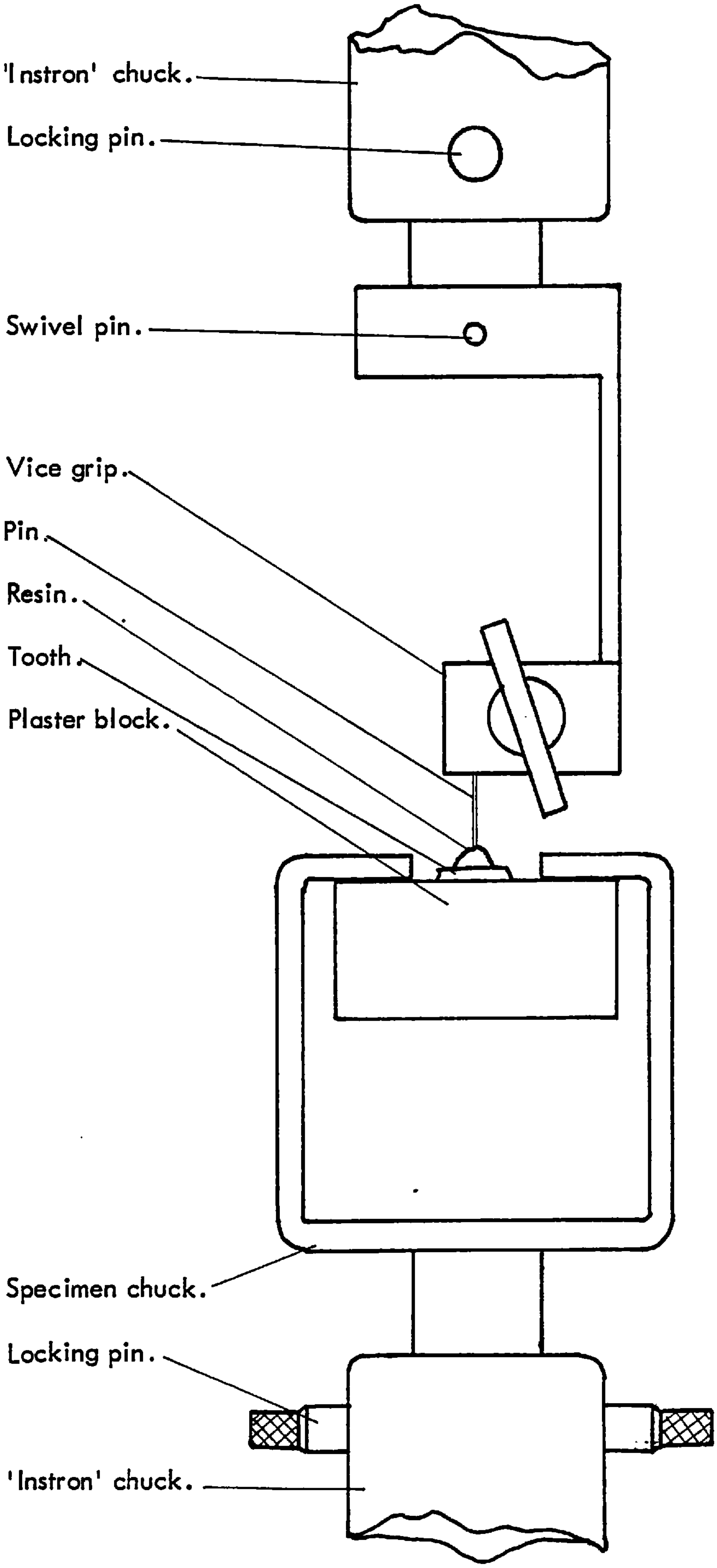
4.104 METHOD OF TENSILE TEST

The tensile tests were carried out with the use of an INSTRON testing machine. A block and tooth were suspended, by means of the attached pin, from a vice grip mounted on the upper chuck of the machine. This allowed the block to hang vertically and allowed the tensile stress to be directed along the axis of the pin, perpendicularly to the joint interface at the dentine surface. The plaster block was pulled downwards by means of a specially designed grip mounted in the chuck of the moving crosshead of the machine (Fig. 4:3). The grip was made to contact the upper face of the plaster block, again in order to ensure that the stress was applied perpendicularly to the joint interface.

The crosshead of the Instron machine was driven downwards at a rate of 1 mm per minute, and the stress registered by the load cell carrying the upper chuck was recorded upon a moving pen chart recorder. The recorder was adjusted to read zero load, before the block was attached to the upper grip, but it was found that the weight of the block was negligible when compared with the forces used to induce fracture. The crosshead chart recorder was examined to give a measure of the stress applied to the specimen at fracture.

The area of the fracture surface was determined by placing the fractured surface of the now detached resin upon

FIGURE 4:3


'Instron' chuck.
Locking pin.
Swivel pin.
Vice grip.
Pin.
Resin.
Tooth.
Plaster block.
Specimen chuck.
Locking pin.
'Instron' chuck.

a grid of mm squares, and counting the number of squares and half squares covered. From these measurements, the tensile force per unit area at the time of fracture was calculated.

4.2 RESULTS OF TENSILE STRENGTH MEASUREMENTS AND DISCUSSION

4.201 RESULTS

The results of the tensile tests are presented in tables 4:1 and 4:2. They are also presented graphically in fig. 4:4. It can be seen that for both groups the results are fairly widely distributed. There is however a difference between the mean values of each group and there is no overlap between the two groups. In other words the highest figure recorded for the untreated samples (group 1) is lower than the lowest figure for the treated samples (group 2). It is interesting to note that for each group the highest value is approximately seven times the lowest value; this would seem to suggest that the results in each group are of similar distribution.

Statistical analysis of the results for the two groups using the Student t test for independent variables gives a t statistic of 4.3075. This indicates that the probability of the results obtained for the group of treated amples (group 2) being of the same group as the untreated samples (group 1) is less than one in ten thousand.

TABLE 4:1

TENSILE STRENGTHS OF ADHESIVE JOINTS OF RESIN BONDED TO UNTREATED DENTINE. (GROUP 1)

BOND AREA $m^2 \times 10^{-6}$	FRACTURE STRESS N	TENSILE STRENGTH $N\ m^{-2} \times 10^5$
25	14.7	5.88
18	6.37	3.53
23	4.90	2.13
16	3.43	2.14
24	17.64	7.35
19	3.43	1.80
22	6.86	3.11
18	11.76	6.53
21.5	8.33	3.87
17.5	12.74	7.28
24	10.29	4.28
16	7.35	4.59
19	13.72	7.22
22	2.45	1.11
14	8.82	6.3
Mean Value		4.47

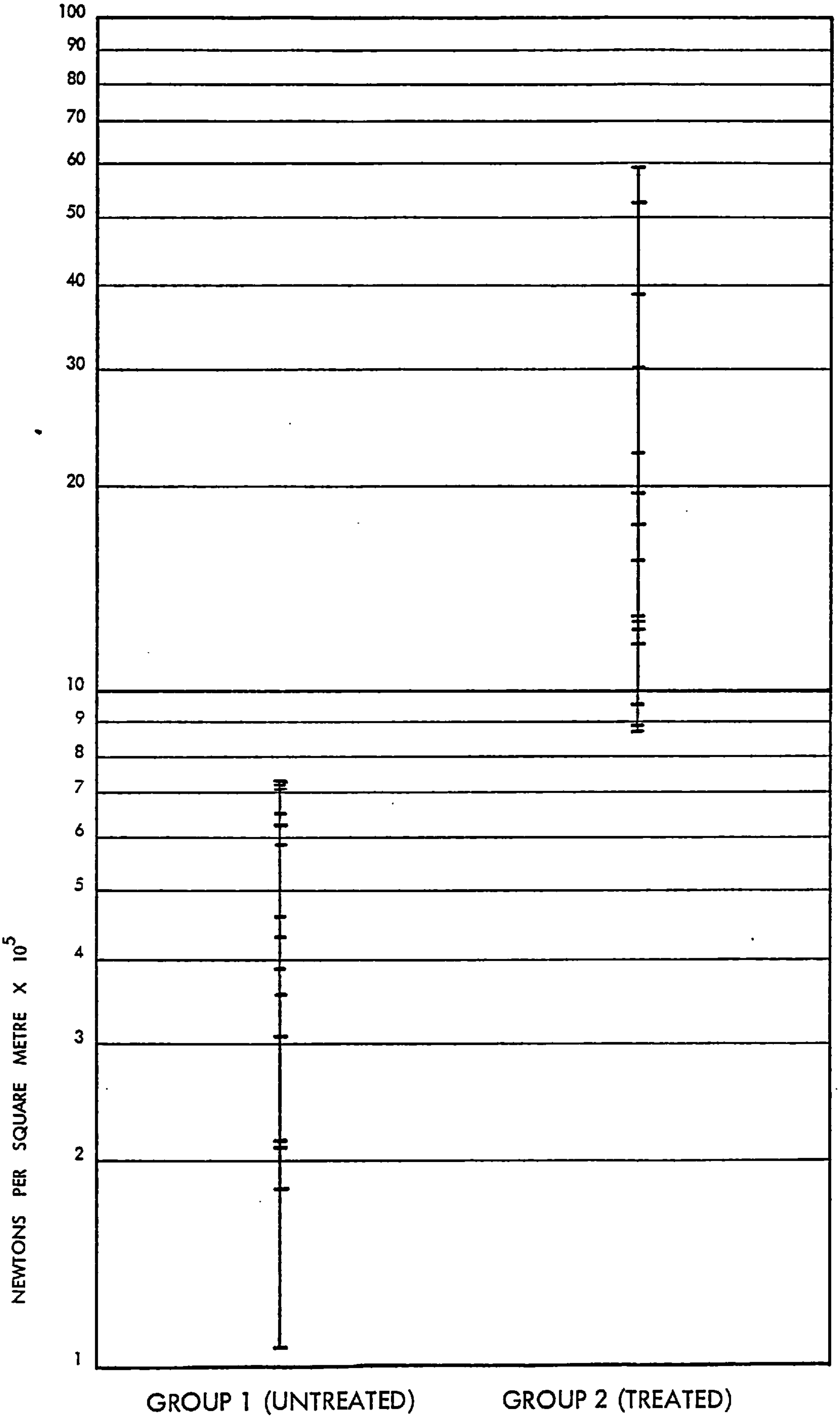
TABLE 4:2

TENSILE BOND STRENGTHS OF ADHESIVE JOINTS RESIN BONDED TO DENTINE TREATED WITH COUPLING AGENT. (GROUP 2)

BOND AREA $m^2 \times 10^{-6}$	FRACTURE STRESS N	TENSILE STRENGTH $N\,m^{-2} \times 10^5$
18	24.5	13.61
20	25.97	12.98
25	30.87	12.34
16	84.28	52.67
15.5	92.12	59.94
20	17.64	8.82
23	51.94	22.58
19	16.66	8.76
16	48.02	30.01
21	38.22	18.2
21	41.16	19.6
18.5	30.38	16.42
25	33.32	13.32
20	61.74	30.87
16.5	15.68	9.50
	Mean Value	21.9

FIGURE 4:4

RESULTS OF TENSILE STRENGTH TESTS.



4.202 DISCUSSION

From the results obtained for the experiment, it is possible to conclude that the triazine coupling agent does affect the adhesion of poly(methylmethacrylate) resin to dentine. Specimens of adhesive joints prepared with the use of the coupling agent show a higher tensile strength after 72 hours immersion in water than similarily stored specimens prepared without the coupling agent. This difference has been shown to be significant.

It is not possible to say that the figures presented are accurate measures of the strength of adhesion of resin to dentine. As explained in the introduction, the geometry of the system is such that the interfacial force at the point of fracture initiation cannot be determined and may be different from the overall tensile force by a very large margin. Nevertheless the experiment does show that the triazine coupling agent does improve adhesion of a dental resin to dentine and does fulfil the hypothesis put forward in chapter 1.

4.3 MEASUREMENT OF ADHESIVE FRACTURE ENERGY

4.301 INTRODUCTION

As explained earlier, it was decided to use the 'blister' test method to try to obtain a measure of the strength of adhesive joints made with and without the triazine coupling agent. This test method produces debonding of an adhering lamina from a rigid solid surface by means of a 'blister' technique. WILLIAMS et al. (1973) claim that the method gives a true measure of the specific fracture energy, γ_a, for an adhesive system. This quantity, γ_a, is a function of the adhesive system and is independent of any test geometry, or loading.

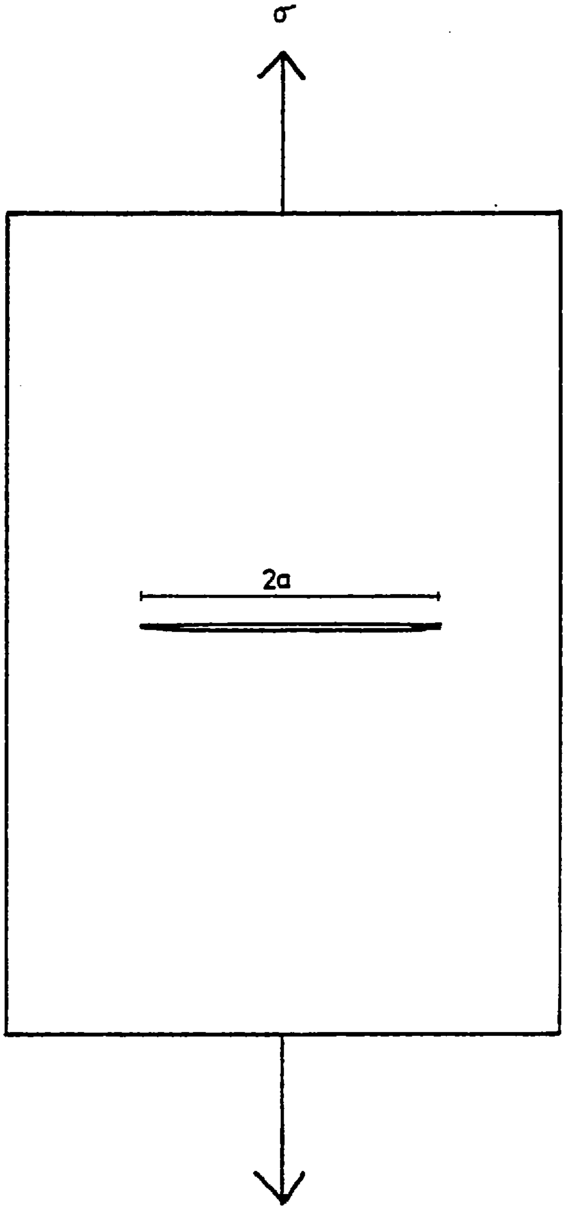
4.302 CRACK PROPAGATION THEORY - COHESIVE FRACTURE

The theory of the 'blister' test is based upon the work of GRIFFITH (1924) which established an energy balance in the case of crack propagation. GRIFFITH's theory applies to a crack in a two-dimensional sheet, (fig. 4:5) and relates the growth of the crack to stress applied to the sheet perpendicularily to the crack. Knowing the elastic modulus of the material, E, the specific surface energy of the material γ_c and the crack half length, a, it is possible to use GRIFFITH's equation to calculate the critical stress, σ_{cr}, which produces unlimited crack propagation, or fracture of the material. Stresses below σ_{cr} will merely lengthen the crack to a point where a new equilibrium is established. Once σ_{cr} is reached or exceeded, equilibrium is inattainable, as the energy released by relaxation of the sheet as the crack lengthens is more than that required to extend the crack and create a new crack surface. This balance is independent of the size of the sheet, provided that the crack length a, when the stress is less than σ_{cr}, is less than the width of the sheet. At stress levels above σ_{cr}, the crack will automatically extend across the whole sheet.

The strength of the material is related to the specific surface energy, γ_c. This is defined as the energy required to create a unit area of fracture surface and is peculiar to the material being stressed.

FIGURE 4:5

$$\sigma_{cr} = \sqrt{\frac{2E\gamma_c}{\pi a}}$$



GRIFFITH'S CRACK PROPAGATION THEORY.

4.303 CRACK PROPAGATION THEORY - ADHESIVE FRACTURE

WILLIAMS (1969; 1970) developed the relationship, advanced by GRIFFITH, in a new situation where the materials either side of the crack were dissimilar. He envisaged that a crack would propagate along the interface between the two materials, thus producing adhesive failure; and that the system was very similar to that where cohesive failure occurred. In the new case, however, the energy to produce the new fracture surfaces must be defined as γ_a, the specific adhesive fracture energy. The elastic moduli of the materials will of course be dissimilar, but provided allowance is made for this it is clear that an energy balance, similar to that proposed by GRIFFITH, can be calculated. The property γ_a will be a property of the particular adhesive system occurring between the two materials.

4.304 'BLISTER' TEST TO MEASURE ADHESIVE FRACTURE ENERGY

WILLIAMS then adapted the energy balance to a three-dimensional system, where the interfacial crack becomes a circular crack between plates of two dissimilar materials, one being more flexible than the other. Instead of applying a tensile force across the interface, the descriptive force is considered to come from an increase of pressure within the interfacial crack. This will cause the more flexible of the plates to 'blister' and the circular crack will increase in radius (Fig. 4:6). The relationship that describes this situation is given by the equation:-

FIGURE 4:6

THE BLISTER BETWEEN TWO DISSIMILAR FLEXIBLE PLATES.

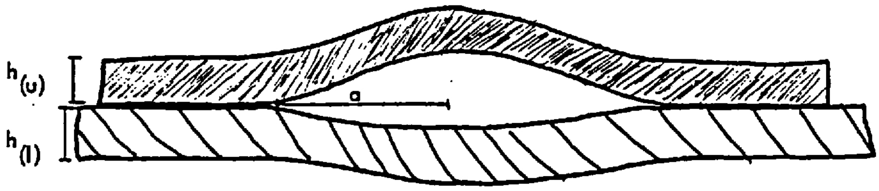
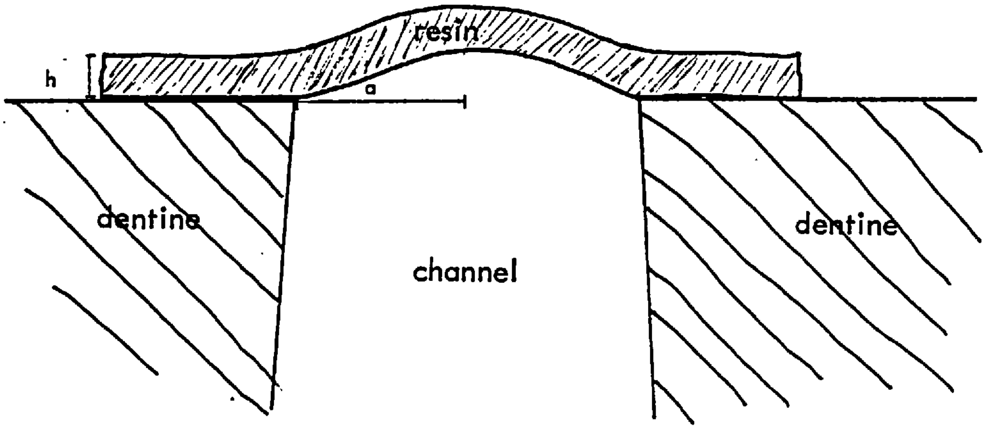


FIGURE 4:7

THE BLISTER TEST AS USED TO MEASURE DENTAL ADHESION



$$P_{cr} = \sqrt{\frac{32}{3(1 - \nu_u^2)} \left(\frac{h_u}{a}\right)^3 \left[\frac{E_u \frac{\gamma_a}{a}}{1 + \left[\frac{D_u}{D_i}\right]}\right]}$$

where

P_{cr} is the pressure in the flaw at which fracture occurs

ν is Poisson's ratio

h is the plate thickness

a is the crack radius

E is the E elastic modulus

D is the plate modulus

such that

$$D_i = \frac{E_i \, h_i 3}{12 \left[1 - \nu_i{}^2\right]}$$

the superscripts u and ℓ apply to the upper and the lower plates respectively, the upper plate being the more flexible.

If the lower plate is considered to be extremely rigid, the D_ℓ tends towards infinity, and $(1 + \frac{D_u}{D_\ell})$ becomes a negligible term. This if the system can be regarded as a flexible plate adhering to a rigid surface, the relationship becomes as follows:-

$$P_{cr} = \sqrt{\frac{32}{3(1 - \nu^2)} \left(\frac{h}{a}\right)^3 \frac{E\gamma_a}{a}}$$

where

P_{cr} is the pressure in the flaw at which fracture occurs

ν is Poisson's ratio of the plate

E is the elastic modulus for the plate

h is the plate thickness

a is the crack radius

This relationship has been shown by WILLIAMS to be correct, by means of experiments with rubber discs cast on to glass plates.

It will thus be seen that to obtain a value for the adhesive fracture energy of an adhesive system, it is necessary to measure only three variables - the plate thickness, the crack radius and the pressure at which interfacial fracture occurs (Fig. 4:7).

4.305 DENTAL ADHESION MEASUREMENT BY THE 'BLISTER' TEST

WILLIAMS, De VRIES and DESPAIN (1973) describe ho- the blister method may be used for measuring adhesion to dental surfaces. They describe a method of producing a flat dentine surface, with a circular flaw, the opening of a channel through the dentine, through which compressed gas may be admitted. The channel is temporarily blocked with a steel pin to allow a disc of dental resin to be cast on the dental surface and when this is set, the pin is removed. A simple apparatus then admits compressed gas to the channel and the pressure is increased until fracture occurs at the interface between the resin and the dental surface. A dial gauge records the gas pressure within the channel.

DESPAIN et al. (1973) present results of experiments to measure the adhesive strength of various dental cements using this method. A figure of 7.183 x 10^{-2} J m^{-2} (4.11 x 10^{-4} in lb/in^2) is given as the adhesive fracture energy of acrylic dental resin adhering to bovine dentine. This figure must be called into question though as a figure for the adhesive fracture energy of acrylic resin to poly(methylmethacrylate) sheet it is also given as 17.5 J m^{-2} (10^{-1} in lb in^{-2}). This is in conflict with the published figure for the cohesive fracture energy for poly(methylmethacrylate) of 0.5 J m^{-2} (GUY, 1972). As the acrylic resin chemically combines with the acrylic sheet, the final adhesive joint can be regarded as a cohesive joint, though with perhaps a larger number of defects than the bulk material. Certainly the interface will not be stronger than the bulk. Thus a figure of 17.5 J m^{-2} cannot be a correct value of adhesive fracture energy. If it were to be assumed that the error is simply one of multiplying factors, i.e. the error is one of 10^2, this would give a figure of 0.175 J m^{-2}, a plausible value, and would suggest that the result for adhesion of resin to bovine dentine should be 7.183 x 10^{-4} J m^{-2}.

It was with this uncertainty that the 'blister' test method was adopted for measuring adhesion strength of acrylic resin to dentine both with and without the use of the triazine coupling agent.

4.306 EXPERIMENTAL DESIGN

An experiment of two parts was designed. The first part was to prepare and test a number of specimens of resin adhering to human dentine without the use of the triazine coupling agent. The second part was to prepare and test a similar number of specimens of resin adhering to human dentine which had been treated with the coupling agent. Between the preparation and the testing, each specimen was to be stored in water at 37°C for a period of 72 hours, to allow any water induced breakdown of adhesion to occur. The results obtained would then be compared between the two groups, and with the results of DESPAIN et al. (1973).

For the purposes of the experiment an apparatus was designed which performed the function of that described by WILLIAMS et al. (1973) but which produced a graphical record of the pressure within the flow at fracture.

4.4 METHODS AND MATERIALS FOR ADHESIVE FRACTURE ENERGY MEASUREMENTS

4.401 MOUNTING OF TEETH

Extracted human molar teeth were mounted in brass mounts in a manner similar to that used by WILLIAMS et al. (1973). The brass mounts were standard plumbing fittings, having an open "compression" type fitting at one end which retained the embedding resin, and a ¾ inch BSP make thread at the other end. This latter thread allowed the whole mount to be quickly attached to the testing apparatus and also to the specimen holder of the grinding machine used in preparing the specimens.

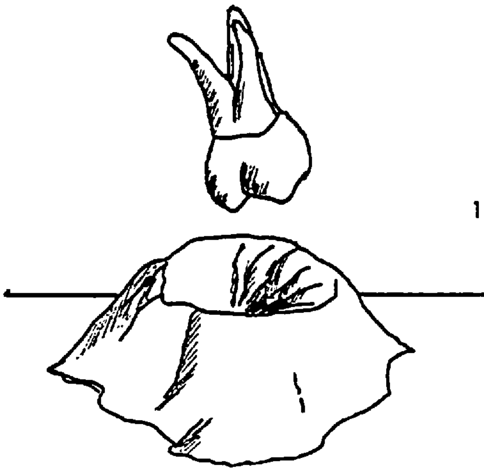
The teeth were embedded in the mount with the following technique (Fig.4:8). A tooth was removed from water storage, dried and then placed, roots uppermost, in a mound of "plasticine" modelling clay. About ¾ of the crown was buried in the clay and the clay was carefully pressed around the tooth to form a good seal. A brass mount was then placed over the tooth, thread uppermost, and seated into the modelling clay. Self curing acrylic resin was then poured into the mount until the roots of the tooth were covered. When the resin had cured, in about ten minutes, the mount was lifted from the plasticine and the crown of the tooth revealed. The mounted specimen was then stored in distilled water at a temperature of 37°C.

4.402 PREPRATION OF DENTINE SURFACES

The preparation of the mounted specimens consisted of three main steps: grinding a smooth flat dentine surface, preparing a tapering circular channel through the tooth and applying the adhering dental resin (Fig. 4:9).

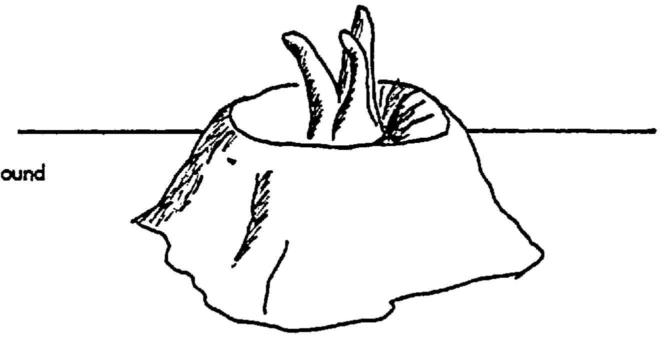
The grinding was performed with rotating discs of silicon carbide paper. A specimen holder was made, which aligned each specimen against the disc in a repeatable manner. This was achieved by screwing the mount into a hole, drilled and tapped into the end of a cylinder of stainless steel, diameter about 38 mm. The cylinder was a sliding fit in a hole in an aluminium block, thickness 18 mm, which was calmped to a pillar on the grinding machine. The cylinder was thus free to move perpendicularly to the surface of the abrasive disc

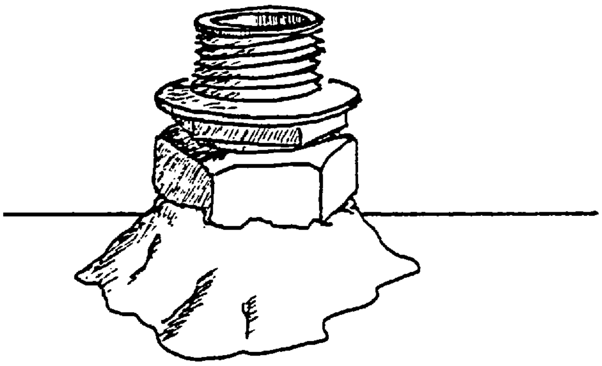
FIGURE 4:8



1. The tooth is placed in a mound of modelling clay.

2. The clay is moulded around the tooth.





3. A plumbing joint is placed over the tooth, bedded into the clay and acrylic resin poured around the roots of the tooth.

4. The embedded tooth removed from the modelling clay.

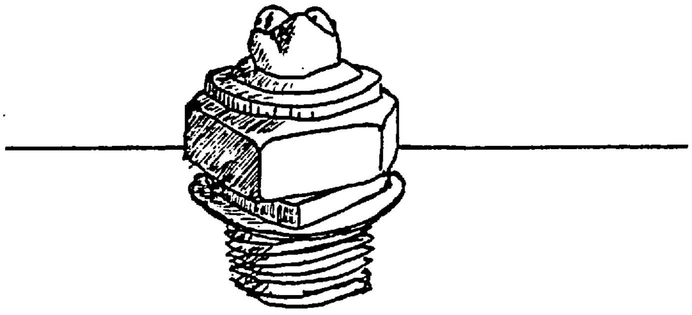
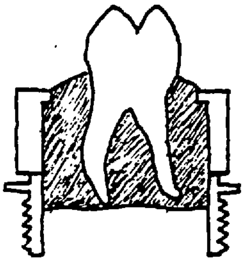
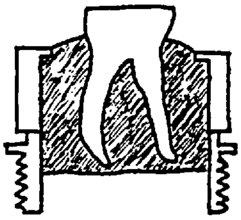


FIGURE 4:9

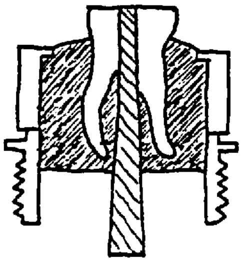


1. A cross section through a mounted tooth.

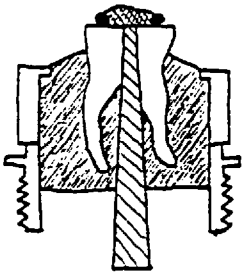


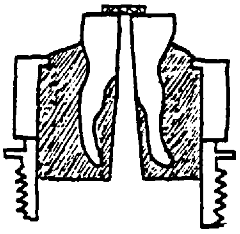
2. The tooth is ground to give a flat dentine surface.

3. A hole is drilled through the tooth and reamed to a taper. A steel pin . is then fitted and ground flush.



4. An 'O' ring is placed on the dentine surface as a mould and resin poured in.





5. When the resin is set, the 'O' ring is taken away and the pin removed. The resin is then ground to a plate of uniform thickness.

and any specimen placed on the end of the cylinder would be ground by the abrasive disc. If the specimen was removed, it could be later replaced and grinding continued in exactly the same plane as before. Water was sprayed onto the disc to remove the debris and to cool the tooth. Discs of silicon carbide of 150 grit and 400 grit were used; the coarser 150 grit to produce the dentine plane from the bulk shape of the tooth, the smoother 400 grit to provide a smooth surface of dentine.

Each specimen was ground until a smooth dentine surface was obtained free from defects. After grinding the teeth were returned to water storage.

4.403 PREPARATION OF CHANNEL THROUGH SPECIMENS

Each specimen had a hole drilled through the centre of the dentine surface by means of a $^7/64$ inch twist drill. The hole was extended to pass through the tooth and the mounting resin. A tapered reamer was then used to enlarge the hole and to taper it, the smaller diameter of the hole being at the dentine surface. This left a circular, tapered channel opening in the centre of the dentine surface.

4.404 OCCLUSION OF CHANNEL THROUGH SPECIMENS

Before producing the adhering lamina of dental resin for each specimen, it was necessary to temporarily occlude the "channel" in the dentine surface. This was done in the manner described by WILLIAMS et al. (1973) with a tapered steel pin. This was pushed into the tapering hole and ground flush with the surface, using the grinding machine. When the dental resin had been cast onto the dentine surface and had set, the pin was removed, thus re-establishing the cylindrical channel.

4.405 PREPARATION OF ADHERING RESIN LAMINA

The prepared dentine surface, with its occluded "channel" was carefully dried with a blast of gas from a cylinder of nitrogen. If the specimen was one selected to receive the couping agent, it was applied at this point. The coupling agent was prepared as the standard solution at 37°C (3:203) and was applied for one minute with the use of a copper wire loop as applicator. After application the specimen was washed with distilled water and dried again.

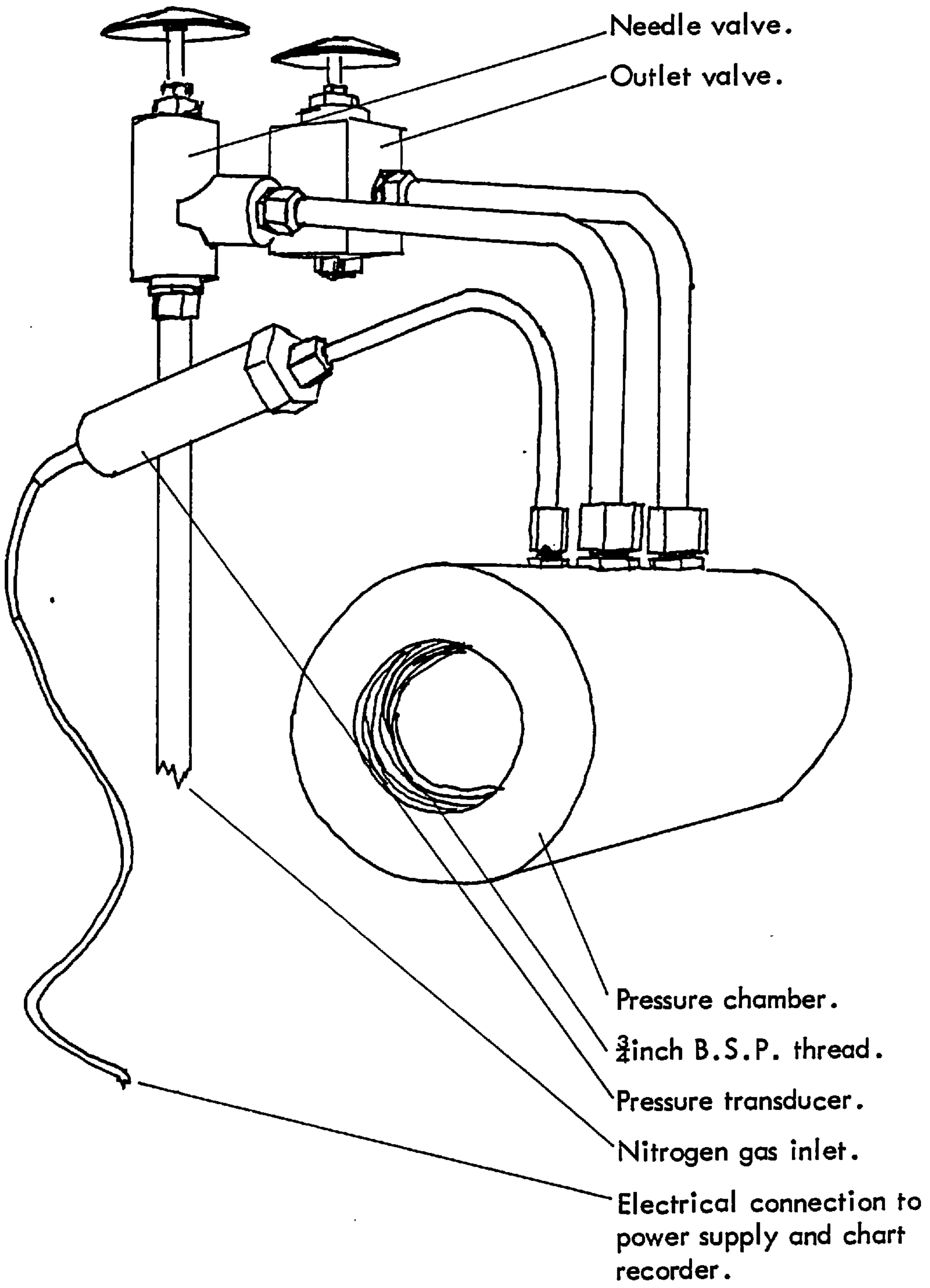
A rubber 'O' ring, internal diameter 8 mm, was placed on the dentine surface around the opening of the channel to act as a mould and a measure of the standard dental resin mixture (3:509) poured into the centre of the ring. When the resin had set, the ring was carefully removed and the steel pin carefully extracted. The specimen was then placed in the holder of the grinding machine, and the resin was ground gently with the 400 grit disc, until it was in the form of a disc about 0.7 mm thick. The self alignment of the grinding machine made the ground surface of the resin parallel with the dentine surface. The completed specimen was then returned to water storage for a period of 72 hours.

4.406 'BLISTER' TEST APPARATUS

The testing apparatus was built to perform the function of that described by WILLIAMS et al. (1973) but with modifications that allowed automatic graphical recording of the pressure within the channel of the specimen, Fig. 4:10. The main part of the apparatus was a pressure chamber, made from a solid cylinder of stainless steel 50 mm diameter and 100 mm length. A hole of about 25 mm diameter was bored into the cylinder axially from one end to a depth of about 75 mm and was tapped to a thread of ¾ inch B.S.P. to a detph of 3 cm. Two copper pipes, $^{3}/8$ inch diameter led into the upper side of the cylinder via brass fittings. One pipe led to a strop valve which vented.to free air, thus acting as an air outlet for depressurising the chamber. The other pipe led to the outlet of a needle valve, which was in turn connected to the outlet of a pressure regulator mounted on a cylinder of oxygen free nitrogen.

A third copper pipe of $^{3}/16$ths inch diameter led from the pressure chamber to a SANGAMO-WESTON pressure transducer type SE-792-500 p.s.i. This contains a silicon diaphragm which has a resistor bridge network formed upon it. If the diaphragm is stressed by an increase of gas pressure admitted via its inlet, the bridge is put out of electrical balance and a voltage will appear, across the output of the bridge, that is proportional to any voltage across the bridge input and in linear relationship with the gass pressure. For the experiments, a stable input voltage was applied to the bridge. This was achieved by connecting a reverse biased zener diode across the bridge input and applying a voltage across the input from a dry

FIGURE 4:10



THE ACTIVE COMPONENTS OF THE APPARATUS BUILT TO PERFORM THE 'BLISTER' TEST.

battery, via a current limiting resistor. The output of the transducer was taken to the Y-axis input of a Y.E.W. Type PRO-21 Chart Recorder. The chart recorder was adjusted so that an output of 1 mv from the pressure transducer produced a deflection of the pen of 1 cm.

4.07 CALIBRATION OF TEST APPARATUS

The apparatus was calibrated using the manufacturers' test data for the pressure transducer, Table 4:3. The input voltage used with the transducer was measured with a digital voltmeter as 5.37 v. The temperature at which the experiments were conducted was 25°C. This was half way between the two test temperatures used by the manufacturers and the mean of the manufacturers' measurements at these two temperatures was calculated and used as the figure for 25°C. This gives the results presented in Table 4:4, which have also been corrected to give the output for an input of 5.37 v. This means that the transducer gives an increase in output voltage of 38.1 mv per 250 psi pressure increase. As 1 psi is equivalent to 703.12 kg m^{-2} pressure and g (the gravitational constant) is 9.80555 m sec^{-2}, the output sensitivity is 1 mv increase per 45244.4 N m^{-2} increase in gas pressure.

4.408 EXPERIMENTAL PROCEDURE

Each specimen was tested with the apparatus in the following manner. A mount was removed from water storage and surplus water shaken off. A rubber O-ring was placed upon the thread of the mount and the mount then screwed tightly into the pressure chamber. The outlet valve of

TABLE 4:3

MANUFACTURER'S TEST DATA FOR SANGAMO WESTON PRESSURE TRANSDUCER TYPE:-SE 792 - 500psi.

SUPPLY VOLTAGE :- 5.0 volts

PRESSURE p.s.i.	OUTPUT at 0° C. millivolts	OUTPUT at 50° C. millivolts
0	+ 0.53	- 0.05
250	+ 35.83	+ 35.60
500	+ 71.10	+ 71.20

TABLE 4:4

PRESSURE TRANSDUCER OUTPUT CORRECTED FOR TEMPERATURE AND SUPPLY VOLTAGE.

PRESSURE p.s.i.	OUTPUT at 25° C. INPUT = 5.0 volts millivolts	OUTPUT at 25° C. INPUT = 5.37 volts millivolts
0	+0.24	+0.2577
250	+ 35.715	+ 38.3579
500	+ 71.15	+ 76.4151

the apparatus was at this stage open and the inlet needle valve closed. The pen on the chart recorder was adjusted to read zero mv and the recorder started so that the pen traced along the X-axis at a rate of 1 cm per ten seconds. The outlet valve was closed and the inlet needle valve opened slowly, so that the nitrogen from the cylinder entered the chamber and increased the pressure within the chamber. The pressure was allowed to increase slowly, such as to produce an increase in output recorded by the chart recorder of about 10 mv per 10 seconds. When the pressure reached a certain point, the acrylic dental resin disc became debonded from the dentine surface and the pressure in the chamber immediately decreased.

The acrylic disc was collected and put aside for measurement together with the specimen. The apparatus was then readied for use with another specimen.

The maximum output voltage recorded by the chart recorder was noted and measurment made with a travelling microscope of the thickness of the acrylic disc and the diameter of the opening of the "channel" in the dentine surface. The mount and its specimen were then returned to water storage. The specimens were revised after grinding the dentine surface to provide a fresh face.

4.5 RESULTS OF ADHESIVE FRACTURE ENERGY MEASUREMENTS AND DISCUSSION

4.501 RESULTS

The results for one group of samples of acrylic resin adhering to dentine without the use of the coupling agent, are presented in Table 4:5. These are also presented in graphical form, Fig. 4:11. The results were calculated from the measurements according to the equation:-

$$\gamma_c = \left[P_{cr}\right]^2 \times \left[\frac{a}{E}\right] \times \left[\frac{32}{3(1-\nu^2)}\right] \times \left[\frac{a}{h}\right]^3$$

where P_{cr} is the critical pressure of debonding.

E is the elastic modulus for acrylic resin

ν is Poisson's ratio

h is the acrylic disc thickness

a is the flow radius

γ_c is the specific fracture surface energy

The constants used were as follows:-

$E = 1.862 \times 10^9$ N m^{-2}

$\nu = 0.328$

P_{cr} as shown earlier = output in mv x 45244.4

Thus

$$\gamma_c = \left[\text{output in mv} \times 45244.4\right]^2 \times \left[\frac{a}{1.862\times10^9}\right] \times \left[\frac{1}{11.95257219}\right]\left[\frac{a}{h}\right]^3$$

TABLE 4:5

ADHESIVE FRACTURE ENERGY VALUES OBTAINED FROM 'BLISTER' TEST.

a (metres)	h (metres)	P_{cr} (millivolts)	γ_a (Joule metres^{-2})
0.00174	0.00076	2.65	1.34×10^{-2}
0.00166	0.00062	6.80	1.35×10^{-1}
0.00183	0.00066	0.80	2.29×10^{-3}
0.00182	0.00056	0.35	7.04×10^{-4}
0.00190	0.00056	7.16	3.50×10^{-1}
0.00187	0.00070	1.80	1.06×10^{-2}
0.00168	0.00068	10.10	2.37×10^{-1}
0.00177	0.00058	12.20	6.88×10^{-1}
0.00168	0.00064	4.53	5.73×10^{-2}
0.001705	0.00087	2.20	5.71×10^{-3}
0.001715	0.00112	8.65	4.23×10^{-2}
0.00169	0.00069	3.35	2.56×10^{-2}
0.00177	0.00059	9.25	3.76×10^{-1}
0.00173	0.00057	9.45	3.97×10^{-1}
0.00181	0.00154	4.00	4.32×10^{-3}
0.00184	0.00054	0.73	3.56×10^{-3}
0.00183	0.00082	1.78	5.93×10^{-3}
0.00179	0.00062	6.00	1.42×10^{-1}
0.00183	0.00034	1.95	9.98×10^{-2}
0.00162	0.00091	8.35	5.86×10^{-2}
0.00176	0.00055	3.23	5.53×10^{-2}
0.001735	0.00048	12.60	1.19
0.00178	0.00060	15.70	1.05
0.001695	0.00056	9.94	4.27×10^{-1}
0.001605	0.00050	6.00	1.75×10^{-1}
0.001745	0.00047	1.82	2.72×10^{-2}
0.00187	0.00042	2.90	1.27×10^{-1}
0.00171	0.00046	1.54	1.91×10^{-2}
0.00174	0.00048	0.30	6.86×10^{-4}
0.00180	0.00038	0.84	1.24×10^{-2}

VALUES OF ADHESIVE FRACTURE ENERGIES OF JOINTS BETWEEN ACRYLIC RESIN AND UNTREATED DENTINE OBTAINED BY THE USE OF THE 'BLISTER' TEST.

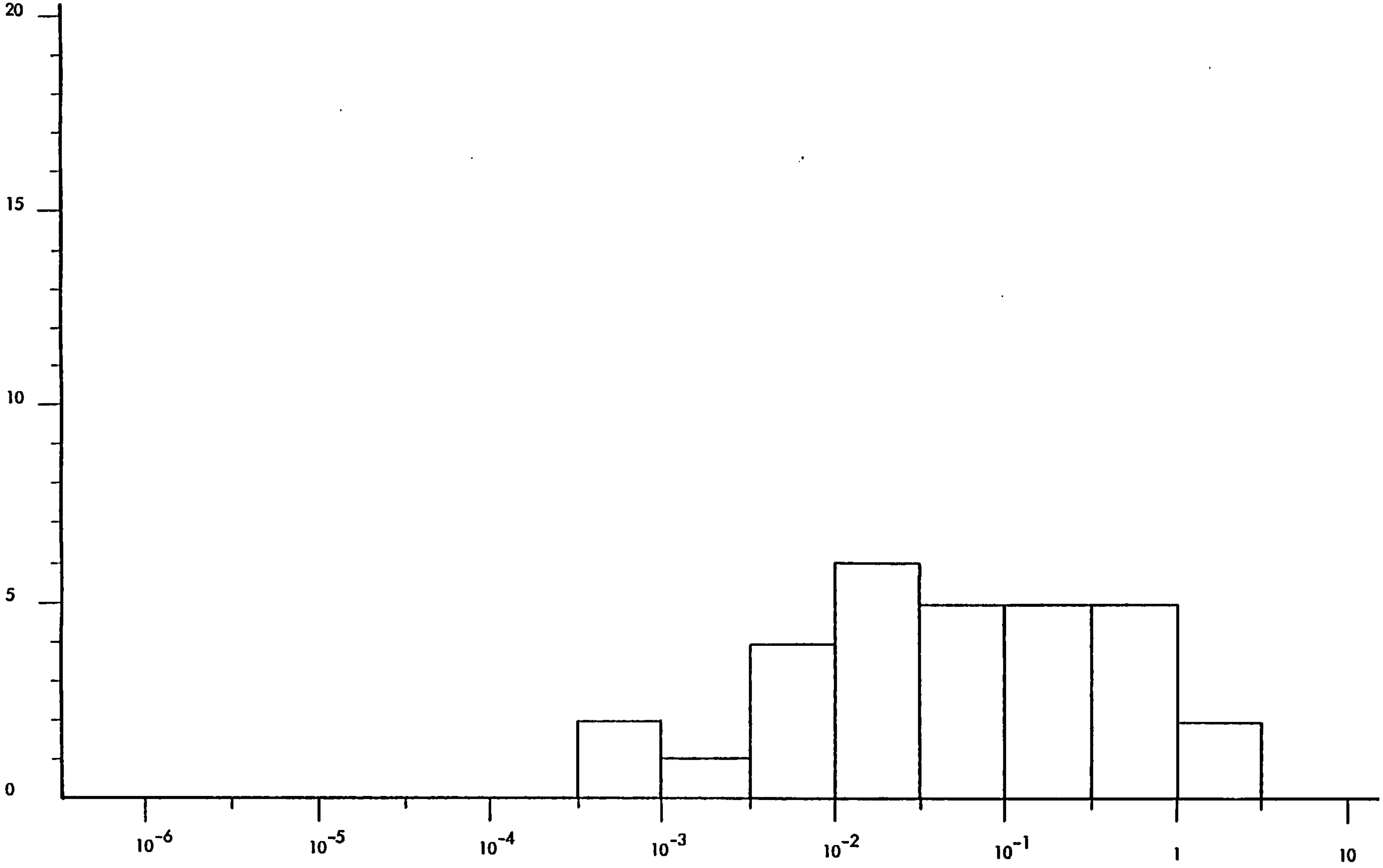


FIGURE 4:11

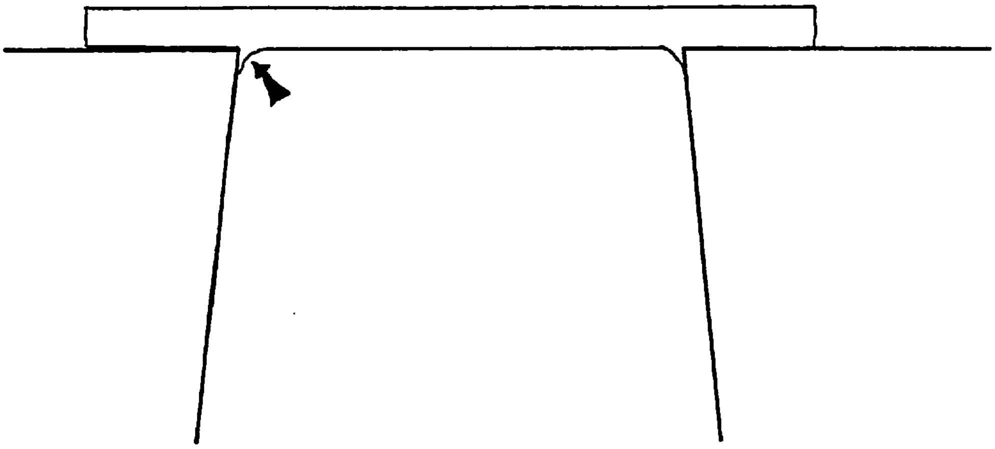
As will be seen from the table the results show a very wide range from 1.20 to 6.86 x 10^{-4} J m^{-2}.

4.502 DISCUSSION

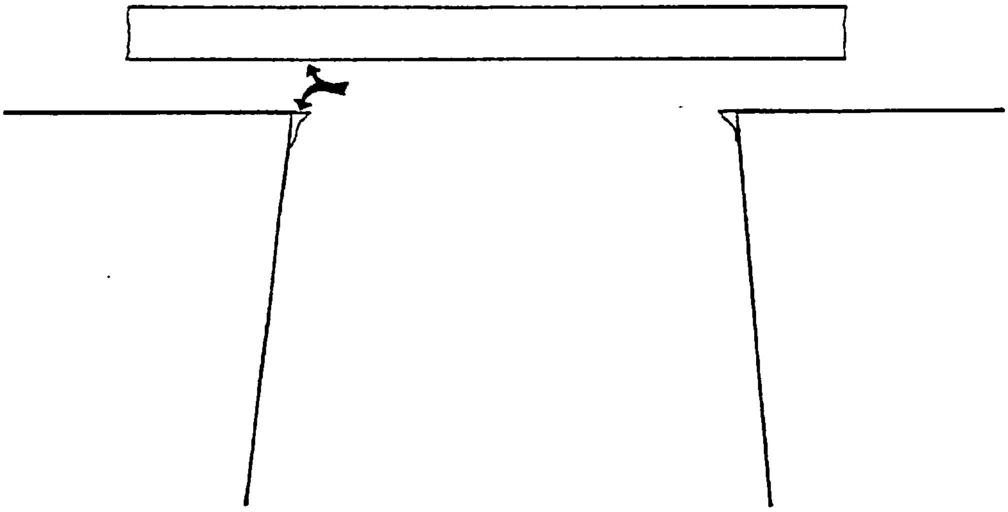
The results obtained appear to be in error, as they are very high in value. As stated earlier, the cohesive fracture surface energy for poly(methylmethacrylate) is 0.5 N m^{-2}. Some of the results obtained for adhesion of the resin to dentine are greater than this. If these figures were correct it would imply that failure of resin dentine adhesion should not occur, as the adhesive joint would be stronger than the resin itself. This is plainly not the case and so a reason for the results being so high was sought.

Upon close investigation of the debonded resin discs, and the dentine specimens, it became clear that the pin was not in fact fitting the channel accurately and that resin was flowing between the pin and the dentine, Fig. 4:12. Around the perimeter of the channel on some specimens could be seen a ring of retained resin and on some of the debonded discs could be seen the outline of the channel. The fracture was not occurring at the interface between resin and dentine but was occurring in resin. This apparently explained the anomalously high results. It was therefore necessary to alter the experimental method, so as to prevent this effect occurring.

FIGURE 4:12



1. The acrylic resin has 'leaked' around the steel pin to form a mechanical attachment to the dentine.



2. After fracture, resin has been left around the rim of the channel. Cohesive fracture within the resin has occurred and not adhesive fracture at the dentine - resin interface.

4.6 METHODS AND MATERIALS FOR MODIFIED 'BLISTER' TEST

4.601 MODIFIED 'BLISTER' TEST - METHOD 1

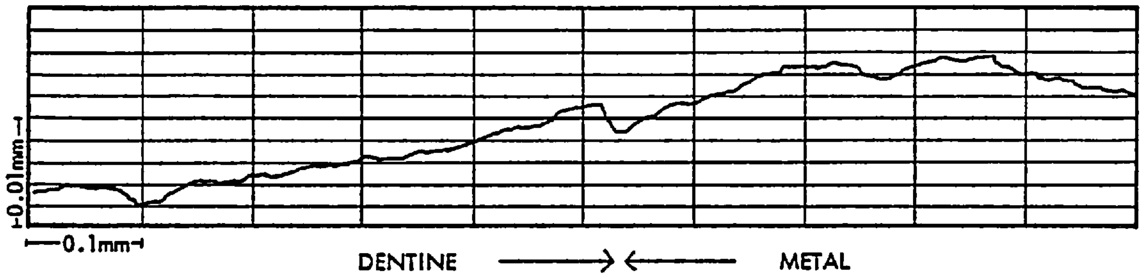
The first attempt to modify the method of WILLIAMS et al.(1973) was to replace the steel pin with a pin of polythene. Polythene being flexible would be able to adopt itself to the sides of the channel and prevent the resin from leaking around it. To this end $^1/8''$ diameter polythene welding rod was obtained and a length used to occlude the channel in one specimen. It was then ground flush with the dentine surface using the grinding machine. An attempt was made to assess this technique in comparison with the steel pin. Two specimens were examined using a TALYSURF surface profile tracing machine. The results are presented in Fig. 4:13. It will be seen that the polythene plug was less successful at sealing the channel than the steel pin. It appears that the resilience of the polythene allowed it to be compressed during the grinding stage and when released from the abrasive surface it expanded and stood proud of the surface.

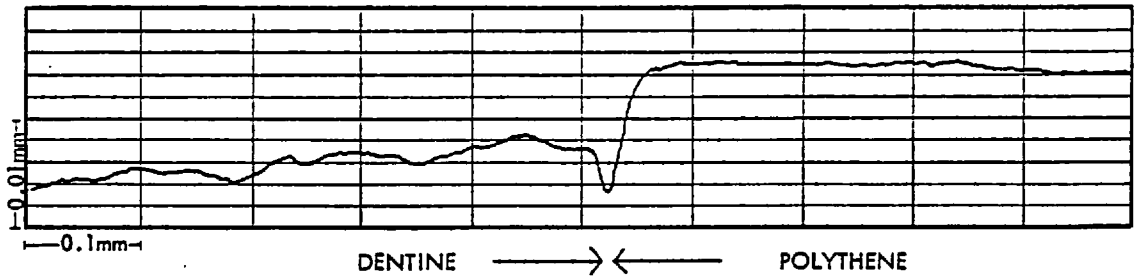
4.602 MODIFIED 'BLISTER' TEST - METHOD 2

The next method investigated was the use of a self-vulcanising silicone rubber. It was envisaged that this could be poured into the channel and would then set. The surface of the rubber could be moulded flush with that of the dentine, by standing the specimen upon a clean glass plate. No finishing of the silicone rubber would be required and the dental resin would not bond to the silicone rubber.

FIGURE 4:13

'TALYSURF' PROFILES OF CHANNELS IN DENTINE SURFACES BLOCKED WITH A STEEL PIN AND WITH POLYTHENE WELDING ROD.



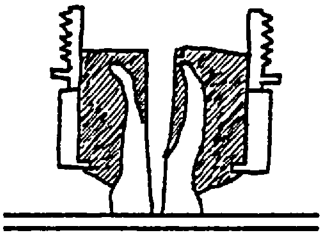


Accordingly a silicone rubber was obtained which was of sufficiently low viscosity to be poured into the tapering hole without trapping air bubbles. This was made up from DOW-CORNING SILASTIC 3110 RTV diluted with 10 per cent by volume DOW-CORNING Silicone fluid DC 200/20 cs. When mixed with its catalyst the rubber hardened in about five minutes. A specimen being prepared was stood, dentine surface downwards, upon a clean glass surface and a No. 19 gauge hypodermic needle inserted into the tapered hole to act as an air vent. A measure of the mixed silicone was poured into the channel, time was left for it to flow to the bottom of the hole and then the needle was withdrawn. When the silicone had set, the sample was carefully lifted from the glass plate and placed in water storage before use, Fig. 4:14.

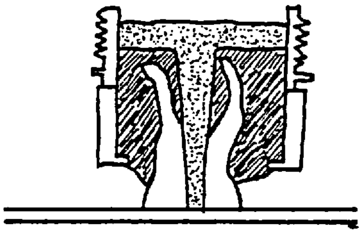
It was not possible to test the adaptation of the silicone to dentine with the TALYSURF instrument as the silicone was not strong enough to bear the weight of the skid, but microscopic examination of the surface suggested that the adaptation was excellent.

With care, it was possible to produce the specimens, ready for the application of the dental resin, or the coupling agent solution and then the dental resin, with a failure rate of about three samples in ten. Most of the failures were due to air bubbles preventing the silicone rubber from filling the whole length of the tapering space.

FIGURE 4:14

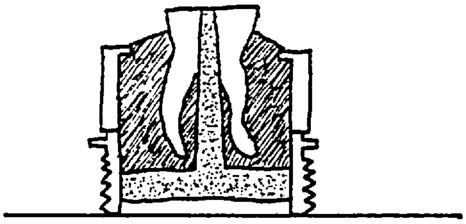


1. The mounted tooth with its prepared dentine surface is stood face downwards on a flat glass plate.



2. Silicone rubber is poured into the tapering hole and left to set.

3. When the silicone rubber is set, the tooth and mount are righted and are ready for the application of resin (stage 4 , Fig. 4:9).



4.603 MODIFIED 'BLISTER' TEST PROCEDURE

Using this method of preparation, the experiments were recommended and two groups of specimens tested, one untreated with coupling agent, the other group treated with the coupling agent. It was found that it was necessary to improve the resolution of the chart recorder to record the very small output voltages from the pressure transducer. This was done with the use of a type 741 operational amplifier connected to give a fixed gain of ten times. This was checked with the use of a millivoltmeter and found to be accurate. The chart recorder now recorded a pen displacement of 10 cm per mv and could reliably record as little as 0.01 mv output from the transducer.

4.700 RESULTS OF ADHESIVE FRACTURE ENERGY MEASUREMENTS (MODIFIED METHOD) AND DISCUSSION

4.701 RESULTS

The results of the experiments are shown in Tables 4:6 and 4:7. They are also presented in graphical form in Figs. 4:15 and 4:16.

In the case of the group of untreated specimens, 18 failed before they were tested, or before any pressure was registered by the chart recorder. The lowest figure measured is 9.64×10^{-7} J m^{-2} and this must represent about the lowest bond strength measurable with the technique in this form. All the results of those that failed before being tested or without registering were classified as below this strength.

TABLE 4:6

ADHESIVE FRACTURE ENERGY RESULTS OBTAINED FROM MODIFIED 'BLISTER' TEST. (UNTREATED SPECIMENS)

a (metres)	h (metres)	P_{cr} (millivolts)	γ_a (Joule metres^{-2})
0.00174	0.00072	0.08	1.44×10^{-5}
0.00181	0.00063	0.02	1.58×10^{-6}
0.00169	0.00084	0.06	4.55×10^{-6}
0.00174	0.00077	0.07	9.05×10^{-6}
0.00175	0.00059	0.05	1.05×10^{-5}
0.00180	0.00061	0.035	5.21×10^{-6}
0.00177	0.00048	0.04	1.30×10^{-5}
0.00171	0.00053	0.055	1.59×10^{-5}
0.00169	0.00081	0.10	1.41×10^{-5}
0.00176	0.00078	0.085	1.34×10^{-5}
0.00175	0.00051	0.04	9.37×10^{-6}
0.00169	0.00070	0.06	7.87×10^{-6}
0.00171	0.00064	0.10	3.00×10^{-5}
0.00174	0.00059	0.035	5.03×10^{-6}
0.00171	0.00056	0.04	7.16×10^{-6}
0.00176	0.00071	0.11	2.98×10^{-5}
0.00180	0.00052	0.09	5.56×10^{-5}
0.00172	0.00064	0.065	1.29×10^{-5}
0.00174	0.00073	0.04	3.46×10^{-6}
0.00175	0.00071	0.02	9.64×10^{-7}
0.00174	0.00048	1.00	7.62×10^{-3}
0.00178	0.00072	0.10	2.47×10^{-5}
0.00171	0.00064	0.22	1.45×10^{-4}
0.00176	0.00058	0.26	3.05×10^{-4}
0.00174	0.00044	0.05	2.47×10^{-5}
0.00184	0.00060	0.05	1.22×10^{-5}
0.00171	0.00070	0.04	3.67×10^{-6}
0.00178	0.00074	0.72	1.18×10^{-3}
Plus 18 specimens that failed before test and are valued at			0.00
MEDIAN VALUE			5.2×10^{-6}
MODAL VALUE			$1.00 - 1.77 \times 10^{-5}$

TABLE 4:7

ADHESIVE FRACTURE ENERGY RESULTS OBTAINED FROM MODIFIED 'BLISTER' TEST. (TREATED SPECIMENS)

a (metres)	h (metres)	P_{cr} (millivolts)	γ_a (Joule metres^{-2})
0.00181	0.00071	0.91	2.28×10^{-3}
0.00176	0.00068	1.26	4.45×10^{-3}
0.00175	0.00069	0.30	2.36×10^{-4}
0.00173	0.00083	0.76	8.32×10^{-4}
0.00182	0.00059	1.14	6.38×10^{-3}
0.00172	0.00071	0.09	1.82×10^{-5}
0.00171	0.00063	1.01	3.20×10^{-3}
0.00169	0.00082	0.84	9.60×10^{-4}
0.00175	0.00068	0.79	1.71×10^{-3}
0.00174	0.00074	1.03	2.20×10^{-3}
0.00174	0.00048	0.24	4.39×10^{-4}
0.00186	0.00070	0.87	2.43×10^{-3}
0.00178	0.00072	1.03	2.62×10^{-3}
0.00171	0.00064	1.00	3.00×10^{-3}
0.00171	0.00058	0.13	6.81×10^{-5}
0.00174	0.00044	0.02	3.96×10^{-6}
0.00184	0.00060	0.19	1.76×10^{-4}
0.00171	0.00070	1.21	3.35×10^{-3}
0.00178	0.00074	0.94	2.01×10^{-3}
0.00182	0.00064	0.79	2.40×10^{-3}
0.00184	0.00053	0.84	4.99×10^{-3}
0.00173	0.00076	0.77	1.11×10^{-3}
0.00172	0.00048	1.03	7.72×10^{-3}
0.00184	0.00067	0.09	2.84×10^{-5}
0.00169	0.00065	1.14	3.55×10^{-3}
0.00175	0.00071	0.96	2.22×10^{-3}
0.00177	0.00074	0.91	1.84×10^{-3}
0.00181	0.00053	1.01	6.76×10^{-3}
0.00171	0.00059	0.06	1.34×10^{-5}
0.00179	0.00071	0.74	1.44×10^{-3}
0.00173	0.00052	1.02	6.09×10^{-3}
0.00172	0.00072	1.24	3.31×10^{-3}
0.00161	0.00080	0.01	1.20×10^{-7}
0.00181	0.00078	0.93	1.80×10^{-3}
0.00180	0.00066	0.09	2.72×10^{-5}
0.00177	0.00042	1.09	1.44×10^{-2}
0.00178	0.00059	0.83	3.09×10^{-3}
0.00173	0.00058	0.64	1.73×10^{-3}
0.00166	0.00042	0.45	1.91×10^{-3}
0.00184	0.00069	0.93	2.77×10^{-3}
MEDIAN VALUE			2.20×10^{-3}
MODAL VALUE			$1.77 - 3.16 \times 10^{-3}$

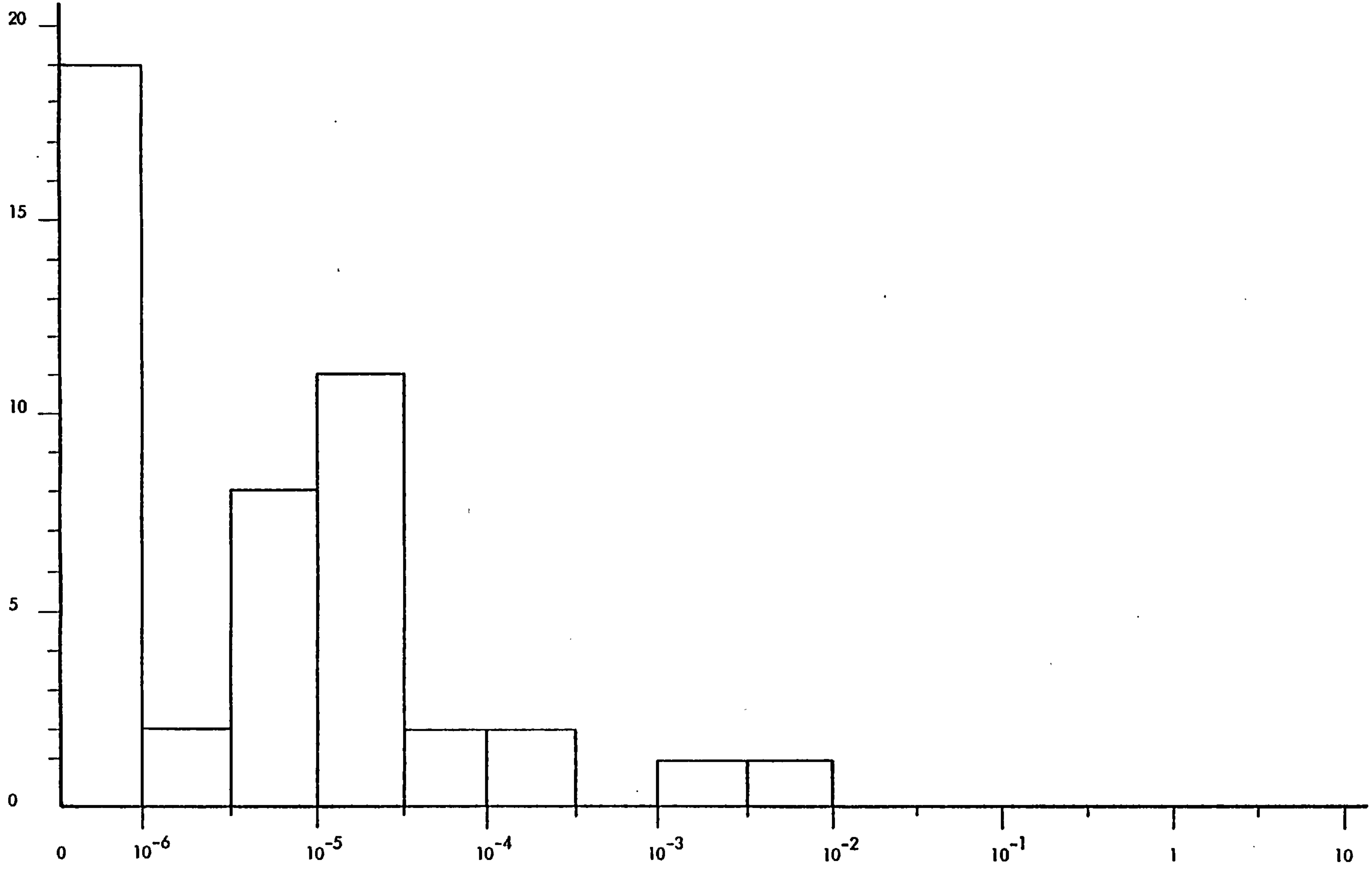


FIGURE 4:15

VALUES OF ADHESIVE FRACTURE ENERGIES OF JOINTS BETWEEN ACRYLIC RESIN AND UNTREATED DENTINE OBTAINED BY THE USE OF THE MODIFIED 'BLISTER' TEST.

VALUES OF ADHESIVE FRACTURE ENERGIES OF JOINTS BETWEEN ACRYLIC RESIN AND DENTINE TREATED WITH COUPLING AGENT OBTAINED BY THE USE OF THE MODIFIED 'BLISTER' TEST.

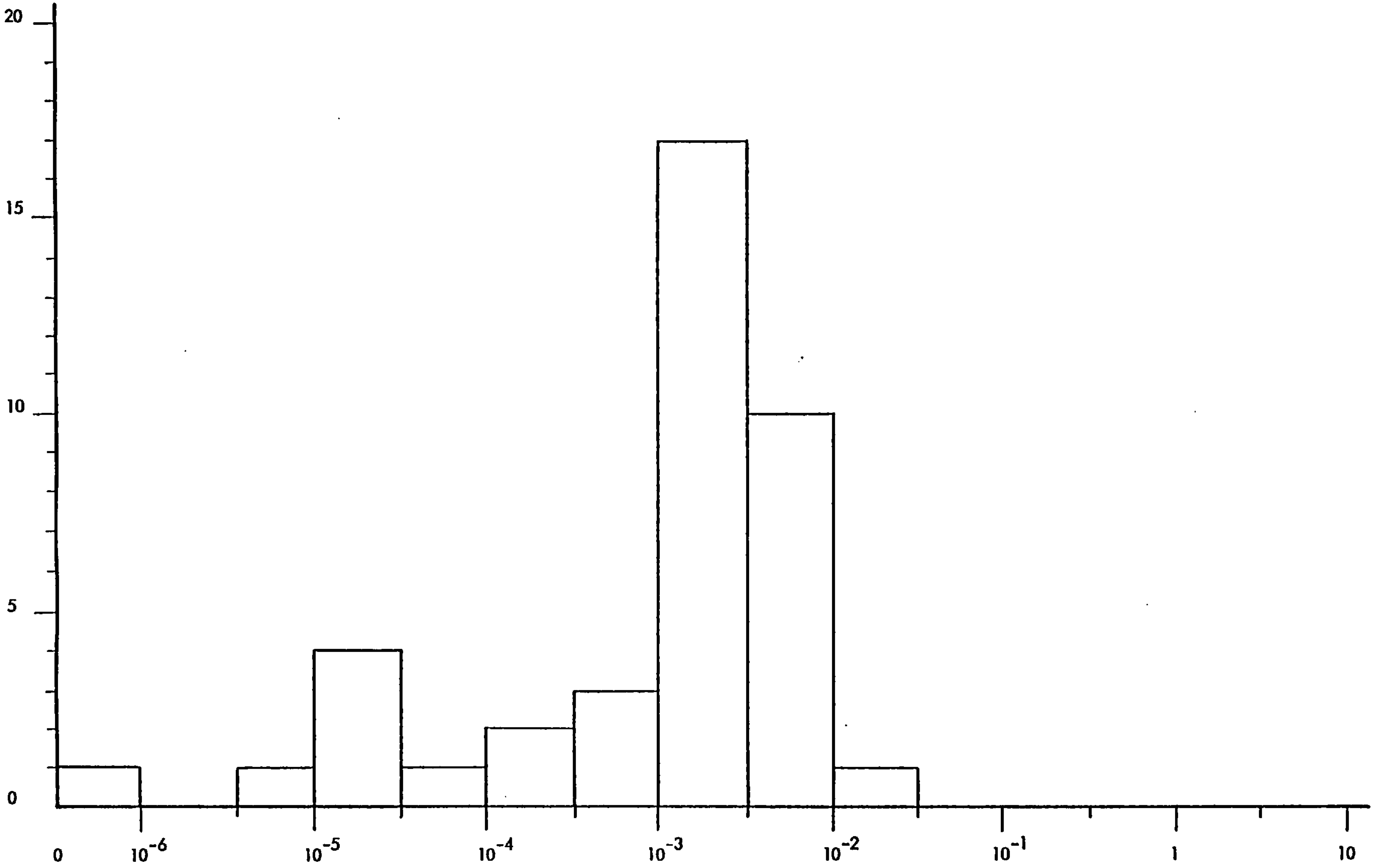


FIGURE 4:16

In the group of treated specimens one has a calculated figure of 1.207 x 10^{-7} J m^{-2}. This is by far the lowest figure obtained of all of the results and may be anomalous. Despite this it has been included in the results.

The results of each group cover a fairly wide range. When plotted on a logarithmic scale they show an almost normal distribution within each group. As in this case an arithmetical mean value does not have great significance, the modal and the median values have been calculated.

4.702 DISCUSSION

From the results given it is apparent that there is a difference between the two groups of specimens and this can be shown by applying the Student t test for independent variables to the results. Testing for the probability of the results of the group of treated specimens being of a similar group as the results of the untreated specimens, gives a t statistic of -4.9264 indicating a probability of less than 0.001. For this test 6 of the zero values were excluded from the untreated group to make the groups of equal size.

As stated in the presentation of the results, the median and modal values have been calculated as these have more meaning than the mean values for each group of results. Where there is a non linear distribution, as is common in many natural phenomena, the median or the modal values tend to give the more reliable estimates of the normal value of the group. In this experiment the modal values have been calculated after distributing discrete values into ranges of one quarter of an order of magnitude.

Of the results of the group of specimens of acrylic resin bonded to dentine without the use of the coupling agent, the median value is slightly less than the modal value. This is due to the large number of specimens which have an adhesive energy given as zero. The difference between the median and modal values is not very great and the median value is probably the more useful figure as it reflects a measure of the large number of joints that failed before test.

The results of the group of treated specimens show less variation, the median value falling well within the range of the modal value. Thus again the median value can be used as a representative result. When these results are compared with the published figure for the cohesive fracture energy of poly(methylmethacrylate), which as stated earlier is 0.5 J m^{-2}, they appear to be of the correct order of magnitude. This is in contrast to those results given by DESPAIN et al. (1973).

It is possible, however, to make a further comparison which appears to confirm the accuracy of the results presented here. DESPAIN et al. (1973) mention that the fracture stress of a joint, σ_f, bears a linear relationship to the square root of the adhesive fracture energy of the joint. Thus the ratio between the fracture stresses of two similar joints will be equal to the ratio between the square roots of the adhesive fracture energies of the two joints. This can be expressed thus:

$$\frac{\sigma_{f_1}}{\sigma_{f_2}} = \frac{\sqrt{\gamma_1}}{\sqrt{\gamma_2}}$$

If this relationship is applied to the values of adhesive fracture energy of a dentine to resin joint and to the cohesive fracture energy of the resin itself, a value for the ratio of fracture stresses between the two cases can be calculated. This may then be used to calculate from the published value of the tensile strength of poly(methylmethacrylate), an estimated value for the tensile strengths of the dentine to resin joint. In Table 4:8 values are presented of the ratio

$$\frac{\sqrt{\gamma_c}}{\sqrt{\gamma_a}}$$

for adhesive joints between resin and dentine, treated and untreated with the coupling agent.

These values have then been used, together with the published value of the tensile strength of poly(methylmethacrylate) of 5.0×10^7 N m^{-2} (GUY, 1972), to calculate the estimated tensile strengths of the same joints, which are presented in Table 4:9.

If comparison is made between the estimated values of tensile strength and those obtained by measurement (and shown in Fig. 4:4), it will be seen that both of the estimated values fall well within the ranges of the respective measured values. This would seem to add much weight to the reliability of the results obtained from the two different experiments.

TABLE 4:8

	UNTREATED	TREATED
Cohesive fracture energy γ_c of poly(methylmethacrylate)	5.0×10^{-1} J m^{-2}	5.0×10^{-1} J m^{-2}
Adhesive fracture energy γ_a of dentine - resin joint	5.2×10^{-6} J m^{-2}	2.2×10^{-3} J m^{-2}
$\dfrac{\sqrt{\gamma_c}}{\sqrt{\gamma_a}}$	310	15

TABLE 4:9

Tensile strength of poly(methylmethacrylate)	5.0×10^{7} N m^{-2}
Estimated tensile strength of resin to dentine joint made without use of coupling agent.	1.6×10^{5} N m^{-2}
Estimated tensile strength of resin to dentin joint made with use of coupling agent	33.0×10^{5} N m^{-2}

5.0 INVESTIGATION BY SCANNING ELECTRON MICROSCOPY

5.001 INTRODUCTION

In recent years, use of the scanning electron microscope has produced much evidence in the investigation of bonding of dental resins to enamel. It was decided to use this technique of investigation to try to observe any changes in the physical nature of the bond between resin and dentine that the use of the coupling agent might produce.

Although enamel to resin bonding has been very fully investigated, little work has been directed towards dentine to resin bonding. HOPPENBROUWERS et al. (1974) present work and micrographs which show that acrylic resins are able to fully "wet" dentine, and produce tags of resin corresponding to the dentinal tubules. Upon fracture of the dentine resins bonds they concluded that an "adhesive" facture occurred. In the same year RETIEF (1974) give evidence that resins will flow into dentinal tubules, and similarly presented micrographs of the effect.

A study of adaptation of composite resins to dentine has been made by BARNES (1977 a) as part of a larger study involving enamel as well as dentine. BARNES shows penetration of dentinal tubules by resin to a depth of up to 200 μm but the resin was placed against the dentine under pressure, and this may have helped produce such a profusion of long resin processes. In the same specimens BARNES (1977 b) shows what he believes may be collagen fibres in the gap between dentine and a resin restoration.

5.002 EXPERIMENTAL AIMS

The coupling agent is designed to form a bond between a resin and the organic component of dentine. If the coupling agent is producing this type of bond, it may be possible to find visible evidence of coupling between the resin and the collagen fibres within the dentine. Alternatively, the improved attraction between the dentine surface and the resin, as demonstrated by the change in contact angle between resin and dentine caused by the use of the coupling agent (3.602), may be apparent in an alteration of the adaptation of the resin to the dentine surface. It was decided that the best method of approach would be to produce examples of resin bonded to dentine, both with and without the use of the coupling agent; and then to try to look at the interface by removing some of the dentine by the use of an acid. It was also decided that some specimens would be separated mechanically, and the previously adhering surfaces examined for evidence of any interaction between the resin and the dentine.

5.003 EXPERIMENTAL METHODS

In all cases the dentine used came from extracted human molar teeth, that had been stored in distilled water. Pieces of dentine of a size small enough to fit on the mounting stub of the electron microscope were produced by grinding the teeth with a water cooled disc of 150 or 400 grit silicon carbide paper. In some cases the dentine was first reduced to size by fracturing the tooth and then ground to give a flat dentine surface. The orientation of the ground surface to the direction of the dentine tubules was not controlled, so that samples of differing orientation were obtained. Those samples that were to be treated with the coupling agent were immersed in a freshly mixed sample of the standard solution (3.203) at a temperature of 37°C, for one minute. The resin used in the experiments was the standard acrylic resin used in all the previous experiments (3.509). A drop of the resin was placed upon the ground dentine surface, and then left to set. No pressure was applied to the resin to make it spread, or adapt to the dentine surface. When the resin had set the specimen was placed in concentrated lactic acid for up to 30 minutes so that some of the dentine would be etched away, thus exposing the resin surface which was bonded to the dentine.

A few specimens were not etched, but the resin was prised from the dentine surface, thus exposing the adhering surfaces, so that they could be examined.

Some specimens were prepared from pieces of fractured dentine without grinding, and were placed into a bead of resin, after treatment with the coupling agent in the standard manner. These were subsequently etched in a similar manner to remove some of the dentine and to show the interface, but from a different angle.

All of the specimens were mounted upon aluminium stubs, with a cellulose cement, and then coated with a film of gold, under vacuum, in the normal manner of preparation for scanning electron microscopy. The specimens were examined in a CAMBRIDGE STEREOSCAN Model 600 scanning electron microscope.

5.1 RESULTS AND DISCUSSION

5.101 RESULTS

Figures 5:1, 5:2, 5:3 and 5:4 show specimens which have received no coupling agent treatment. A gap is apparent between the resin and the dentine, where the acid has etched away the dentine. Fig. 5:3 shows grooves running across the dentine surface which are a result of the grinding process. The etching has not completely removed the roughness and scratching left by the abrasive. The resin, in all of the specimens can be seen to consist of beads of polymer which have fused together under the influence of the monomer liquid. These, together with the dentinal tubules help to give an idea of scale when comparing one view with another.

No processes of resin can be seen passing into the dentinal tubules in the manner demonstrated by HOPPENBROUWERS et al. (1974) and BARNES (1977).

Figures 5:5, 5:6 and 5:7 show specimens which have been treated with the coupling agent. Fig. 5:6 shows a specimen which was prepared by placing the dentine on a bead of resin, thus its appearance differs from the other figures. The major difference that is apparent between the treated and the untreated specimens, is the presence in the treated specimens of filaments, or processes between the resin and the dentine. In nearly all instances they appear identical to the processes demonstrated by HOPPENBROUWERS et al. (1974) and BARNES (1977). They can be seen to pass from the resin, into the dentinal tubule, and appear to be continuous with the resin. Fig. 5:8

is of a specimen prepared in a similar manner to Figs. 5:5, 5:6 and 5:7, but the dentinal tubules are orientated differently, and do not appear to open onto the surface as discrete round apertures. It is possible though to see filamentous structures extending between the resin and the dentine. They appear to be much finer than the resin processes in the earlier figures, with the exception of a few very fine strands apparent in Fig. 5:5. Figs. 5:9 and 5:10, two views of one specimen, again show the fine strands, but here they are not continuous between the resin and the dentine. This specimen was etched with 50% phosphoric acid, instead of lactic acid, and this may be the reason for the discontinuity.

The identity of the fine filaments is difficult to state with certainty. The most likely explanation is that they are filaments of collagen fibre from the dentine, and do in fact appear similar to those demonstrated by BARNES (1977 b). Another alternative is that they are fine strands of resin, but it is hard to postulate a mechanism for this explanation.

In an attempt to demonstrate the presence of fibres within the dentine, some specimens of dentine only were prepared in a special manner. Figs. 5:11 and 5:12 show the appearance of these fibres. The dentine has been subjected to treatment with the coupling agent solution for 1 minute, in an attempt to fix the organic material, and then decalcified with lactic acid for five minutes. This regime was repeated twice, before mounting and gold coating the specimens. Fig. 5:11 shows dentine on the pulped wall, and many large fibres can be seen lying on and passing into the dentine. This can be compared with Fig. 5:12 which shows dentine cut parallel to the dentinal tubules, and fibres running at right angles to the course of the tubules. It is possible that the fibres seen in Figs. 5:11 and 5:12 are similar to those seen in Figs. 5:5, 5:8, 5:9 and 5:10, or of similar origin.

Figs. 5:13 and 5:14 show samples of dentine treated with the coupling agent, placed in the dental resin and which have then been mechanically disturbed before the resin was finally cured. In Fig. 5:13 filamentous web-like structures can be seen, which give the appearance of a sticky viscous "glue" having been pulled away from a solid surface. It is hard to determine the origin of the web, but it is more likely to be strands of resin, than organic material pulled from the dentine. The specimen shown in Fig. 5:14 gives an appearance similar to Fig.5:6, but the processes appear to have broken in many instances.

Figs. 5:15 and 5:16 show the surface of a bead of resin that was adhering to dentine treated with the coupling agent. The resin has been prised away from the dentine. In Fig. 5:15 can be seen the remains of many processes that extended into the dentinal tubules, and have broken. There are occasional processes that have pulled away from the dentine and are lying on the resin surface. Fig. 5:16 is a view of part of Fig. 5:15, at higher magnification. The broken processes can be seen more clearly, and at the same time can be seen very many small protruberances in the areas between the processes. Examination of the dentine surface from which the resin has been fractured gives the view shown in Fig. 5:17. Several large dentinal tubules can be seen, but in between are many smaller features that appear to be shallow holes.

A further view of this at higher magnification is given in Fig. 5:18. This 'mottling' does not appear in any of the other views of dentine surfaces. It is possible to speculate that the mottling of the dentine is produced by collagen fibres being pulled from the dentine surface by the resin. This would imply that the many small protruberances on the resin surface are pieces of collagen fibre, firmly bound to the resin. More work is required before positive identification of these features can be made.

5.102 DISCUSSION

That the use of the coupling agent produces a change in the nature of the adhesive interface cannot be denied. The mechanisms producing the change in the nature are, however, not so easily proven, yet it would seem reasonable to propose that the results show two phenomena attributable to the use of the coupling agent. These are an increase in the spreading power or wetting power of the resin, and an ability of the coupling agent to interact with collagen fibres of the dentine.

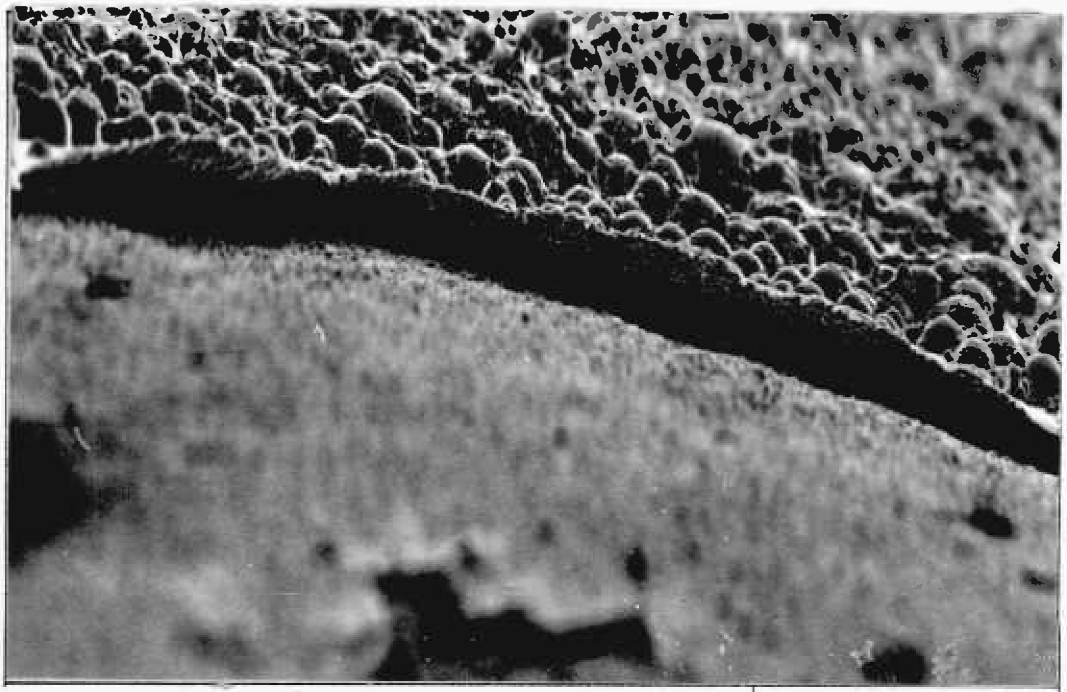
The increase of spreading power is demonstrated in the way use of the coupling agent has produced penetration of the dentinal tubules by the resin. Although BARNES (1977) shows penetration of dentinal tubules by resin without any such pre-treatment, he prepared his specimens in a manner that applied pressure to the unset resin. This would have the effect of forcing the resin into the tubules. In the case of the results presented here, no such pressure was applied, the resin being allowed to flow naturally across the surface of the dentine. Figs. 5:1 to 5:4 show that when the coupling agent was not used no penetration occurred, and Figs. 5:5 to 5:8 show that use of the coupling agent produces tubule penetration.

This result can be compared with the results presented in chapter 3 (3.602), where it was shown that the same resin was able to set up a lower contact angle on dentine treated with the coupling agent. Both results can be attributed to the same cause, the greater affinity of the resin for a dentine surface that has been treated with the coupling agent than an untreated surface. This conclusion would support the hypothesis of chapter 1 (1.311).

The ability of the coupling agent to interact with collagen fibres within the dentine is best demonstrated by the appearance of Figs. 5:11 and 5:12, where fibres can be seen quite clearly as part of the dentine. The use of the coupling agent as a fixative has been successful in preserving the fibres throughout the acidic decalcification.

The appearance of the fibres is such that they are most probably identical to the fibres visible in Figs. 5:5, 5:8, 5:9 and 5:10. If this is so, then it is possible to make the further observation that the use of the coupling agent produces an interaction between dental resin and collagen fibres. This interaction is not to be seen in any of the micrographs of the untreated specimens. This is strong evidence in support of the hypothesis of chapter 1 (1.311) but it depends upon the correct identification of the fibrous structures. Further work is necessary before such a definite identification can be made.

FIGURE 5:1



The interface between acrylic resin (above) and an untreated, ground dentine surface, with subsequent etching of the dentine in lactic acid to expose the interface.

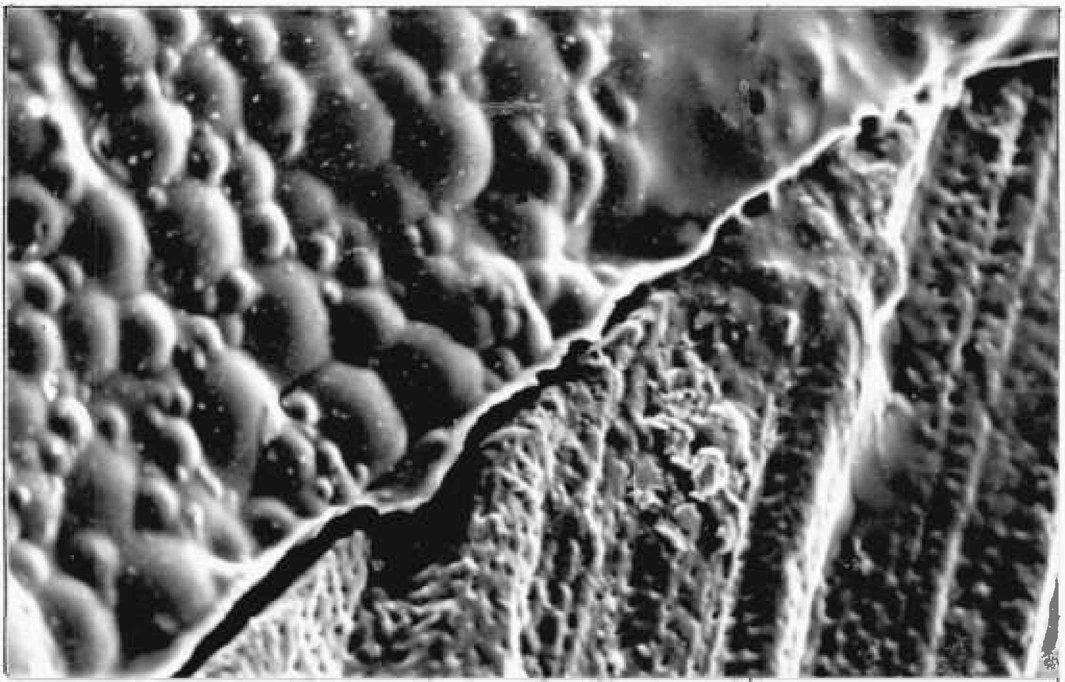
100 μm

FIGURE 5:2

A view of a specimen similar to that shown in Figure 5:1.

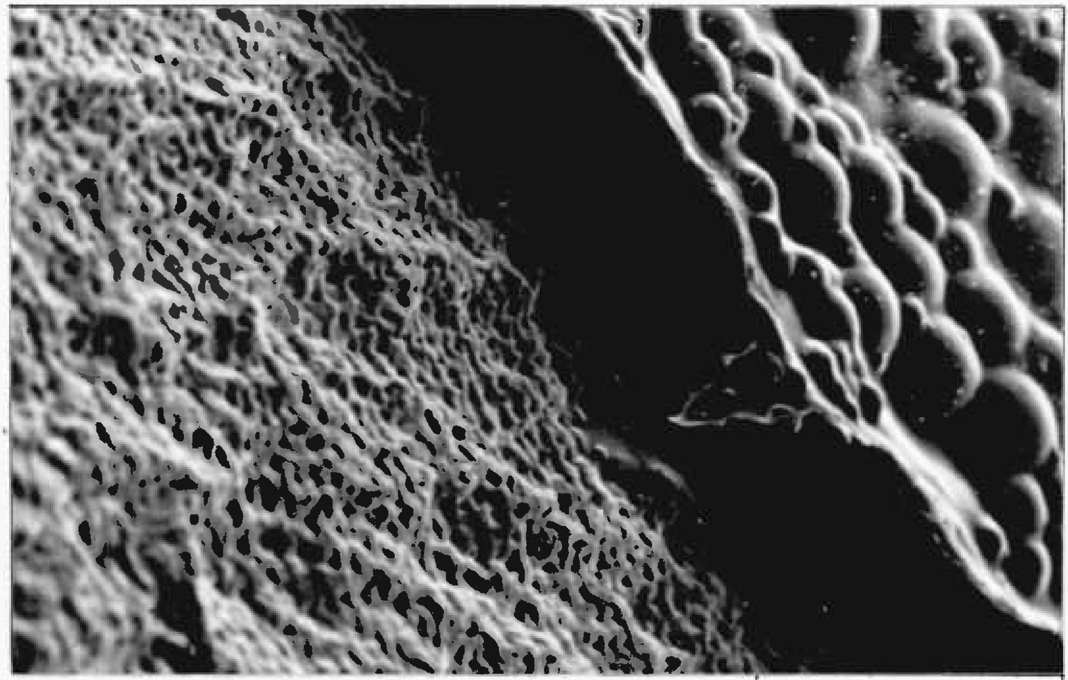
20 μm

FIGURE 5:3



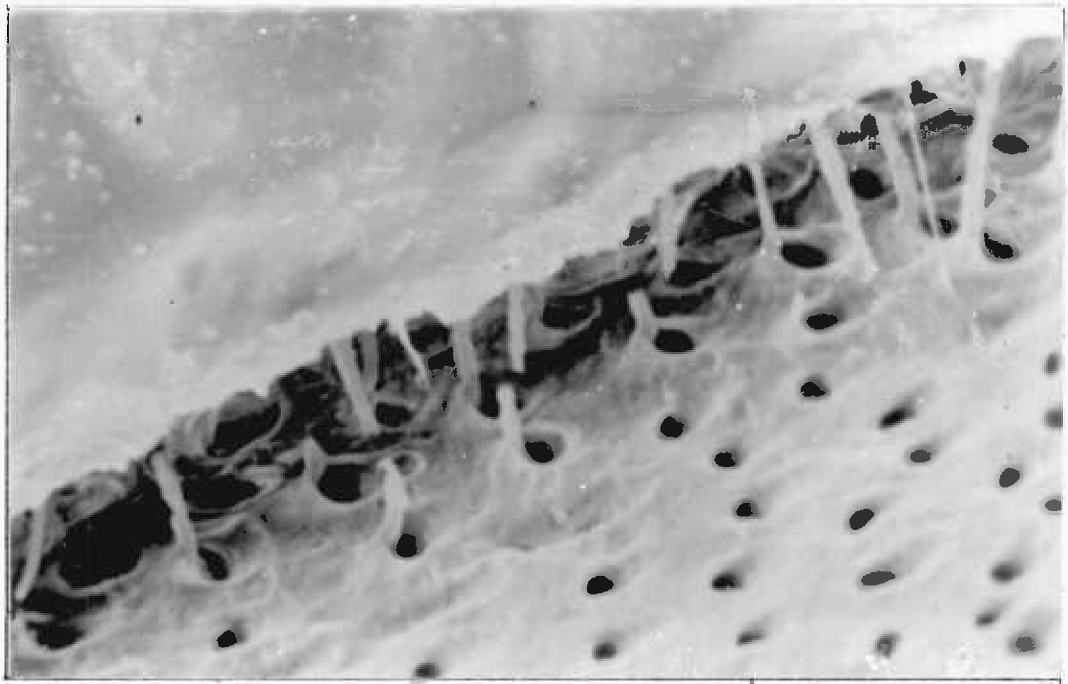
Acrylic resin on an untreated, ground, dentine surface, with subsequent etching of the dentine in lactic acid to expose the interface. Grooves left by the grinding are still visible.

FIGURE 5:4



A view of a specimen prepared in a manner similar to the specimen show in Figure 5:3.

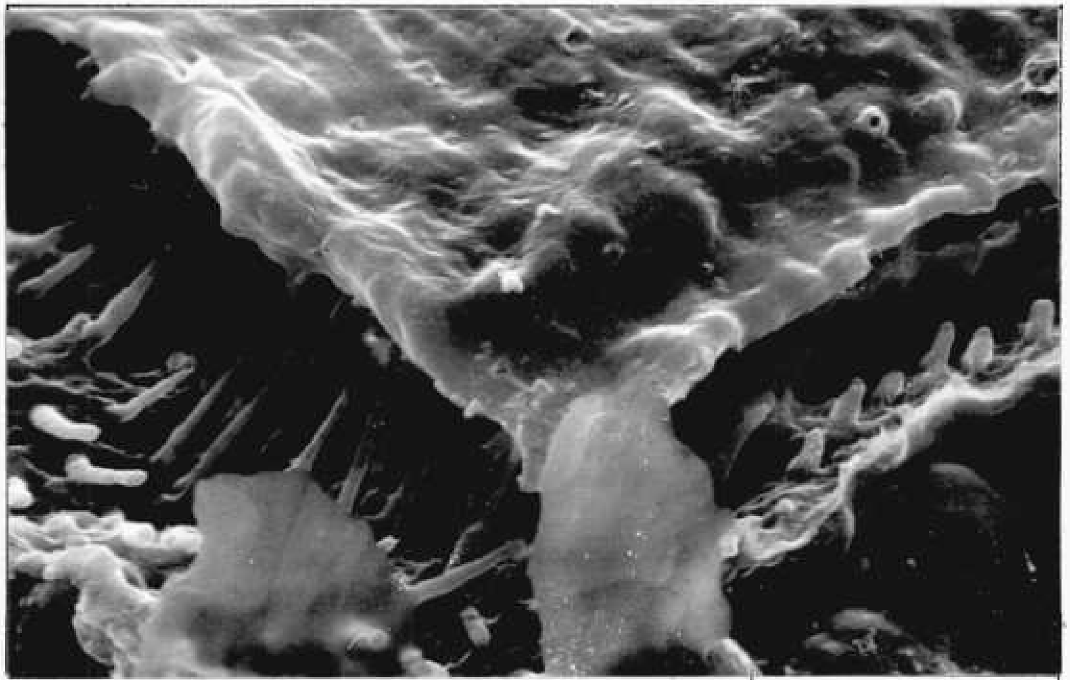
FIGURE 5:5



The interface between acrylic resin (above) and a dentine surface that has been treated with the coupling agent, with subsequent etching to expose the interface. Many resin processes can be seen passing into dentinal tubules as well as some 'fibres'.

10 μm

FIGURE 5:6



The interface between acrylic resin (below) and a dentine chip that has been treated with the coupling agent. Subsequent etching in lactic acid has revealed the interface with its many resin processes.

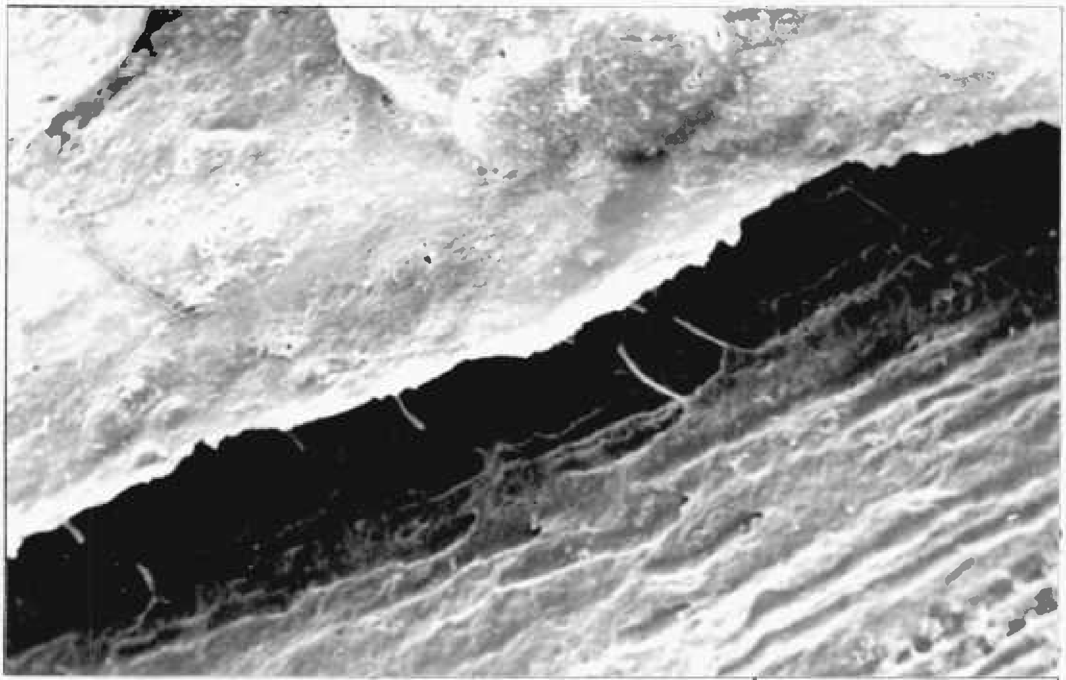
10 μm

FIGURE 5:7

Resin processes passing into dentinal tubules, in a specimen prepared in a similar manner to the specimen shown in Figure 5:5.

8 μm

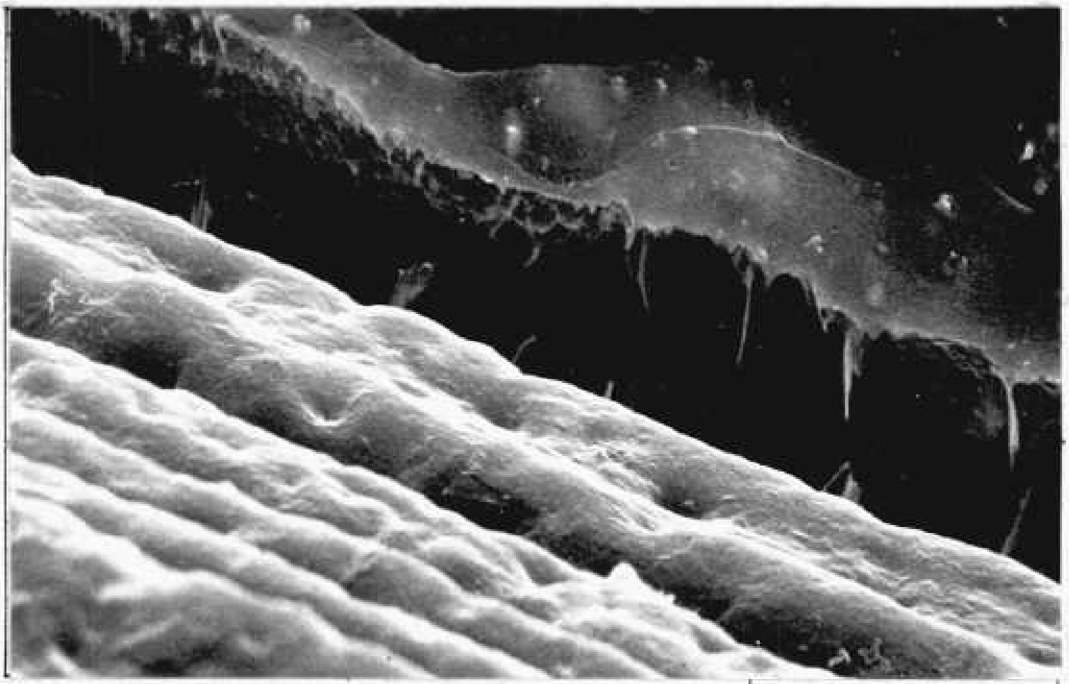
FIGURE 5:8



The interface between acrylic resin and dentine treated with the coupling agent. The dentinal tubules are orientated nearly parallel to the surface of the dentine.

10 μm

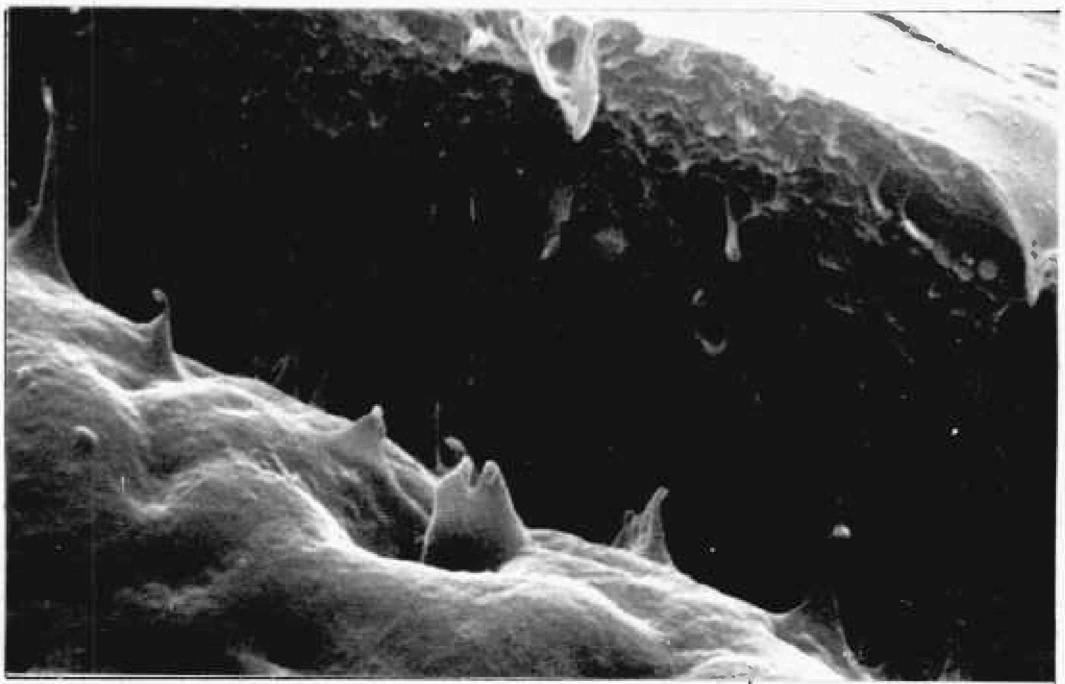
FIGURE 5:9



The interface between acrylic resin (above) and dentine treated with the coupling agent, subsequently etched with phosphoric acid. Fibrous structures can be seen.

10 µm

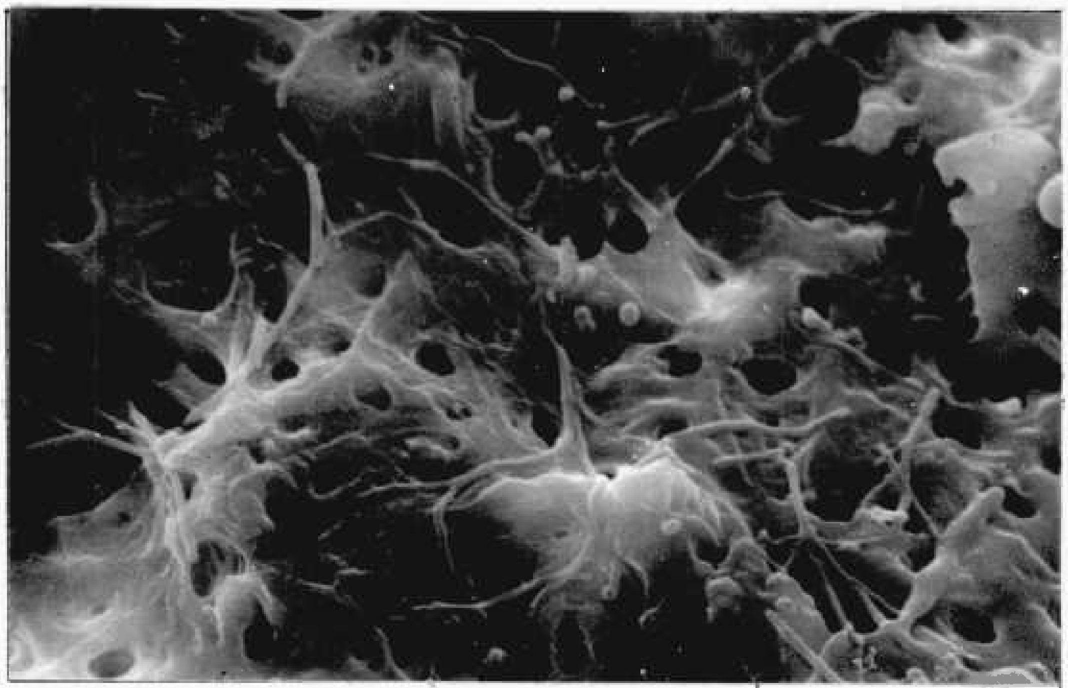
FIGURE 5:10



Another view of the specimen shown in figure 5:9.

3 µm

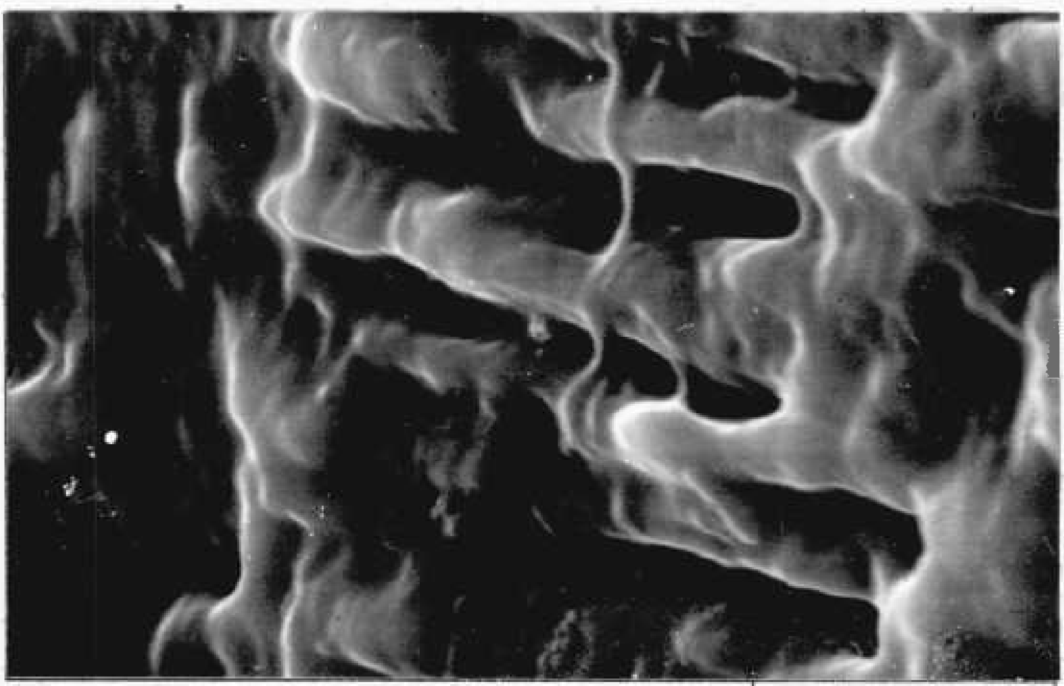
FIGURE 5:11



Dentine 'fixed' with the coupling agent and decalcified with lactic acid, showing fibres passing from and lying across the dentine.

10 µm

FIGURE 5:12



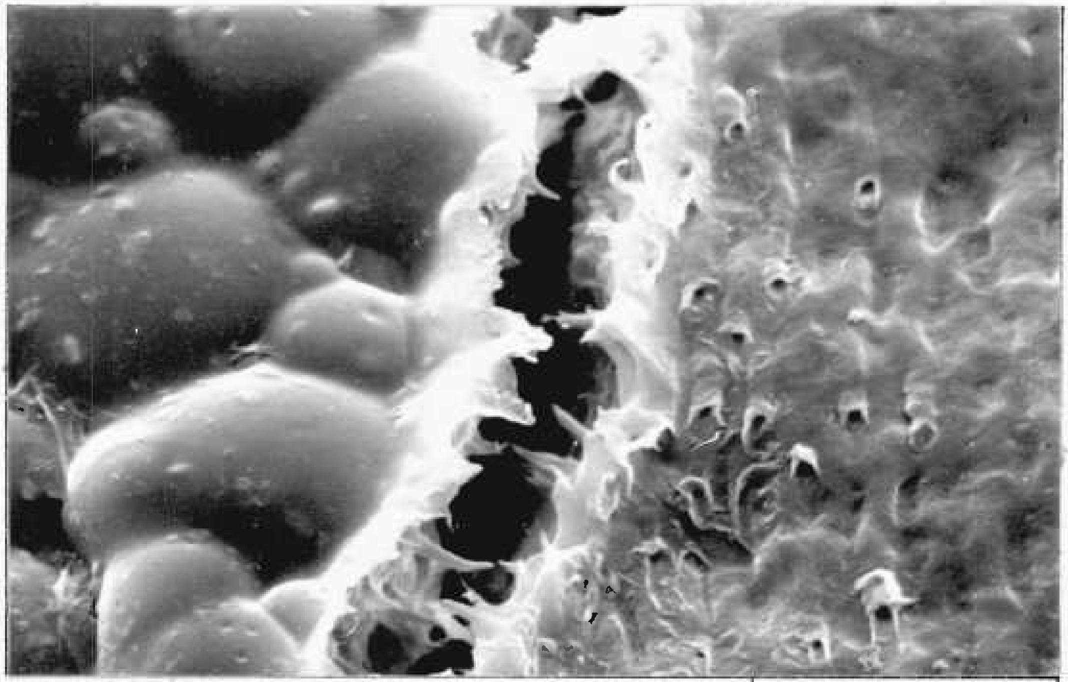
Dentine 'fixed' with the coupling agent and decalcified with lactic acid, showing fibres in the dentine at right angles to the dentinal tubules.

4 µm

FIGURE 5:13

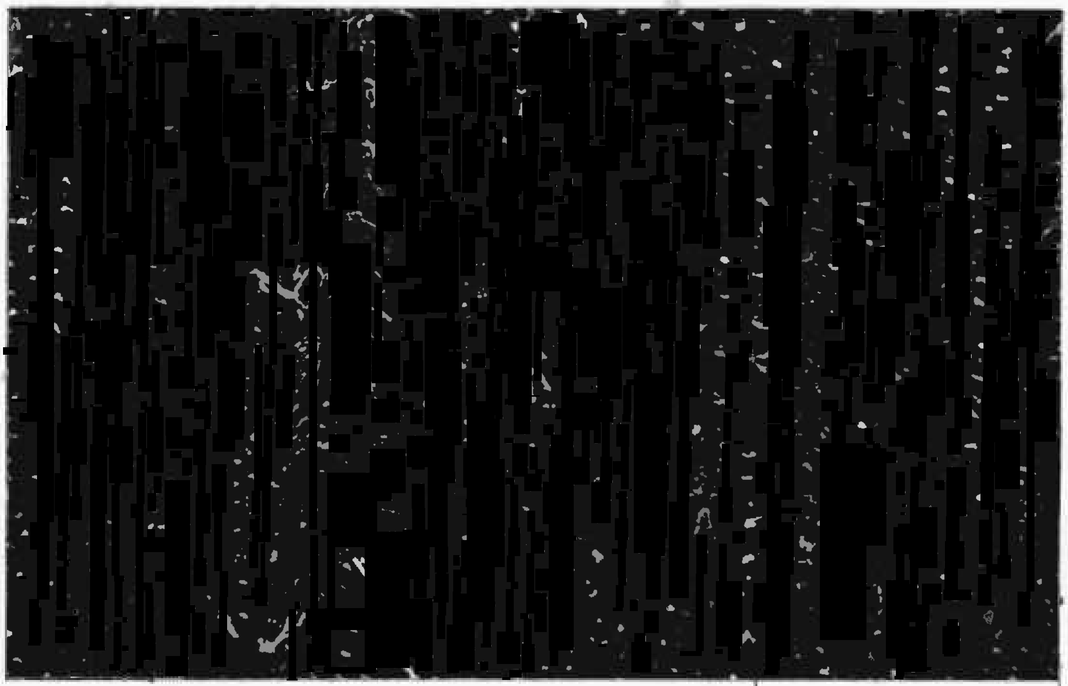
The interface between acrylic resin and dentine treated with the coupling agent. The specimen has been moved whilst setting, and strands of resin have appeared across the gap thus created.

FIGURE 5:14



The interface between acrylic resin and dentine treated with the coupling agent, and moved just before the resin has set.

FIGURE 5:15



The surface of acrylic resin that has been debonded from a dentine surface treated with the coupling agent. A few resin processes have not fractured and have left their tubules to lie across the resin surface.

40 μm

FIGURE 5:16

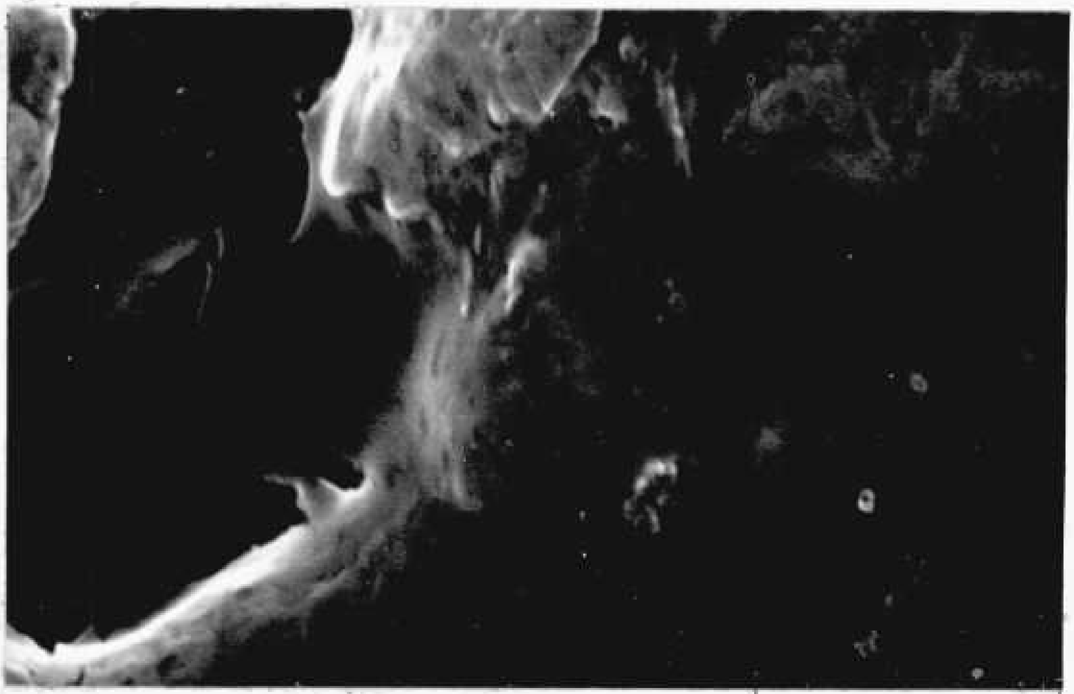
An enlarged view of part of Figure 5:15. It is possible to make out the presence of many smaller protruberances on the surface between the resin processes.

6 μm

FIGURE 5:17

The dentine surface from which the resin shown in Figure 5:15 was removed.

FIGURE 5:18



An enlarged view of part of Figure 5:16. A speckled pattern is visible on the dentine surface.

6.0 CONCLUSIONS

A coupling agent to produce chemical bonds between dental tissue and a dental resin has been synthesised, and used to test the hypothesis set out in chapter 1 (1.311). Knowledge of the method of synthesis, together with the evidence derived from infra-red spectroscopic examination enables the conclusion to be made that the synthesised coupling agent is 2-N'-allylamino, 4,6 dichloro - s - triazine. This is believed to be a novel compound as no reference can be found to its previous synthesis.

The coupling agent has been shown to react with a dentine surface in a manner that is, most probably of a covalent nature. The reaction takes place under conditions of temperature that are found in an oval environment, and occurs within a time that could be considered acceptable in a clinical situation.

Dentine surfaces that have been treated with the coupling agent have been shown to interact with an acrylic dental resin in a manner different from untreated dentine surfaces and in a manner that displays an increased attraction between the treated dentine and the resin. It is suggested that the presence on the surface of the treated dentine of the polymerisable olefinic double bonds of the coupling agent is responsible for this increased affinity, and that a copolymerisation reaction is occurring.

It has also been shown that adhesive joints between a dental resin and dentine that has been treated with the coupling agent and stored for 72 hours in simulated oral conditions, have a higher specific energy of adhesion than similar joints made without use of the coupling agent and subjected to similar storage conditions.

It is therefore proposed that the hypothesis of chapter 1 (1.311) has been tested and found to be proven.

The evidence used to support this claim has been used in an application for the granting of a BRITISH PATENT (CRANFIELD, 1975).

6.1 POSSIBLE FURTHER RESEARCH

As explained in chapter 1, the ability to produce an adhesive bond between a resin and dentine should prove to be of great use in clinical dentistry. The experiments performed in vitro and described in this thesis suggest that 2 N'-allylamino, 4,6 dichloro - s - triazine may be used as a coupling agent for clinical dental use. To confirm this it would be necessary to conduct a clinical experiment, to assess the effect of the use of the coupling agent. If the agent is to be of value it must be demonstrated that its use does improve the performance resin of dental restorations. It is possible to envisage a clinical trial, similar to that carried out by CHANDLER et al. (1974), in which subjective assessment of pairs of restorations would be made. In each pair, one restoration would have revived the coupling agent, whilst the other would be untreated and would act as a control.

At the same time it would be necessary to carry out experiments to determine whether the coupling agent produced any undesirable effects upon the pulp of any tooth it was used on. It is not likely that untoward effects would occur, as the coupling agent has been shown to be very reactive, and would therefore bind itself to the many available sites before it was able to reach the dental pulp.

The coupling agent produced for these experiments is only one of a large family of possible compounds. If the substitution of the trichloro - s - triazine were carried out with a longer chain alkenylamine, a different product would result but it would in theory be capable of reacting in a similar manner to 2 N'-allylamine, 4-6-dichloro - s - triazine. However its different physical shape might improve its ability to react and thus give an even better performance as a coupling agent. Before any further compounds are synthesised, it would be advisable to complete a clinical experiment that would determine the value of the coupling agent when used clinically to produce resin dental restorations.

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