



EPOXY RESINS FOR BONDING ORTHODONTIC ATTACHMENTS TO TEETH

D. H. RETIEF AND C. J. DREYER

Joint Council for Scientific and Industrial Research / University of the Witwatersrand Dental Research Unit, Johannesburg.

SUMMARY

An epoxy resin formulation has been developed to bond orthodontic attachments to enamel surfaces.

The disruptive force required to break the bond under experimental conditions was in excess of the forces exerted on the orthodontic attachments during treatment.

This formulation has been subjected to a limited number of clinical trials. These tend to substantiate the experimental findings.

BANDING of teeth for orthodontic treatment provides the means of connecting the attachments to the teeth. This technique has certain drawbacks: it is time-consuming; the inter-dental space occupied by the band material and cement is not only a source of discomfort to the patient but may also hamper the treatment; and gingival irritation and enamel decalcification are not uncommon.

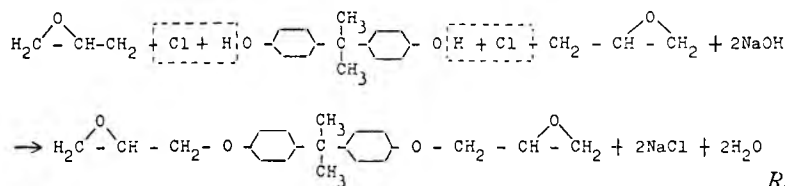
These disadvantages would be obviated

if a suitable adhesive material was available to bond orthodontic attachments directly to enamel surfaces. Many such materials, including the epoxy resins, have been evaluated for this purpose (Bowen 1956, Newman 1965, Phillips 1966 and Mitchell 1967).

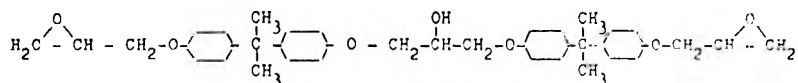
The application of these resins to dental tissues, however, presents special problems. Because of the high temperature often required for curing, the toxicity of the curing agents and the length of the cure, most of them cannot readily be used intra-orally. In addition previous work has shown that optimum bonding is obtained and maintained only under dry conditions.

I. THE EPOXY RESINS

These are synthetic materials manufactured from by-products of the petroleum industry, most of them by reacting epichlorohydrin with diphenylolpropane in an alkaline medium as shown below.



Reaction 1.



Reaction 2.

Between the terminal epoxide groups only two kinds of linkages are present: carbon-carbon and carbon-oxygen-carbon. As they are stable and inert, Skeist (1964) has suggested that this molecule be symbolized thus:



The two terminal reactive epoxide groups are represented by the two triangles. He calls this intermediate "diepoxide O", the "O" indicating absence of hydroxyl groups in the molecule.

The condensation product of a liquid epoxy resin must have a small molecular size. To achieve this the epichlorohydrin must be present in excess during the manufacturing process; the diphenylolpropane would otherwise react with the epoxy groups in the "diepoxide O" to lengthen the chain.

Skeist (1964) is of the opinion that the reactions which take place when diphenylolpropane is increased progressively give rise to different products.

If two molecules of diphenylolpropane react with three of epichlorohydrin, they give rise to Reaction 2. (See top of page).

This compound can be designated as:



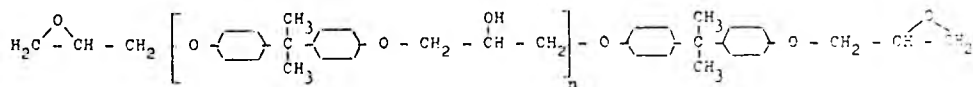
In addition to the two terminal epoxide groups, this compound, "diepoxide 1" contains one hydroxyl group.

A further increase of diphenylolpropane will result in Reaction 3. (See bottom of page).

Each molecule of the resin described here has two epoxy groups. These are equivalent to four hydroxyl groups since one epoxide can esterify two molecules of monobasic acid.

According to Skeist (1964) the sum of the hydroxyl groups and the four derived from the two epoxy groups gives the hydroxyl functionality of the epoxy resin, or the number of molecules of monobasic acid required to completely esterify one molecule of epoxy resin.

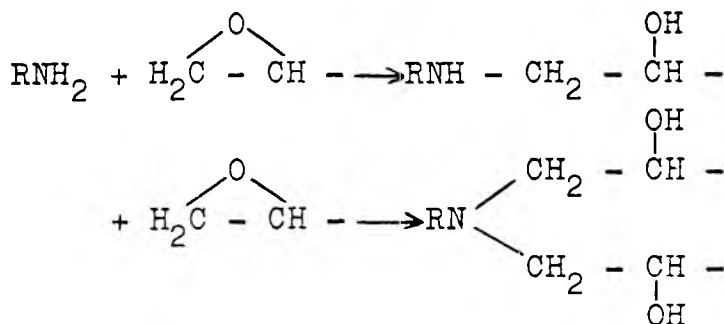
The physical properties of the epoxy resin depend on the degree of cross-linking that has occurred in the cured resin; this takes place via the epoxy and hydroxyl groups, hence its functionality is important. Manufacturers obtain a high func-



Reaction 3.



where $n = 2-15$.



Reaction 4.

tionality in a resin by incorporating in it far more epichlorohydrin than actually is required for its synthesis.

If other phenols or alcohols are used instead of diphenylolpropane, epoxy resins with different physical properties are produced.

II. CURING THE LIQUID EPOXY

The epoxy resins may react with various other chemicals to give an infusible product which forms powerful bonds with many materials.

The uncured resins are either liquids or brittle solids. Although the former contain varying diepoxides their predominant component is "diepoxide O". When cured or hardened their molecules are joined together at their ends and sides to form large cross-linked structures.

The epoxy and hydroxyl groups take part in the cross-linking (Skeist 1964). Most of the intermediate molecules have epoxy groups at both ends, and all but the shortest of the intermediates have hydroxyl groups spaced at regular intervals along the chains.

There are two types of linkages by means of which a liquid resin is converted to a solid end-product:

- (a) A *reactive hardener* which combines with one or more additional molecules of resin.
- (b) Other epoxy intermediate molecules, with the aid of a *catalyst*.

(a) *Reactive hardeners*

The aliphatic polyamines function by

reacting with the epoxides. Each active hydrogen atom attached to a nitrogen atom is capable of opening the epoxide ring; for example diethylenetriamine ($\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$), which has five active hydrogen atoms attached to its three nitrogen atoms, can join with as many as five epoxy molecules.

By means of a further reaction the primary amine *reacts* with the epoxide to form a secondary amine and the latter can react with another epoxide. (Reaction 4, see top of page).

It is believed that the secondary alcohols formed during the reaction do not combine with other epoxide groups but catalyze a similar reaction between the remaining amine and epoxide group.

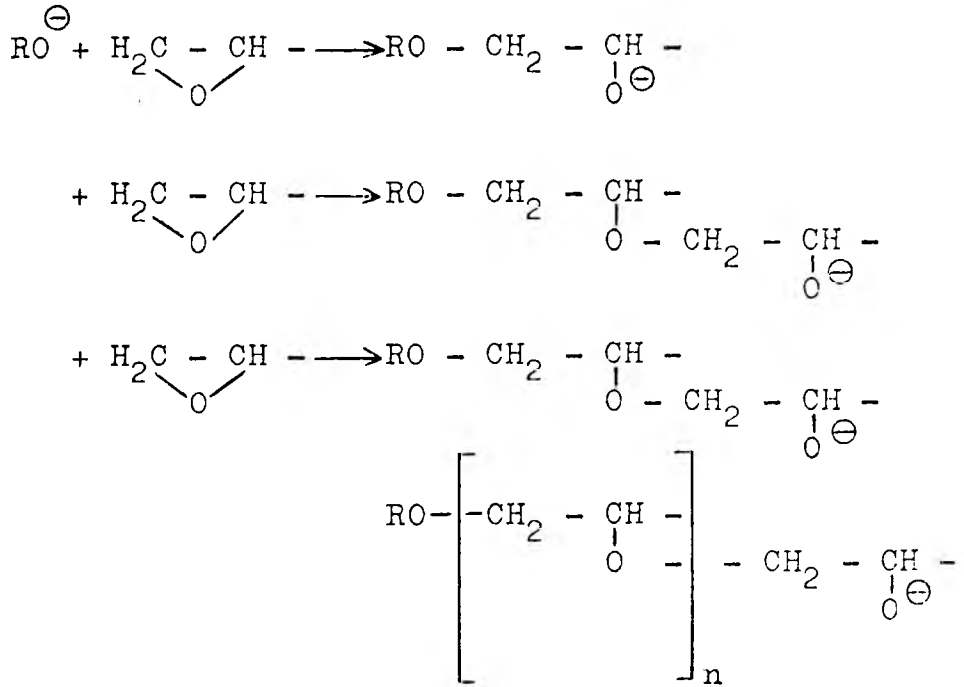
(b) *The catalyst*

The catalyst may be strong bases such as tertiary amines; and hydroxyl groups as generated in Reaction 4 or as provided by the addition of compounds containing hydroxyl groups — for example hydroxy-substituted amines, phenol or phenolic tertiary amines — have a catalytic effect on the curing reaction.

Shechter and Wynstra (1965) described the base-catalyzed cure as polymerization reaction which proceeds thus:

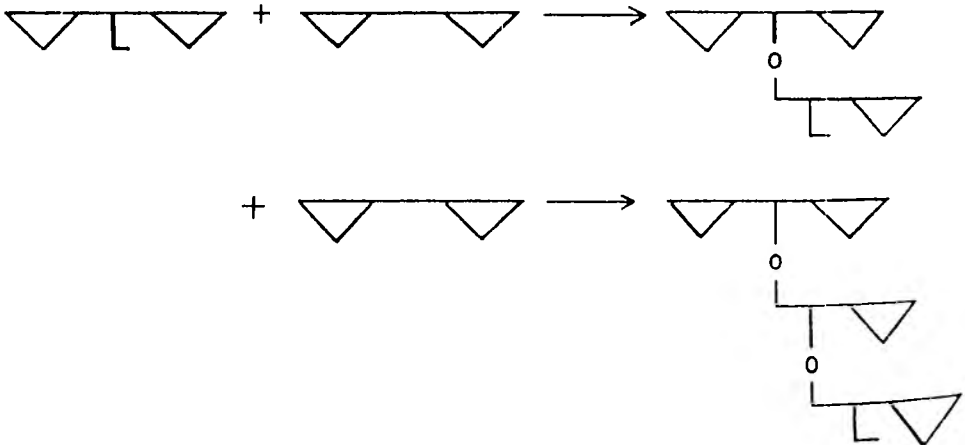
The tertiary amine converts the hydroxyl group to an alkoxide ion. This anion then reacts with the epoxide to form a new alkoxide ion. The latter combines with another epoxide to form an ether and regenerates the alkoxide ion which is capable of further reaction with epoxide

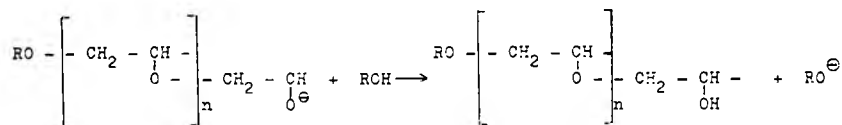
groups to lengthen the chain as hereunder:



Reaction 5.

This may be represented as:





Reaction 6.

Contact with another molecule containing a hydroxyl group results in the termination of this polymer chain and the generation of a new alkoxide ion to restart a polymerization reaction. (Reaction 6, see top of page).

The catalyst or reactive hardener may be blended, or catalysts which have both reactive and catalytic groups in the same molecule may be used.

The cure, as described above, is exothermic and results in a three-dimensional cross-linked thermostat polymer.

III. THE CURING AGENTS

A wide range of chemicals, chiefly amines, amine adducts and acid anhydrides, fall into this category.

Amines

1. *Primary-secondary aliphatic amines*: Include ethylenediamine and higher members of its series. They act at room-temperature and are extensively used in the curing of epoxy resins. Their toxicity is a disadvantage but it can be reduced by introducing a hydroxyl group into the polyamine molecule.

2. *Aliphatic primary-tertiary amines*: Combine the reactive hardening action of a primary amine with the catalytic action of a tertiary amine.

3. *Cyclic secondary amines*: Include piperidine, which is one of the oldest of the amine curing agents and is used when a softer end-product is required.

4. *Aromatic primary amines*: Cure at an elevated temperature.

5. *Phenolic tertiary amines*: Usually employed as catalysts with the acid anhydride curing agents.

An example of this group is tris-(dimethylaminomethyl) phenol — K-54*. It promotes a very fast reaction because the

*K-54. Anchor Chemical Company Ltd., England. Supplied by D. K. Croxton (Pty.) Ltd., Johannesburg.

catalytic action of the tertiary amine is enhanced by the hydroxyl group.

Aliphatic amine adducts are modified polyamines. It is claimed that "Epikure-U"**, which belongs to this group, is less irritating than the pure primary-secondary aliphatic amines and, in addition, has a low sensitivity to moisture during the curing process.

Acid anhydrides require high temperatures for the cure of epoxy resins.

IV. THE EFFECT OF TEMPERATURE ON CURING

The curing of epoxy resins is an exothermic reaction because heat is liberated when the epoxide ring is opened. The temperature at which curing of the resin occurs at a satisfactory rate is determined by the reactivity of the curing agent. Reactive hardening agents are available which will cure some epoxy resins at room temperature. The process can be accelerated by increasing the temperature, but the quality of the cured product will be impaired if it is raised too high.

During the initial stage of the curing process the mixed resin is converted to a gel and then to a solid. In the final stage the solid product is hardened by additional polymerization.

V. REINFORCEMENTS, FILLERS AND THIXOTROPIC AGENTS

A variety of inert solid additives are capable of altering the properties of the epoxy resins.

Reinforcements and *fillers* of mineral, synthetic or metallic origin are added to produce cured resins possessing specific physical properties. For example there is a marked difference in their coefficient of thermal expansion with and without a filler. In the former, when fused quartz is

**Epikure-U. Supplied by Shell Chemical (S.A.) (Pty.) Ltd.

used, it is equivalent to that of tooth structure (Bowen 1956); in the latter it is much higher.

Thixotropic agents are materials which are added to the resin/curing agent mix to reduce its flow from an inclined surface; a small amount 2.0 – 10 per cent by weight, suffices. For the liquid epoxy resins use is made of colloidal silicas such as "Aerosil"* — a silicon dioxide of extremely fine particle size. Because of their large surface area, these particles tend to link together to form short fibres; and they in turn may make contact with other fibres to produce a web, which, it is believed, accounts for the thixotropic effect of silica compounds in the curing resin.

VI. SURFACE PREPARATION

To obtain maximum adhesion the surfaces to be bonded require special preparation. In industry they are degreased, etched by chemicals and dried. The surfaces of dental structures and other materials to be bonded intra-orally must be similarly treated.

Buonocore (1955) found that an 85 per cent phosphoric acid solution produced a strong and lasting bond between acrylic restorative materials and enamel. Gwinnett and Buonocore (1965) showed adhesion to be most satisfactory when a modified 50 per cent phosphoric acid solution was applied to the enamel surface prior to the application of the adhesive. Under these conditions the authors found that the adhesive material penetrated superficially into the enamel.

To improve the adhesion between an epoxy resin and an enamel surface, Newman (1965) prepared the latter with a 40 per cent phosphoric acid solution before placing the adhesive. In discussing the possible deleterious effects of phosphoric acid pretreatment for 60 seconds, he pointed out that this need not cause undue anxiety as most dental cements used at present contain 35 – 55 per cent phosphoric acid.

VII. TOXICITY

Kydd (1960) investigated the toxic effects of a polyamine curing agent by employing the routine patch test with diethylenetriamine. The results indicated

*Degussa, Germany. Supplied by Jacobson and Van den Berg (S.A.) (Pty.) Ltd., Johannesburg.

that they vary from one individual to another. In the same article he mentioned the finding of Lea and his co-workers: that uncured epoxy resins can cause skin irritation in humans.

Kapsimalis (1960) examined some cured epoxy resin formulation by means of a tissue culture technique, and found them to be non-toxic.

These experiments indicate that the materials tested do not have marked toxic properties. The results, however, are not conclusive; the toxicity of a particular epoxy formulation can be evaluated only after that of the component parts, the intermediates and the final products have been determined.

VIII. THE NATURE OF ADHESION

Adhesion is defined as the attraction existing between molecules at an interface (Eley 1961). The forces of attraction include Van der Waal's forces, hydrogen bonding and those resulting from the formation of electrovalent and covalent bonds.

According to Eley, the Van der Waal's forces of molecular attraction are due to three main factors: the interaction between permanent dipoles in the molecules known as the orientation effect — Keesom forces; the induction effect that takes into account the influence of the dipole moments which induce an additional dipole moment in a neighbouring molecule — Debye forces; the dispersion effect which results from the interaction between the random motions of the electrons of two molecules, ions or atoms in close contact leading to the formation of instantaneous dipole moments — London forces. The first two of these depend upon the existence of permanent dipole moments in the molecules and therefore play no part in a medium consisting of non-polar molecules.

The hydrogen bond may be regarded as a special type of dipole-dipole interaction, and the mechanism involved is thought to be electrostatic. The necessary condition is for an electronegative atom to be in the neighbourhood of a hydrogen atom which is itself bonded to an electronegative ion. It may be envisaged as two negatively charged ions linked together by a positively charged hydrogen ion (proton).

The forces of attraction when electrovalent or covalent bonds are formed are

considerably stronger than those referred to above. In the first-mentioned there is an electron transfer from the one atom to the other, leading to the formation of positively and negatively charged ions; the bonding is due to the electrostatic attraction between the oppositely charged ions. On the other hand atoms might gain inert gas structures — not by complete transference of electrons but by sharing them. The shared pair constitute the covalent bond.

As adhesion relies on the forces of molecular attraction it is evident that it can take place only at short distances of separation in the order of Angström units. Thus surfaces which are flat at an atomic level will adhere spontaneously to each other if brought into contact, without the need of an intermediate layer of adhesive (Buonocore 1963). In practice it is impossible to get such atomically smooth surfaces, hence a liquid adhesive must be used to wet the surfaces to be bonded (De Bruyne and Houwink 1951).

The degree of wetting depends on the contact angle at which the boundary of the liquid adhesive meets the solid surface; it must increase as the contact angle decreases. The contact angle is small if the attraction between the liquid and the solid is equal to or greater than the cohesive forces of the liquid. It is large if the forces of molecular attraction between the liquid and the solid surface are less than the strong mutual attraction between the molecules of the liquid. When this condition obtains no wetting takes place and droplets of adhesive form on the solid surface. The viscosity and the surface tension of the liquid and the nature of the solid surface influence the wetting. Even if the surface of the adherent is rough and porous, wetting is necessary to enable the liquid to enter its pores or depressions. This will expand the actual area over which the molecular forces of attraction can operate; and the interlocking of the set adhesive in the irregularities of the adherent will, by mechanical means, offer greater resistance to displacement.

For a number of reasons, the thinner the adhesive layer, the stronger is the joint. First there is less chance of flaws occurring; these may cause stress concentrations when the joint is subjected to a load, leading to

its failure. Next, a thin layer resists deformation under a load. Finally, there is a reduced risk of shrinkage of the adhesive during hardening or polymerization, or of its swelling due to absorption of fluids, or of a significant difference in the thermal expansion of the adhesive and the adherent. De Bruyne and Houwink (1951) suggest it is these factors that are a major cause of joint failure; they produce tangential vectors of force which are proportional to the thickness of the adhesive layer and counteract the molecular forces of attraction between adherent and adhesive at the interface.

INVESTIGATION

The aim of this investigation was to determine whether an epoxy resin* can be used for bonding orthodontic attachments to teeth. Those which can be satisfactorily cured only at high temperatures were excluded from the experiments.

A. *The Adhesion of the Resin*

1. *To the enamel surface:* Extracted teeth, either fresh or preserved in formalin, were cleaned with pumice on a lathe, washed and placed in a physiological saline solution until they were needed. As formalin fixation did not appear to affect adhesion, teeth so treated were used almost exclusively.

Preliminary work shows that the epoxy resin forms a far better bond with a conditioned enamel surface than with one that is untreated. The authors, after trying a number of conditioning agents, arrived at the same conclusion as Gwinnett and Buonocore (referred to earlier in this article) and therefore decided to use that recommended by them: a 50 per cent phosphoric acid solution. The acid was left for one minute and washed off with water prior to the application of the resin. The effect of this procedure on the enamel surfaces will be discussed in a later paper.

2. *To the orthodontic attachment.* Manufacturers stress that it is essential to prepare metal surfaces to obtain maximum bond strengths. All stainless steel attachments used in this investigation were etched with a 40 per cent sulphuric acid solution.

*Donated by Chrysler Corporation (Cycleweld Chemical Products Division, Michigan) and Shell Chemical (S.A.) (Pty.) Ltd.

When a bracket was placed directly in the resin on the tooth surface its flow invariably obliterated the grooves and flanges; and when the amount deposited on the enamel surface was reduced it led to an unsatisfactory bond. To overcome the problem the bracket was enlarged by welding it to a section of orthodontic band material, to which was welded an additional base of stainless steel gauze. Besides ensuring adequate union, this type of base has an additional advantage: the orthodontic attachment can be placed in the resin on the mixing slab and sufficient material will adhere to it to obviate the need of applying any to the tooth.

B. *The Time of Cure*

Experiments showed the curing time of liquid epoxy resins with room temperature curing agents to be far too long for them to be used clinically. The following methods of reducing the curing time were investigated:

1. *Heat treatment of the mixed resin.* First there was determined the time required for the several curing agent combinations to reach the initial setting stage at room temperature; and next the effect of heating the different combinations at temperatures ranging from 37° C. – 70° C. for varying periods. As expected, heating the resin after mixing shortened the time needed for it to reach the initial stage.

Since such heat treatment may affect the adhesive quality of the material, the adhesion of preheated mixed resins to conditioned enamel surfaces was tested. In this way a preheat schedule (temperature and time) was arrived at which would give optimal bonding under simulated clinical conditions.

2. *The use of catalysts.* Of the accepted catalysts only phenol, salicylic acid and tris-(dimethylaminomethyl) phenol were tested. The results proved phenol to be the most satisfactory in regard to both curing time and adhesion.

C. *Effect of Water on Adhesion*

Most of the epoxy resins are adversely affected by water while curing. In the course of bonding attachments to an enamel surface a resin may come into contact with water from one or more sources:

the enamel surface, the adjacent soft tissue and the saliva.

After conditioning the enamel surfaces, water was removed by drying the teeth in an oven for five minutes at 50° C. Excellent adhesion resulted, but as this procedure cannot be applied clinically, it was decided to use cotton wool; it produced a state of dryness comparable with that which can be obtained in the mouth.

The resin was covered with water during various stages of the curing process to study its effect on the adhesive property of the cured material. Immersion of a tooth with its attachments at room temperature (\pm 22° C.) and at 37° C. produced different effects. Raising the temperature to the latter degree usually reduced, and in some instances annulled, the adhesive property of the cured resin. For this reason all subsequent immersion tests were carried out at that temperature.

It was found that the more advanced the curing process when the resin was placed in water, the less it was affected. The most obvious changes occurred in the superficial layers, which became white and brittle. These changes were accompanied by a reduction in the adhesion of the cured resin. As it is anticipated that teeth to be bracketed can readily be isolated from the saliva for more than five minutes, those used in all subsequent tests were immersed in water at 37° C. that length of time after placement of the bracket.

Three months have elapsed since the epoxy resins used in this investigation were subjected to the immersion tests, and there are no apparent signs of their having deteriorated. However, it is not yet possible to determine the effect on their adhesive properties if they remain submerged at a constant temperature of 37° C. for a prolonged period.

D. *Placement of the Orthodontic Attachment*

The orthodontic attachment when placed in the desired position on the conditioned enamel surface shifted due to the flow of the resin. Such movement can be decreased by the use of thixotropic agents.

Glass slides placed in a vertical position were used to compare the rate of flow of untreated resin with that of resins containing respectively 2.5, 5.0 and 10 per cent of Aerosil. It was found that when the con-

centration of this thixotropic agent exceeded the first-mentioned figure there was a slowing down of the flow rate. Further, experiments disclosed that the adhesive quality of the resin with 10 per cent Aerosil was as good as that without it; in fact at times it was even better.

E. Results

In the initial phase of the work the adhesion between the various epoxy resin formulations and conditioned enamel surfaces was assessed. To gather comparable results in the subsequent experiments the enamel surfaces were smoothed with a stone and polished with pumice before conditioning. The specimen joints made on these surfaces and cured as previously described (preheated and immersed in water at 37° C.) were tested to failure by applying a tensile disruptive force.

The following formulation yielded the best results:

Part I	{	Epikote-828	1 ml. (1.12 gm.)
		Aerosil	0.10 gm.
Part II	{	Epikure-U	0.3 ml. (0.31 gm.)
		Phenol	0.07 gm.

Each part was mixed separately until it reached a homogeneous consistency. The two parts were then mixed together for two minutes and preheated for five minutes at 50° C. The working time was limited to approximately three minutes; after that the resin became too sticky to handle and the adhesion was markedly reduced.

A tensile strength of up to 1,000 p.s.i. was obtained on specimen joints prepared with this formulation. As mechanical removal of the resin and the attachment from the tooth surface was difficult, the

effect of certain organic solvents was examined. A few drops of chloroform applied to the resin proved a simple solution to the problem.

The epoxy resin formulation treated in the manner described has been subjected to a limited number of clinical trials. Although of short duration, the results are most encouraging.

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