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ENAMEL DEMINERALIZATION AND ORTHODONTIC THERAPY

A Thesis embodying original work, submitted in partial fulfillment of the requirements for the Degree of Master of Dental Science in the Faculty of Dentistry, University of Sydney, December 1968.

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ENAMEL DEMINERALIZATION AND ORTHODONTIC THERAPY.

Introduction.

After removing orthodontic bands the enamel surface of one or more teeth may exhibit areas of demineralization which were not apparent at the time of band cementation. This phenomenon has been reported in the literature and has been responsible for people, inside and outside the dental profession, viewing full-banding with apprehension.

Clinical observations permit a classification of these areas which is related to their etiology:

- A Areas of enamel demineralization between the gingival margin of the orthodontic band and the soft tissue. These areas have been attributed to plaque formation and subsequent dental caries.
- B Areas of enamel demineralization at the margins of the orthodontic band. These areas have been attributed to marginal cement solubility, a caries-susceptible site thus being formed.
- C Areas of enamel demineralization beneath the orthodontic band. These areas have been attributed to:
 - i Surface demineralization due to enamel etching by the phosphoric acid in cements.
 - ii Sub-surface demineralization due to the development of a caries-susceptible site following a breakdown in the function of cement, which is to fill the gap between band and enamel.

Both the orthodontic appliance and the dental cement

have been criticized for contributing to these lesions on the enamel surface. Many believe the arrival of the bonded bracket will be followed by a reduction in the number of these areas.

There exists sufficient evidence to suggest that attempts to cement the maximum number of orthodontic bands by using thin mixes of cement (so prolonging the working time) contribute to the formation of areas of demineralization.

The aim of this study is to ascertain from the literature what factors encourage the production of areas of demineralization during orthodontic therapy and how best to eliminate them. A description will then be given of an original investigation into the effects of varying the powder/liquid ratio of cement used in band cementation on:

1. Enamel etching potential.
2. Cement working time.
3. Cement setting time.
4. Cement Solubility.

REVIEW OF THE LITERATURE

A. Brief Historical Account.

Castello and co-workers (1948) treated ground and unground enamel surfaces with various mixes of cement and later examined these same surfaces with a microscope (16x and 32x) using reflected light. Microimpressions were also taken and examined under the microscope (50x and 45x). Some of their conclusions were:

- i. The enamel surface was etched markedly and homogeneously by cement liquid alone.
- ii. Various mixes of cement "more or less affected" all enamel surfaces.
- iii. The degree of etching did not seem to increase after the cement was completely set.
- iv. Ground surfaces were more affected than unground surfaces.

Gross (1951) referred to the decalcification of the enamel tooth structure as the "scars of orthodontic therapy". He thought the tooth structure was exposed to acid influence until the cement had finally set. In his own experiments he identified a decalcified area "upon the development of a white, chalky appearance of the area exposed to cement". He regarded the cement under the orthodontic band to be the responsible factor but "concluded that cement under an orthodontic band can be prepared so that etching is not inevitable".

Bodecker (1951) suggested that some variable factor must be involved in the formation of these areas, otherwise they would occur more regularly. As some teeth were more susceptible to etching than others he thought the variable factor might possibly be "enamel resistance". He concluded by saying: "Patients and general practitioners will realise that it is the character of the enamel which is

responsible for etching and not the orthodontic technique".

Docking (1952) used a surface finish meter for measuring surface roughness produced by decalcification. The up and down movements of the meter stylus as it rode across the tooth surface under a load of about .1gm were converted into a correspondingly varying electric current which was amplified and recorded graphically to give a highly magnified picture of surface contour along the line of traverse. He also used microimpression techniques to examine enamel surfaces which had been under orthodontic bands. Some of his conclusions were;

- i. At standard consistency no alteration in the surface of the tooth could be detected with any cement used.
- ii. Actual breakdown of the surface could be detected only with the thinnest mix ($P/L = .5\text{gm/cc}$)
- iii. A ground and polished enamel surface was more liable to attack than an intact surface.
- iv. The susceptibility to attack by cement might conceivably be due to variations in the subject rather than in the technique.

In an essay representing his clinical observations on cementation Adams (1955) said "the apparent lack of interest in a subject which should be of paramount concern to us in our field" probably resulted from an unjustified contempt for a fool-proof procedure. He made inquiries of various orthodontists and arrived at two conclusions from the results of his poll;

- i. Orthodontists were not so much worried over the areas covered by the bands, but were definitely concerned over the areas between the bands and the gum margins. (Some commented that they were looking forward to the arrival of the bonded bracket).

- ii. Any protection which varnish offered the enamel surface was offset by the bands coming loose more frequently, for filling up surface irregularities removed the only source of retentive power the cement possessed.

Among the advantages of epoxy adhesives over dental cements, Newman (1965) included "decreased decalcification". He believed the disintegration of dental cement under bands allowed the ingress of bacterial and oral debris, which resulted in eventual decalcification.

Graber (1967) said one of the advantages of dentofacial orthopedics was the elimination of decalcified areas associated with more usual appliances.

Sakamaki and Bahn (1968) thought the elimination of banding and attaching the bracket directly to the enamel surface would be desirable. "As far as the decalcified areas are concerned", they concluded, "many of these areas apparently have become inactive with the removal of bands. Other areas may be the result of other factors such as the action of the acid used in the cement".

B. Possible Contributing Factors.

1. Lowered Enamel Resistance.

Whether an area of demineralization is the result of dental caries or acid attack, or a combination of both, the variable factor suggested by Bodecker, enamel resistance, must be considered. As the varying degree of immunity to dental decay is a daily observation, he asked if there might be a correlation between incidence of dental caries and incidence of chalky spots following band removal.

Brudevold (1948) used a quantitative method for the estimation of the phosphate solubility in acid of intact enamel surfaces. Variations in phosphate solubility were found from area to area on the same tooth and between various areas on different teeth. Unerupted permanent teeth were found to be more soluble than erupted permanent teeth and ground surfaces were more soluble than untreated enamel surfaces. The first test on an intact enamel surface averaged lower in solubility than the second test but the reverse was true for solubility tests on ground surfaces.

Sullivan (1954) subjected surfaces of enamel to applications of acid and found the external layers of enamel were less soluble than the corresponding subsurfaces. He concluded that the relative insolubility indicated the existence of a hypercalcified zone of enamel at the external surface.

Ericsson (1953) experimented with extracted teeth by exposing them to radioactive "tracers" (Ca^{45} and P^{32}) for periods of 16 to 28 hours. In every single test, carious enamel had taken up much more of the isotope than intact enamel. He found no indication of any difference in uptake

between surfaces judged as "arrested" or "acute".

Johansen (1963) studied carious lesions with the electron microscope. He found the morphology, size and electron density of crystallites within individual enamel rods suggested regional differences in these characteristics. The crystallites located at the periphery of rods appeared larger, more electron dense and generally better preserved than those within the enamel rods. He speculated that such crystallites may have been selectively spared from dissolution.

Using the electron microscope Osborn (1968) found a sudden change in direction of prisms at the surface of the enamel in the transverse plane of the tooth. He thought that an equivalent change in crystalline orientation might account for some of the differences, shown by polarization microscopy, between this sometimes prismless area and the subsurface enamel.

An intact enamel surface would appear to contribute to the tooth's defence against any form of acid attack.

There may be influences beyond the control of the orthodontist. Jackson, Sutcliffe and Burch (1967) studied the prevalence and anatomical site-distribution of clinical dental caries in the mandibular incisor region. In their population sample the prevalence of attack followed a symmetrical pattern. In individuals the number of asymmetrical attacks was equal to, or greater than, the number of symmetrical attacks. In the population the prevalence of attack was the same on each member of a pair of adjacent surfaces, but in individuals this was not so. They said that the pattern of dental caries could be genetically-determined, just as predisposition to disturbed-tolerance autoimmunity is genetically-based.

2. Dental Caries.

Apart from the difficulty of cleaning behind archwires, lockpins, coil springs or vertical loops, orthodontic patients are under definite instructions not to damage appliances and a lowered standard of oral hygiene inevitably results.

Bach (1953) studied the incidence of dental caries during orthodontic treatment and found a decided increase in the number of fillings required by patients who had had orthodontic treatment.

Hill and Blayney (1965) found lactobacillus colony counts to be a reliable index of dental caries attack rates in large populations. The percentage of high and low lactobacillus counts might reflect the intensity of caries attack, but their data would not permit the appraisal of the role of lactobacilli as the etiologic agent of dental caries.

Sakamaki and Bahn (1968) found the lactobacillus index increased fivefold after band placement and returned to original levels when the bands were removed. They concluded that orthodontic banding directly influenced the number of oral lactobacilli. The occurrence of most of the lactobacillus growth sites on the edges of the bands, particularly the gingival band margin, suggested that these regions had increased susceptibility to caries.

3. Cement Breakdown.

a. Cement Dissolution.

Skinner and Phillips (1967) considered solubility and disintegration of cement to be the one property of greatest clinical significance. They regarded cement solubility as the main factor contributing to recurrent caries around the margins of an inlay or crown.

A well-fitting orthodontic band could present a similar situation.

Jorgensen (1963) tested the solubility of selected cements in lactic acid and concluded that a cement with a relatively high solubility in distilled water may have a relatively low solubility in acid or saliva at the physiologically most relevant pH levels 4.5 - 6.5. He therefore doubted whether solubility rates of cements, as measured in distilled water, were of value as an indication of their resistance to dissolution in the oral cavity.

b. Cement Fracture.

Skinner and Phillips (1967) said that any dental cement exposed to the forces of mastication will fracture and finally disintegrate if lacking in compressive strength. Any subsequent band loosening would leave the enamel prone to decay due to the protection offered, debris and bacteria between band and enamel.

Cameron et al (1963) questioned the possibility of dental cements ever failing under pure compression and thought a series of complex stresses would be responsible. They objected to compression tests by loading over relatively long periods as the rates of force application occurring in the mouth more closely resembled impact forces. They noticed that a slower setting cement also exhibited low strength.

c. Loss of Retention.

Skinner and Phillips (1967) described adhesion as being a bonding between unlike molecules. They said there was no adhesion between dental cement and the enamel surface or any other restorative materials with which it is employed. Instead of adhesion there was a mechanical locking at both cement-enamel and cement-metallic surfaces. Any loosening of bands permits the accumulation of debris and bacteria between band

and enamel.

Adams (1955) reported that some orthodontists using varnish to protect enamel had noticed an increase in the number of loosened bands.

Berkson (1950) tested "the tensile strength of a comparatively flat surface bond between enamel and gold." "He luted cast gold plates to the buccal enamel of molar teeth. Although the cementing surfaces of the plates were roughened with a stone prior to cementation, after each test the cement was found to be adhering to the tooth enamel and not the metal plate. He concluded that cement had a certain amount of specific "adhesion" to enamel and a much lesser amount to gold and that he had actually been testing the retentive force between the cement and the plate rather than between the cement and the tooth.

During these tests black copper cement did not exhibit superior properties to zinc phosphate cement.

Docking (1952) and Williams (1965) noticed how tenaciously particles of cement adhered to enamel surfaces during their respective experiments.

Berkson thought it was likely that some cements microscopically etched the surface enamel and created greater "adhesion" in this manner. This would occur in areas where there was optimal chemical composition and where optimal pressure was being applied.

Matsui and Minoguchi (1963) increased the "adhesion" of phosphate cement, silicate cement and self curing resin to both enamel surfaces and metal surfaces. The enamel was treated with glycerophosphoric acid dimethacrylate and the metal band dipped in a warm liquor containing concentrated sulphuric acid.

Cameron and co-workers (1963) thought the particular importance of cement was "to fill the void between the tooth and the orthodontic band, thus preventing the formation of bacterial plaques and resultant decalcification under the band".

d. Dimensional Changes.

Expansion and contraction in the band - cement - enamel system can lead to the formation of a caries - prone area either by the loosening of a band or by setting up an area of no contact between cement and enamel surface.

Skinner and Phillips (1967) said that mechanical retention was also dependent upon the dimensional changes occurring in the cement during setting as a result of the water gain or loss.

Nelsen and co-workers (1952) thought that marginal percolation might explain the recurrence of caries at the margins of some restorations. They noted that the range of temperature encountered in the mouth was from 4 degrees centigrade to 60 degrees centigrade. With dental materials expanding or contracting with thermal change at a different rate from that of the tooth structure a space could develop between the tooth and material. When the tooth was wet fluids could occupy this space. Nelsen said the fluid itself then expanded and contracted with variation in temperature.

Although the limit of visual acuity is 50 microns Nelson considered defects of 10 microns to be large cavities when compared to the diameter of the lactobacillus, 2 microns. He believed these defects ultimately became choked with debris.

4. Exposure of Enamel to Acids.

a. Cement Liquid.

Castello (1948) and Docking (1952) observed the damage to enamel surfaces from the action of cement liquid alone.

Apart from the obvious presence of excess liquid in wet mixes of cement, enamel could be exposed to attack from acid in incorrectly mixed cement or mixes where the powder particle size was too large.

Jorgensen (1960) studied the structure of the film of zinc phosphate cements. While carefully mixed cements gave the impression of forming a suspension of evenly distributed powder particles in the liquid this was not so with thin films of cement. He prepared a mix of cement and expressed it to a thin film between two plane glass plates. Films of approximately 20 microns were examined under the microscope (100x) and in nearly all cases, peripherally to the powder lumps, an area was found which was deficient or lacking in powder. He considered this area to consist chiefly or wholly of phosphoric acid. Jorgensen regarded the powder lump as a filter between the two glass plates. When the plates were compressed the lump separated the two phases of the cement mix the moment the width of the space between became smaller than the lump. He thought this filtration process could be responsible for the cement film being displaced over rather large areas of tooth surface by a liquid film.

The degree of filtration could be reduced by using low cementation pressures, by avoiding cement mixes of low viscosity and by minimising the time of pressure application during cementation.

Brudevold (1948) demonstrated the higher solubility in acid of enamel surfaces which had already been attacked by acid.

F. Relation of pH to Enamel Demineralization.

Hals and co-workers (1956) studied the effects of lactate buffers on dental enamel in vitro. They said that Miller's theory of acid dissolution of the inorganic content of enamel might explain the progress of dental caries but nothing was known of the initial lesion. They concentrated on first changes in normal enamel, noting that earlier experiments had been handicapped by the fact that the acid used had been quickly neutralized by salts from the reaction with the tooth substance.

Experiments were conducted on newly extracted premolars, from patients 10 - 14 years of age, utilizing lactate buffers of 3.51 - 5.70 pH. Thin sections of these teeth were then examined microscopically using polarized light. Hals described inner and outer spots of decalcification on the tooth enamel surface. Inner spots appeared microscopically to be slightly opaque spots with a shiny, apparently intact enamel surface. Outer spots appeared as dull whitish spots, with or without a loss of tooth substance.

Between pH 3.51 and pH 4.00 only outer spots appeared.

Between pH 4.12 and pH 5.25 inner and outer spots appeared.

Between pH 5.43 and pH 5.70 only outer spots appeared.

Hals and co-workers found there was a time limit, varying with the pH value, for the production of an inner spot, and where exceeded, the original inner spot became an outer spot. Also, the higher the pH the longer the time of exposure required before the inner spot changed to an outer spot.

These workers believed the inner spot represented a certain phase of the decalcification process and occurred only within a certain pH range and within a relatively brief

b. Fruit Juices.

Stafne and Lovestedt (1947) noticed that the total quantity of acids introduced into the oral cavity was increasing with increased consumption of citrus fruits, acid beverages and acid confections. Whether mineral was removed by chelation or surface etching, they said all these acid substances accelerated mechanical wear, particularly wear by brushing.

Mannerberg (1960) investigated the effect of fruits rich in citrate and subsequent tooth brushing on the appearance of the tooth surface. He found that orange juice had hardly any appreciable effect on the appearance of the tooth surface but in certain cases lemon juice produced a complete change. He examined the tooth surfaces by ~~reviewing~~ metal shadowed replicas under the microscope.

Sognnaes (1963) said "there can be no question that the hard tissues of the mouth are susceptible to destructive actions of mechanical or chemical nature or both. Calcium phosphate is obviously soluble in calcium - binding chemical agents, whether these be of exogenous or endogenous origin, as long as the agents are present sufficiently long, in adequate quantities, and in susceptible locations".

These effected surfaces would again be more vulnerable to attack by cement liquid.

C. Composition of Cements.

1. Cement Liquid.

Paffenbarger and co-workers (1933) reported on zinc phosphate cements and found the cement liquids consisted of phosphoric acid solutions buffered with various quantities of zinc oxide and aluminium hydroxide. They analysed the liquids of 16 phosphate cements and found the free phosphoric acid content ranged from 38 per cent to 59 per cent while the average water content was 33 ± 5 per cent.

Paffenbarger and co-workers found that exposing the cement liquid to the atmosphere of the laboratory resulted in a loss in the water content.

Skinner and Phillips (1967) said the amount of water present was a factor in the control of the ionization of the liquid and was also an important ingredient concerned in the rate and type of the liquid - powder reaction. The added buffers reduced the reaction rate of the liquid with the powder.

In 1938 Paffenbarger and co-workers investigated the physical and chemical properties of dental silicate cements. The silicate cement liquids were found to be very similar to the zinc phosphate cement liquids although the water content was generally higher and the free phosphoric acid content ranged from 38 per cent to 48 per cent. The silicate cement liquids were "very acid".

Skinner and Phillips (1967) said that the cement liquids of copper cements were basically zinc phosphate cement liquids, the difference between the two cements being in the cement powders.

Simmons and co-workers (1968) tested a relatively new

zinc phosphate cement in which distilled water rather than phosphoric acid was used as the liquid component. Compared to a commercially available zinc phosphate cement the hydrophosphate cement proved inferior in almost all properties investigated.

2. Cement Powder.

Paffenbarger and co-workers found zinc phosphate cement powders contained from 75 per cent zinc oxide to 100 per cent zinc oxide, the principal modifier being magnesium oxide.

The silicate cement powders contained mainly silica and alumina with smaller amounts of calcium, fluorine and sodium.

Skinner and Phillips (1967) attributed the unique anticariogenic property of silicate cements to the fluorine content (12 to 15 per cent). They thought this property was the result of a reduction in enamel solubility, similar to the effect of topically applied fluoride solutions.

The same authors said that the chemistry of copper cements was very similar to that of the zinc phosphate cements, black copper cement being formed by replacing some of the zinc oxide of the powder with cupric oxide. The addition of cupric salts was supposed to increase the antiseptic properties of the cement.

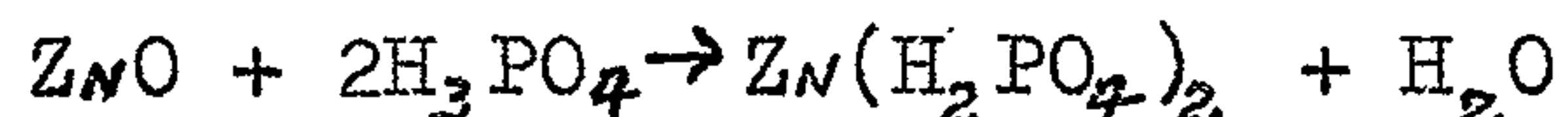
For his experiments Gross (1951) chose a cement at random because he believed all cements were alike in their basic constituents since they had to comply with dental specifications.

The compositions of cement powders and liquids as presented by Paffenbarger and co-workers might not represent the composition of present day cements but Skinner and Phillips

believe "they are sufficiently typical for all practical purposes".

3. Chemistry of Setting.

Skinner and Phillips saw the reaction of zinc phosphate cement powder and cement liquid as a solution of the surface of powder particles in the phosphoric acid to saturation, followed by the formation of primary zinc phosphate;



Thus at the time of placing the cement in the mouth the mixture would consist of undissolved powder particles and a solution of phosphoric acid and primary zinc phosphate.

The setting process was a further chemical reaction in which the stable water - insoluble tertiary zinc phosphate precipitated in crystalline form from a superaturated solution.

Skinner and Phillips said the final structure of the cement was a core of undissolved zinc oxide powder in a matrix of tertiary zinc phosphate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$).

Higashi and co-workers (Part I - 1966) believed this inorganic chemical reaction interfered with any mixing procedure calculated to obtain a uniform product, as the reaction took place instantaneously. Also the possibility of existing free phosphoric acid and free zinc oxide remained. These authors observed physical changes during the setting process of zinc phosphate cement and found that as long as the environmental temperature remained at a constant level the setting time was slower in proportion to an increase of phosphoric acid liquid. As a result of tests of setting time on setting zinc phosphate cement at various temperatures the authors thought "the accepted notion concerning the setting mechanism of zinc phosphate cement will have to be re-examined".

Higashi and co-workers (Part 2 - 1966) believed it could be assumed that the setting of zinc phosphate cement was not due to the generation of phosphate salt crystals through a chemical reaction of zinc oxide and phosphoric acid but due to the gelation of colloids.

Grant and co-workers (1968) studied the structure of zinc phosphate and silicate cements which had been allowed to set. Using the electron microscope they concluded that morphologically zinc phosphate cement (and silicate cement) conformed with the accepted classical picture of these materials.

The phosphoric acid attacks the powder particles forming silicic acid (Si(OH)_4) during the mixing of silicate cements and Skinner and Phillips said the set cement consists of a core of unattacked powder particles surrounded by a silicic acid gel matrix. The sheath formed around the powder particles at the beginning of the reaction appeared to prevent further diffusion of acid more effectively than the zinc phosphate sheath and free phosphoric acid is therefore present for a much longer time after the initial set of silicate cements. Skinner and Phillips said the final structure of set silicate cement consisted of 20 - 30 per cent gel matrix the remainder of the mass being undissolved powder particles.

Hybrid combinations of zinc phosphate cement powders with silicate cement powders were referred to as silico - phosphate or zinc - silicate cements by Skinner and Phillips. They are manipulated in a manner similar to the silicate cements, have a higher pH than silicate cement and are stronger and less soluble than zinc phosphate cements, and usually contain a fluoride.

D. Availability of Free Acid.

Svare and Meyer (1965) carried out in vitro experiments to discover whether a silicate cement had enough available acid to cause a pulpal response when placed in dentine. They found:

- (1) 5.72 per cent of acid incorporated in the silicate cement was available for diffusion and
- (2) .6 per cent of this available acid was surface acid, the remainder being leachable acid.

Axelsson (1964) studied the dissolution of six silicate cements used in Sweden. After immersing them in distilled water for one week he concluded all components of the cement were leachable.

Wilson and Batchelor (1967) tested silicate cements in demineralized water containing carbon dioxide in equilibrium with the atmosphere and having a pH of 5.7. They found a quantity of material had been eluted within 24 hours but that the chemical composition of the eluate bore little relationship to that of the parent cement. Altering the pH of the solution from 5.5 to 7.5 had little effect on cement erosion. The leaching pattern of phosphate from the cements suggested a simple washing out of the soluble salts from the cement gel and Wilson and Batchelor thought the amount of phosphate leached probably depended on the degree of attack by the liquid on the powder, and the amount would be greatest where the relative amount of liquid used in the cement preparation was high.

The results of their experiments indicated that in solutions such as they used, the erosion of cement in the first two or three weeks after preparation was alone of significance.

de Freitas (1968) said that no answer had as yet been found to the problem of cement dissolution in oral fluids. He mixed specimens of silicate cements according to the manufacturer's specifications, submerged them in distilled water and analysed the distilled water from time to time. All extracts were clear and free from particles and the first extract (one week) did not show the low pH value that may have been expected due to the extraction of free phosphoric acid. He saw this higher pH (6.08) as the effect of other soluble ions dissolving in the same period and providing a buffering action. The dissolution of the silicate cements was brought about by preferential solubility of the matrix and final disintegration was effected by attritional dispersion of the less soluble core particles.

From his experiments de Freitas concluded:

- (1) The rate of solution as shown by individual extractions was not uniform.
- (2) Solution of any fluoride content into the oral fluids would continue throughout the life of the cement, thus reducing enamel solubility.
- (3) The abrupt termination of soluble phosphate indicated that only incompletely reacted phosphate was dissolved and that phosphate in full chemical combination with cement powder was highly insoluble material.
- (4) Lower solubility figures were obtained by following the manufacturer's directions for proportioning powder and liquid.
- (5) Test specifications should involve testing in dilute acids instead of distilled water.

Skinner and Phillips said the mixing of zinc phosphate cements should be initiated by the addition of a small amount of powder, such a procedure neutralizing the acid, thus complementing the buffering action of the salt in the cement liquid. Solubility of zinc phosphate cements could be reduced by using the maximal amount of powder for the purpose at hand.

E. pH. of setting Cement.

Using antimony electrodes (.5mm diameter) Norman and co-workers (1966) determined both the surface pH and the pH of the internal mass of dental cements during hardening. A variety of cements was used, they were stored under varied conditions and pH readings were taken at intervals ranging from 3 minutes to 48 hours.

Silicate and zinc phosphate cements both gave higher pH recordings in 100 per cent humidity and the internal pH was always greater than that at the surface. Compared with the zinc phosphate cement, silicate cement maintained a lower pH during an extended period. The pH of the silico - phosphate cement used was always slightly lower than the pH of the phosphate cement.

Skinner and Phillips (1967) have summarized the pH recordings in table 1.

*Table 29-6. The pH of Dental Cements at Various Time Intervals after Mixing**

CEMENT	pH					
	3 MIN.	1 HR.	24 HRS.	48 HRS.	7 DAYS	28 DAYS
Zinc phosphate	3.5	5.9	6.6	6.8	6.9	6.9
Silico-phosphate	3.2	5.4	6.1	6.3	6.5	6.7
Type II copper	2.5	5.0	5.8	6.3	6.5	6.5
Silver cement	2.7	5.7	6.7	6.8	—	—
Silicate	2.8	3.7	5.0	5.2	5.2	5.2
Type I copper	0.8	3.0	4.7	5.1	5.2	5.3

* A standard consistency mix was used and the pH was determined by means of micro-antimony electrodes.

In a later study Norman and co-workers (1966) carried out similar pH tests of setting cement using thin, thick and standard cement mixes. They found from data accumulated over one month that the pH of all cements tested became relatively stable in 48 hours, and the choice of storage medium had only a slight effect on the pH change of the cements.

The pH of thin cement mixes was initially lower than the pH of standard and thick mixes and remained so for a longer period. The pH of standard cement mixes did not increase with as great rapidity as did that of the thick mixes, but by the end of the test period pH values for standard and thick mixes were comparable. Thin mixes of cement never reached the pH of standard or thick mixes, their pH remaining .5 to 1.0 pH below, even after one month.

Norman and co-workers found thick and standard mixes of zinc phosphate and silico - phosphate had a pH of 7 while an equivalent mix of silicate cement had a pH of 5.5.

They concluded that powder/liquid ratio exerted the most pronounced influence on pH during setting. In contrast, contact with tooth structure or temperature alteration had only a minimal influence on the pH of setting cements.

Gross (1951) gave the pH of cement liquid as pH2 while Docking (1952) estimated the pH of cement liquid to be 1.

period of exposure.

The relationship between pH value and enamel dissolution was earlier observed by Stephen (1940). He said that calcium phosphate in saliva would not permit enamel dissolution above 5.0 - 5.5 pH.

Stephen (1938) had noted the ability of dental plaque to reach a pH as low as 4.6 and stated that enamel would actively dissolve at this pH under mouth conditions.

Gray (1962) repeatedly exposed enamel for short intervals to acid solutions. He found the initial solubility rate of human dental enamel increased as the pH decreased.

G. Contribution of Enamel Structure to Demineralization

Both the surface demineralization produced by acid attack and the sub-surface decalcification seen in an incipient carious lesion have been related to the structure of the enamel.

Sognnaes(1963) carried out enamel demineralization experiments (in vivo) using rhesus monkeys. He thought it would be of interest to determine to what extent the structure of enamel contributed to its own dissolution in chemicals. He noted that the typical pattern of incipient enamel caries was one of a relatively intact enamel surface overlying a considerably demineralized subsurface zone. This could be due to the high fluoride content and lower carbonate content of the outer enamel surface but Sognnaes thought that the pattern might be brought about by organic, natural surface coatings that influence the physical chemistry of the enamel.

Sognnaes said the destruction of enamel was not entirely a one way process, for there was evidence of redeposition of calcified matter at certain stages. Redeposition of some mineral phase with different solubility properties from enamel could partly influence the pattern of dental caries or acid demineralization of enamel.

Sognnaes concluded that the pathway of the carious process was intimately related to certain preformed structural patterns within the enamel. These were:

the incremental lines of Retzius

the interprismatic substance

the cross striations of the individual enamel prisms

As the subsurface demineralization can reach a depth

of 1000 microns prior to surface enamel breakdown Sognnaes felt the alterations in enamel could not be predicted from inspection and replicas of enamel surfaces.

Darling (1963) described structural changes in enamel in early dental caries. He said that proteolytic breakdown of the insoluble keratinous organic matrix began at about the time of the breakdown of the enamel surface. But at that stage there was already evidence of demineralization of the enamel, so observations of lesions showing intact enamel surfaces would not involve proteolytic changes. He estimated the zone of relatively unaffected enamel to be about 30 microns in width at the surface.

Darling thought the pattern of demineralization would be influenced by several factors - variations in chemistry of enamel components, variations in orientation of crystallites or variations in the accessibility of the demineralizing agent.

Frank and co-workers (1966) compared caries - resistant and caries - susceptible enamel by means of electron probe studies. They found that the superficial enamel layer contained the same amount of calcium and phosphorus and that there was no significant difference in the distribution of these two elements in the two groups.

They also studied enamel caries before cavity formation and confirmed the loss of calcium and phosphorus in the subsurface, principally along the striae of Retzius. The superficial enamel layer had a normal chloride, calcium and phosphorus content.

Lenz (1967) used the electron microscope to show that while an incipient carious lesion resulted in a demineralization

of the enamel, the texture of the enamel was loosened by spaces appearing between the individual crystals. Demineralization in vitro with relatively concentrated acids resulted in an etching of the crystals. In the initial phase of caries there was a reduction of the size of the crystals without any trace of etching. Lenz thought the course of the demineralization seemed to be conditioned by the effect of the organic substances which entered the enamel during the process of demineralization and enveloped the individual crystals and so retarded the diffusion of the substances that dissolve the enamel.

Frank (1967) studied the ultrastructure of tooth enamel using the electron microscope. He found that in the adult enamel the prism and the interprismatic substance were composed of the same ultrastructural elements, one difference being the orientation of the axes of the apatite crystals. He noticed the aprismatic layer at the enamel surface was composed of apatite crystals side by side with their axes perpendicular to the enamel surface. There was a progressive decrease in mineralization from enamel surface to dentino - enamel junction.

Frank also studied carious enamel and noticed that demineralization was shown by a diffuse destruction of apatite crystals, accompanied by a widening of the intercrystalline spaces. The destruction of an apatite crystal was brought about sometimes by progressive dissolution, sometimes by fragmentation of an apatite crystal. In the enlarged intercrystalline spaces there was a marked increase of organic material, amorphous in appearance and probably originating from bacteria or saliva.

Demineralization of enamel by acid "in vitro" could be

distinguished from caries "in vivo" by the absence of precipitated organic material in the intercrystalline spaces.

Frank believed the first stage of caries in the enamel involved the appearance of a white or brown spot, which always developed in contact with a bacterial plaque. In this initial lesion an apparently intact superficial layer of enamel was overlying a demineralized sub-surface zone.

Johnson (1967) examined ultra - thin sections of selected areas of carious enamel with the electron microscope. In the course of tissue breakdown he found the prisms themselves and the interprismatic substance were affected equally. As there was now general agreement that the fundamental structure of the tissue between the prisms was identical with that inside, Johnson thought the term interprismatic enamel more suitable. The only visible difference between the two was found to be in the orientation of the crystallites.

During the carious process Johnson found the demineralization of the bulk of the tissue to be diffuse, intra - and interprismatic enamel both being affected. Enamel structure did not appear to be so important, and the cores of the hydroxyapatite crystallites themselves appeared to dissolve more rapidly than the peripheral parts, resulting in the production of a large number of hollow remnants. There was evidence that some recrystallization took place as part of the carious process.

Poole and Johnson (1967) noticed that enamel surfaces prepared in a plane perpendicular to prism direction were more seriously damaged than those surfaces prepared in a plane parallel with prism direction when exposed to demineralizing

solutions. All of the acids used preferentially dissolved the axial portions of prism heads leaving a honeycomb appearance on surfaces transverse to prisms.

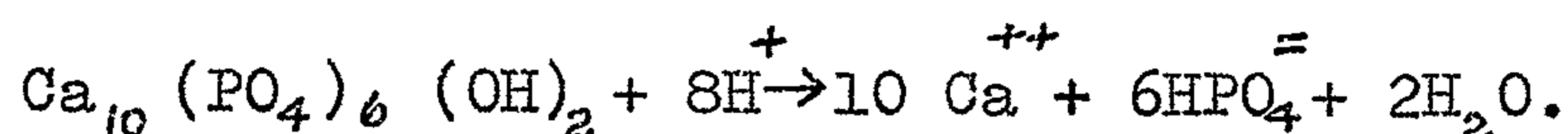
Poole and Johnson concluded that the orientation of crystallites relative to the direction of attack, together with compositional variations within the enamel structure, contribute to the pattern of etching.

Osborne (1968) said there were many sources of error in estimating prism directions using techniques that were solely dependent on the interpretation of two - dimensional images. Without accurate knowledge of the three - dimensional layout of prisms it would not be possible to know the degree of inaccuracy (or accuracy) of previous descriptions of enamel structure.

H. Chemistry and Dynamics of Acid - Enamel Reaction

1. Chemistry.

Gray (1962) described the dissolution of enamel in acid as the result of reaction between the hydrogen ion and the inorganic hydroxyapatite which forms the principal part of the enamel. For convenience he treated the enamel as hydroxyapatite and wrote the equation for the reaction as:



The dissociation of the phosphate ion so formed would be determined by the pH of the system. Gray said this chemical reaction was irreversible and in his own acid etching experiments he completely accounted for the decrease in solubility rate of enamel with time by the accumulation of reaction products and the rise in pH. With the accumulation of the products of reaction chemical equilibrium approached. He found the calcium and phosphate of the enamel were dissolved in the same ratio as they were found in enamel and that the dissolution rate could be retarded by the addition of almost any cation. The effectiveness of the cation varied directly with the insolubility of the phosphate salt of the cation agent.

Gray believed that the reaction rate depended on how fast the hydrogen ions reached the enamel surface, the rate being increased slightly by temperature rise and markedly by agitation.

The addition of fluoride ions to the buffer retarded the rate of enamel dissolution in Gray's experiments but the initial solubility rate of enamel with a significant fluoride content was identical with that of normal enamel. He concluded that the difference in solubility between the

two types of enamel was insufficient to remove the reaction out of diffusion control. However, the equilibrium solubility of the enamel with the fluoride was less than that of enamel without fluoride.

2. Dynamics.

Hals (1956) stated that enamel decalcification by lactate buffers was caused by the hydrogen ions only. As the hydrogen ions reacted with the apatite there was a drop in hydrogen ion concentration, in addition to the normal drop which is determined by diffusion formulae.

As the prism sheaths were more permeable than the prisms proper, the penetration would first occur in the prism sheaths. Thus the penetration into the prisms would occur both from the prism sheaths and from the surface of the enamel. Hals thought the penetration was via the organic material while the crystallites presented obstacles to the penetrating ions. As the crystallites were dissolved he assumed the enamel as a whole became increasingly permeable. The action of the hydrogen ions was diminished as the buffer inside the enamel became more or less saturated with calcium salts. These calcium salts would diffuse inwards as well as out of the enamel and so the action of the acid depended not solely on the penetration of the hydrogen ions but on the diffusion of calcium salts out of the enamel.

Gray (1962) found during his enamel etching experiments that any speed of solution agitation, when exceeded, resulted in an increased rate of enamel dissolution. He accepted this as clear evidence that the acid - enamel reaction was diffusion controlled.

Gray and Francis (1963) produced incipient carious lesions of enamel, typical of those formed in vivo, by purely chemical reagents. Two factors were found to be necessary, an acid to dissolve the hydroxyapatite and an organic polymer to protect the external surface of the enamel. When the reaction products (calcium and phosphate) were included in the system, the effects ranged from complete inhibition of the reaction to subtle alterations in subsurface decalcification. Gray and Francis saw the surface reaction in vivo as being uniformly retarded by enamel cuticle, bacterial plaque and saliva. They obtained similar effects in vitro by using proteins, polysaccharides and mucopolysaccharides.

They thought it logical that when enamel was exposed to acid, the acid would diffuse both to the enamel surface, and into the enamel. If acid was consumed rapidly at the enamel surface, little or no acid would remain to diffuse into the enamel. But if the surface reaction was retarded acid would diffuse into the enamel, producing a subsurface reaction. Thus there would be a competition between surface reaction and diffusion into the enamel, incipient carious lesions being formed when the surface reaction was reduced.

Holly and Gray (1968) constructed a diffusion model to describe the dependence of depth of decalcification on:

- i Hydrogen ions and acidic buffer concentration
- ii The inhibiting effect of the reaction products
- iii The effects due to complexing of calcium reaction products by the acid anion.

Their model simulated enamel under plaque, hence there was no agitation; for agitation leads to surface breakdown. Acidic reactant was transported through a double membrane.

One membrane of constant thickness represented the relatively sound outer layer of enamel, and the subsurface decalcified region was represented by another membrane, the thickness of which increased in time.

They developed mathematical equations, based on their model, which described the time-dependence of the acid consumption and the depth of decalcification during the formation of an incipient carious lesion.

I. Bonded Attachments and the Enamel Surface.

1. Conditioning of Enamel.

Lefkowitz (1940) said there could be no doubt that islands of decalcification or white spots would be attacked more readily than normal enamel "because they form a zone of lowered resistance to the inroads of caries".

Brudevold and co-workers (1957) studied the reaction of tooth surfaces to sodium fluoride solutions. The uptake of fluoride varied in different teeth and different areas on the same tooth, but pumiced, ground or acid - etched surfaces showed greater uptake than intact surfaces. Slightly demineralized areas, such as brown or white spots, also showed greater uptake than sound enamel.

Nevertheless, if orthodontists hope to attach brackets directly to enamel surfaces, and so dispense with the orthodontic band, an acid-etched enamel surface would appear, up until the present moment, to be a necessary part of any bonding technique.

Throughout the literature the problem of obtaining adhesion centres upon the permanence of the bond between any two surfaces.

Rose and co-workers (1955) examined the adhesive properties of many materials used in dentistry and quickly found that dry testing had no relation to clinical conditions. None of the products they tested consistently maintained adhesion after prolonged water immersion.

Buoncore (1955) experimented to obtain increased adhesion between acrylic material and intact enamel surfaces. He felt that perhaps an acid treatment of the enamel surface might render it more receptive to adhesion in the same manner

as it does for metals in industry. In one experiment 85 per cent phosphoric acid was used intraorally and washed off the enamel surface after 30 seconds. The duration of adhesion of the acrylic filling material was increased from 11 hours to 1,070 hours.

When the acrylic was removed mechanically, "the underlying enamel appeared as a sharply defined area of clean enamel which appeared white and opaque by contrast with the surrounding enamel". Buoncore said that in a few days the treated area of enamel appeared normal again, except for a faint loss of lustre. Such treatments were regarded as clinically safe because of the absence of any lasting noticeable effects on the enamel.

The increased adhesion was explained as being due to:

- i. A tremendous increase in surface area due to the acid etching action.
- ii. The exposing of the organic framework of enamel which serves as a network in and about which the acrylic can adhere.
- iii. The removal of old fully reacted, and inert enamel surfaces, exposing a fresh, reactive surface more favourable for adhesion.

Buoncore thought the acid - etching of enamel was clinically safe when one realized that similar concentrations of phosphoric acid were used in phosphate cements.

Buoncore and co-workers (1956) found the increased adhesion of resins to acid - etched enamel surfaces was destroyed within 24 hours of immersion in water.

Sadler (1958) tested several commercial adhesives to

determine the possibility of placing metal attachments directly onto the tooth, thus eliminating the bands completely. Edgewise brackets were attached to extracted human teeth with each of 9 preparations - dental cements, rubber - base cement, metal adhesives and general adhesives. Tension, shear and torque force was applied to the brackets but none of the products tested was capable of holding metal attachments directly to the teeth with a stability required for clinical orthodontics.

Swanson and Beck (1960) etched enamel with 85 per cent phosphoric acid, using one drop for 60 seconds, prior to affixing plastic attachments. For best results they said the enamel surface must be clean, etched with acid and dry.

Swanson and Beck said the characteristics of an adhesive satisfactory for clinical application were so exacting that most really good bonding agents were ruled out on the basis of setting time alone.

They listed four requirements of a satisfactory adhesive:

- i. adhesiveness to tooth structure
- ii. resistance to mouth fluids
- iii. lack of toxicity to living tissue
- iv. a setting time practical for operating room conditions and patient comfort.

In their investigations they improved bond strength by:

- i. altering the substrate (acid etching the enamel surface)
- ii. choosing a malleable metal attachment which permitted adaptation.
- iii. choosing an adhesive whose viscosity was related to the accuracy of fit between substrate and adherent

- iv. protecting the bonded margins from moisture by a waterproof surface coating.

None of the materials they tested produced a bond which would be useful under oral conditions, and while moisture was by far the greatest problem there was no known material which could be applied as a surface coating to the bonded margins to provide the necessary moisture seal from without.

Swanson and Beck found the maximum bonding was not obtained during the initial set and so the slower hardening took place in the presence of oral fluids. The significant reduction of bond strength in the presence of moisture did not necessarily indicate a breakdown of the adhesive. They thought it could be due to water absorption by the resin carrying the metal attachment, thus weakening the bond between adhesive and resin. Most of the separations were found, however, to be between the enamel and adhesive rather than at the junction of adhesive and resin.

Bernstein (1965) added two requirements to those laid down by Swanson and Beck for a suitable adhesive!

- i. the agent must have an adequate shelf-life.
- ii. the agent and attachment should be easily removed when desired with little or no alteration to the underlying tooth surface.

Bernstein (1965) decided against etching enamel surfaces prior to attaching resin materials because of the criticism that some members of the profession had for this procedure. But, he asked how was more enamel lost? By etching and placing an attachment for some months and isolating the areas or by constant wear from tooth brushing and mastication

during the same period of time. Bernstein found the attachment would hold longer with greater contact area between tooth surface and attachment and greater adaptation between tooth surface and attachment.

Newman (1965) examined hundreds of teeth to which epoxy resins and curing agents had been applied (not industrial adhesives), and he found no deleterious effects on the enamel surface, macroscopically or microscopically. He pretreated tooth surfaces by pumicing and by applying 40 per cent phosphoric acid, thus improving the joint strength. The reaction of teeth to 40 per cent phosphoric acid and the resultant joint strength depended upon the type of tooth surfaces. Newman said the use of 40 per cent phosphoric acid for 60 seconds on tooth surfaces should remind us that dental cements (which are non-adhesive) contain 35 to 55 per cent phosphoric acid and that the pH of dental cement during band cementation is about 1.6 and that an acid pH may be maintained for 15 to 45 minutes after cementation.

Newman (1965) studied epoxy adhesives for orthodontic attachments. He pumiced the tooth surface to remove remnants of the organic cuticle or dental plaques, acid - etched the enamel surface to strengthen the bond, but found variations in forces needed to break the bond because of variations in tooth size, shape, contour, surface topography as well as the subjective human technique.

Newman selected epoxy resins that were solvent free, 100 per cent solids and so there was no problem of solvent evaporation after joining the surfaces. They possessed shear strength and rigidity, displayed excellent wetting properties, and were resistant to the acids and alkalies

of oral fluids. He thought further research was needed to accelerate the curing time of these resins. By combining an epoxy resin of high molecular weight with one of low molecular weight he accelerated the curing process and reduced the possibility of irritation.

Curing was also accelerated by heating the adhesive to hasten the room - temperature cure.

By bonding a tooth - coloured plastic which covered the entire labial surface Newman could see two advantages, esthetic and hygienic.

The hygienic advantage came from two sources:

- i. There could be no decalcification resulting from poor tooth brushing of the gingival areas.
- ii. While cement disintegrated and allowed the ingress of bacteria and debris so producing decalcification, the adhesive joint would break in toto.

Gwinnett and Matsui (1967) said there was no known material capable of forming a permanent attachment to untreated enamel surfaces under oral conditions, but satisfactory union could be achieved after etching the enamel surface. They applied zinc phosphate cement liquid to the enamel surface for two minutes. They found the depth of etching was no more than 2 - 3 microns, with a total histologic change of about 10 microns.

Docking (1967) said that the science of bio-materials had led to closer co-operation on the part of the materials and the biological scientists. The bio-materials concept favoured an adhesive system, either in the dental material itself or provided by a coating solution giving adequate attachment. The emphasis was placed on adhesion to avoid

marginal leakage which was inevitable where a dental material had a coefficient of thermal expansion which did not match that of tooth enamel. If an impervious material permanently adhered to the enamel, marginal percolation could not occur.

Docking said enamel etching treatment could provide mechanical keying or expose some of the protein fibrils which might provide attachment.

Mitchell (1967) tested polymerizing adhesives and general purpose adhesives in vitro but none of them could maintain integrity of bond in a moist environment. Some protection was obtained by coating the bonded margins with silicone grease but Mitchell developed the M - bracket - a hat shaped 24 - karat sheet gold bracket base. Orthodontic attachments were soldered on top of the bracket band. All brackets remained in place during minor orthodontic movement, but the operation was only partly successful. Mitchell said the adhesive was still the weak link, the rupture occurring at the bracket adhesive junction. He suggested improved mechanical locks on the metal bracket base.

Buoncore and co-workers (1968) studied the penetration of methyl cyanoacrylate into enamel surfaces and found there was no union with unconditioned surfaces, but acid conditioning enhanced adhesion. Two additional possible explanations for increased adhesion were given:

- i. the creation of spaces in depth along interprismatic areas into which the resins could penetrate.
- ii. the incorporation on the enamel surface of an absorbed layer of highly polar phosphate groups, derived from the acid used, which might enhance

adhesion of the resin through increased wettability of the surface.

Newman and co-workers (1968) changed hydrophobic (water repellent) enamel surfaces to hydrophilic enamel surfaces by applying 40 per cent phosphoric acid for one minute. This increased wettability was necessary to achieve a satisfactory bond between adhesive and tooth enamel surface.

2. Physical Nature of Bond.

Gwinnett and Matsui (1967) studied the physical relationship between enamel and adhesive after acid - etching of enamel. Eight different materials were selected and the interface between enamel and adhesive was repeatedly examined under the optical and electron microscopes as the specimen was slowly demineralized in 5 per cent hydrochloric acid.

All specimens examined under the optical microscope showed filamentous "tag - like" extensions at the interface where the material had contacted an etched enamel surface. Each "tag" was continuous with its neighbour by means of a relatively translucent sheet to form a continuous structure. No "tags" were observed on untreated areas or at sites of "prismless enamel" and all "tag - lengths" were fairly comparable, varying from 15 - 25 microns.

Under the electron microscope (6000x and 13,000x) Gwinnett and Matsui noticed that immediately beneath the adhesive there was a zone whose density of crystallites was greater than that of the underlying enamel. The adhesive had penetrated into and polymerized in the prism boundaries,

The origin of the "tag - extensions" was attributed to the liquid monomer which had penetrated into the boundaries and cores of the prisms and polymerized therein. The crystallite components of the enamel were thus encapsulated and so provided an effective and permanent mechanical bond.

The extent of the penetration by liquid monomer would depend on:

- i. The number of spaces in the enamel into which the material can flow after acid-etching.
- ii. The speed of polymerization of the material.
- iii. The post - eruptive age of the tooth.

Gwinnett and Matsui pointed out that tooth enamel which has been exposed to the oral environment only 1 - 2 years has not completed ^{ed}maturation and readily demineralizes when treated with acid.

They found that if the bulk of the material was lost from the tooth surface, then that which has penetrated the enamel remained in situ. The stability of this remaining material would ultimately determine the effectiveness of the adhesive.

Gwinnett and Matsui saw tremendous potential for adhesives as a caries preventive measure by sealing off pits and fissures. They demonstrated in vitro that enamel containing the remnants of adhesive was less soluble in acids than normal enamel. Hence they saw penetration of the adhesive into the enamel as desirable both from the stand-point of the formation of mechanical and chemical bonds with all the enamel components and also to impart

surface protection to the enamel in the event that the bulk of the material might be lost.

Buoncore, Matsui and Gwinnett (1968) studied resin penetration into conditioned enamel surfaces by dissolving away the enamel, leaving prism-like "tags". They could not find "tags" where the resin contacted unconditioned enamel. These "tags" were considered to be a combination of resin and entrapped organic matter of the enamel.

Buoncore and co-workers tested the resin - enamel surface for penetration by dyes and radioisotopes and concluded their failure to penetrate the interface indicated a chemical union between enamel and resin forming a relatively impermeable interface which would also contribute to the enhanced bonding.

While successful bonding seemed to depend on enamel conditioning and "tag" formation, the strength and durability of the bond depended on such factors as viscosity, surface tension, and dimensional changes due to temperature and water absorption.

Buoncore, Matsui and Gwinnett concluded that a material should be sought that has high wettability for enamel surfaces, a high surface tension for effective filling of capillary spaces, and which will polymerize in situ to a tough, impermeable, abrasion and bacterial resistant layer.

Martin (1968) suggested that one of the prerequisites of a bonding material should be "no enamel etching required".

J. Prevention of Areas of Demineralization.

1. Reduction of Enamel Solubility.

Immediately prior to band cementation clinical inspection of enamel surfaces may reveal intact enamel surfaces, intact enamel surfaces with subsurface decalcification (the demineralized agent may be endogenous or exogenous in origin) or ground enamel surfaces as seen in "spot - grinding" or "interproximal stripping".

More recently erupted teeth might not as yet be fully matured.

Martin (1968) has said there is nothing artificial about introducing the fluoride ion into the enamel structure. At one time the role of these ions was considered purely anti-enzymatic but it is now realised that the fluoride ion combines with the enamel structure, the properties of the enamel being changed by this chemical reaction. It is no accident that the new calcium phosphate which now contains fluoride is the most stable form of biological hard tissue. The fluoride content of fossils is very high as over a period of time there is a constant attempt by nature to replace as much of the non-fluoridated hard tissue in the human body as is possible.

Calcium phosphate hydrate: $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ has a particular form when it crystallizes, which is biologically the same as that found in nature. The replacement of the hydroxyl group by fluorine converts the hydroxyapatite into fluorapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ which is more stable, and is caries resistant. The hydroxyapatite and fluorapatite exist together, the

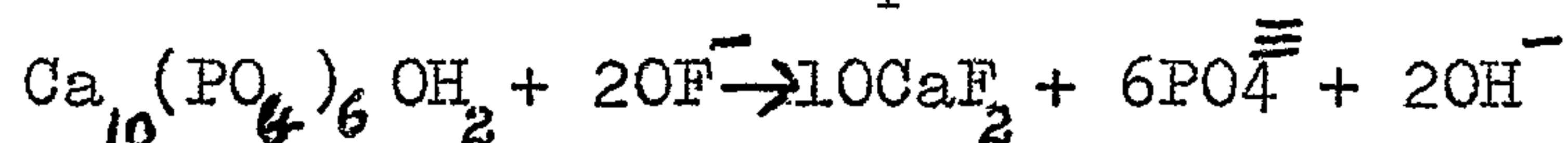
proportion of the latter increasing with time.

As the fluoride relation with enamel is natural and chemically based, the more that is taken up, the better for the enamel. There might be trace elements capable of imparting this skeletally stronger property, but at the moment Martin says only fluorine is known to have this property, and the better the enamel the more fluorine is incorporated.

Fluoridation of water supplies is simply an attempt to provide natural conditions. As the enamel is being formed the presence of fluorine is assured along with calcium and phosphorus. Martin refers to the uptake of primary fluoride at the dental sac stage, secondary fluoride at the pre-eruptive stage and tertiary fluoride once the tooth is exposed to the oral cavity. This tertiary fluoridation would continue in solutions of 1 p.p.m., for the bombardment of the enamel surface by highly active fluoride ion is far more active than the hydrogen ion is during the course of enamel dissolution.

This substitution reaction whereby the hydroxyl group is displaced by fluoride will only take place at low concentrations of fluoride.

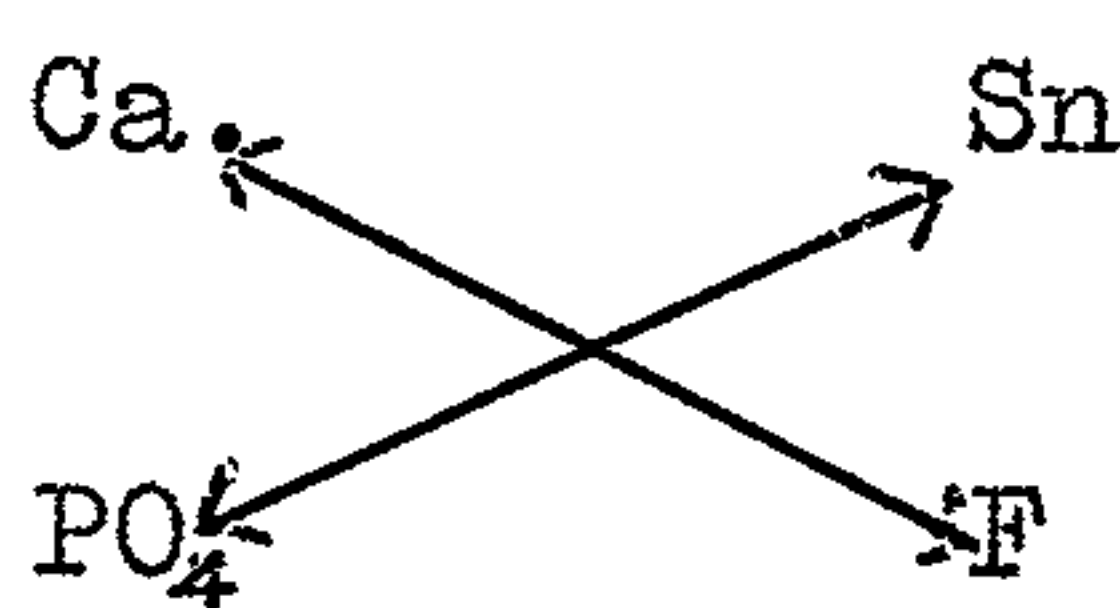
Applications of high concentrations of fluoride, be it by gel or solutions, produce a different change in the enamel - a double decomposition:



The enamel is completely broken down, the calcium fluoride forming as a precipitate on the enamel surface later to be bound by plaque. Calcium fluoride (solubility in water, 16 p.p.m.) is never found in the human body.

Such double decompositions of enamel follow application of 2% Sodium Fluoride solutions as these solutions represent 20,000 p.p.m. NaF and that is 10,000 p.p.m. fluoride.

Martin said that acidulated fluoride solutions, containing sodium fluoride, orthophosphoric acid and hydrofluoric acid may enable the enamel to take up more fluoride than solutions of stannous fluoride, but the treated enamel is more soluble. This is because decomposition of enamel by stannous fluoride produces two insoluble end products, calcium fluoride and stannous phosphate.



With applications of fluoride solutions of high concentration the double decomposition of enamel is followed by the substitution reaction seen with solutions of low concentration due to a drop in the concentration of fluoride on the enamel surface.

Once the relative insolubility has been conferred on the enamel the objective is to keep all the contents of the enamel within the surface of the enamel.

For over 25 years evidence has been accumulated of the advantages to tooth enamel of water supplies containing 1 p.p.m. fluoride whether these proportions were found endemically or dispensed mechanically. Here only reference will be made to the Norrkoping fluoridation study. Due to technical difficulties only one - third of the population's drinking water was fluoridated (1.2 p.p.m. in the form of sodium fluosilicate). This was temporarily discontinued following a dispute as to its

legality, and an objective statement was required urgently. Based on school dental records, Sellman and Syrrist were able to demonstrate a reduction in DMF surfaces of nearly 40 per cent in seven year old children who had had access to the fluoridated water.

While studying the methods of application of stannous fluoride to tooth enamel Muhler (1957) noted that the clinical effectiveness of stannous fluoride depended on preventing its oxidation to the stannic state. He believed the solution should be prepared fresh and used immediately. He performed a thorough prophylaxis since clinical evidence suggested that the effectiveness of the topical treatment was also decreased if a prophylaxis did not precede the initial treatment.

In 1958 Muhler observed the effects of single applications of 10 per cent unbuffered aqueous solutions of stannous fluoride.

Bixler and Muhler (1946) studied the effect on dental caries in children of three agents containing stannous fluoride. They obtained superior results using:

- i. stannous fluoride in a compatible prophylactic paste.
- ii. topically applied aqueous stannous fluoride solution.
- iii. the home use of stannous fluoride in a compatible dentrifice.

Bernier and Muhler (1966) said present evidence strongly indicated that the use of multiple stannous fluoride procedures would result in caries reductions in

the order of 70% in both children's and adults' permanent teeth. Recent studies, they said, suggested the length of solution application could be reduced to as little as 15 seconds.

Muhler and co-workers (1967) conducted a study to evaluate specifically the influence of multiple stannous fluoride therapy on the subsequent rate of progression of incipient dental caries in young adults. After 30 months their results indicated that multiple stannous fluoride therapy reduced the rate of caries progression by 80.3 per cent.

In 1968 Muhler and co-workers tested the clinical effectiveness of stannous hexafluorozirconate as an anticariogenic agent. They used freshly prepared solutions (8 per cent and 16 per cent) and used them immediately. Their clinical studies supported their laboratory findings which were that stannous hexafluorozirconate was 50 per cent to 70 per cent more effective than stannous fluoride.

Brudevold (1957) demonstrated that pumiced, ground, acid - etched surfaces and white spots showed greater uptake of sodium fluoride than sound enamel.

Gray (1965) tested the acid dissolution rate of sound and white spot enamel treated with various fluoride compounds. He found that regardless of the technique used stannous fluoride was always superior in its effects to stannous chloride and sodium fluoride. Also he noted the large amounts of stannous fluoride taken up by areas of defective enamel and thought this "reservoir of antisolubility" could exert a prolonged effect.

2. Correct Manipulation of Cement.

Relative to areas of demineralization, two factors emerge when considering cement manipulation, elimination of free phosphoric acid and utilization of the optimum physical properties offered by the cement manufacturer.

Skinner and Phillips (1967) emphasized that as a group, the physical and chemical properties of cements leave much to be desired and their manipulative techniques should be designed to provide the optimal behavior. All of the cements shrink during setting, they said, and they all slowly disintegrate in the oral fluids.

Gross (1951) said the 20 per cent excess liquid provided for by dental specifications should be discarded when the unit of powder has been used up. The cumulative changes in the concentration of the liquid, resulting from repeated opening and closing of the liquid container, would increase more rapidly as the ratio of the exposed surface of the liquid to its total volume increased.

Skinner and Phillips said changes in the water content of the liquid would markedly affect the setting time. They said that in addition to keeping the bottle sealed, the liquid should not be left sitting on the slab prior to mixing.

Skinner and Phillips placed the responsibility for specifying the proper powder - liquid ratio upon the manufacturer and added that from the standpoint of the physical properties of the cement, a mix of thick consistency was the best.

Savignac and co-workers (1965) studied the powder/liquid

ratios and time of mixing of zinc phosphate cement as used by 31 dentists in band cementation. The total number of mixes was 186 and the range of powder/liquid ratio was from .64gm/.5ml to 1.67gm/.5ml. The range for the mixing time was 40 seconds to 196 seconds. The setting time varied from 14 minutes to 6 minutes, thicker mixes setting more quickly.

The compressive strength varied from 8,900 p.s.i. to 17,000 p.s.i. for thicker mixes. Solubility and disintegration decreased with an increase in powder/liquid ratio.

Savignac and co-workers thought that for any particular cement the need for proportioning devices was indicated. From their studies of the effects of powder/liquid ratio variation on the physical properties of zinc phosphate cement they concluded further standardization of the mixing technique was indicated.

Skinner and Phillips make the following observations on cement manipulation:

Contact with Moisture: Because of the critical nature of the water content of the cement liquid, the area near the cement must be kept dry during mixing, during insertion in the mouth, and during hardening. Phosphoric acid will be leached out if cement is allowed to harden under a film of saliva and the set cement will be easily dissolved by the oral fluids. After the cement has set it should not be allowed to dry out as this results in shrinkage and crazing of the surface and finally disintegration.

In the case of silicate cements alteration in the water content of setting cement decreases the strength and

increases the solubility of the set cement. There is also a greater shrinkage of the cement if it is allowed to harden in the presence of moisture. Again phosphoric acid is leached out and the water replaces it in the weak gel framework.

Strength: The strength of the cement is dependent upon the liquid/powder ratio, the compressive strength increasing rapidly as the amount of powder is increased. The zinc phosphate cements attain 75 per cent of their maximal strength during the first hour and their maximal strength within 24 hours. When exposed to the oral forces zinc phosphate cements exhibit brittleness and a definite lack of strength leading eventually to fracture and disintegration.

The compressive strength of silicate cements is also directly proportional to the powder content because the more powder particles in the hardened cement the greater binding action of the matrix or gel, as the binding action is dependent upon the surface area of the core. All the powder particles must react with the liquid, as powder particles not chemically attached result in a weak cement. Silicate cements harden more slowly than zinc phosphate cements and the strength decreases as the cement dissolves in water or oral fluids.

Solubility and Disintegration: The layer of exposed cement should be kept to a minimum and the material handled in such a manner that its solubility is as low as possible. During dissolution of zinc phosphate cement the matrix is probably attacked first and erosion results as the cement crumbles and disintegrates. Obviously the greater the amount

of powder incorporated into the liquid, the less is the disintegration.

Silicate cements are more soluble in distilled water than zinc phosphate cements but zinc phosphate cement disintegrates more rapidly in lactic and acetic acids. With acids such as lactic and acetic present in plaque material it can be expected that zinc phosphate cement will be attacked more rapidly in the mouth than silicate cement. Silicate cements exposed to the washing action of the saliva and to mechanical wear remain relatively intact but disintegration occurs adjacent to gingival areas where debris and food plaque collect. While the durability of silicate cement depends on diet and bacterial flora of the mouth, the type and pH of the acids in the oral environment are very important.

The solubility of silicate cement is related to the gel matrix and not to the core of undissolved particles. Therefore the less gel matrix present in the set cement, the less its solubility. The gel matrix probably dissolves and the particles are washed away. The solubility decreases with an increase in the amount of powder incorporated, but beyond a certain powder/liquid ratio the cement becomes more soluble. The more powder employed, the less is the amount of matrix formed, but each undissolved powder particle must be surrounded by gel, otherwise the oral fluids will penetrate the voids formed by the absence of silica gel, and the exposed surface of the cement increases considerably.

The maximal strength and minimal solubility do not occur with the same powder/liquid ratio.

Setting Time: If zinc phosphate cement sets too rapidly, the crystal formation is disturbed and broken up during the

mixing of the cement or during band cementation. A cement mix made on a cool slab lengthens the setting time and this probably offers the dentist the best method for control of setting time. However a temperature below the dew point of the room would introduce moisture into the mix.

The setting time may be influenced by the rate at which the powder is added to the liquid. The more slowly the powder is added, the longer is the setting time, the matrix probably forming when the mixing is completed.

The longer the mixing time, the longer is the setting time, any matrix formation being broken up during mixing, the final matrix forming after the mixing is completed.

The more liquid employed in ratio to the powder, the slower is the setting rate of cement. Apparently the acid attenuates the mixture, and more time is required for intermeshing of the crystals.

Lengthening of the setting time by use of higher liquid /powder ratio and possibly by prolongation of the mixing should be avoided because of the adverse effect on the strength and solubility of the cement.

Recommended mixing techniques involve the gradual addition of small amounts of zinc phosphate cement powder to the liquid to assist in neutralizing the acid thus complementing the buffering action of the salts in the acid. The desired consistency should always be attained by the addition of more powder and never by allowing a thin mix to stiffen. Such a procedure fractures the crystals already formed and the final cement is weak and

will disintegrate in oral fluids.

Silicate cements set more slowly where a longer mixing time is employed. Probably the gel is broken up, thus producing a cement of decreased strength and increased solubility.

Increasing the liquid/powder ratio prolongs the setting time but weakens the set cement. The rate of addition of the powder to the liquid is not so significant with silicate cements, and as with zinc phosphate cements, the best method for the dentist to control the setting time is to change the temperature of the mixing slab, but not below the dew point of the room.

Eichner and co-workers (1968) investigated the solubility of dental cements and listed factors influencing cement solubility as:

- time of dissolution
- Concentration of solute in dissolving medium.
- Specimen shape
- type of dissolving liquid
- surface polish of specimen
- turbulence of the dissolving medium
- powder - liquid ratio of cement.

Changing the specimen shape did not significantly affect the solubility of the cements they tested.

Wilson and Batchelor (1967) studied the solubility of silicate cements and found that the amount of phosphate in the eluate depended on the degree of attack by the cement liquid on the powder and was greatest where the relative amount of liquid used in cement preparation was high and its phosphate concentration was high. The leaching pattern

of phosphate from cements suggested that the dissolution process was a simple washing out of the soluble salts from the cement gel.

Cameron and co-workers (1963) said the practicing orthodontist was probably more clinically aware of the setting time than of any other physical property of cement. They said the setting time was directly related to the working time and the working time of a cement was of critical importance in the cementation of orthodontic bands.

Cameron and co-workers made the following recommendations to assist the orthodontist in establishing a proper standardized technique for the manipulation of cement.

- i. Select one powder/liquid ratio for a given dental cement which will yield acceptable physical properties consistent with the clinical working time requirements.
- ii. Employ the same powder/liquid ratio in all cement mixes regardless of the number of bands being set.
- iii. Adopt a standard mixing technique.

Such adherence to a standardized procedure, they said, would consistently produce cement mixes having the desired physical properties.

3. Accurate band fitting.

Berkson (1950) said that band construction was a far greater factor than cement in band retention. Yet no matter how skilfully an orthodontic band might be shaped it would not keep its retention on a tooth throughout functional use without the aid of cement. The orthodontist called upon the cement to protect the tooth under the band from

caries.

Berkson said structural faults were always present in adhesive materials and the thinner the film the fewer the faults likely to be present as it was quite impossible to produce a mixture that was homogeneous throughout. Microscopic faults such as gas bubbles, areas of excess acid or powder or foreign particles were always present.

Skinner and Phillips (1967) said that the thickness of the cement film was determined to some extent by cementation pressure, the viscosity and temperature of the cement, as well as the taper of surfaces between enamel and band. They added that accurately fitting restorations (bands) kept the area of exposed cement to a minimum and so kept cement solubility as low as possible.

The work of Nelsen and co-workers (1952) on fluid exchange at the margins of dental restorations suggests that the smaller the bulk of cement between orthodontic band and enamel surface the smaller the space developed between cement and enamel due to thermal changes.

Norman and co-workers (1963) studied the properties of films of dental cements. They investigated films less than 40 microns thick as this was generally considered to be the maximum limit acceptable. They found there was less marginal leakage of silicate cements than zinc phosphate cements and while zinc phosphate films and silico phosphate films were produced at 9 microns and 13 microns respectively they had little resistance to load at these dimensions.

Fusayama and Iwamoto (1960) tested the shearing resistance of dental cements. They designed an apparatus

to test the retention of inlays to enamel surfaces and found a film thickness of 38 microns gave the maximum retaining force.

4. Choice of Cement.

While the choice of cement for band cementation will finally be determined by the suitability or otherwise of its physical properties and ease of manipulation, Skinner and Phillips said the clinical significance of the presence of fluorine in cement was tremendously important. The incidence of recurrent caries and contact caries (caries on surfaces approximating silicate restorations) was markedly less around cement restorations containing flouride. This anticariogenic property was more likely due to reduction in enamel solubility than to any germicidal property of fluorine and it was probable that some fluoride was continually available at the leaking cement enamel interface.

5. Non - Dehydration of Enamel.

Referring to cavity preparation in dentine, Skinner and Phillips said that a condition of complete desiccation was not desirable when placing cements, as if the walls of a prepared cavity were desiccated with alcohol and hot air more phosphoric acid could be absorbed from the cement liquid into the tooth structure.

Ziegler (1959) investigated the comparative merits of cementing orthodontic bands on non-dehydrated and air - dried teeth. He examined tooth surfaces under and around bands in vivo and concluded that there was no statistical difference in the incidence of decalcification or breakdown in retention between the air - dried and non - dehydrated teeth.

6. Protection of Cement Surfaces.

Jorgensen (1963) studied the effect of polishing on the solubility of cements. Test specimens were gently polished under water with an emery cloth of the same coarseness as clinically used dental strips. Standard solubility tests were made and Jorgensen found a higher solubility for unpolished test samples, probably due to the amount of gel matrix present in the surface of such specimens, whereas polished cement surfaces would consist largely of undissolved powder particles.

However a polished (rough) surface in the mouth would probably offer poorer hygiene and involve a greater risk of dissolution than an unpolished surface and for this reason Jorgensen made no recommendations for clinical practice.

Smith (1967) said the durability of dental cements in the mouth was influenced by manipulative and clinical factors. Abrasion and fracture were important considerations but the principal cause of cement failure was generally accepted to be dissolution of the material in saliva and other oral fluids.

Smith studied the effects of various protective agents upon the solubilities of silicate cements in water and citric acid. Silicate cement specimens were coated with greases (1 mm thick) and varnishes (.05 to .15 mm thick) and solubilities compared with unprotected specimens.

All the films of the varnishes were soft after drying in air and a loss of 10 to 20 per cent by weight occurred on soaking the films of varnish in water for 24 hours. The permeability of the varnishes was affected by minute

cracks, very rapid drying varnishes being more prone to these defects.

Soft paraffin wax floated off the solubility discs after one hour in water at 37 degrees centigrade, silicone grease after 1.5 hours and wax after 4 to 8 hours. Similar results were found in the mouth. Existing dental varnishes gave good protection (up to 4 weeks) to silicate cements and remained well-adapted although they could be flaked off readily. They did not affect the surface of the silicate material.

Smith speculated that repeated varnishing might well give a long life in mouths where rapid dissolution normally occurred. Alternatively, a permanent coating could be applied when a sufficiently durable varnish is found.

Marjorie Swartz and co-workers (1968) studied the penetration of dentine by the constituents of silicate cement in cavities prepared in monkeys. As they found in their in vitro tests as well, three coats of varnish afforded somewhat more protection than a single coat.

7. Improved Oral Hygiene.

Johansen (1963) saw carious lesions as manifestations of a complex disease phenomenon affecting the calcified tissues of teeth. Numerous factors, including the saliva, would influence the course of the disease, and the basic process by which lesions developed were generated by microbial metabolism in localized areas on external tooth surfaces. The acid environment thus erected by metabolism of carbohydrates favoured dissolution of dental tissue. Johansen said it could be assumed that the ultrastructural

and chemical changes which occurred in dental caries were mainly the result of the carious process with modifying influences from the fluid environment of the oral cavity.

Leach (1967) said that when a tooth surface was thoroughly cleaned with a toothbrush and toothpaste (in vivo or in vitro) it was possible to rub away all the various integuments until the individual crystallites of surface enamel were exposed. If the tooth surface were then exposed to saliva for a period of minutes, an acellular, bacteria - free layer was deposited on the tooth surface. He said this was the "pellicle" and was derived from the glycoproteins in the saliva. Hours later bacteria became deposited on the surface of the pellicle, surrounding themselves with a matrix very different from the pellicle. The aggregation of bacteria and its matrix was defined as "dental plaque."

Leach demonstrated the presence of sugar in the matrix of the dental plaque by means of the electron microscope. He found plaque tended to form during fasting, particularly at night.

Silverman and Kleinberg (1967) studied factors affecting the aggregation of microorganisms in human dental plaque and they considered the first step in plaque formation to be the deposition of protein material from the saliva on the teeth followed by the adhesion and subsequent penetration of this material by bacteria from saliva.

Baker Dirks (1966) believed the plaque protected the enamel surface by its buffering capacity and also acted as a reservoir for minerals. In a negative way,

plaque acted as a place of accumulation of substrate for acid production by bacteria.

Frank and Brendel (1966) believed there was little doubt that bacteria were the aetologic agents of dental caries because oral bacteria could attack enamel in vitro, and antibiotics acting specifically on bacteria reduced the incidence of caries in man.

Frank (1967) said the first stage of caries in the enamel was characterized by the appearance of a white or brown spot, which always developed in contact with a bacterial plaque. By microradiography he demonstrated in these initial lesions a superficial layer, apparently intact, overlying a demineralized sub-surface zone.

Schatz and Martin (1962) advanced the proteolysis-chelation theory of dental caries. They noted that organic matter in normally calcified tissues could be attacked by certain microorganisms and enzymes without preliminary decalcification. Such action produced the initial lesion in caries and the products of this attack possessed properties which would permit a more or less simultaneous dissolution of apatite at the time of breakdown of organic matter.

Schatz and Martin said only enzyme reactions, not acid digestion of protein or acid decalcification were sufficiently specific to account for the host specificity in terms of the substrate attacked in the initial stage of caries and other microbial infections.

Poole and Johnson (1967) said that although it was commonly accepted that the destructive agents in dental caries were organic acids (mainly lactic acid),

there was a belief that the initial destruction of mineral was caused by chelating agents and that this was preceded by proteolysis.

Eggers Lura (1967) defined caries as "a microbiological degradation and utilization of the tooth substance in a neutral or alkaline milieu caused by the presence of abnormally high sugar accumulation in the plaques which inhibit the bacterial metabolism and, at the same time, produce soluble calcium saccharates and calcium complexing intermediates and which require abnormal quantities of inorganic phosphate enzymatically extracted from the enamel apatite by phosphorylations".

Keyes (1968) reviewed the research in dental caries. He said some investigators regarded dental caries primarily as the lysis of enamel by acids produced from carbohydrate bacterial interactions, and the therapeutic treatment was to render the enamel surface more resistant to demineralization or to reduce the production of acids. Other investigators regarded the formation of carious lesions as the pathological consequence of invasive microbial diseases. Keyes called these diseases odontopathic infections.

He said the elimination or dispersion of bacterial masses appeared to be as important as attempts to produce acid - resistant teeth or to control acid formation.

Keyes said many questions remained unanswered:

- i. What types of microorganisms had the potential to colonize on "smooth" enamel surfaces?
- ii. What substrates (from food residues or other sources) did these microorganisms metabolize?
- iii. What kinds of acids, polysaccharides and toxins did they produce?

- iv. How did the various bacterial by - products interact with tissues of the host or other microorganisms in the plaque population?
- v. What was the eventual fate of the microorganisms?

Keyes added that treatments of dental caries that did not include control of microbic deposits represented the abatement of symptoms rather than the control of the disease, namely, bacterial plaque infections. Therapeutic programs should control the formation of odontopathic plaques or at least keep these deposits below the level at which toxic reactions occur.

Fanning and Henning (1967) investigated the design of toothbrushes (available in Adelaide) in relation to oral health. They deplored the disappearance of the ethical interest in the standard of the products available and of 51 brushes available for adults only five were acceptable in design. Eight brush types were available for children, but not one was entirely acceptable.

Henning and Fanning (1968) evaluated methods of oral hygiene instruction. They thought it quite apparent that dogmatic teaching of cleaning techniques failed to motivate patients to care for their mouths. Many patients became frustrated and did not follow instructions. They welcomed the change in approach where patients were taught why they should clean their teeth rather than to follow a particular method.

Henning and Fanning condemned the use of mouth washes without treatment or instruction in oral hygiene. They believed the dentist's teaching should not be restricted to a single technique of oral hygiene; but modified to meet the

individual needs of different patients, using the natural teeth for demonstration and not models. Supervision of oral hygiene they considered to be a ^{continuing} process.

Fanning and co-workers (1968) demonstrated the efficacy of fluoride dentrifices as a method of controlling dental decay. They thought it important, nevertheless, to stress the value of the cumulative benefit of other well-established methods of caries prevention, such as dietary control, water fluoridation and regular dental care.

8. Dietary Control.

Any recommendations from orthodontists which are relevant to the patients' diet usually stress the physical nature of foodstuffs. While this is essential, the biochemical nature of the diet must be considered during orthodontic treatment, a period of increased caries incidence.

Harris (1963) reported on the dental status of a group of children living in a Home at Bowral, Australia. While dental care was minimal, the dietary regimen in the Home was vegetarian with great emphasis on dairy products, and much of the food was eaten in the uncooked state. Annual clinical and radiographic examinations of the teeth were made of children between ten and fifteen years and the percentage of caries - free mouths for the Home children ranged from 71.4 - 6.1 per cent and for a comparable group of State school children, from 4.6 - 0.0 per cent.

Sugar, white flour, and products made from these were rarely included in meals, but as the children became old enough to earn wages there was a degeneration in dental

health due to the deviations from the original lacto - vegetarian diet of which the carbohydrates were unrefined.

Harris and co-workers (1967) studied the cariostatic effect of calcium sucrose phosphate in children aged 5 -17 years. The addition of this salt to carbohydrate food at the rate of 4.3 gm per day demonstrated a beneficial effect when results were compared with those obtained from a control group of children aged 5 - 17 years.

Harris and co-workers (1968) said that calcium sucrose phosphates were safe, soluble and readily incorporated in various foods.

Carroll and co-workers (1968) studied the clinical effectiveness of phosphate - enriched breakfast cereals on the incidence of dental caries in adults. By adding a 1 per cent mixture of sodium dihydrogen phosphate and disodium hydrogen phosphate to ready-to-eat breakfast cereals the incidence of D.M.F. teeth was reduced 47 per cent after 12 months.

De Paola and Lax (1968) studied the caries inhibiting effect of acidulated phosphate - fluoride chewable tablets in young children. The tablet consisted of sodium fluoride, sodium biphosphate and hexamic acid and one tablet per day over two years produced a caries reduction rate of 20 per cent compared with a control group. De Paola and Lax concluded that the ingestion of fluoride supplements did not appear to produce a cariostatic effect as favourable as that of water fluoridation.

K. Remineralization and Decalcified Areas.

1. Brief Review of Literature.

Ericsson (1953) thought the greater depth of penetration of carious enamel ("acute" or "arrested") by radioactive calcium was due to the enlarged total surface of the corroded crystallites and the greater facilities for diffusion. He expected that there would be a correspondingly greater uptake of fluoride by enamel surfaces which had been subject to incipient carious dissolution.

Koulourides and co-workers (1961) softened extracted teeth in acetate buffer (pH 5.5, 37°C for 2 -12 Hours) and tested their surface hardness using Knoop hardness measurements. The softened teeth were kept in rehardening solutions and the tooth surface hardness determined at various time intervals. In some cases a return to initial hardness was observed after eight days.

They believed this evidence of enamel rehardening emphasised the dynamic nature of the enamel surface and the importance of the oral fluid in the carious process. If the softening process had proceeded beyond a critical limit, complete rehardening did not occur. Koulourides suggested 150 Knoop hardness could be the boundary between sound and carious enamel and could mark the limit of the natural reparative processes for enamel. The rate of rehardening was more rapid with solutions containing a calcium/phosphorus ratio of 1.67. The rate of rehardening was also accelerated by using solutions containing fluoride (1.p.p.m.), for in addition to producing a more insoluble enamel, Koulourides thought the fluoride ions disturbed the

dynamic equilibrium between tooth surface and fluid.

Koulourides and co-workers concluded that "prevention and healing of initial carious lesions seem possible by modification of the composition of the oral fluid either systemically or locally".

Sognnaes (1963) conclusively demonstrated the capacity of the enamel to take up radioactive elements from the salivary circulation and to a lesser degree from the internal connective tissue fluid of the pulp, depending upon the stage of dental calcification and eruption. He used high levels of various radioactive isotopes on live rhesus monkeys. He found the final submicroscopic maturation of the enamel was to a large extent controlled by the liquid - solid equilibrium between the salivary environment and the enamel structure.

Sognnaes then asked whether the physiological mechanism which can bring the enamel mineralization from the stage of the recently erupted tooth up to the more highly mineralized stage may be duplicated if the enamel of fully calcified teeth were to be drained of some of its lime salt content, either experimentally or pathologically,

In his own experiments with rhesus monkeys, where teeth were tested with five per cent nitric acid for five minutes and extracted after various periods of exposure to saliva, the enamel changes were sub-surface and along the Retzius lines without any alteration of gross appearance of enamel. After only two days there was an increase in microdensity of the demineralized enamel, and after one week, in addition to a further increase in microdensity, the previously pronounced Retzius lines had disappeared.

After 7½ months there was no evidence of chalkiness on dried enamel surfaces.

Thus from a clinical and æsthetic point of view it did appear that the teeth of normal animals could experience an incipient surface etching and regain the normal glossiness of a healthy tooth surface.

Sognnaes said it should not be assumed that the partially demineralized tooth substance could become completely reconstructed to its precise original physical and chemical state. Firstly, there was not necessarily a direct correlation between the physical and chemical properties of teeth. Secondly, while the microdensity appeared to be recovered in the remineralized specimens, there appeared to be a greater microscopic dye - binding capacity within these areas of "rehardened" enamel. He thought the affinity for the dye, toluidine blue, suggested the presence of an amorphous mucous substance which could be contributed by saliva, the normal organic - inorganic linkage of enamel not being reconstituted.

Sognnaes concluded that if the enamel surface was partially destroyed - within a certain degree and depth - there appeared to exist a limited capacity for reconstitution to clinically normal quality and appearance. This chemical repair appeared to operate whether the original enamel surface had been destroyed by chemical action (acid), pathological demineralization (incipient caries), or by mechanical abrasion (remodelling malshaped teeth).

Pickel (1965) and co-workers felt that as there was a continuous exchange of ions between enamel surface and saliva, a modification of this exchange could be expected

from changes in the composition of saliva. This would be followed by a change in enamel surface hardness. They added auxiliary substances to saliva in vitro and, like Koulourides, etched enamel, collected Knoop hardness measurements and compared these with measurements taken after immersion in the saliva.

They found that saliva alone could accomplish a modest rehardening and so, to be effective, any rehardening agent should reharder softened enamel significantly better than saliva alone and it should perform quickly. They improved the rehardening activity of the saliva by the direct addition of dicalcium phosphate dihydrate.

Birgit Johansson (1965) suggested that use of too strong an etching agent could remove surface enamel in toto and so "fail to produce the porous highly selective type demineralized enamel seen in carious lesions". She etched enamel by immersion in acetate buffer and later exposed these surfaces to saliva and calcifying solutions. From her experiments (subjecting tooth sections to polarized light microscopy) she found that remineralization was rapid during the first 24 hours and tapered off during the next 48 hours. No further increase in mineral deposition was observed after additional exposures to the calcifying solution or saliva for periods of up to three weeks. The rate of remineralization was similar in the inorganic calcifying solution and the parotid duct saliva. The decreased opacity was due to mineral deposition in the outer enamel as shown by polarizing microscopy. Remineralized areas of "white spots" were penetrated by dyes to a lesser extent than the control areas of "white

spots". She thought the remineralized surface was impermeable and would limit toxic diffusion and remineralization of underlying enamel.

Backer Dirks (1966) studied the posteruptive changes in dental enamel, changes before the caries process began (posteruptive maturation), the caries process itself, and the changes thereafter. These changes in the enamel and the speed of the changes were different for the various tooth surfaces.

In more than 50 per cent of the proximal surfaces that showed enamel lesion radiographically, the caries process did not progress. He thought this caries arrest could be the result of an altered environment or a newly acquired resistance of the enamel.

Backer Dirks said the disappearance of white opaque spots could take place by remineralization or surface abrasion or both. The opaque spot might represent a recrystallization of the surface of apatite crystals into tricalcium phosphate, leading to the loss of one calcium ion. The disappearance of the white spot would then be a reversal of this process - a process where a favourable pH would be of far greater importance than the availability of calcium ions.

Backer Dirks carried out a longitudinal study on seven year old children until they were 15 years. He found "an important number" of incipient carious areas in enamel did not progress within his period of observation. A small fraction of the white spots soon progressed to a cavity.

The other white spots either seemed to be unchanged,

to have regained their normal surface gloss, or to have disappeared completely. Backer Dirks believed it most likely that remineralization or a process of recrystallization or both, took place.

Koulourides and co-workers (1968) obtained a rehardening solution by dissolving synthetic hydroxyapatite ($\text{Ca/P} = 1.67$) in .1M hydrochloric acid. The range of pH of the effective rehardening solutions indicated that the newly formed mineral could fill microspaces in the enamel structure over a wide pH range. They said that whether the mineral was identical in chemical composition or crystal structure with the original enamel material could not be determined from hardness data, but as the rehardening rate did increase in a regular manner with the increasing supersaturation the formation of one solid phase seemed likely.

They thought there was little doubt that at pH above 6.8 the mineral formed was apatite, and very likely the same type of mineral was formed throughout the pH range studied.

Lilienthal and co-workers (1968) said that as the hydroxyapatite in tooth enamel existed in dynamic equilibrium with its fluid environment and retardation of demineralization inhibited dental caries, then it was likely that the opposing reaction of the equilibrium, remineralization, could also influence the progress of a carious lesion. They carried out experiments with rehardening solutions on softened enamel surfaces using Knoop hardness measurements as their basis for comparison. Some of the conclusions were:

- i. The presence of calcium sucrose phosphate in a tooth paste led to significant rehardening of

- softened enamel, the hardness increasing with higher concentration of calcium sucrose phosphate.
- ii. The hardening due to calcium sucrose phosphate was not increased by the addition of saliva or stannous fluoride.
 - iii. Calcium ions alone, phosphate ions alone and sucrose phosphate anions alone do not harden softened enamel but the combination of all three ions is effective.
 - iv. The rehardening produced by calcium sucrose phosphate can be attributed to the calcium ions which it contains.
 - v. Enamel rehardening with calcium sucrose phosphate can be a rapid process, being virtually complete in five minutes under certain conditions.
 - vi. Calcium sucrose phosphate in solution and in toothpastes can increase the hardness of unsoftened tooth enamel.
 - vii. In the presence of .05 per cent and .5 per cent calcium sucrose phosphate the softening rate of tooth enamel in normal acid buffer was markedly reduced.
 - viii. Teeth rehardened with calcium sucrose phosphate did not possess any enhanced or reduced susceptibility to acid attack.

Frank (1967) studied the ultrastructure of the remineralization process using the electron microscope. He defined remineralization, from the ultrastructural point of view as "an inorganic crystalline precipitation in

normally mineralized and subsequently demineralized areas. In principle it can be a crystalline growth, completely identical with the normal apatite crystals of the enamel and the dentine or differing from these by their size".

Darling (1967) thought that mineral salts might be redeposited in carious enamel but there was no evidence of any reconstruction of the tissue or increased resistance to caries.

Lenz (1967) interpreted remineralization as meaning that "enamel that has been partially demineralized by artificial means or by caries 'regenerates' through taking up calcium phosphates, primarily from the saliva". He found that spaces opened up between the enamel crystals through decomposition of the crystals in the early stages of caries were not closed through renewed surface growth of the crystals (as in mineralization). In vitro a granular precipitation of the added substances was formed, but apatite crystals were formed in vivo in the same manner as calculus. The enamel was not restored to its former structure during the in - vitro or in - vivo remineralization processes. Covering of enamel defects by colloidal - viscous layers from the saliva was not remineralization, Lenz said. In genuine remineralization the existing spaces in the texture of the enamel were filled by substances originating from saliva which, under suitable conditions, became the matrix for the formation of crystal - nuclei.

Wei (1967) reviewed the literature on remineraliation of enamel. He thought the term remineralization should include "attempts to replace the lost hydroxyapatite with

minerals other than the original calcium and phosphate by chemical processes of exchange, substitution and other means of physical and/or chemical bonding". He concluded that there was considerable evidence to show that remineralization of partially demineralized enamel was possible, but he felt the mode of treatment, the type of remineralizing solution and medium of application required further investigation.

2. After Band Removal

The removal of orthodontic bands should be routinely followed by the chipping away of adhering cement, by a thorough prophylaxis and by a dental examination and bitewing radiographs.

Backer Dirks (1966) noted how white opaque spots on buccal surfaces disappeared by remineralization or surface abrasion or both. He thought it most likely that remineralization or a process of crystallization took place, a lost calcium ion being returned to the tricalcium phosphate crystals from the saliva.

Martin (1968) said that white spots treated with stannous fluoride solutions became more insoluble areas of enamel than healthy enamel treated with the same solutions. However, the white spot remained.

Muhler (1960) compared the results of clinical examinations before and after the application of stannous fluoride as a topical anticariogenic agent.

He found in every clinical test (without reference to the former examination) the disappearance of lesions was constantly observed. He said, from his tests, it was an established fact that once the precarious or carious

area became pigmented with the characteristic light brown colour, the lesion would fail to increase in size.

Thus there is the responsibility of complementing the natural reparative processes of the saliva with Muhler's multiple fluoride therapy.

No reference was found for the treatment of enamel surfaces to which plastic attachments had been bonded, nor any describing the fate of the adhesive "tags" encircling the crystallites.

Original Work.

Laboratory Observations on Some Properties of Dental Cements Mixed to Standard and Thin Consistancies.

Aim.

To record the effect of altering powder/liquid ratio of dental cement on:

1. Enamel etching potential.
2. Cement working time.
3. Cement setting time.
4. Cement solubility.

Materials and Methods.

A. Materials.

Three popular orthodontic cements were selected for this study:

- i. A zinc phosphate cement.
- ii. A black copper cement.
- iii. A silico - phosphate cement.

All bottles of powder and liquid were new and unopened. Batch numbers were recorded. Extracted teeth were collected and kept dry in a glass - stoppered jar. These teeth came from all areas of the mouth and from young and old patients.

Prior to use the enamel surface selected for study was cleaned for 30 seconds with a dry prophylaxis brush on a dental engine, rinsed in tap - water and dried with compressed air. Each selected surface was then examined under the optical microscope (X16) to be sure it was free from any defects, such as mechanically or pathologically induced mineral loss.

B. Methods.

1. Enamel Etching Potential of Cement.

Experiment i.

Three clinically and radiographically perfect first bicuspid were extracted from a fourteen year old patient requiring orthodontic treatment.

After cleaning, as previously described, each of the three buccal surfaces was covered with a piece of bite-wax of standard thickness and a round "window" about four millimetres in diameter made with a thin hollowed metal tube.

Into one opening onto the buccal enamel was placed a drop of silicate cement liquid, a small amount of freshly mixed silico-phosphate cement into another, and a portion of silico-phosphate powder into the opening on the buccal surface of the third tooth.

The three teeth were placed horizontally on a stick of softened wax, covered with a plastic box and left at room temperature for 21 days.

When the cement mix and powder were removed the original intact glossy enamel surface was observed under the optical microscope.

The drop of colourless cement liquid had now become a white, tacky paste of apparently the same original volume and shape, and too viscous to flow off the enamel surface. This tooth was then washed and brushed thoroughly under tap water and dried with compressed air. The buccal surface now exhibited a circular area of etched

enamel, the depth of which appeared uniform to the naked eye, and the margins were sharp to finger touch. Viewed from the proximal aspect there was definite interruption of the curvature of the buccal surface.

Silicate cement liquid obviously had the capacity to attack some tooth enamel.

Experiment ii.

Thirty extracted teeth were selected from the glass jar. They included carious teeth and caries-free teeth, anterior and posterior teeth, and teeth from young patients and old patients. Mesial, distal, labial and lingual defect-free surfaces were selected and over each chosen surface a wax cover was marginally sealed. The "window" was again made in the wax and onto each selected enamel surface a drop of silicate cement liquid was placed. By holding the dropper vertical on each occasion the same volume of liquid was dispensed. The teeth were placed on wax, covered and left for 21 days at room temperature.

After this period of time every colourless drop of cement liquid had become the white, tacky paste seen in Experiment i. The consistency of the paste seemed to be the same for each tooth.

Every tooth surface showed a circumscribed area of etched enamel readily examined with the naked eye. (Fig.1)

Silicate cement liquid appeared to attack most human enamel surfaces. The fact that a tooth was apparently caries-resistant did not appear to add to its protection from acid attack.



Fig. 1. Enamel surfaces etched by silicate cement liquid. (Stain-alizarin red S)

Experiment iii.

Ten carious or restored upper canines with perfect labial surfaces were selected. In this and subsequent experiments only carious or restored teeth were used, thus minimizing the possibility of encountering acid-resistant enamel and possibly fully exposing any enamel-etching properties of dental cements.

Each of the ten canine labial surfaces was divided into three sectors by means of thin lines of sticky wax in Y form. The teeth were grouped in five pairs and onto each labial surface three drops of liquid were placed, one drop of zinc phosphate cement liquid, one drop of black copper cement liquid and one drop of silicophosphate cement liquid. The position of each drop on the labial surface was rotated as progression was made from one tooth to the next.

All teeth were placed in a room at 37 degrees centigrade and pairs were removed at intervals of 6, 10, 15 minutes, 1 hour and 2 hours. As each pair of canines was removed from the room, the wax and cement liquid drops were removed. All the liquid drops appeared to be still clear, but even to the naked eye every one of the thirty areas showed evidence of etching, even if only loss of lustre. There was a tendency for the etching by silicate cement liquid to be the most prominent.

All three cement liquids being considered had the capacity to etch enamel, even within a period of 6 minutes at 37 degrees centigrade.

These observations were confirmed with the optical microscope (X16).

Experiment iv.

Five carious upper central incisor teeth were selected. Under the optical microscope (X16) the labial surfaces were free of defects, and each of these surfaces was divided into three sections with Y - shaped sticky wax lines.

A "mix" of each cement was prepared by incorporating .25 gm. powder into .5 cc. liquid over a period of 1.5 minutes and on each labial surface one drop of each "cement" was placed.

The five teeth were placed on wax, covered and left for 7 days at 37 degrees centigrade. After 7 days the black copper and silicate cements were still sticky, but the phosphate cement mix had hardened to a fragile solid.

The "cements" and wax were removed and the teeth washed and dried. The surfaces under the "cements" were unaffected except for a slight loss of lustre under the silico-phosphate cement.

These observations were confirmed by viewing under the optical microscope (X16).

The powders of all three cements appeared to have a strong buffering action when mixed with their respective liquid, even when the "cement mix" was too thin to set.

Experiment v.

Seven carious upper molars having at least one broad surface free of defects were selected. The chosen enamel surface was partitioned into three sections with Y lines of sticky wax.

A mix of each of the three cements was prepared with a powder/liquid ratio of .64gm/.5cc. The mixing time was 1.5 minutes.

A drop of each mix was placed in an appropriate division on each tooth, the teeth mounted and placed immediately in a room at 37 degrees centigrade.

After 72 hours the cement and wax were removed, and the teeth washed and dried.

Neither with the naked eye nor the optical microscope was any loss of lustre noticed under any cement.

Thus at magnification of 16 there was no evidence of enamel etching using mixes of cement as thin as .64 gm/.5cc.

Experiment vi.

Twenty one carious upper lateral incisors with microscopically (X16) perfect labial surfaces were selected. All cavities were filled with wax and accurately fitting orthodontic bands fabricated from .003X.125 inch stainless steel band material.

The teeth were divided into three groups and bands in each group were cemented with a mix of one of the three cements being considered. The powder/liquid ratio was .64 gm/.5cc and the mixing time was 1.5 minutes.

Immediately after cementation the banded teeth were placed on one of three strips of marked wax, placed in a room at 37 degrees centigrade and left for 72 hours.

Prior to the removal of the bands a thin line on the enamel surface was made just above and below the band with a fine diamond point.

The bands were then removed from the teeth, the cement washed away with brush and water and the teeth dried.

No evidence of enamel etching was found when the area of enamel that was beneath all bands was viewed under the microscope (X16). All 21 teeth were then sectioned transversely at the cervical margin and the crowns embedded in resin in such a manner that longitudinal sections of the crowns could be made in a labio - lingual direction.

Four sections of each tooth were then made using the Gillings-Hamco machine. The resin was removed from around the section and the specimen cleaned in solvent. Each section had a thickness of two hundred microns.

Only 75 per cent of sections remained at this stage and these were viewed in distilled water under the polarizing microscope (X25).

No evidence of any mineral loss from the enamel was observed. (Figs. 2, 4, 6).

The three ground sections photographed under the polarizing microscope were then placed side by side in the centre of the emulsion-surface of a radiographic slide (Agfa-Gevaert, Scientia Platen). The long axis of each section was parallel to the long axis of the slide (3 inches x 1 inch) and the section held by tape at the upper and lower border.

The slide was then taken to the X-ray diffraction generator (Phillips PW 1008) and mounted at a focus-object distance of 12 inches. Exposure was for 12 minutes using 25 milliamperes and 35 kilovolts.

The tape and sections were then removed from the slide, and the slide developed, washed and dried. The radiograph of each section was viewed and photographed under the microscope (X 25).

Figures 3, 5, 7, confirm that these very thin mixes of cement had no effect on the tooth enamel, even in thin films under orthodontic bands.



Fig. 2. Ground section of tooth enamel that was beneath zinc phosphate cemented band seen under polarized light. (.64gm/.5cc)

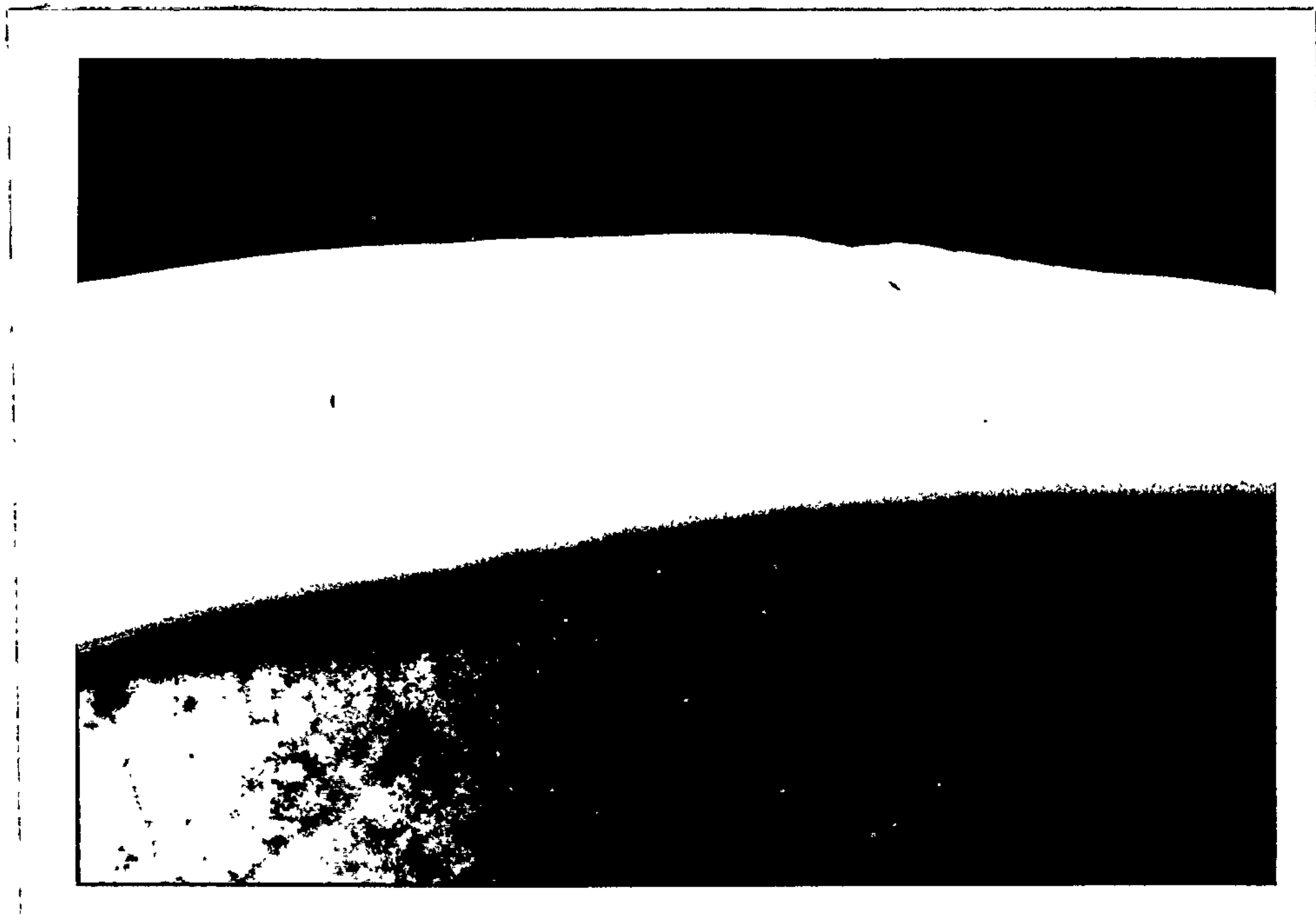


Fig. 3. Micro-radiograph of enamel seen in fig. 2.

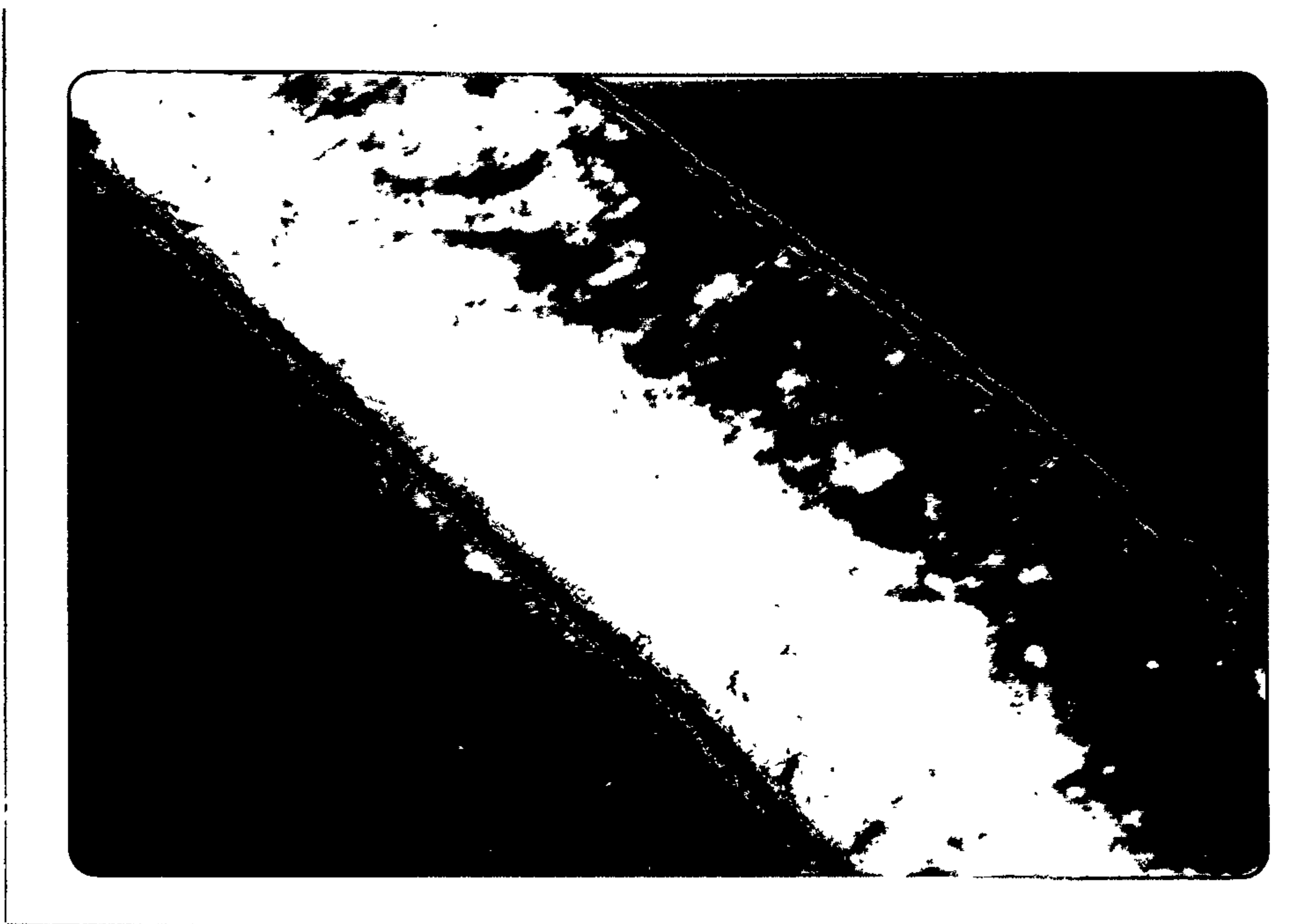


Fig. 4. Ground section of tooth enamel that was beneath black copper cemented band seen under polarized light. (.64gm/.5cc)

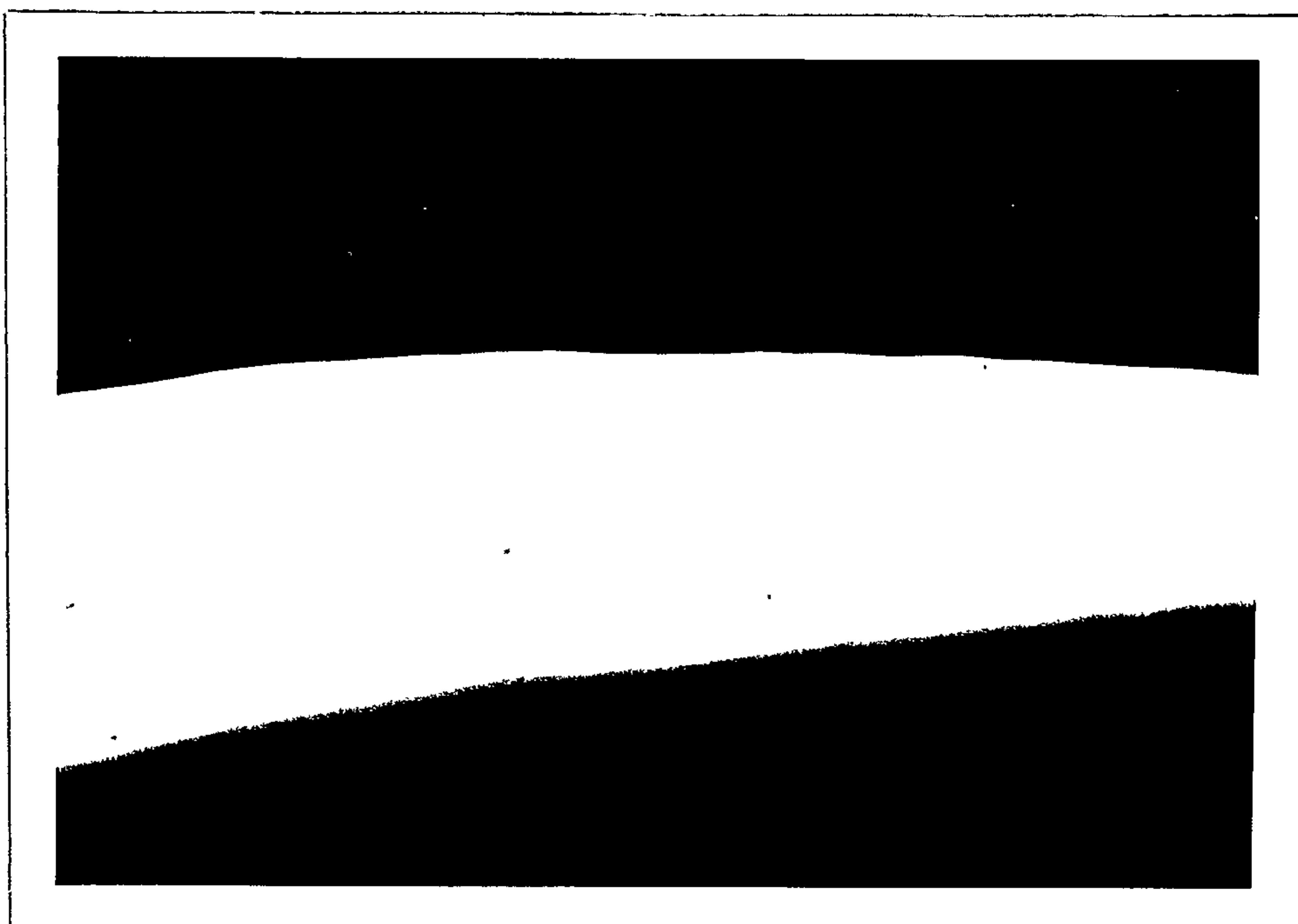


Fig. 5. Micro - radiograph of enamel seen in Fig. 4.

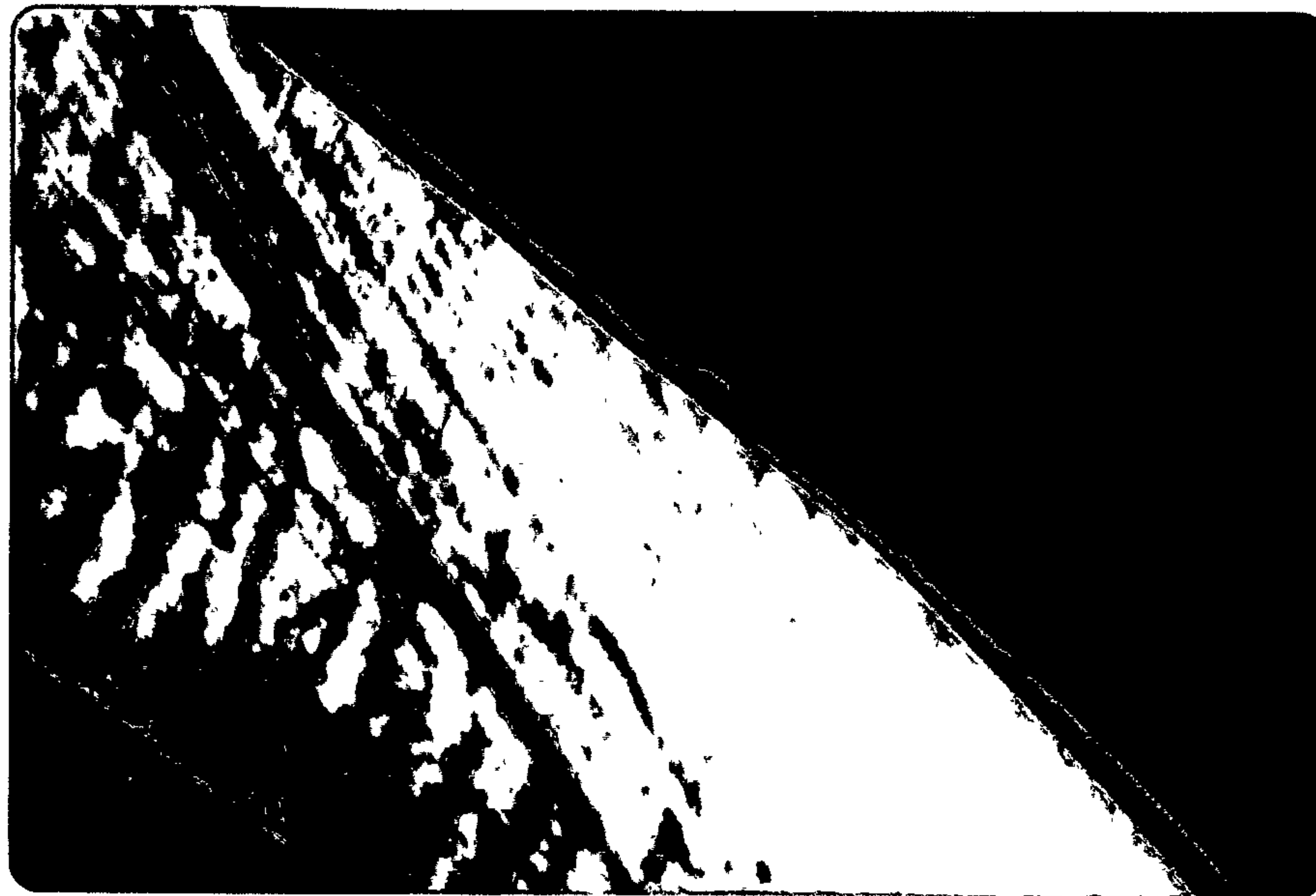


Fig. 6. Ground section of tooth enamel that was beneath silico - phosphate cemented band seen under polarized light. (.64gm/.5cc)

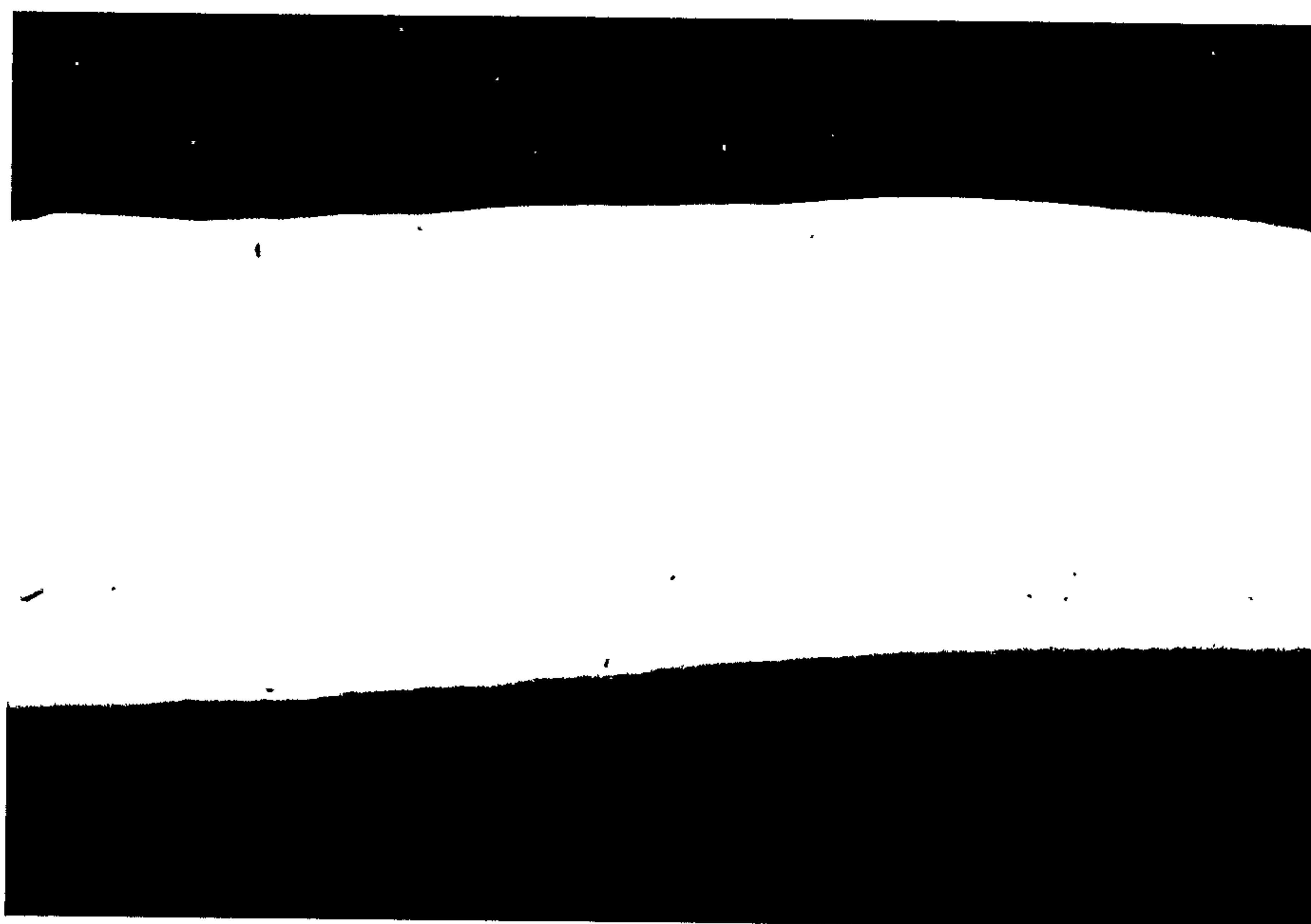


Fig. 7. Micro - radiograph of enamel seen in Fig. 6.

2. Cement Working Time.

From the moment of introducing the first powder particles to the cement liquid until the point in time beyond which the setting cement on the mixing slab could not be satisfactorily placed as a lining inside the band was regarded as the working time.

Preliminary tests showed that a round plastic rod about one centimeter in diameter, rounded and highly polished at one end, could be used advantageously in a manner similar to its usage in the testing of setting alginate impression materials.

Firstly thin mixes of cement were tested i.e. .64gm powder/.5cc liquid for zinc phosphate cement, black copper cement and silico - phosphate cement.

Then standard mixes of cement were tested - proportions as recommended by the manufacturer. These were;

zinc phosphate cement - 1.3gm/.5cc.

black copper cement - 1.1gm/.5cc.

silico - phosphate cement - 1.5gm/.4cc.

The mixing of the cements was standardized in the following way. The room temperature was maintained at 21 degrees centigrade and the mixing slab (three inches square) and spatula (stainless steel) were always cooled under tap water before mixing. The powder was weighed out to the nearest centigram and the liquid dispensed from a pipette measuring to one-tenth cubic centimetre.

The rate of incorporating powder into liquid was

found to be most critical and the rate and mode of spatulation had to be consistent if consistent mixes were to be obtained. For this purpose a stop - clock with second hand was utilized.

For zinc phosphate and black copper cements the powder was divided into three equal fourths and two eighths. When the clock was started one eighth part of powder was drawn into the liquid, the next eighth at 15 seconds, one quarter at 30 seconds, the next at 45 seconds and the last at 60 seconds, the whole mixing being completed at 90 seconds.

With the silico - phosphate cement the powder was divided into one half and two quarters. At the start of mixing one half the powder was added to the liquid, one quarter at 15 seconds, the remaining powder at 30 seconds, and the mixing completed at 60 seconds.

As soon as each mix was completed the mixed cement was allowed to flow onto a clean glass slide where a dome - shaped mass was formed. The rounded end of the plastic rod was then lowered lightly onto the cement, when initially some of the cement came away on the end of the rod. As the cement continued to harden, the polished end of the rod could leave an impression in the cement, but this would not remain for long. The rod was applied at 30 second intervals and when the spherical indentation would remain, with well - defined margins, for 30 seconds the working time of that cement was considered to have expired. Examination of cement consistencies at that stage confirmed that at about that point in hardening, cements could be considered no longer suitable for band cementation.

Three tests were performed with the zinc phosphate and black copper cements but only two with the silico - phosphate cement, as further studies were required from the same batches.

The results are tabulated in Table 2.

TABLE 2

Working Time of Dental Cements in Minutes

Cement	Consi- stency	Test 1.	Test 2.	Test 3.	Average
Zinc Phosphate Cement	Thin	21.5	22	22	22
	Stand	5	5	5	5
Black Copper Cement	Thin	52	51.5	52.5	52
	Stand.	13.5	14	14	14
Silico- Phosphate Cement	Thin	30.5	31		31
	Stand.	4.5	4.5		4.5

3. Cement Setting Time.

All powders and liquids used in testing cement setting time were from the same bottles used in the working time tests. The same standardized mixing technique was again employed, and while the thin and standard mix proportions were the same, double quantities were required.

When the mixing was completed within the appropriate number of seconds the cement was poured into a copper ring standing at 21 degrees centigrade on a glass slide. The ring was .25 inches high and .5 inches outside diameter, the metal thickness being .0625 inch. Excess material was removed from above the border of the ring thus leaving a flattened surface. Three minutes after starting the mix the cement - filled ring and slide were removed to an atmosphere of 100 per cent relative humidity at 37 degrees centigrade. A standard Gillmore needle was then carefully lowered vertically at half minute intervals onto the cement surface and allowed to rest under its own weight. When the needle failed to make a perceptible indentation on the cement surface, the cement was considered to be set, and the setting time was taken as the time that had passed from the commencement of mixing up until that point.

Three readings were taken for thin and standard mixes of zinc phosphate and black copper cements but only two were possible for the silico - phosphate cement, the limitation being brought about by the low density of the contents of the silico - phosphate cement powder bottles.

The results are tabulated in Table 3.

TABLE 3

Setting Time of Dental Cements in Minutes

Cement	Consistency	Test 1.	Test 2.	Test 3.	Average
Zinc Phosphate Cement	Thin	15.5	15.5	16	16
	Stand.	6	6	6	6
Black Copper Cement	Thin	65	66	62	64
	Stand.	12.5	13	13	13
Silico - Phosphate Cement	Thin	20	20		20
	Stand.	3	3		3

TABLE 4

Comparisons of Cement Working Time and Setting Time in Minutes.

Cement	Consistency	Working Time	Setting Time
Zinc Phosphate Cement	Thin	22	26
	Stand	5	6
Black Copper Cement	Thin	52	64
	Stand	14	13
Silico- Phosphate Cement	Thin	31	20
	Stand	4.5	3

4. Cement Solubility.

The solubility of a zinc phosphate cement, a black copper cement and a silico - phosphate cement was tested in distilled water and a .001 M solution of lactic acid. The pH of the lactic acid was established at 4 by titration with a .2N solution of sodium hydroxide.

For each cement two consistencies were used, a thin mix and a standard mix, each having the same powder/liquid ratio as that used in the setting time tests.

New bottles of powder and liquid were obtained and their contents used for both solubility tests. Because of the low density of the silico - phosphate powder, a new bottle of powder and a new bottle of liquid were required for the second test.

Room temperature was maintained at 21 degrees ~~centigrade~~ and the mixing technique was standardized in the same manner as the cement mixing in the setting time tests.

Stainless steel ligature wires were then selected and weighed individually. Consistently the weight for a ligature wire was found to be .090 gm, for approximately 100 wires were weighed and only a few had to be discarded.

A clean glass slide was placed upon a bronze disc .80 inches in diameter. When the cement was mixed it was poured into a glass tube bearing a metal plunger and by this means approximately .5 cc of mixed cement could be placed on the metal disc. A looped ligature wire was then embedded in the cement and a clean glass slide placed on top. By gentle pressure the cement mass was flattened into a circular disc just covering the bronze disc.

Three minutes after the commencement of mixing the glass plates and the cement were placed for one hour in an atmosphere having a relative humidity of 100 per cent at 37 degrees centigrade.

Five tests were carried out with each mix in each solvent, but only four for the silico - phosphate cements as it was desirable that all cements tested for the one solvent came from the same batch.

After one hour the cement specimens were withdrawn from the humidor, removed from the glass slides and placed on a clean sheet of paper. Fine sand - paper was then used to trim away all feathered margins at the circumference of the discs, a smooth border remaining.

At this stage fragments of varying size were accidentally broken off the main body of the disc, the difference between the strength of discs made from thin and standard cement mixes being very obvious.

After 15 minutes on the sheet of paper the discs were considered to be at room temperature. They were then dried with compressed air and weighed to the nearest milligram.

Into a clean glass beaker 50 ccs of the solvent were then poured and the five discs lowered into the solution by means of ligating the wires to a brass rod which rested across the top of the beaker. The position of each disc was recorded by its sequence number on the rod and by the number of knots around the rod.

The beaker containing the fully submerged cement discs was then placed in an atmosphere of 100 per cent

relative humidity at 37 degrees centigrade for 23 hours. After this period the discs were removed and placed on a clean sheet of paper for 15 minutes. Each specimen was then dried with compressed air and weighed again.

All solvents were perfectly clear after removing the discs.

In both solvents the standard mix of silico-phosphate cement actually increased in weight during the solubility test.

The solubility was calculated to the nearest .1 per cent from the following formula;

$$\% \text{ Solubility} = \frac{\text{Weight Loss}}{\text{Original Weight less Wire}} \times \frac{100}{1}$$

The results appear in Tables 5 - 10.



TABLE 5

Solubility of zinc phosphate cement in distilled water.

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.244	1.242	.002	1.154	.2
2	1.127	1.126	.001	1.037	.1
3	1.611	1.608	.003	1.521	.2
4	1.512	1.510	.002	1.422	.1
5	1.430	1.428	.002	1.340	.2
Solubility Mean			.2	S.D.	.07

Powder/liquid = 1.3gm / .5cc

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.005	.986	.019	.915	2.1
2	.980	.958	.022	.890	2.5
3	.980	.960	.020	.890	2.2
4	1.074	1.053	.021	.984	2.1
5	1.059	1.038	.021	.969	2.2
Solubility Mean			2.2	S.D.	.17

Powder/liquid = .64 gm / .5cc

TABLE 6

Solubility of Black Copper Cement in Distilled Water

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.375	1.371	.004	1.285	.3
2	1.470	1.466	.004	1.380	.3
3	1.419	1.416	.003	1.329	.2
4	1.432	1.428	.004	1.342	.3
5	1.470	1.466	.004	1.380	.3
Solubility Mean			.3	S.D.	.05

Powder/Liquid = 1.1 gm/.5cc

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.123	1.100	.023	1.033	2.2
2	1.123	1.098	.025	1.033	2.4
3	1.103	1.078	.025	1.013	2.5
4	1.119	1.096	.023	1.029	2.2
5	.859	.840	.019	.769	2.5
Solubility Mean			2.4	S.D.	.16

Powder/Liquid = .64 gm/.5cc

TABLE 7

Solubility of Silico-Phosphate Cement in Distilled Water

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	2.562	2.584	-.022	2.472	-.9
2	2.760	2.786	-.026	2.670	-1.0
3	2.488	2.510	-.022	2.398	-.9
4	2.374	2.394	-.020	2.284	-.9
5	-	-	-	-	-
Solubility Mean			-.9	S.D.	.06

Powder/Liquid = 1.5 gm/.4cc

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.008	.958	.050	.918	5.4
2	1.076	1.020	.056	.986	5.8
3	.956	.906	.050	.866	5.8
4	.870	.830	.040	.780	5.0
5	-	-	-	-	-
Solubility Mean			5.5	S.D.	.38

Powder/Liquid = .64 gm/.5cc

TABLE 8

Solubility of Silico-Phosphate Cement in Lactic Acid

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	2.326	2.346	-.020	2.236	-.9
2	2.750	2.778	-.028	2.660	-.1.1
3	2.744	2.772	-.028	2.654	-.1.0
4	2.458	2.481	-.023	2.368	-.1.0
5	-	-	-	-	-
Solubility Mean			-1.0	S.D.	.08

Powder/Liquid = 1.5 gm/.4cc

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.006	.972	.934	.916	3.7
2	.940	.908	.032	.850	3.8
3	1.068	1.032	.036	.978	3.7
4	1.029	.997	.032	.939	3.4
5	-	-	-	-	-
Solubility Mean			3.7	S.D.	.18

Powder/Liquid = .64 gm /.5cc

TABLE 9

Solubility of Zinc Phosphate Cement in Lactic Acid

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.610	1.590	.020	1.520	1.3
2	1.678	1.654	.024	1.588	1.5
3	1.630	1.604	.026	1.540	1.7
4	1.628	1.600	.028	1.538	1.8
5	1.578	1.552	.026	1.488	1.7
Solubility Mean			1.6	S.D.	.20

Powder/Liquid = 1.3 gm/.5cc

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.152	1.104	.048	1.062	4.5
2	1.096	1.052	.044	1.006	4.5
3	1.174	1.128	.046	1.084	4.2
4	1.120	1.072	.048	1.030	4.7
5	.998	.960	.038	.908	4.2
Solubility Mean			4.4	S.D.	.22

Powder/Liquid = .64 gm/.5cc

TABLE 10

Solubility of Black Copper Cement in Lactic Acid

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.415	1.398	.017	1.325	1.3
2	1.473	1.456	.017	1.385	1.2
3	1.460	1.444	.016	1.370	1.2
4	1.390	1.376	.014	1.300	1.1
5	.781	.773	.008	.691	1.2
Solubility Mean			1.2	S.D.	.071

$$\text{Powder/Liquid} = 1.1 \text{ gm} / .5\text{cc}$$

Test	Weight Before	Weight After	Weight Loss	Corrected Weight	Solubility Per Cent
1	1.122	1.072	.050	1.032	4.8
2	1.180	1.128	.052	1.090	4.8
3	.854	.820	.034	.764	4.5
4	1.022	.976	.046	.932	4.9
5	1.048	.998	.050	.958	4.8
Solubility Mean			4.8	S.D.	.16

$$\text{Powder/Liquid} = .64 \text{ gm} / .5\text{cc}$$

Statistical Analysis.

The variables involved in the solubility tests were the solutions, cements and powder/liquid ratios.

The prime consideration in this study is to simply establish whether there is any statistically significant difference between thin and standard cement mixes, in terms of percentage solubility. Let u_1 , u_2 and S_1 , S_2 be the respective means and standard deviations for the percentage solubilities of the standard and thin mix samples. Values for each data set are presented below:

<u>Data Set.</u>	<u>u_1</u>	<u>u_2</u>	<u>S_1</u>	<u>S_2</u>
A 1	.2	2.2	.07	.17
A 2	.3	2.4	.05	.16
A3	.9	5.5	.06	.38
B 1	1.0	3.7	.08	.18
B 2	1.6	4.4	.20	.22
B 3	1.2	4.8	.071	.16

A1, A2 and A3 indicate data obtained from solubility tests in distilled water.

B1, B2 and B3 indicate data obtained from solubility tests in lactic acid.

An inspection of these results suggests that there is a significant difference between the two mixes.

However, each data set (the sample) consists of only four or five readings. Because it is desired to make an inference about the whole population of readings which could have been performed in the study, it is correct

to apply a suitable test of significance.

Choice of Statistical Test.

It would be appropriate to apply the Student's 't' test to this data, having first checked by the Variance Ratio 'F' test that the data may be assumed to have been drawn from the same 'population'.

However the non-parametric ('distribution-free') equivalent of the 't' test, the Mann-Whitney U test (Siegel, 1956) is perhaps the most suitable test to apply to the data of this experiment.

This tests whether two independent groups have been drawn from the same population. That is, it is tested whether any two samples are statistically different from one-another.

The Mann-Whitney test (Siegel, 1956) avoids the assumptions which are required to be made when using the 't' test concerning population distribution. Applied to the present data, the U test also avoids much unnecessary computation.

The Mann - Whitney U Test - Method and Results.

The test is applied to the two samples of any given data - set. For each data set the method is similar, so that results for one data set only need be presented. Results for each data set having the same number of replications in each sample are identical.

Consider set B2 (Table 9). The standard and thin mix samples each have 5 replications. Let the standard and thin mix solubilities be denoted by X and Y respectively.

The null hypothesis is made that the standard and thin mix solubilities have the same distribution (ie., we hypothesise there is no difference between the samples).

The observations from set B2 are combined and ranked in order of increasing size as shown:

Value	1.3	1.5	1.7	1.7	1.8	4.2	4.2	4.5	4.5	4.7
Sample	X	X	X	X	X	Y	Y	Y	Y	Y

The value of the Statistic 'U' is calculated, in this case, by the sum of the number of Y values which precede each X value.

$$\text{Thus } U = 0+0+0+0+0 = 0$$

Note: If we had counted the number of X values which precede each Y value, we would find.

$$U = 5+5+5+5+5 = 25$$

Consulting the appropriate Table of Probabilities associated with each sample, we see that $U = 25$ does not appear. This means we have focussed on the wrong sample group in determining U. We therefore denote the observed value as $U' = 25$ and transformed by:

$$U = n_1 n_2 \quad \text{---} \quad U' = 5 \times 5 - 25 \\ = 0$$

as determined previously

($n_1 = n_2 = 5$ = sample size here)

For a value of $U = 0$, it is seen from the tables that the probability of occurrence under the null hypothesis is .004. A satisfactory significance level is .05. The null hypothesis is therefore rejected. That is,

it may be assumed with statistical certainty that the thin and standard mixes are different. There is only a 0.4% chance that our decision is incorrect.

This result also applies to data sets A1, A2 and B3.

Similarly we find for data sets A3 and B1 that there is a significant difference between the two mixes. In this instance ($n_1 = n_2 = 4$ = sample size) the probability of our decision being wrong is only .014.

The overall conclusion is that thin and standard mixes gave significantly different percentage solubilities in every case.

Discussion.

During this study an opinion poll was conducted among ten Sydney orthodontic specialists, each of whom answered the following three questions:

- Q. 1. From clinical experience what complaints, if any, would you make about dental cements?
- Q. 2. Are you looking forward to the arrival of bonded brackets?
- Q. 3. If so, why?

Some of these answers will be discussed and related to the findings during this enquiry into enamel demineralization.

A. Answers to Q. 1.

Six of the ten orthodontists were "quite happy" with dental cements with minor reservations, which are reflected in the following emphatic replies:

- 1. "Mixed too thin, it etches the enamel surface".

The etching of the enamel surface by cement liquids alone has been observed during this investigation, and the effect was quite marked. However, the addition of .25gm of cement powder to .5cc liquid neutralized the phosphoric acid, for after seven days (when two of the three "cement mixes" were still liquid) the enamel surface was unaffected, except for a faint loss of lustre when the silico - phosphate cement was employed. The consistencies of cement obtained with P/L ratio of .64gm / .5cc have not been observed clinically but were selected as minimum P/L ratios based on the results of a survey

reported in the literature (Savignac,1965). Such cement mixes must be called "too thin" (relative to the manufacturer's recommendation), but these consistencies were employed to cement accurately fitted orthodontic stainless steel bands to enamel surfaces.

When the bands were removed the enamel surfaces were observed under the optical microscope. The teeth were sectioned and the sections viewed under polarized light. Soft - X-rays were then taken of sections and viewed under the microscope. Not one enamel surface, during any of the above three examinations, showed any evidence of demineralization.

The consistencies referred to endanger the enamel surface, but for reasons other than any power to etch enamel.

2. "The adhesion could be better and the setting time longer".

There is no adhesion between dental cements and enamel or metal surfaces, yet other orthodontists offered a different explanation for loose bands.

"Setting time" of cement on the mixing slab has been referred to as working time in this study, and it is this time in which band cementation is still possible with the available cement mix that concerns orthodontists. Methods of lengthening working time invariably affect the physical properties of cements adversely. The most frequently used method of increasing the working time of any cement is to decrease the powder/liquid ratio. On the other hand orthodontists want the cement under bands to set quickly once they are positioned on the teeth, and decreasing the powder/liquid ratio increases the

setting time of the cement. There is thus the possibility of dismissing the patient with setting cement exposed to saliva.

From the study of setting time and working time of cements in this work, two facts emerge:

- i. It is possible to mix cement at very thin consistencies, which allow more than twenty minutes for band - cementation, and these cements will still set in the mouth.
- ii. Using cements mixed in accordance with the manufacturer's recommendations there was evidence of a correlation between the working time and setting time of any one cement. When the cement was of no further use for cementation, it had almost set under the band. With thin mixes of cement there was no useful relation between working time and setting time.

As recommended in the literature, a standardized mix of cement should be used on all occasions, and the orthodontist must accept the limit to the number of bands he can cement because of this.

3. "It disintegrates and washes out-but that might be my fault".

All the orthodontists had reservations about the solubility of cements, but thought this could be reduced with care. Two of them, however, had repeatedly noticed that their problems of loose bands always occurred in mouths where the standard of oral hygiene was low.

The marked increase in solubility of all three cements when mixed at low P/L ratio was recorded in both

solvents, distilled water and lactic acid. The silico - phosphate cement was less soluble than the zinc phosphate and black copper cements in lactic acid. The build up of plaque in mouths where oral hygiene is poor, and the associated decrease in pH value must directly endanger exposed cement surfaces, the degree of dissolution being influenced by the P/L ratio used in mixing the cement. This degree of cement solubility could then be related to the length of working time or setting time. If the greatest insolubility of any given cement is with a P/L ratio which also provides a working time of four minutes, it is doubtful whether, at time of full - banding, orthodontists always dispense for the patient the most insoluble cement at their disposal.

B. Answers to Q.2.

Eight of the ten specialists interviewed were emphatic in their declared wish to attach the orthodontic bracket directly to the tooth surface. One of them said he would regret the disappearance of the band because "he just happened to like fitting bands". Another said he would need to be satisfied that there was no ensuing increase in the patients caries rate.

C. Answers to Q. 3.

The advantages expected from the availability of bonded brackets were given as:

1. "Time saving - no cementing and no band - fitting".

All orthodontists were in agreement on this remark, yet no reference has been found to support this hope. The acid - conditioning of enamel surfaces in the mouth could prove to be a procedure requiring both time and care. The attachment of lingual and palatal auxiliaries would be individual procedures and their correct positioning rendered suspect. There would be no opportunity to fit attachments in the patient's absence and calculate the degree of tooth - movement required with the aid of models. Moreover, the setting-time of adhesives used to date could well make the whole procedure of fixing brackets to enamel directly too time - consuming.

2. "They will cover less tooth structure."

It is difficult to see how this reduced amount of tooth coverage can be regarded as an advantage. In the presence of archwires, coil springs and loops, the toothbrush cannot be employed with greatest efficiency and the opportunity for plaque formation must be increased. This is particularly significant in the interproximal regions which are fully exposed when bonded brackets are employed. All contact points are protected by the orthodontic band and a case might well be made for the orthodontic band in so far as it could possibly reduce the number of new interproximal cavities when compared with a control population of the same age group.

Many orthodontists believe the most protected part of a tooth during orthodontic treatment is that under the band.

3. "It will offer esthetic improvement".

The complete coverage of the tooth labial surface has been advocated, and irrespective of area covered, bonded brackets will be an improvement upon metal bands esthetically, during treatment.

Any complete coverage of labial surfaces must present gingival problems similar to these observed around ill - fitting crowns and interproximal restorations. The necessary acid - etching of the enamel surface, the physio-chemical nature of the enamel - adhesive union, and the difficulty of bracket removal could well leave the enamel in a condition where any esthetic advantage of bonded brackets could be challenged.

A brighter future for attaching adhesives directly to enamel surfaces could rest in the field of prophylactic dentistry where enamel etching and molecular linkage are still preferable to dental caries.

Summary.

The role of phosphoric acid and dental caries has been considered in the formation of areas of demineralization during orthodontic therapy. The formations of sites favourable to the progress of caries have been considered on the one hand, and the chemical and dynamic action of acid cement liquids with tooth enamel on the other.

The future possibility of reducing the incidence of these white spots by utilizing bonded brackets has been examined.

Possible methods of prevention, and the remineralization of affected areas have been analysed.

Using the optical microscope, polarizing microscope and soft X-ray techniques, enamel surfaces which were exposed to dental cements were studied.

A comparison was made between thin and standard mixes of three dental cements. Properties considered were working time, setting time, and solubility in two solvents, distilled water and lactic acid.

The results of the study were discussed in conjunction with the findings of a poll of orthodontic opinion on the clinical behavior of cement.

Conclusion.

From the literature and the original investigation in this study the following conclusions have been drawn:

1. The human tooth enamel has a defensive barrier in the form of an unaffected outer enamel surface.
- 2. Prior to band cementation, multiple fluoride therapy would rehardened any affected enamel surface and render the dentition more resistant to acid attack and dental caries.
- 3. Where the enamel surface is unaffected or rehardened the etching of enamel due to clinical mixes of dental cement is negligible.
4. Uniform consistency of the cement film is enhanced by using low cementation pressure of short duration.
5. The working time of any dental cement is determined by the manufacturer's recommended P/L ratio, and the maximum number of bands that can be cemented from any one cement mix should be determined by circumstances other than cement consistency.
- 6. The dissolution of thin mixes of cement from under orthodontic bands is very probable and depending on the cement used, could be even greater in mouths where the standard of oral hygiene is low.
- 7. Areas of demineralization should be considered as a caries problem and emphasis placed on the physical properties of cement, oral hygiene

instruction, diet control and a general awareness of the problem involved.

8. The application of any remineralizing solution following the removal of orthodontic bands should be an integral part of the overall treatment.
9. Improvements in composition, physical properties and manipulation technique of dental cement could precede the displacement of orthodontic bands by the bonded bracket.

Footnote.

A comparative analysis of the commercial dental cements available, relative to their working time, setting time and solubility in organic acid, could indicate the most suitable cements for orthodontic purposes. Only cement mixes using P/L ratios and techniques recommended by the manufacturers would be worthy of examination.

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