A comparison of in vitro shear bond strengths of orthodontic bonding units following use of a conventional acid-etch, and a crystal-forming enamel modifier.

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To clarify terms used within this thesis, a few definitions are presented:

Shearing force - the force acting on a member in such a manner that it tends to cause the member to separate along a plane parallel to the applied force. (Bruch, 1978)

Shearing stress (shear) - the internal resisting force opposing the shearing force. (Bruch, 1978)

Shear strength - the ultimate shearing stress (Bruch, 1978)

Orthodontic bonding unit - a unit comprising an orthodontic bonding attachment, bonding adhesive, and enamel surface to the depth of adhesive penetration.

A new surface modifying (conditioning) agent, used to effect orthodontic adhesive bonding to enamel, has recently become available under the trade mark Crystal-Lok[#].

Promotional literature of this agent (Am. J. Orthod., October, 1983) claimed many advantages over conventional phosphoric acid modifying agents. These included:

1) less enamel damage because

a) bonding is facilitated by crystals which "project up from the enamel" instead of "radically etching enamel away".

b) brackets are more easily debonded;

2) lack of gingival irritation if contact with the crystal-forming solution occurs;

3) easier "clean up".

All these advantages with comparable tensile bond strength values.

Reported studies of Crystal-Lok (or its precursors) are few, with even fewer undertaken by independent researchers. An investigation involving Crystal-Lok, therefore seemed to be of potential value. Shear bond strengths created would be relevant since shearing forces are applied to bonded attachments during orthodontic treatment, especially in the incisal region - e.g. intrusive arches induce shearing force components on the brackets -, and since this agent is to replace phosphoric acid, a comparative study seemed appropriate. Thus, a comparative, in vitro study of the shear bond strengths of orthodontic bonding units created following enamel pretreatment with either 37 per cent w/w phosphoric acid solution[*] or Crystal-Lok, was undertaken. Sites of bond failure were also noted.

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A review of the literature enabled this author to gain from others' experience. This lead to avoidance of some previously encountered pitfalls, utilization of previous conceptions, and an understanding of the two systems to be studied. It established a base with which to compare.
The review included:

1) methods of shear testing;

2) a review of acid-etch technique
    - its mechanism of action and associated variables
    - differences in effect upon surface and subsurface enamel, e.g. acid-etch pattern formation (since subsurface human enamel was to be used in this study)
    - the extent and character of enamel damage;

3) a review of Crystal-Lok, its
    - development
    - mechanism of action
    - associated bond strengths compared with those associated with acid-etch
    - associated enamel effects
    - clinical usefulness.

The discussion relates the literature review and the study, and suggests further questions.

Chapter 1: Shear bond strength studies

Reynolds (1975) suggested that shearing forces need consideration when assessing bonded orthodontic attachments.

In vitro shearing forces have been created by using various apparatuses in a tension [1,2,3,4,5,6,7] or compression [8] mode. Hirce, Sather, and Chao (1980)[9] claimed torsion loading could also create shearing forces.

Various authors [1,2,4,5,6,7,8,9] have suggested their in vitro experimental methods tested shear bond strengths, when actually a combination of shear and other bond strengths were assessed because the enamel surface component was not flat. Tavas and Watt (1984) referred to this combination as the shear/peel strength. This may be visualised by considering a mathematical model for describing the force systems produced in the various 'shear' bond experiments reported:

Defintions

Shearing force - a force acting on a member in such a manner that it tends to cause the member to separate along a plane parallel to the applied force.

f_a - applied force

$f_{||}$ - a vector of f_a parallel to the surface at any given point, i.e. the Shearing force.

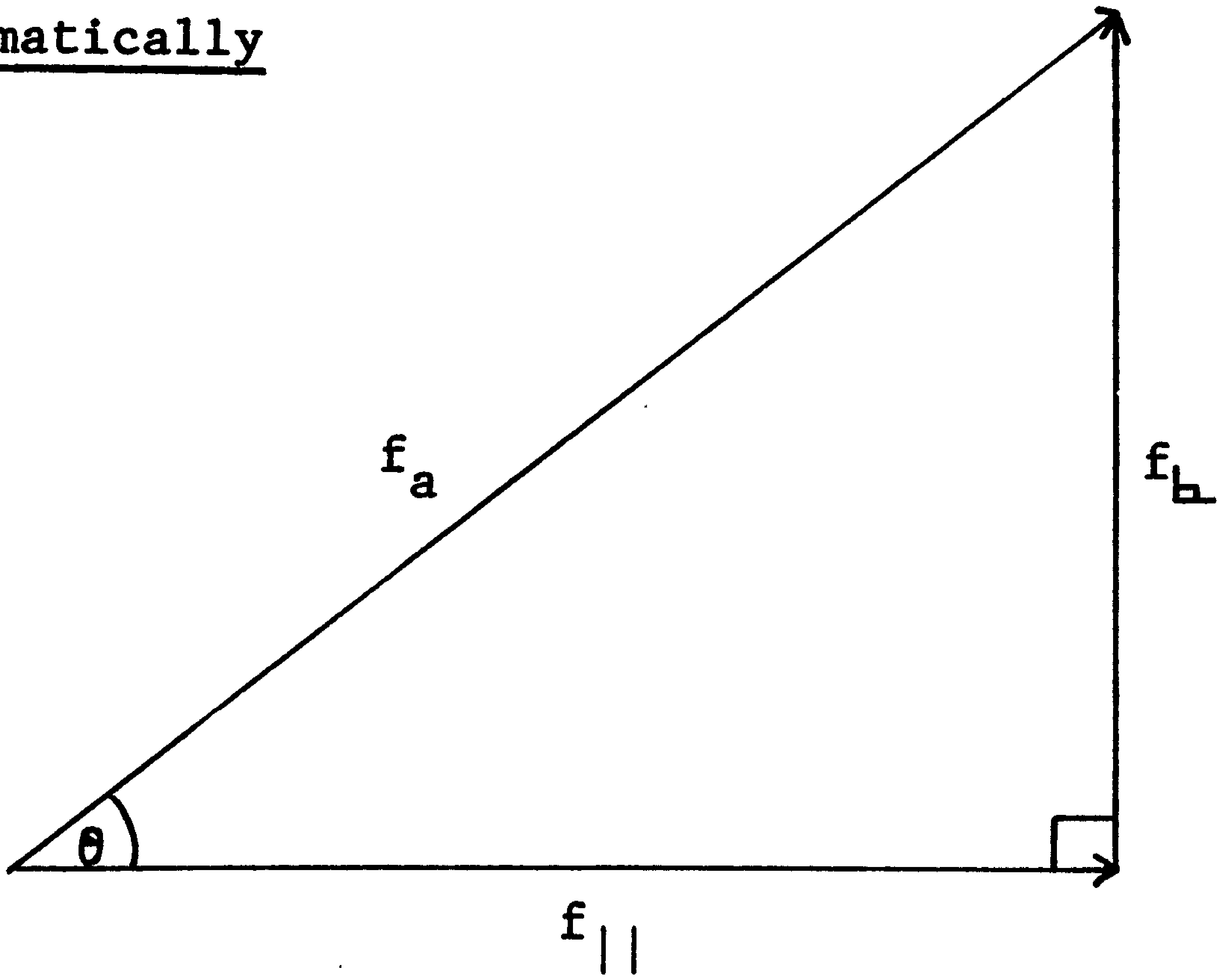
Note: For a curved surface $f_{||}$ will be tangent to that curve at any given point.

$f_{\perp}$ - a vector of f_a perpendicular to $f_{||}$ such that when summed with $f_{||}$, gives the resultant f_a.

θ - the angle between f_a and $f_{||}$

[1] Moin and Dogon (1978)
[2] Alexandre, Young, Sandrik, and Bowman (1981)
[3] Keizer, ten Cate, and Arends (1976)

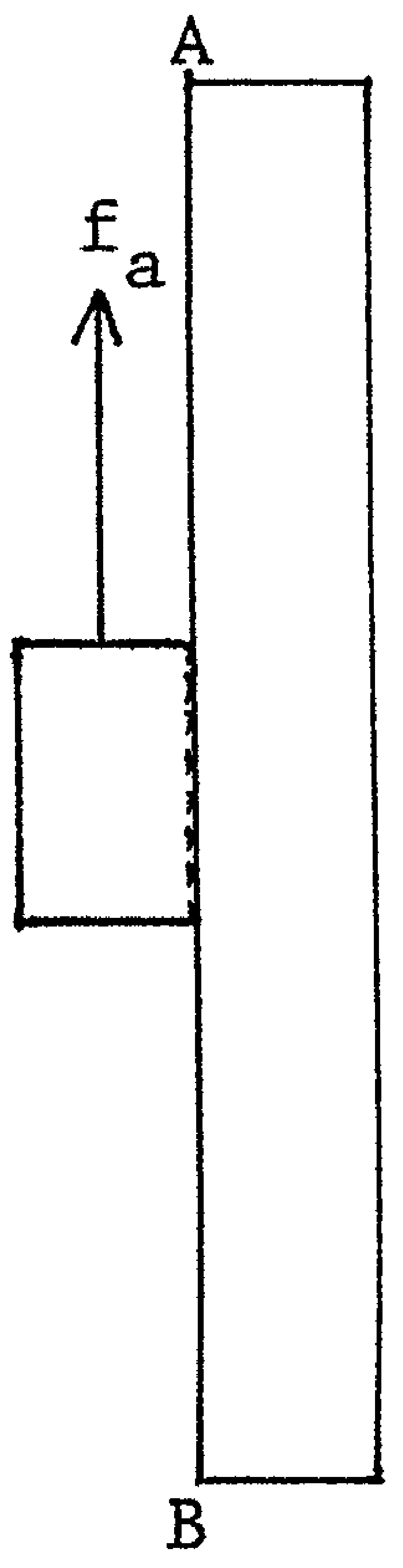
Diagramatically



$$f_{||} = f_a \cos$$

$$f_{\perp} = f_a \sin$$

4. Maijer, and Smith (1981)
5. Johnson, Hembree, and Weber (1976)
6. Lopez (1980)
7. Mascia, and Chen (1982)
8. Thanos, Munholland, and Caputo (1979)



$f_a \parallel \overline{AB}$

For a flat surface

When f_a is parallel to the surface, at any given point on that surface :

$$f_a = f \quad , \theta = 0 \; , f_\perp = 0.$$

$$\text{ie. } f_\parallel = f_a \cos\theta$$
$$= f_\parallel = f_a \cos 0^\circ ; \cos 0^\circ = 1$$
$$= f_\parallel = f_a$$

$$\text{and} \quad f_\perp = f_a \sin\theta$$
$$= f_\perp = f_a \sin 0^\circ ; \sin 0 = 0$$
$$= f_\perp = 0$$

For a non-flat surface

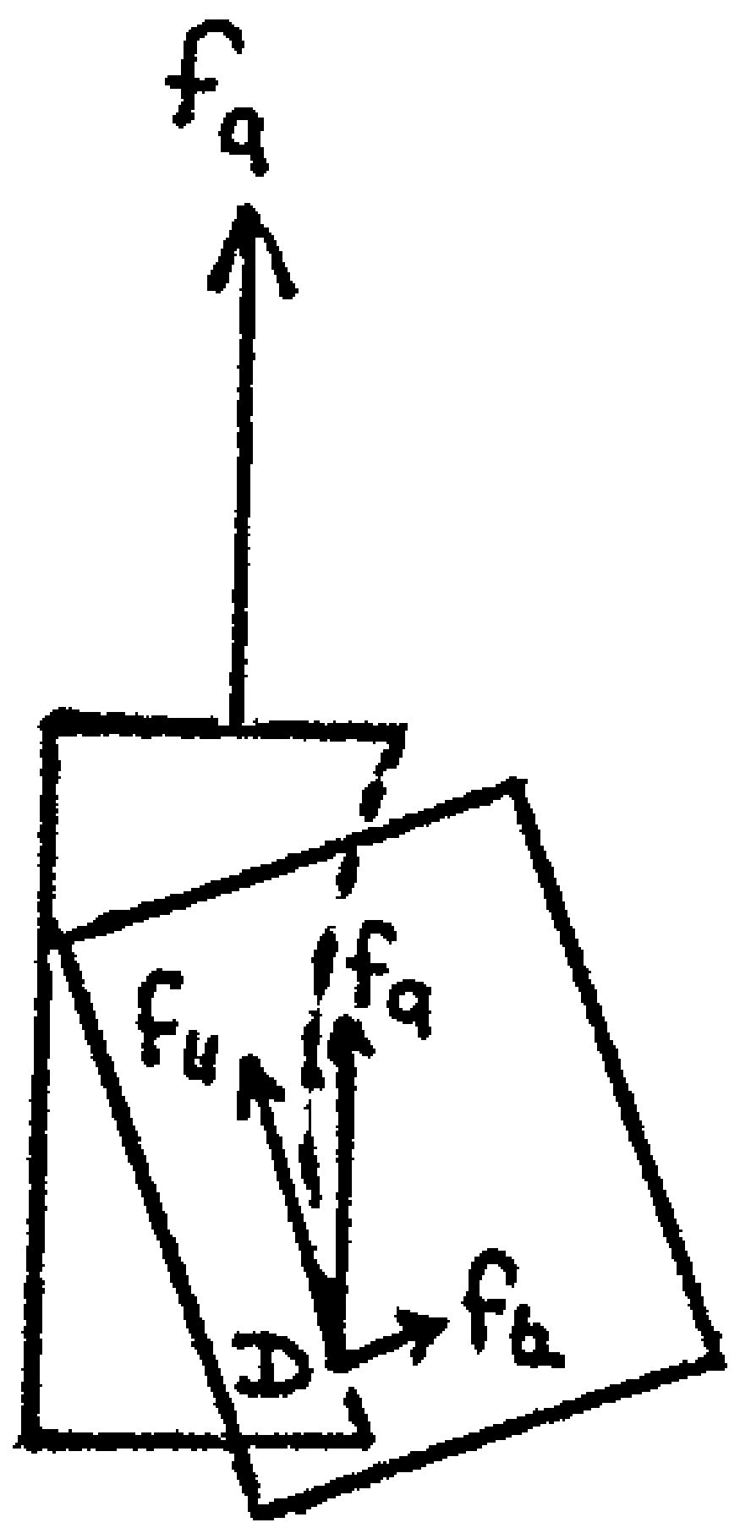
At any given point ,D, on that surface where

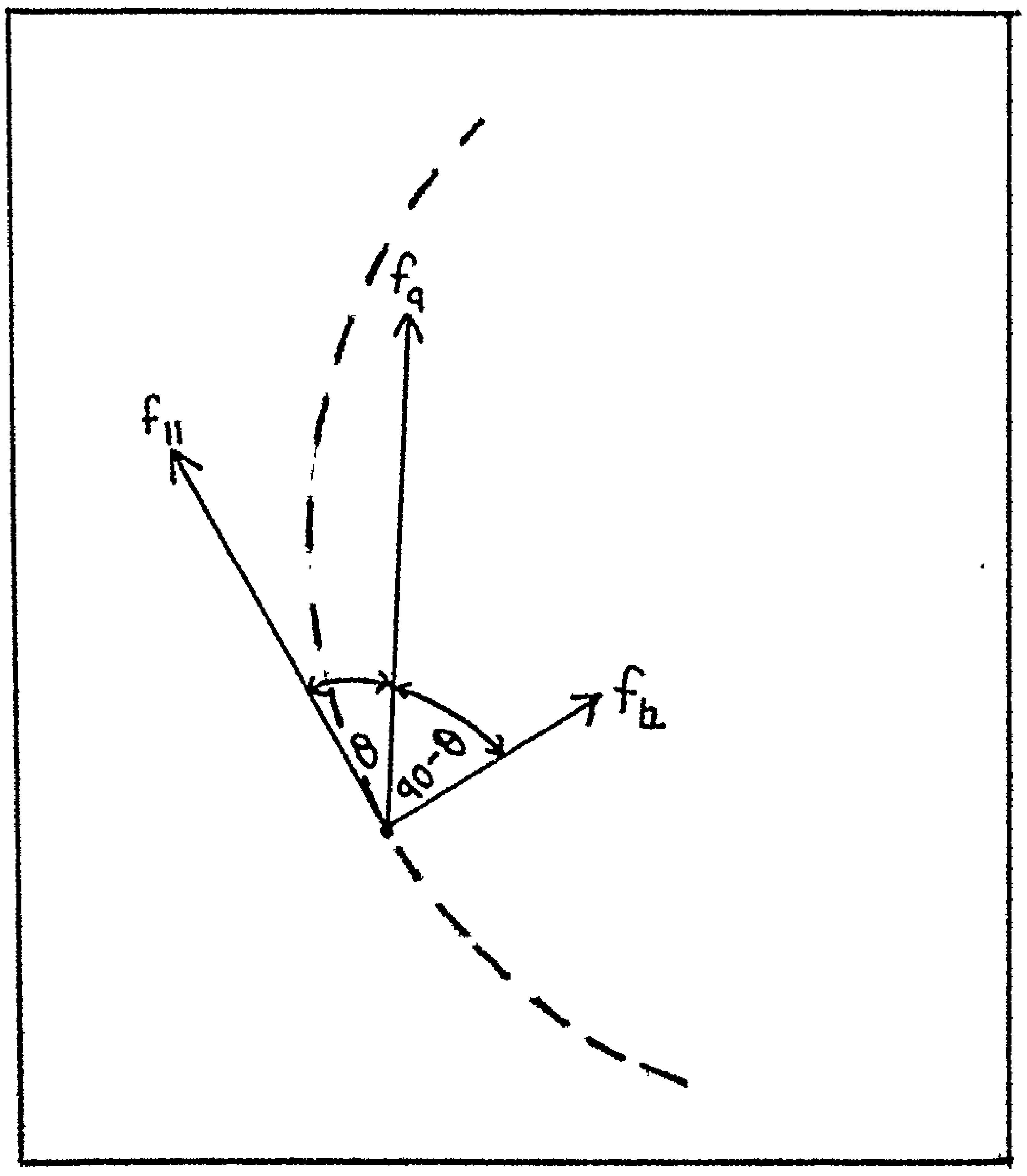
$\theta \neq 0^\circ$; $\cos 0<1$, and since $f_{||} = f_a \cos\theta$

$= f_{||} < f_a$

; $\sin\theta > 0$, and since $f_\perp = f_a \sin\theta$

$= f_\perp > 0$





Explanation

When applying unidirectional force to an orthodontic bonding unit, the shear bond strength will equal the applied force at the time of bond failure if the bonded surface is flat and parallel to the applied force. If the surface is other than flat, the shear bond strength at any given point on that surface will be defined by $f_{||} = f_a \cos \theta$.

For all values of θ, except were $\theta=0^{o}$, $f_{||} < f_a$. In addition, a force ($f_{\perp}$) perpendicular to the shearing force ($f_{||}$) will act, thus the applied force will be the sum of these two force vectors. This means that for other than flat surfaces, pure shear bond strengths will not be measured.

The various studies [1,2,4,5,6,7,8,9] which created orthodontic bonding units on other than flat surfaces, have equated the 'shear' bond strengths with the applied forces at bond failure: this renders their claimed results invalid.

Shear bond strengths reported by Keizer et al (1976), and Marshall(1983) more closely approximate pure shear bond strengths since the enamel surfaces have been abraded flat as assessed by the naked eye.

Chapter 2: The acid-etch technique

Newman (1969) suggested that, for orthodontics, mechanical bond formation between the tooth and resin system is preferable since it is a self-limiting bond. He stated; "we are not seeking a permanent adhesive bond but one that can be readily broken when a desired treatment phase is completed."

2.1 Mechanism of action

2.1.1 Enamel surface properties

Etching an enamel surface with an acid is one way of achieving mechanical bond formation between an adhesive and that surface. Phosphoric acid solutions are the most commonly used, and have the effect of increasing surface wettability by increasing surface roughness and surface energy (Retief, 1973; Reynolds,1975; Soetopo, Beech, and Hardwick, 1978; Jendresen, Glantz, Baier, and Eick, 1981; Council on dental materials, instruments, and equipment, 1982).

Soetopo et al (1978) explained; "etched enamel is a high energy surface upon which polar organic fluids, such as acrylate monomers, spread spontaneously and,in doing so, reduce the surface energy. The free energy of the interface is less than the sum of the surface energies of the dry, etched enamel and acrylate monomer,and a net gain of thermodynamic free energy results. This lowering of the free energy arises from the formation of secondary bonds. Good 'wetting' of the enamel surface results in the adhesive spreading over the maximum area. If the enamel is porous, the monomer will penetrate into the surface. Thus penetration into enamel (i.e. tag formation) will be encouraged by secondary bond formation. Tags are obviously not essential to obtain bonding after short periods of water immersion. It is possible, however, that in the absence of tags long term water immersion, particularly under conditions where the bond is subject to stress, will lead to interfacial

Study	Average tag length (µm)	Maximum tag length (µm)	No. tags counted per tooth (surfaces)	No. teeth (surfaces) per material	Material	[H_3PO_4]	Contact time (s)	Method of observation
Retief (1973)	-	50	-	-	1 - ER	50%	60	SEM Mag: 450 x Direct
Jörgensen (1975a)	8 - 9	22-26	40	1	2 - FR	35%	60	Incident light microscopy with measuring ocular Mag: 1250 x Direct
Jörgensen & Shimokobe (1975)					1 - UR	unbuffered		
Silverstone (1975)	-	50-60	-	-	1 - FR 1 - UF	30% w/w buffered	60	PLM SEM Direct
Pahlavan et al(1976)	5 - 10	15	-	-	3 - FR 1 - UF	50%	60 120	PLM; SEM; Direct Mag: 1000 x
Voss & Charbeneau (1979)	5 - 10	10	-	-	3 - FR	50%	60	SEM; Direct Mag: 1000 x
Reinhardt & Vahl (1979)	-	200-300	-	-	-	-	-	SEM
Diedrich (1981)	70 - 80	100-170	50	5	3 - FR	50%	120	SEM; Direct

PLM: Polarizing light microscopy
SEM: Scanning electron microscopy

ER: Epoxy resin
FR: Filled resin
UR: Unfilled resin

Table 1. Resin-tag lengths

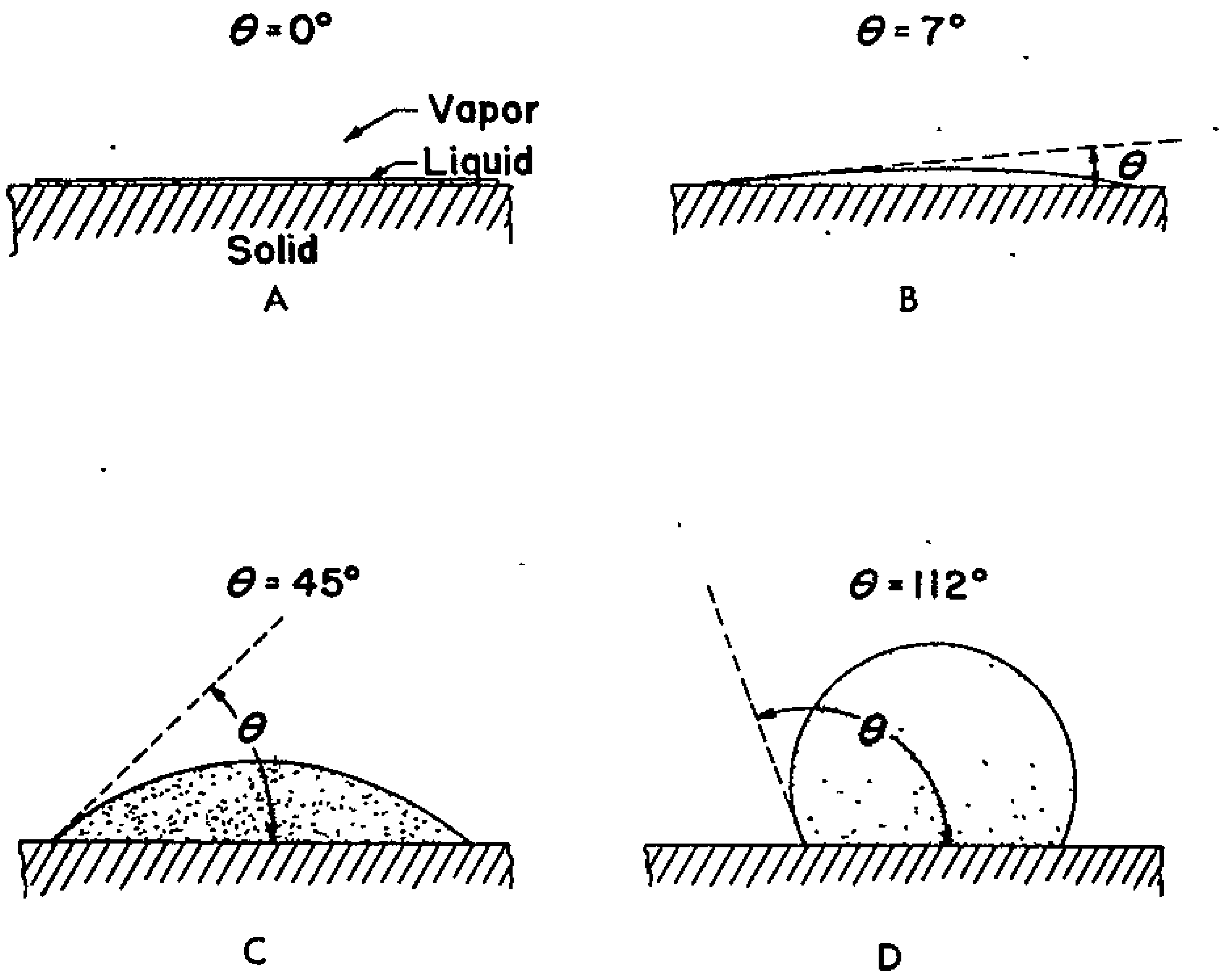


Figure 2–12 To a great extent, adhesion depends on wetting the surface *A*. When the contact angle is 0°, the liquid contacts the surface completely and spreads freely *B*. Small contact angle on slightly contaminated surface. *C*. Larger angle on surface contaminated with an absorbed film *D*. Large angle formed by poor wetting of a solid which has a low surface energy

Figure 1. The relationship between contact angle and surface wettability.
[From: Phillips, R.W.(1982): Skinner's Science of Dental Materials: 8th edition: W.B. Saunders: 25]

failure due to the ingress of water. This is because enamel possesses a greater affinity for water than for acrylate resins. Thus after long term water immersion retention will probably rely primarily on mechanical interlocking via tags."

Jendresen et al (1981) explained how "the surface texture or microtopography of a solid surface may have an overwhelming effect on the wetting characteristics of that solid surface... Increased surface roughness of a solid will increase its wettability if the liquid in contact with a plane surface of the same solid has a contact angle of less than 90°. The converse is true, when the liquid used forms an angle of more than 90° with the plane surface." [Fig. 1]

Reynolds (1975) summarized; "essentially acid-etching changes the enamel surface from a low energy hydrophobic to a high energy hydrophilic surface, showing increased wettability."

2.1.2 Resin tags

Jörgensen (1975a), and Jörgensen and Shimokobe (1975) found that resin tags from composite resins did not contain filler particles, and concluded that resin penetration into the etched enamel surface did not depend on the viscosity of the composite material but, among other factors, on the viscosity of its resin component, and whether this component was sufficiently available on the surface of the composite material.

Diedrich (1981) observed that various orthodontic adhesives showed no varying penetration potentials, and no significant differences in tag formation despite their differing viscosities and compositions.

The reported average length of resin tag penetration into cleaned, phosphoric acid-etched enamel surfaces varied [Table 1]:

i) Pahlavan, Dennison, and Charbeneau (1976), and Voss and Charbeneau (1979); 5 - 10 μm

ii) Jörgensen (1975a), and Jörgensen and Shimokobe (1975);

8 - 9 ± 4 μm

iii) Diedrich (1981); 70 - 80 μm

Silverstone (1975) stated: "between long tags which are seen clearly with the light microscope are smaller ones which are difficult to detect at the light microscope level, but which nevertheless increases further the retention of the material to enamel". These longer tags were demonstrated to be greater than 50 - 60 μm in length.

Maximum tag lengths reported:

i) Pahlavan et al (1976), and Voss and Charbeneau (1979); 15 μm

ii) Jörgensen (1975a), and Jörgensen and Shimokobe (1975); 22 - 26 μm

iii) Silverstone (1975); greater than 50 - 60 μm

iv) Diedrich (1981); 100 - 170 μm

v) Reinhardt and Vahl (1979); 200 - 300 μm

These observations might be explained by:

1) the methods of observation which varied between polarised light microscopy (PLM) and scanning electron microscopy (SEM). However, Voss and Charbeneau (1979) using SEM confirmed the results of Pahlavan et al (1976) where PLM and SEM were used. Silverstone (1975) used PLM and SEM, Reinhardt and Vahl (1979), and Diedrich (1981) utilised the latter.

2) the varying enamel modifying techniques [Table 1].

3) specimen preparation. Silverstone (1975), and Diedrich (1981) suggested that only partial demineralization of the

enamel was necessary so that the fragile, long filamentous resin projections were not deprived of their enamel support, and thus were less susceptible to fracture during subsequent preparation.

The latter author found that as negatives of the etch relief, adhesive matrices showed resin tags with an average length of 14 - 15 μm. The matrix procedure covered only the solid base of the tags.

In the SEM studies, additional factors which may influence observed resin tag lengths have been suggested to include sample damage during sectioning and acid relief, heat production during the coating process, fracture or degradation of resins throughout the procedure, and the variation of the angulation, tilt, and height of the pedestal containing the sample in the microscope (Pahlavan et al, 1976; Voss and Charbeneau, 1979; Diedrich, 1981).

Silverstone (1975) suggested these resin tags had a function in retention of the material to the enamel, and that within certain limits the depth of tag penetration was related to the degree of material retentiveness. Diedrich (1981) considered them a "decisive factor in the mechanical retention phenomenon". Pahlavan et al (1976), and Voss and Charbeneau (1979) concurred. Diedrich (1981) suggested evidence for this could be deduced from the site of bond fracture following debonding. The location of the fracture depended upon the strength of the micromechanical retention. Where enamel fragments had clung to the resin (i.e. fracture within the enamel), tag formation was pronounced.

Young, Hussey, Gillespie, and Stephen (1975) "suggested that the role of long 'tags' of penetrating sealant into the etched enamel surface may have been over-estimated. In particular, one may question whether the presence of longer 'tags' due to a greater degree of etching should be expected to result in better retention of the sealant". Smith (1975) considered it likely that once above a certain minimum value of penetration, retention would not be very dependent upon the tag length.

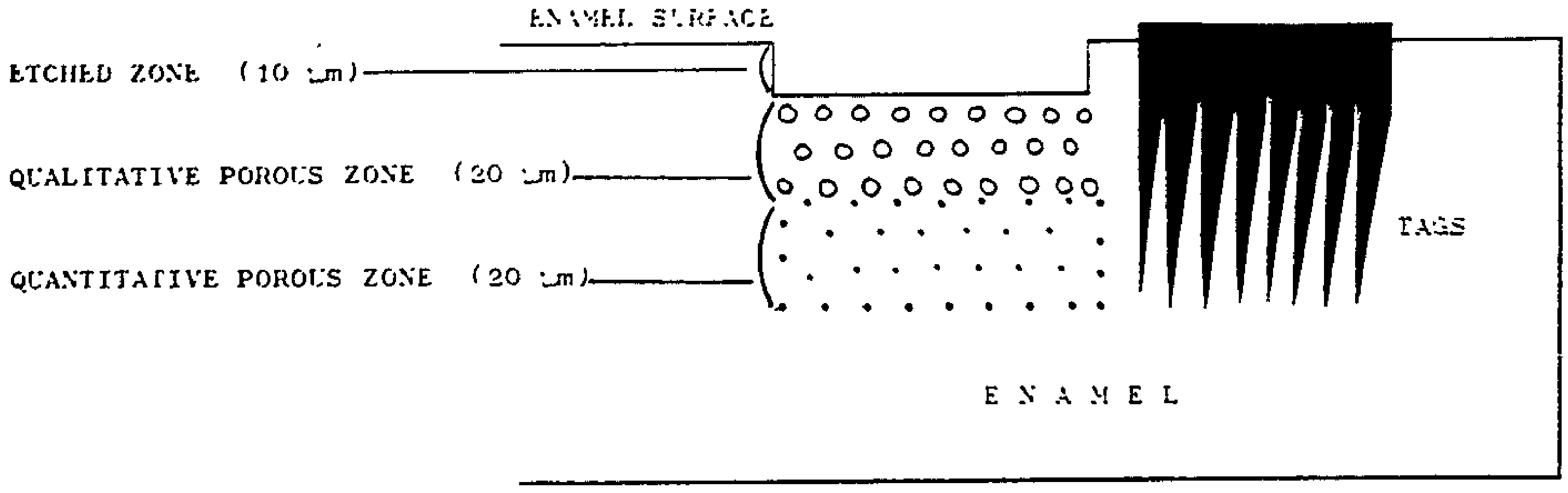


Fig. 25. Diagramatic representation of an etched and porous enamel surface showing the three distinct zones, and the subsequent penetration of tags of resin.

Figure 2. Zones of etched enamel
[From: Silverstone (1975)]

Soetopo et al (1978) stated: "They (the tags) have been studied in detail by both optical and electron microscopy and have been assumed to be of prime importance in bonding. Microscopical observation can give little information on bonding: only the surface adaption can be qualitatively examined. The existence of resin tags in the enamel is not evidence per se for mechanical interlocking being the principal mechanism of adhesion. Although resin tags are usually present when polymers are bonded to acid-etched enamel, it does not necessarily follow that tags are required to obtain satisfactory bonding. However, any adhesive must closely adapt to the bonding surface at a molecular level to function by whatever adhesive mechanism. The presence of tags indicates that the surface area available for bonding has been increased." These researchers and others (Adipranoto, Beech, and Hardwick, 1975) have found that short term bonding does not require tag formation. [It should be noted that they observed the tags using light microscopy to a magnification of x 160.]

2.1.3 Zones

Silverstone (1975) described three zones in the outer enamel following acid-etching with a 30 per cent w/w phosphoric acid solution for 60 seconds, into which resin tags may penetrate [Fig. 2] :

1) an ETCHED zone - approximately 10 μm in depth of enamel was lost;

2) a QUALITATIVE POROUS zone - approximately 20 μm of remaining enamel depth was rendered porous, as demonstrated qualitatively with PLM;

3) a QUANTITATIVE POROUS zone - extending for about 20 μm deep from the qualitative zone. This zone appeared histologically indistinguishable from sound enamel. However, it exhibited a lower birefringence than the corresponding

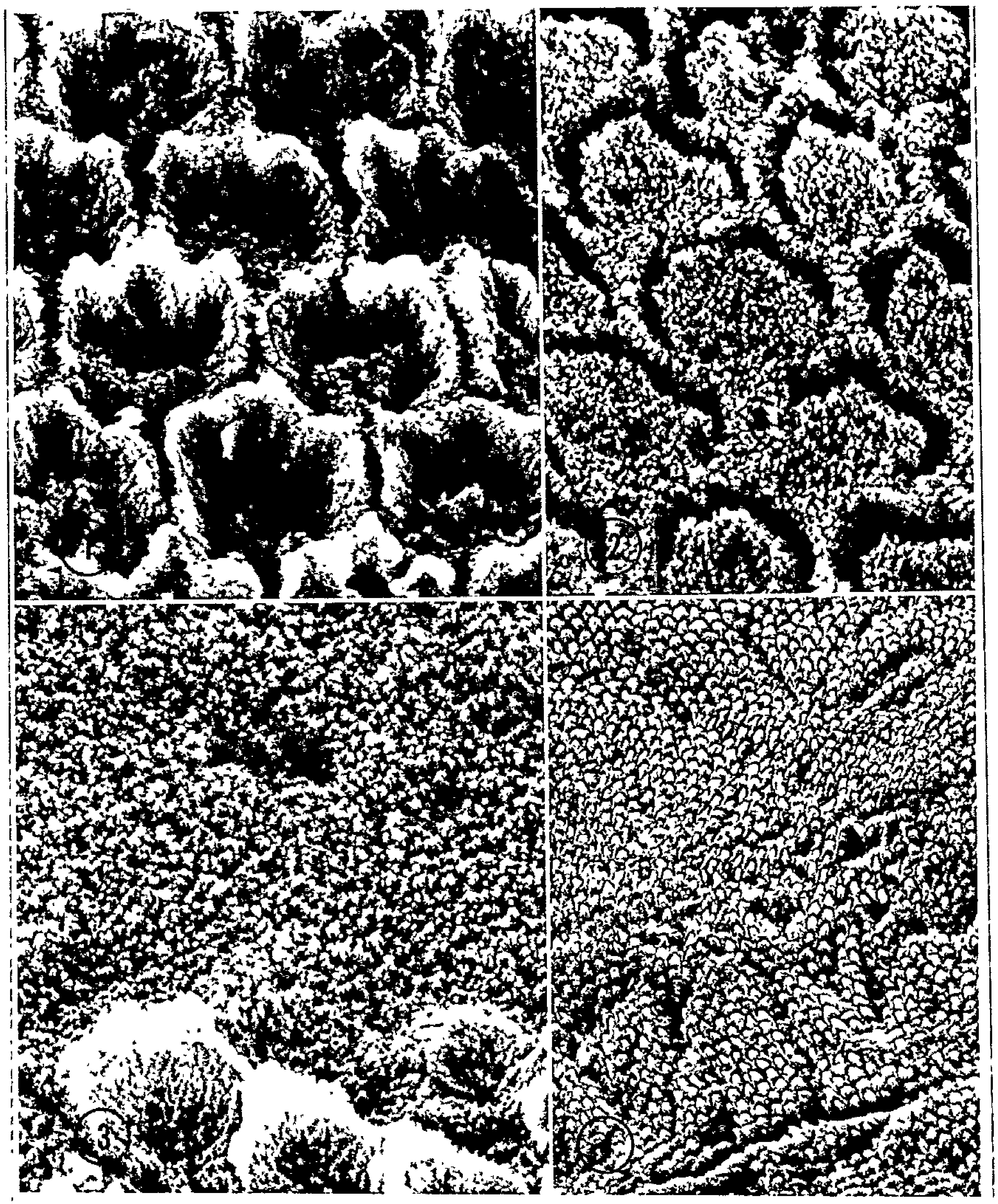


Fig. 4d

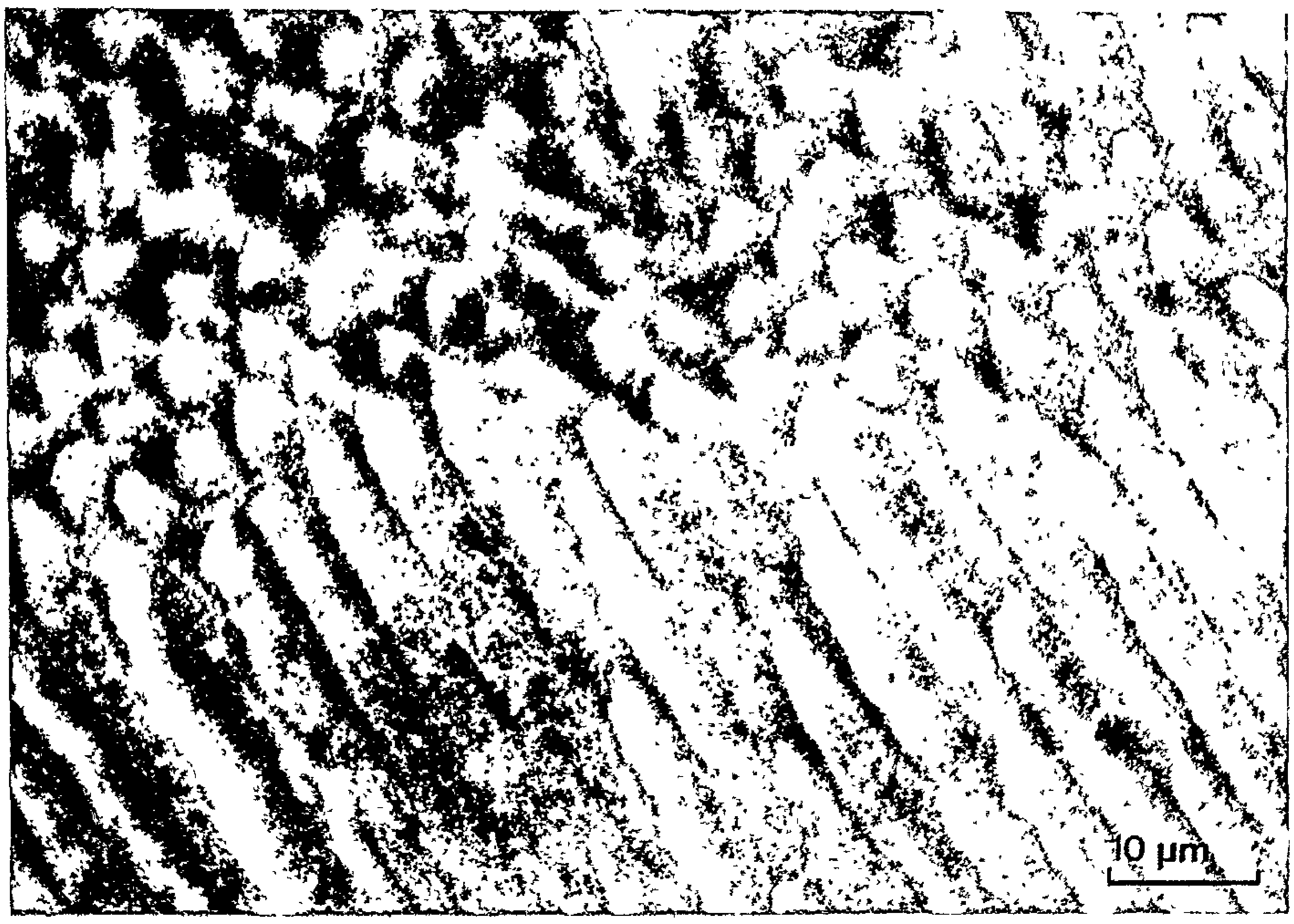
Fig. 1. Enamel area with central etch type. Preferred apatite dissolution within the prism cores. (Two-minute application of 50 percent H_3PO_4. Original magnification, ×3,200.)

Fig. 2. Coherent field of peripheral etch patterns, the marginal fissures within the area of the prism heads are different in width and contour. (Two-minute application of 50 percent H_3PO_4. Original magnification, ×3,200.)

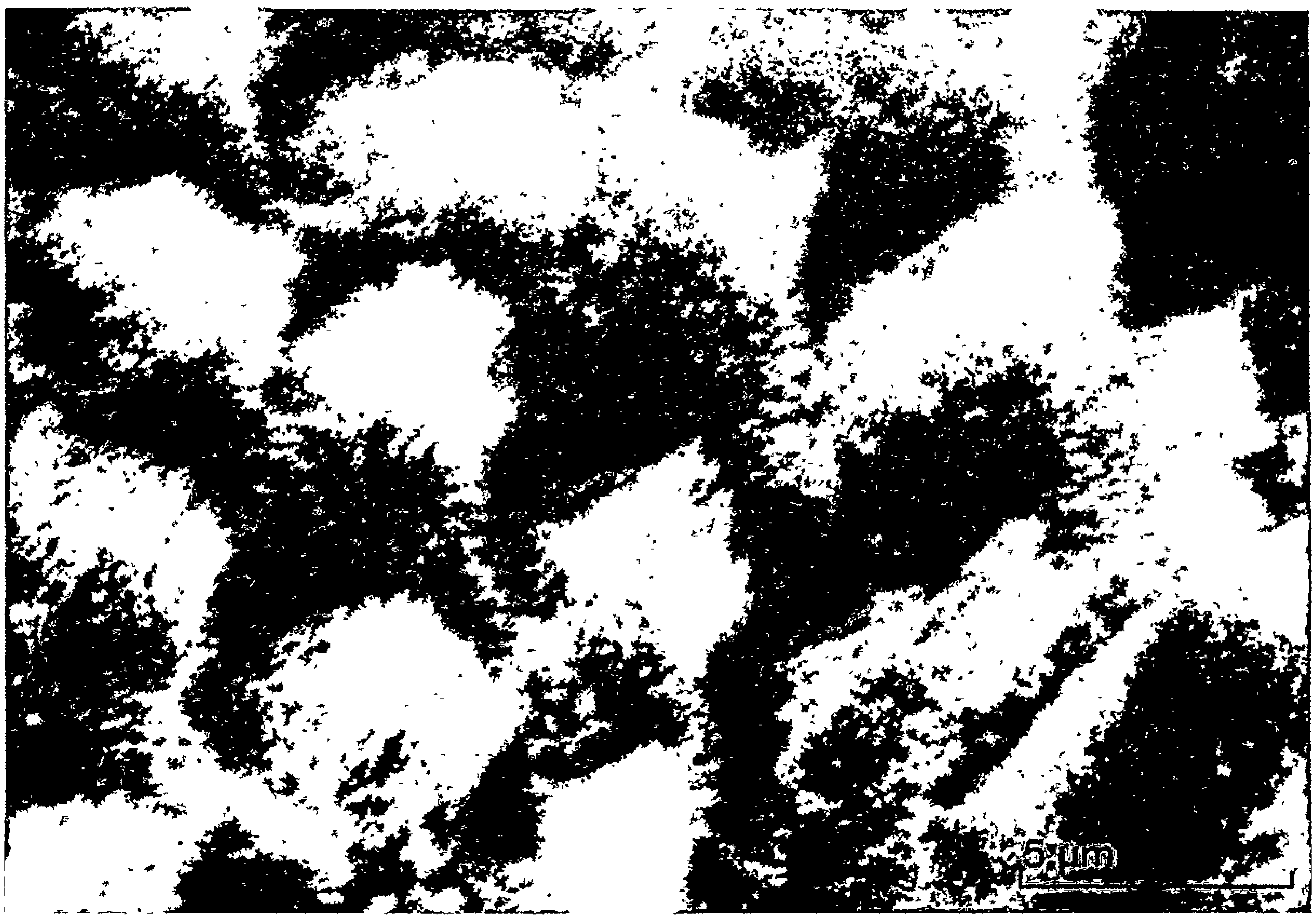
Fig. 3. Next to an area of raised-up prism peripheries, there is a zone of poorly structured etch patterns. Granulated enamel surface with microporosities. (Two-minute application of 50 percent H_3PO_4. Original magnification, ×3,200.)

Fig. 4. Etched prism groups show an irregular superstructure with deep grooves and crests (Four-minute application of 50 percent H_3PO_4. Original application, ×320.)

Figure 4. Acid-etch patterns of human enamel
[From: Diedrich (1981)]



Type 2 etching pattern (lower magnification)



Type 2 etching pattern (higher magnification)

Figure 3 (continued)

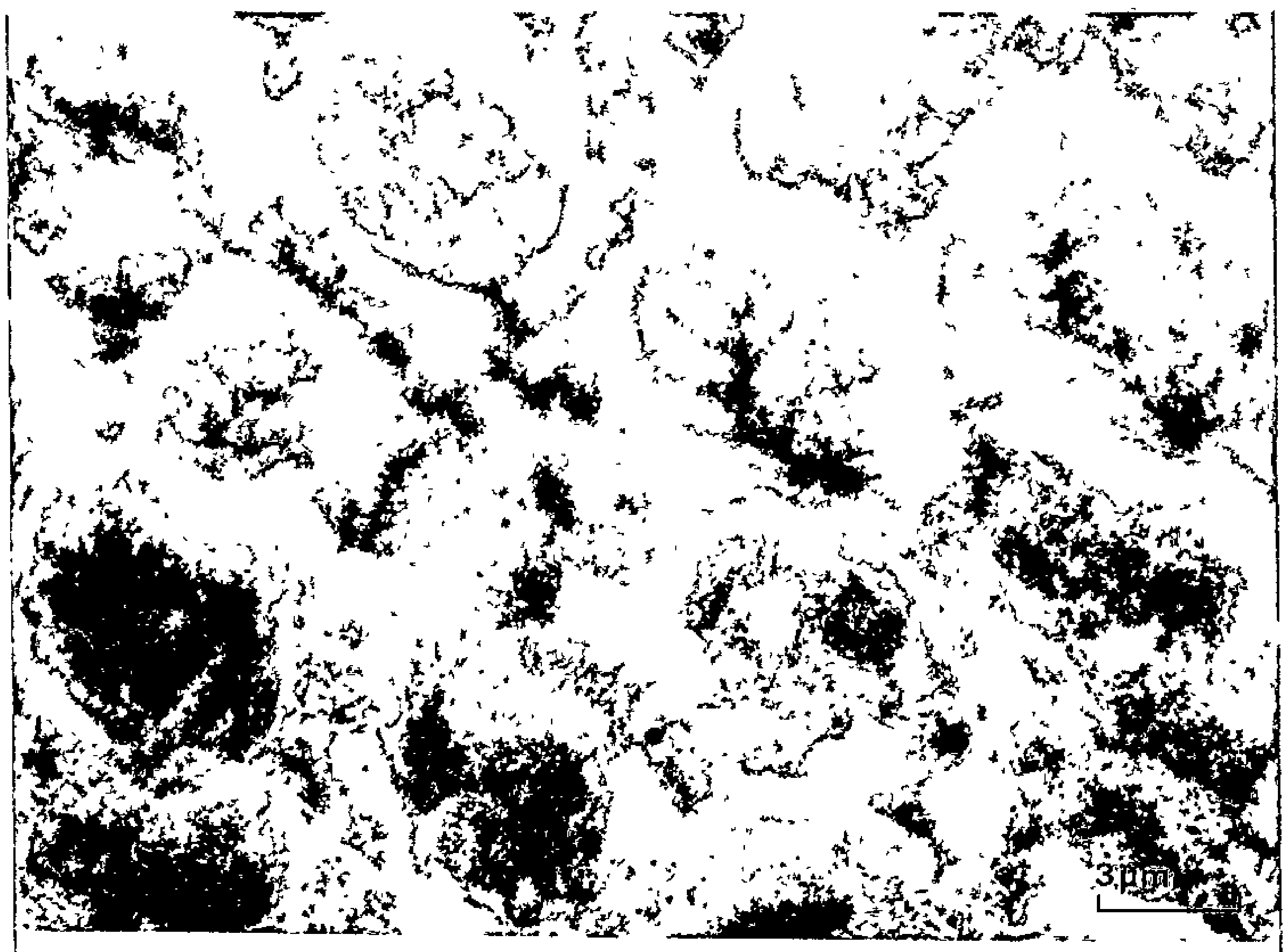


Fig. 1. Scanning electron micrograph of an enamel surface that was exposed to 37-percent phosphoric acid for 1 min. The surface shows a pattern in which there is a distinct hollowing of prism centres with relatively intact prism peripheries. This type of damage, called type 1 etching pattern, was the most common seen in this study.

Type 1 etching pattern

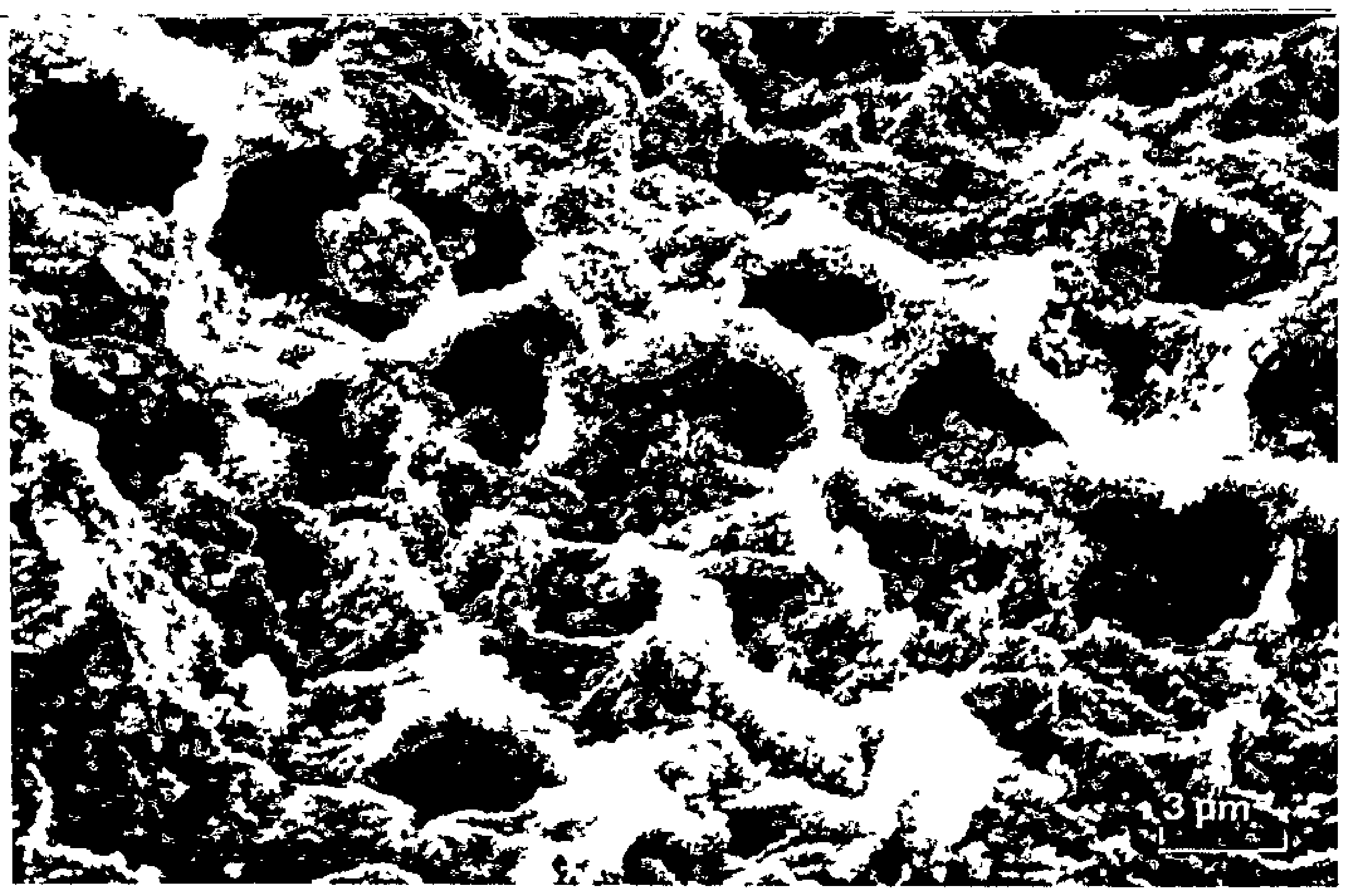


Fig. 4. Scanning electron micrograph of an enamel surface exposed to 30-percent phosphoric acid for 1 min. In this, areas can be seen showing a type 1 etching pattern in which there is a preferential removal of prism cores. However, adjacent regions show a type 2 etching pattern in which the reverse pattern can be seen. In addition, in many areas the pattern of surface damage is difficult to relate to prism structure. Such a field is referred to in this study as a type 3 etching pattern.

Type 3 etching pattern

Figure 3. Acid-etch patterns of human enamel
[From: Silverstone et al (1975)]

control region. This region was rendered slightly porous into which resin tags extended from the enamel surface. It may have been that the natural enamel pores were made available for resin penetration.

Diedrich's (1981) finding of resin tags to an average depth of 70 - 80 μm, with some detectable to 100 - 170 μm, and Reinhardt and Vahls' (1979) detection to 200 - 300 μm raised a question as to the validity or limit of Silverstone's description. The former author suggested that further research was necessary in order to determine more precisely, the depth of resin penetration. Furthermore he questioned the extent to which resin tags represent a complete image of the acid penetration effect.

2.1.4 Etching Patterns

Silverstone, Saxton, Dogon, and Fejerskov (1975) described three basic etching patterns on human enamel surfaces following their exposure to various concentrations of unbuffered phosphoric acid, and buffered lactic acid solutions for varying times. Diedrich (1981), following enamel surface exposure to a 50 per cent gel-like phosphoric acid for various periods, classified four basic etching patterns - three corresponding to those described by Silverstone et al (1975) and one in addition. These two classifications were based on surface morphology defined following examination using SEM.

Silverstone et al (1975) = S
Diedrich (1981) = D

The basic etching patterns described were [Fig. 3, 4]:

1) Type 1 (S) = Central etch type (D);

characterised by generalised surface roughening, with a distinct pattern showing preferential dissolution of prism cores (centres) with relatively intact peripheral regions, thus constituting a "honeycomb-like" image. This was the most

Study	Acid	[Acid]	Contact time (s)	Patterns (Silverstone et al, 1975 classification)	Enamel
Silverstone et al, (1975)	H_3PO_4 (unbuffered) Lactic (buffered, pH 4.5)	20 - 70 % 1, 0.1, 0.001N	1-10 min	1, 2, 3	surface
Silverstone (1975)	H_3PO_4 (unbuffered)	20 - 60 % w/w 30 % w/w	60,90,120 120	1, 2, 3 1, 2, 3	permanent surface deciduous surface
Jörgensen (1975a)	H_3PO_4 buffered unbuffered	35 & 50% 35%	60	1, 2, 3	surface
Hormati et al (1980)	H_3PO_4	37%	60	1, 2	subsurface
Diedrich (1981)	H_3PO_4 unbuffered	50% gel	120	1, 2, 3 starlike/ fernlike	surface
Nathanson et al (1982)	H_3PO_4	37%	60	1, 2, 3	surface subsurface
Bates et al (1982)	H_3PO_4	37%	30,60,120	1, 2, 3	subsurface

Table 2. Acid etch-relationships with acid-etch variables

common pattern.

2) Type 2 (S) = Peripheral etch type (D);
characterised by preferential dissolution at the prism boundaries, leaving prism cores projecting toward the original enamel surface.

3) Type 3 (S) = Less structured type (D);
characterised by generalised surface roughening with regions resembling hollowed prism cores adjacent to areas in which the pattern was more consistent with the loss of prism peripheries. Within these areas were regions in which the etching pattern did not apparently conform to prism morphology. Sometimes the entire surface topography could not be related to prism pattern.

4) Starlike (fernlike) etching type (D);
characterised by an irregular build-up of prism groups into starlike or fernlike patterns [Fig. 4d].

These patterns were confirmed by others [Table 2].

Deviations from these basic etching patterns, such as bizarre fissures, tubes, grooves, pits, or craters, have been noted (Diedrich, 1981).

Diedrich (1981) explained the variable response of enamel surfaces, even following identical pretreatment, to be due to structural variations in the superficial enamel layer - differences in the course of prisms and crystallite orientation, anisotropy of the chemical reaction of single crystallites (Sharpe, 1967; Nygaard and Simmelink, 1972), and local differences in mineral content and in the organic/inorganic composition of prisms (Yaeger, 1976). In addition, the actual/effective H^+ concentration at the enamel surface would participate in determining the etch topography. This may be influenced by acid concentration and pH, duration and mode of acid application, and reaction product formation (Chow and Brown, 1973; Soetopo et al, 1978).

Silverstone et al (1975) found that "such differences produced by acids are difficult to explain on the basis of variation in chemical composition and crystallite orientation", and concluded, "this further highlights the variation in structure that can occur in enamel, not only from tooth to tooth, or surface to surface, but also from site to site on a single surface". Diedrich (1981) concurred.

Interestingly, Jörgensen (1975b) found that a very similar etch pattern was exhibited symmetrically along the midline of contralateral pairs of teeth.

2.1.5 Subsurface enamel

Silverstone (1975) stated: "there seems to be little difference when we etch surfaces where there has been perhaps 100 m removed previously although this region is obviously more susceptible to demineralization compared with surface enamel".

Nathanson, Bodkin, and Evans (1982), Bates, Retief, Jamison, and Denys (1982), and Hormati, Fuller, and Deneby (1980) found that subsurface enamel exhibited the same basic etching patterns as surface enamel. The former authors stated: "It is apparent from this study that one may neither generalize that enamel subsurface etches better than its outer surface nor claim that the opposite is true".

2.2 Optimum phosphoric acid concentration and etching time

When considering the phosphoric acid concentration of solutions it is necessary to define the units of concentration. These may include:

i) weight/weight; (w/w)

ii) weight/volume; (w/v)

iii) volume/volume; (v/v)

iv) molarity; (M), (Duff and El Motayam, 1975; Soetopo et al, 1978) i, ii, and iii may be expressed in percentage terms. However, y per cent w/w is not equivalent to y per cent w/v nor v/v: e.g. a 30 per cent v/v solution would be equal to a 44.5 per cent w/w solution, both would be 5.7 M. A 30 per cent w/w solution would be equal to an 18.6 per cent v/v solution both being 3.6 M. Duff and El Motayam (1975) recommended that concentration be expressed in terms of molarity since this would eliminate confusion.

Few investigators and manufacturers have stated, unambiguously, the concentration units in which their phosphoric acid solutions were expressed (Soetopo et al, 1978). This creates difficulty in relating the results of one study to another.

Gottlieb, Retief, and Jamison (1982) suggested criteria for consideration when an optimal phosphoric acid concentration is advocated for etching:

1) bond strengths;

2) the depth of etch;

3) the reaction products that are formed on the enamel surfaces during the etching procedure.

2.2.1 Bond strengths

Studies investigating optimal phosphoric acid concentrations have related concentrations to tensile bond strengths. Young et al (1975) found only small variation in tensile bond strengths when 10, 30, 50, and 70 per cent w/w concentrations were used on bovine enamel surfaces. Retief (1975) observed no significant difference when using 10, 20, 30, 40, and 50 per cent w/w, but a highly significant decrease with 60 per cent and a further decrease with 85 per cent. Soetopo et al (1978) found maximum tensile bond strength in the range 10 - 30 per cent w/w, 2 and 40 per cent produced similar strengths. Gottlieb et al (1982) reported no significant differences between 10 - 60 per cent w/w, and

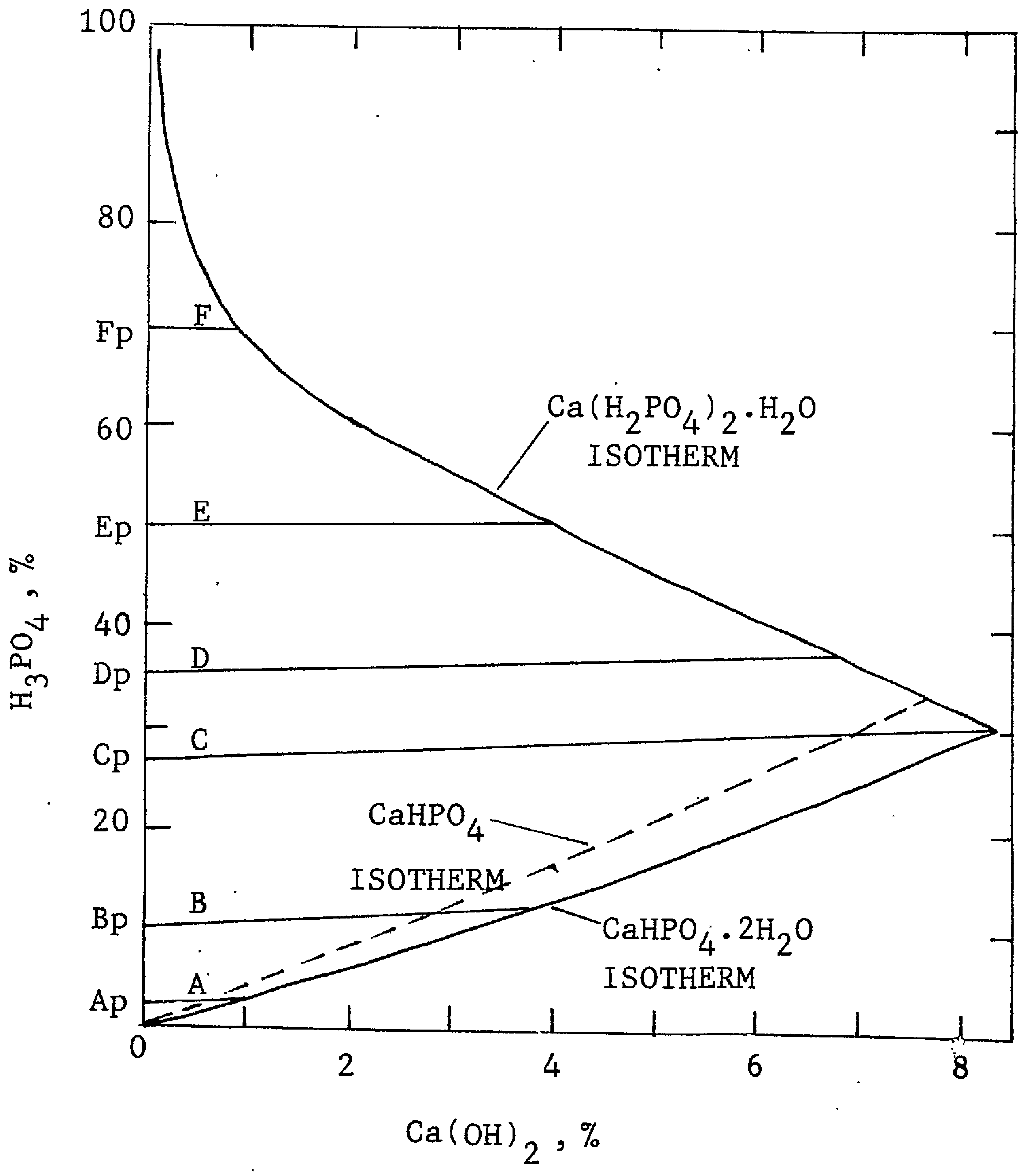


Fig. 5. Solubility phase diagram for systems $Ca(OH)_2$-H_3PO_4-H_2O at 25°C. Lines A through F are hydroxyapatite dissolution lines.

[Adapted from Chow, L.C. & Brown, W.E. (1973) J. Dent. Res., 52 : 1158] a significant decrease with 70 per cent. These latter three studies used human enamel.

Resins used were chemically activated composites (Soetopo et al, 1978; Gottlieb et al, 1982), ultraviolet light activated composite (Soetopo et al, 1978) and unfilled (Young et al, 1975) resins, and an epoxy resin (Retief, 1975).

2.2.2 Deth of etch

Retief (1975), using a surface roughness machine, calculated the depth of enamel loss produced by applying phosphoric acid solutions of different concentrations to human enamel surfaces. Depths between 10 - 12 μm were recorded for concentrations between 10 - 45 per cent w/w, 7 μm for 50 per cent, and 3.5 μm for 60 per cent. Silverstone (1974) used a calibrated eyepiece graticule to measure the depths. Solutions of 20, 30, 40, 50, and 60 per cent w/w caused losses in depth of 14, 10, 9, 7, and 2 μm respectively.

2.2.3 Reaction product formation

Chow and Brown (1973) showed, following the application of a 50 per cent phosphoric acid (H_3PO_4) solution to human enamel surfaces for 1 minute, a white crystalline deposit on those surfaces. Analysis indicated this to be monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2.H_2O$). They explained this result by referring to the phase diagram for the ternary system, H_3PO_4-$Ca(OH)_2$-H_2O [Fig. 5]. The process of hydroxyapatite [HA] ($Ca(PO_4)_3OH$) dissolution in phosphoric acid may be divided into two steps:

1) the dissolution of HA; this would change the solution composition along the dissolution line (A through F)[Fig.5] associated with the initial acid concentration;

2) dissolution of HA and precipitation of $Ca(H_2PO_4)_2.H_2O$ after the composition reaches the isotherm for this product; the combined effect would tend to change the solution

composition along the $Ca(H_2PO_4)_2.H_2O$ isotherm toward greater calcium concentrations. Solutions containing less than approximately 27 per cent H_3PO_4 would probably be accompanied, as the HA dissolved, by an appreciable rise in pH, sometimes to above 2, where dicalcium phosphate dihydrate [brushite] ($CaHPO_4.2H_2O$) and/or monetite ($CaHPO_4$) are stable phases and would precipitate because they are more insoluble than $Ca(H_2PO_4)_2.H_2O$. Therefore, at higher and low concentrations very little calcium is dissolved, the HA being converted into relatively more soluble primary calcium phosphate, or insoluble secondary calcium phosphate respectively (Chow and Brown, 1973; Soetopo et al, 1978).

"Apatite dissolution in Step 1 should proceed more rapidly than in Step 2, because in the latter it is impeded by the $Ca(H_2PO_4)_2.H_2O$ coating that would form. Therefore, if enamel is treated with acid only for a brief period, the amount of apatite dissolve in Step 1 would account for a major portion of the total amount dissolved". (Chow and Brown, 1973)

Relating the above criteria:

The length of the dissolution line from any given point on the vertical axis of Fig. 5 indicates the amount of apatite that would be dissolved by the concentration of phosphoric acid represented by that point. For example, the concentration of phosphoric acid solution F_p would dissolve considerably less HA in Step 1 than would a more dilute solution such as D_p, and the same as A_p. That is, the precipitated phase tends to protect apatite from dissolution, thus at high or low phosphoric acid concentrations the depth of etch is less than for intermediate concentrations. Soetopo et al (1978) considered that deposits formed would, unless removed by washing, tend to prevent adhesives from coming into direct contact with the actual enamel surface thereby reducing tensile bond strengths.

Silverstone (1974, 1975) observed that phosphoric acid solutions in the concentration range 30 - 40 per cent w/w produced the most evenly distributed etch over an enamel surface, and that the 30 per cent solution was the most consistent. The conclusion reached was that this latter concentration produced the most favourable conditions for bonding. Enamel surface assessment was by SEM and PLM: these methods of examination are qualitative and should not be used to quantitate the etching action of conditioning solutions (Gottlieb et al, 1982).

2.2.4 Optimal acid concentration

For long term retention under oral conditions, penetration of polymer into enamel has been considered necessary (Soetopo et al, 1978), therefore minimal, more soluble reaction products would be desirable. In the concentration range between 10 - 60 per cent w/w phosphoric acid, the higher concentrations would be more desirable since less superficial enamel would be removed, and a readily soluble reaction product produced during the etching procedure (Gottlieb et al, 1982).

Retief (1974, 1975) concluded that the etching solution producing optimal bond strength for any resin system should be determined experimentally.

2.2.5 Etching time

Etching times of between 1 - 2 minutes have been recommended (Chow and Brown,1973; Retief, 1974, 1975; Silverstone, 1974, 1975; Brännström and Nordenvall, 1977; Gottlieb et al, 1982).

2.3 Post-etched enamel

Following acid-etching, the enamel surface exhibited increased surface energy and roughness. The question as to the fate of the etched surface not incorporated into the bond unit needed answering.

Arana (1974) concluded that etched enamel was only temporarily decalcified, and within 48 hour it would essentially return to its pre-etched condition. This was based on visual observation of teeth in situ; the criterion being the colour shade of the enamel.

Studies using SEM did not support the above conclusion, but found that the etched pattern remained even after 4 months (Meurman and Asikainen, 1976; Garberoglio and Cozzani, 1979; Diedrich, 1981; Jendresen et al, 1981). That the enamel surface returned to its original state of adhesiveness and roughness in a relatively short time period due to the adsorption of a biofilm, the aquired pellicle (Jendresen et al, 1981).

Meurman and Asikainen (1976) found that the buccal surface of upper molars rehardened in vivo to 84 per cent of initial hardness after 23 days. The subjects used a fluoride containing dentrifice, and the proximity of the parotid salivary duct opening should be noted.

Nasr (1978) showed that abraded, etched mesial surfaces of human molars could, in vitro, exhibit increased hardness following treatment with 2 per cent NaF and/or 8 per cent SnF_2. After 1 minute etching, 5 minutes application of the two fluoride compounds combined, increased surface hardness to 9 per cent greater than the unetched surface hardness.

Kochavi, Gedalia, and Anaise (1975) reported that the precipitates, $Ca_5(PO_4)_3F$ and CaF_2, and $Sn_3PO_4F_3$ and CaF_2 filled the enlarged pores in the phosphoric acid-etched enamel following treatment with NaF and SnF_2 respectively. This may have reduced surface wettability (Lee, Stoffey, Orlowski, Swartz, Ocumpaugh, and Neville, 1972).

Diedrich (1981) summarised the situation: "The etched enamel surface is not completely restored to its original morphology, even after exposure in the oral cavity for 4 months. There is only partial repair by defect filling with organic and inorganic precipitates, and by abrasion of the fragile superficial etching relief."

Based upon the information presented, it would seem appropriate to quote Meurman and Asikainen (1976) : "It is thus highly recommendable to avoid unnecessary conditioning of intact enamel."

Furthermore, application of fluoride immediately following orthodontic bonding would be indicated to enhance remineralization and caries resistance (Diedrich, 1981).

2.4 Debonding and enamel finishing ('clean up')

"In orthodontics, the bonding of attachments to the enamel surface is temporary" (Shey and Brandt, 1982). Newman (1969) concurred.

Debonding involves the removal of the bonded attachment with a variable amount of bonding resin from the enamel surface. Ideally the enamel would be returned to its pretreatment state (Fields, 1982). In practice this has not been found to occur. Essentially debonding may be divided into steps:

1) bonded appliance removal;

2) residual resin removal from the enamel;

3) enamel finishing.

Burapavong, Marshall, Apfel, and Perry (1978) stated: "Perhaps the most important factor to consider in a bracket-removal technique is the damage done to the enamel surface."

Procedures in each of the above mentioned debonding steps may contribute to this damage.

Studies investigating this subject have concentrated on depths of enamel loss and surface roughness. Enamel depths reported lost during debonding included 10 - 20 µm (Burapavong et al, 1978), 16 - 24 µm Pus and Way, 1980), 25 µm (Lee Brown and Way, 1978), and 50 - 64 µm (Fitzpatrick and Way, 1977).

Diedrich (1981) stated: "The location of the fracture site (of the bond) depends on the strength of micromechanical retention produced by acid pretreatment."

He reported observing enamel fractures to a depth of 100 µm, and localised enamel loss of a maximum of 150 - 160 µm due to enamel detachments. The latter may correspond to about 10 per cent of enamel surface thickness.

Enamel surface roughness was diminished following final polishing (Fitzpatrick and Way, 1977; Burapavong et al, 1978; Rouleau, Marshall, and Cooley, 1982).

2.5 Total enamel lost

The total enamel lost due to the acid-etch technique, from initial cleaning to final polishing of the enamel surface, when a filled resin was used, was reported to be 30 - 41 μm (Pus and Way, 1980), 42 - 55 μm (mean) (Lee Brown and Way, 1978), and about 56 m (Fitzpatrick and Way, 1977).

Enamel loss of upto 60 μm would not remove all the resin tags from the enamel (Silverstone, 1975; Diedrich, 1981). However, Silverstone (1975) suggested that these residual tags render the embedding enamel less susceptible to acid dissolution.

Chapter 3: Crystal-Lok

3.1 Crystal-forming solutions

Smith (1971) observed that polyacrylic acid reacted with a clean enamel surface resulting in the crystallization of a material, the morphology of which suggested it was a calcium compound. The reaction appeared to occur readily at certain sites in the enamel surface from which "spherulytic growth" appeared to nucleate or nucleate in part. This crystal growth was profuse on an abraded enamel surface.

Smith and Cartz (1973) noted that purified polyacrylic acid produced slight etching on clean enamel surfaces, but polyacrylic acid containing sulphate ions as a residue from the polymerization initiator (ammonium persulphate) produced a crystalline deposit which gave the surface a whitish appearance. Many of these crystals were nucleated at the enamel surface and resisted mechanical removal.

X-ray diffraction and electron microphobe showed the crystals to be gypsum ($CaSO_4.2H_2O$).

Chemical analysis demonstrated that calcium ions were released from the enamel into the supervening polyacrylic acid.

Crystal formation depended mainly upon sulphate ion concentration $[SO_4^{2-}]$, and was independent of molecular weight and concentration of the polyacrylic acid solution. Smith, Maijer, Keyes, Bennett, and Peltoniemi (1979) reported that polyacrylic acids of various molecular weights facilitated crystal growth if at least 1 per cent sulphate ion was present. Crystal growth density was mainly dependent upon sulphate ion concentration, both could be increased by addition of ammonium sulphate or sulphuric acid, and that increased sulphate ion concentration and polymer molecular weight resulted in increased nucleation site numbers and decreased crystal size.

Maijer and Smith (1979) used a 40 per cent polyacrylic acid solution with an averge molecular weight of 5000 and sulphate ion concentration of 3.8 per cent (assessed by gravimetric analysis), to assess the effect of contact time with enamel, on crystal shape and growth. Exposure for 2 - 4 minutes resulted in long, needle-like crystals. As contact time increased the crystals shortened, became rounder and fatter, and decreased markedly in sharpness.

Smith, Lux, and Maijer (1981)* found that crystal density could be increased slightly with contact time greater than 1 minute, and more readily with increased polyacrylic acid and, therefore, sulphate ion concentrations. Higher concentrations resulted in less squat, more needle-shaped crystals, most likely explained by a greater degree of etching, more rapid calcium ion released, and a larger number of nucleation sites. They concluded that a 35 per cent, 12 x 10^3 molecular weight polyacrylic acid solution was sufficiently viscous to resist flowing off the tooth surface, readily removed by gentle washing with water, and resulted in dense crystal growth after 1 minute application. This was then used as the standard.

Crystals have also been formed on dentine and bone (Smith et al, 1979).

* Note: Many of the tests reported were undertaken on abraded bovine enamel surfaces.

3.2 Crystal growth and resin bond formation

"The principle of bonding in this surface treatment is the formation of a bonded crystal deposit and the penetration of the fluid resin around the crystal" (Maijer and Smith, 1979). Fluid resin penetration around the crystals was first reported by Maijer and Smith (1979), and subsequently confirmed by Smith et al (1979).

Tensile bond strengths for resins bonded in conjunction with crystal formation were similar to those with acid-etch (Maijer and Smith, 1979).

Shaffer (1984) found shear bond strengths for the two systems to be essentially the same.

Fracture under tensile load occurred most commonly in the crystal-resin layer, implying that the crystals were strongly bound to the enamel surface (Maijer and Smith, 1979; Smith et al, 1979). This may be regarded as a chemical bond between crystals and enamel, and a mechanical bond between crystals and resin (Maijer and Smith, 1979).

Maijer and Smith (1979), and Smith et al (1979) produced results which indicated that the crystals may be removed from enamel, leaving no residual resin tags.

Smith (1975) reported measurements of calcium solubilised from standard areas of enamel by phosphoric acid were about ten times those for polyacrylic acid, for comparable concentrations.

Smith et al (1979) found that 5 - 10'u m of surface enamel was lost due to polyacrylic acid.

Maijer and Smith (1984), in a preliminary clinical assessment of crystal bonding in vivo at 18 months, found a 10 per cent loss of acid-etch brackets and a 9 per cent loss of crystal bonding solution brackets.

Claimed advantages of crystal forming over acid-etch solutions as the enamel pretreatment for orthodontic bonding were:

1) much less loss of surface enamel and fluoride, and less surface damage (Maijer and Smith, 1979; Smith, 1982);

2) no residual resin tags in the enamel surface (Maijer and Smith, 1979; Smith, 1982);

3) similar bond strengths attained (Smith, 1982);

4) easier debonding and "clean up" with less enamel damage (Smith, 1982; Maijer and Smith, 1984).

Experiment

Objectives

Primarily, the purpose of this in vitro study was to compare the shearing forces necessary for the disruption of orthodontic bonding units formed following pretreatment of abraded human enamel surfaces with either a 37 per cent w/w phosphoric acid solution or Crystal-Lok: a polyacrylic acid solution containing sulphate ions.

Secondarily, the sites of bond failure were observed.

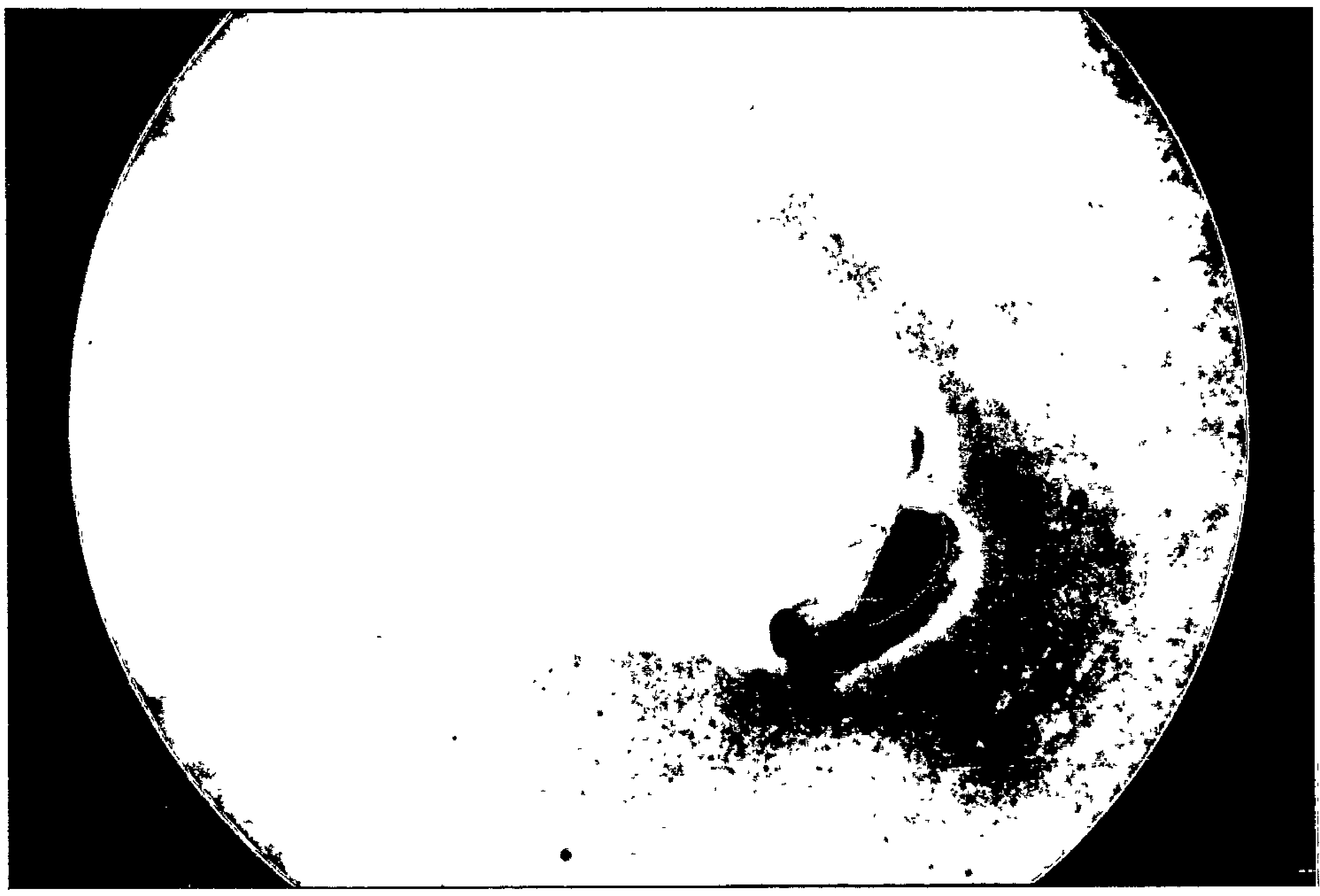


Figure 10. Abraded embedded enamel surface

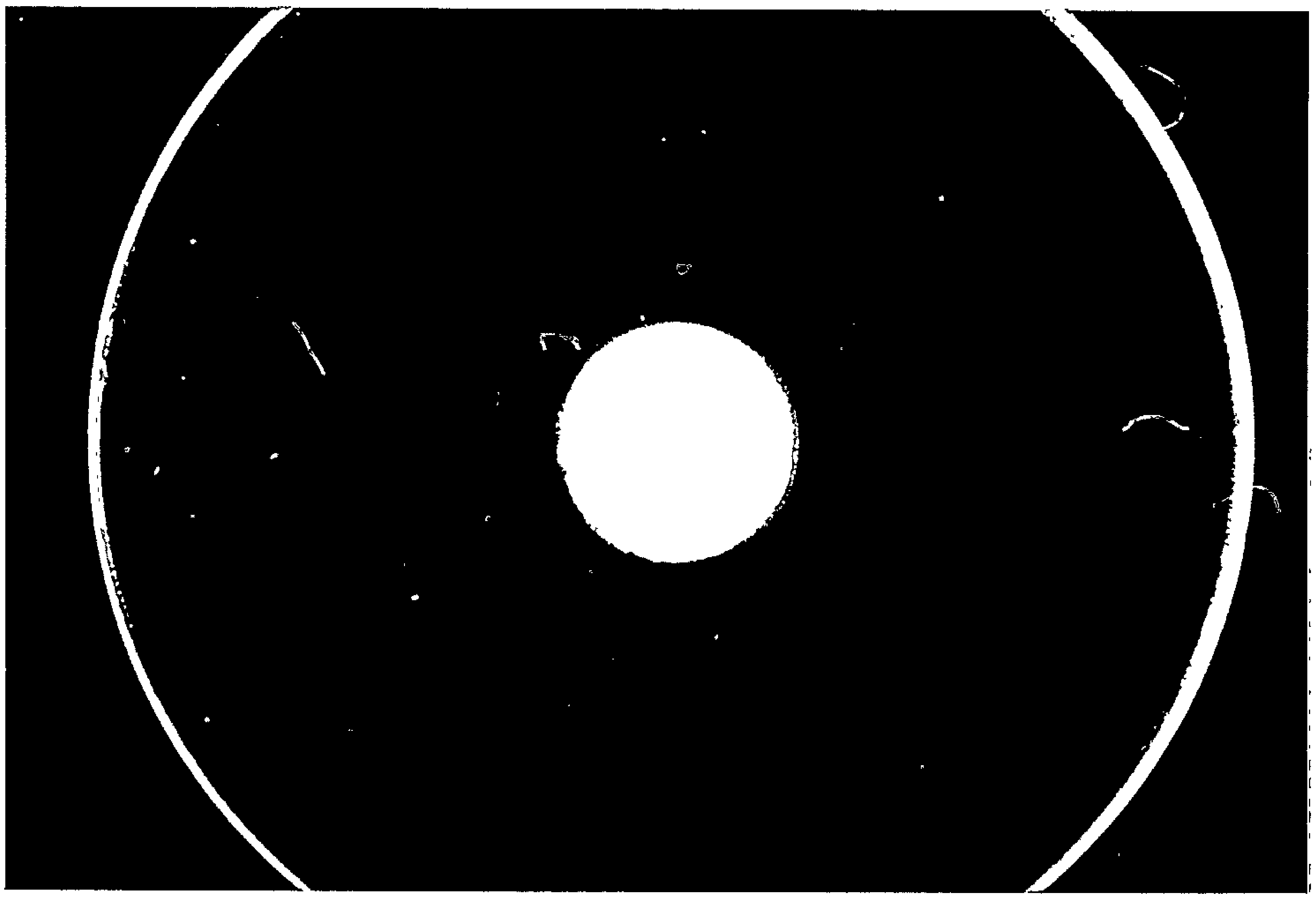


Figure 11. Masked abraded embedded enamel surface

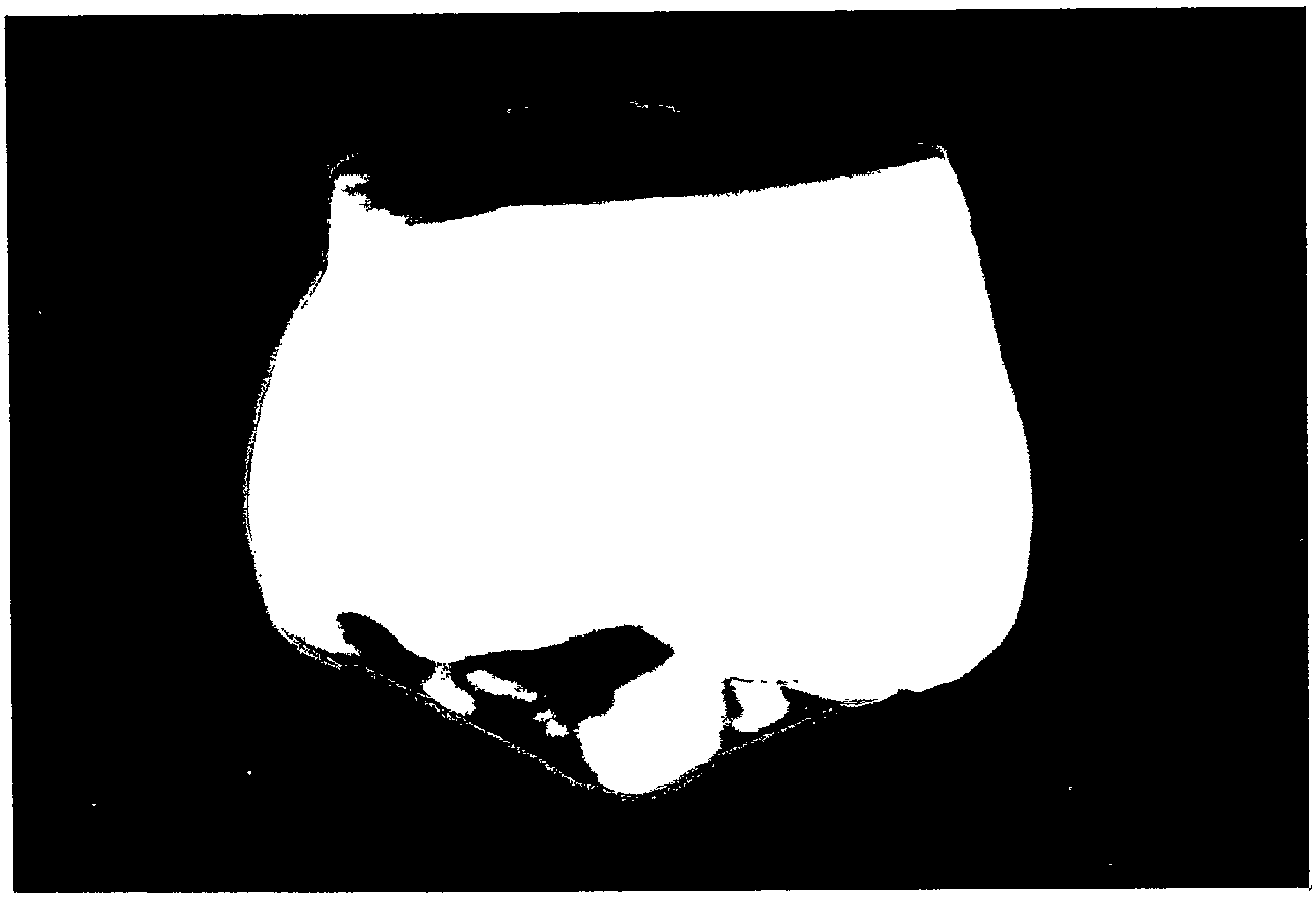


Figure 7. Tooth crown after root removal

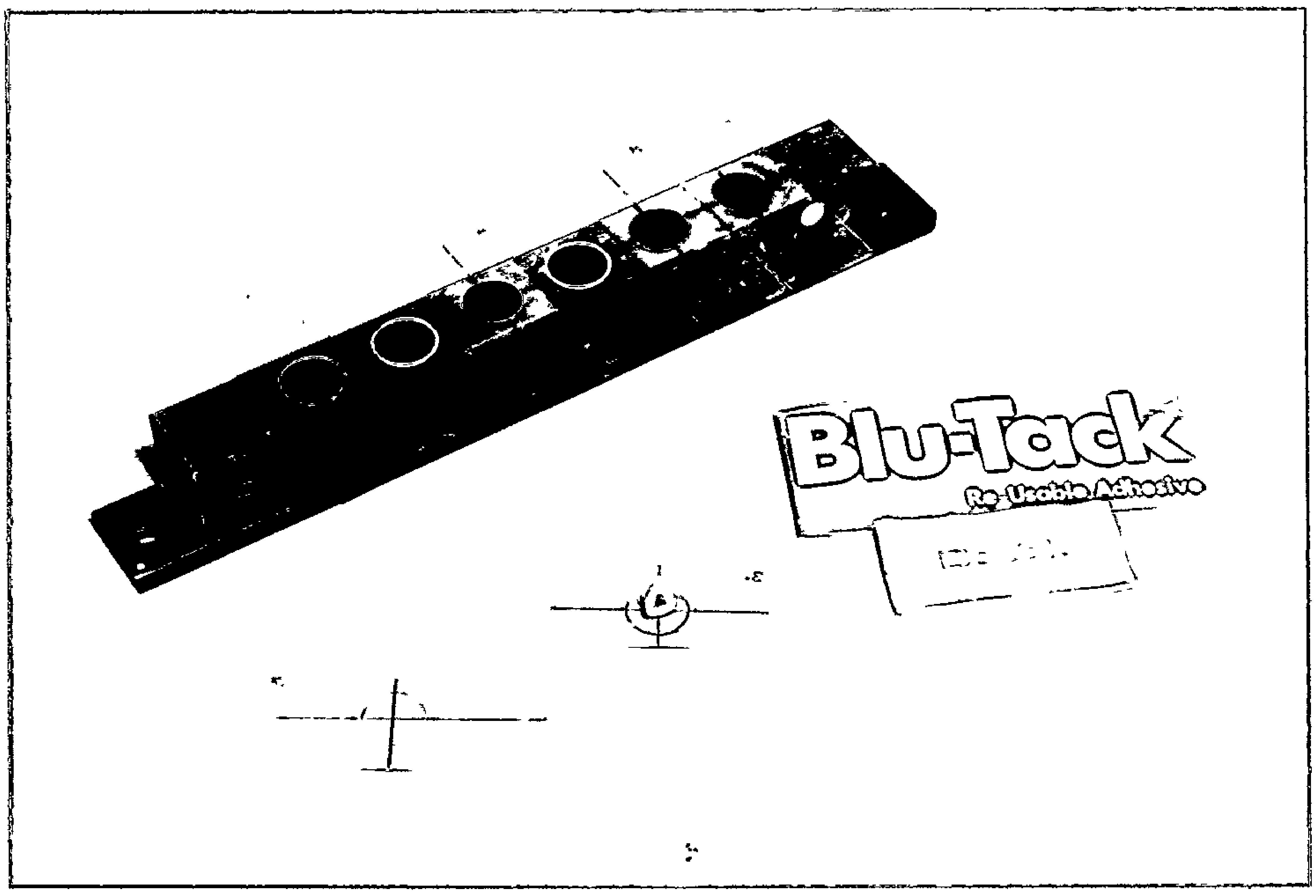


Figure 8. Crown segment oriented and retained on microscope slide prior to embedding in Vel-Mix.

Microscope slide alignment with embedding mould.

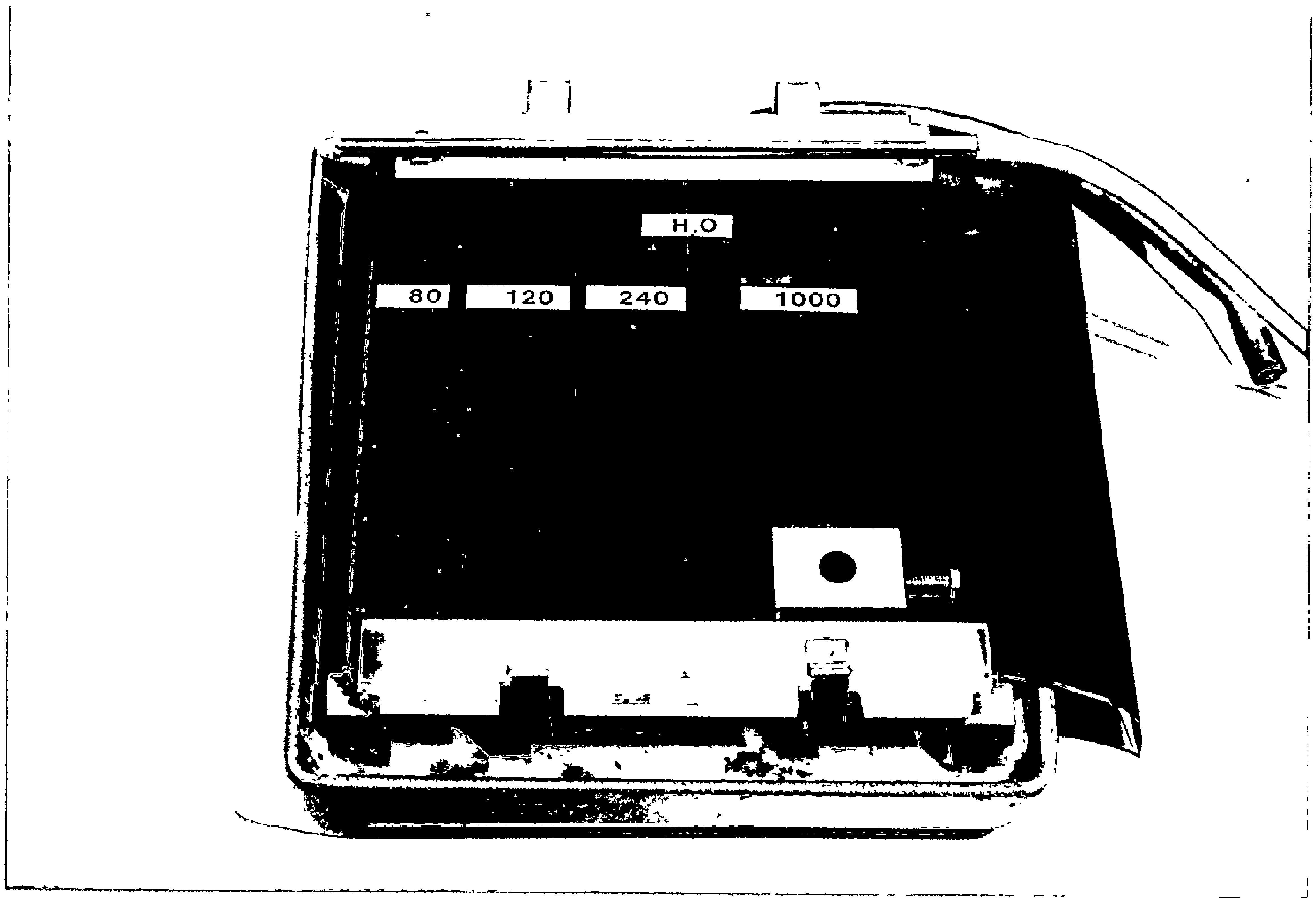
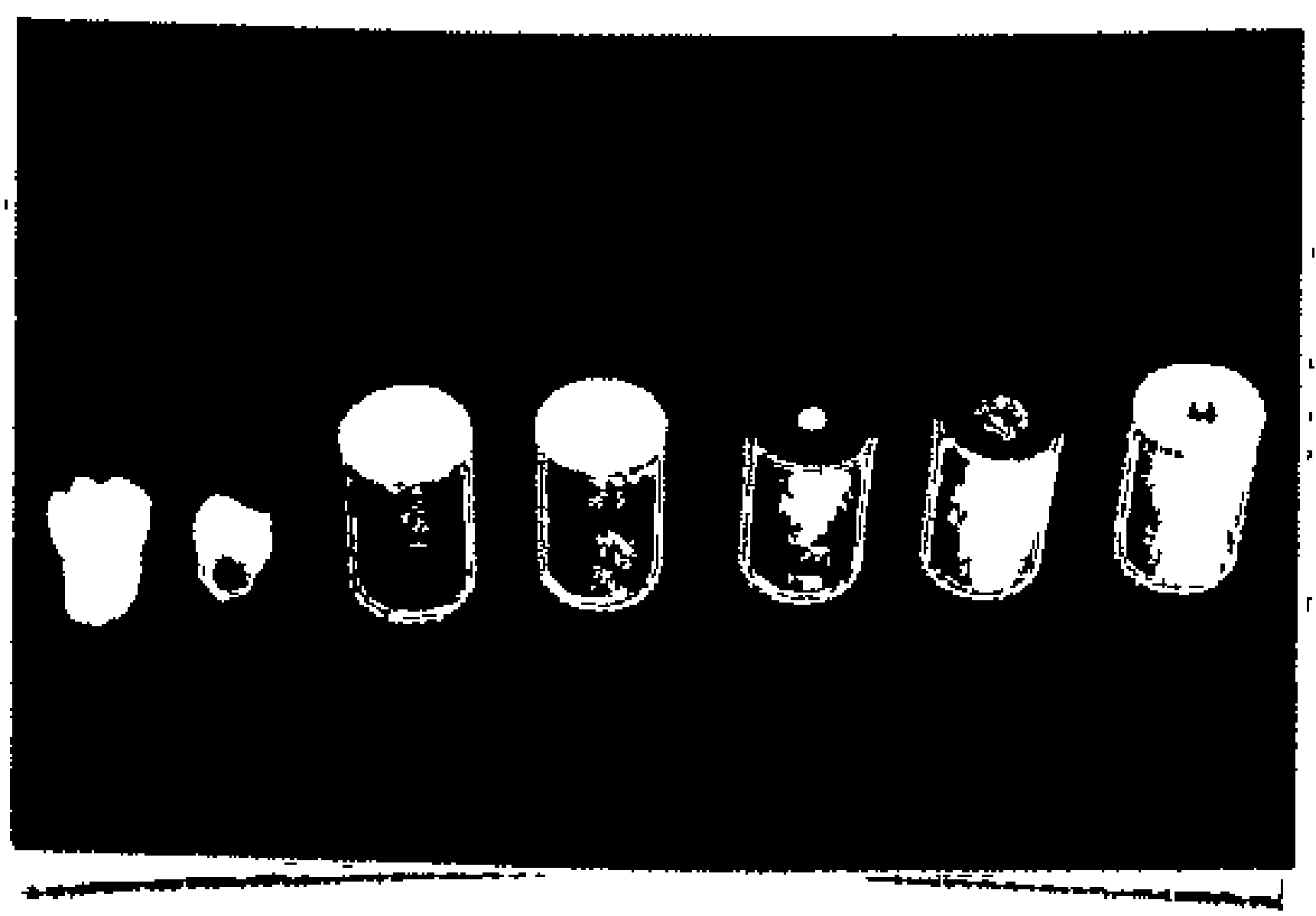


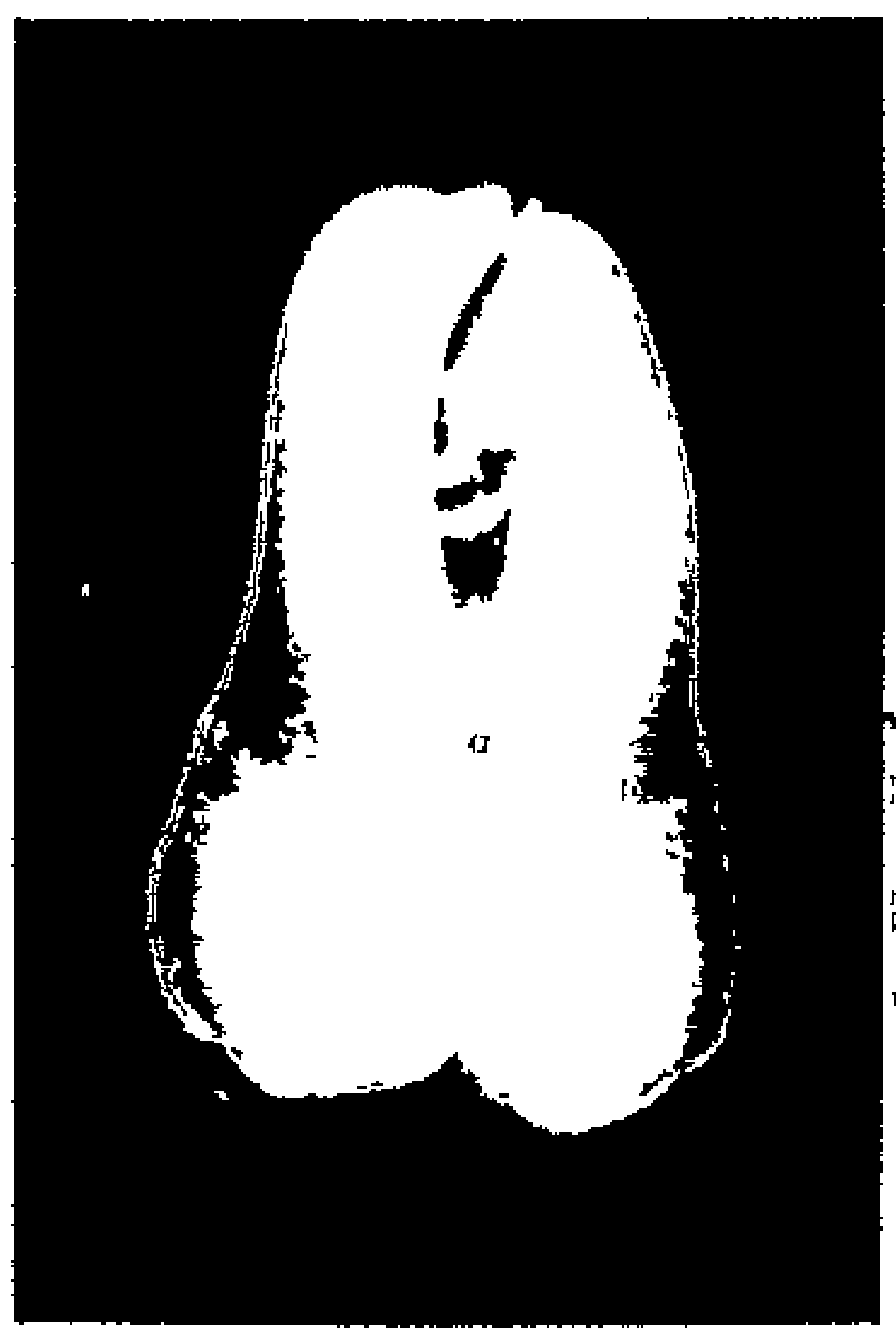
Figure 9. Abrasion apparatus and custom-made steel holder

Materials and Method

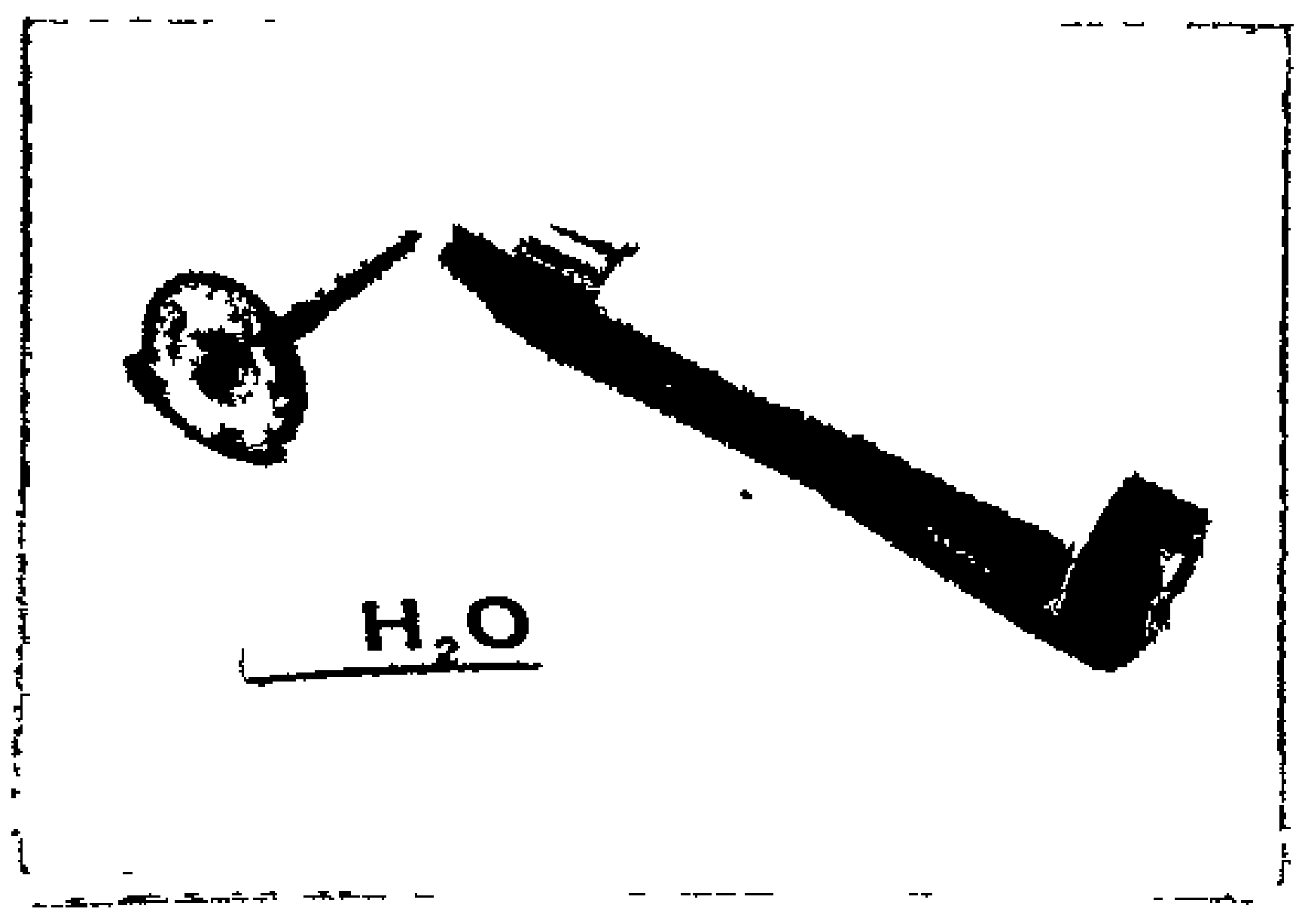
Figure 6a

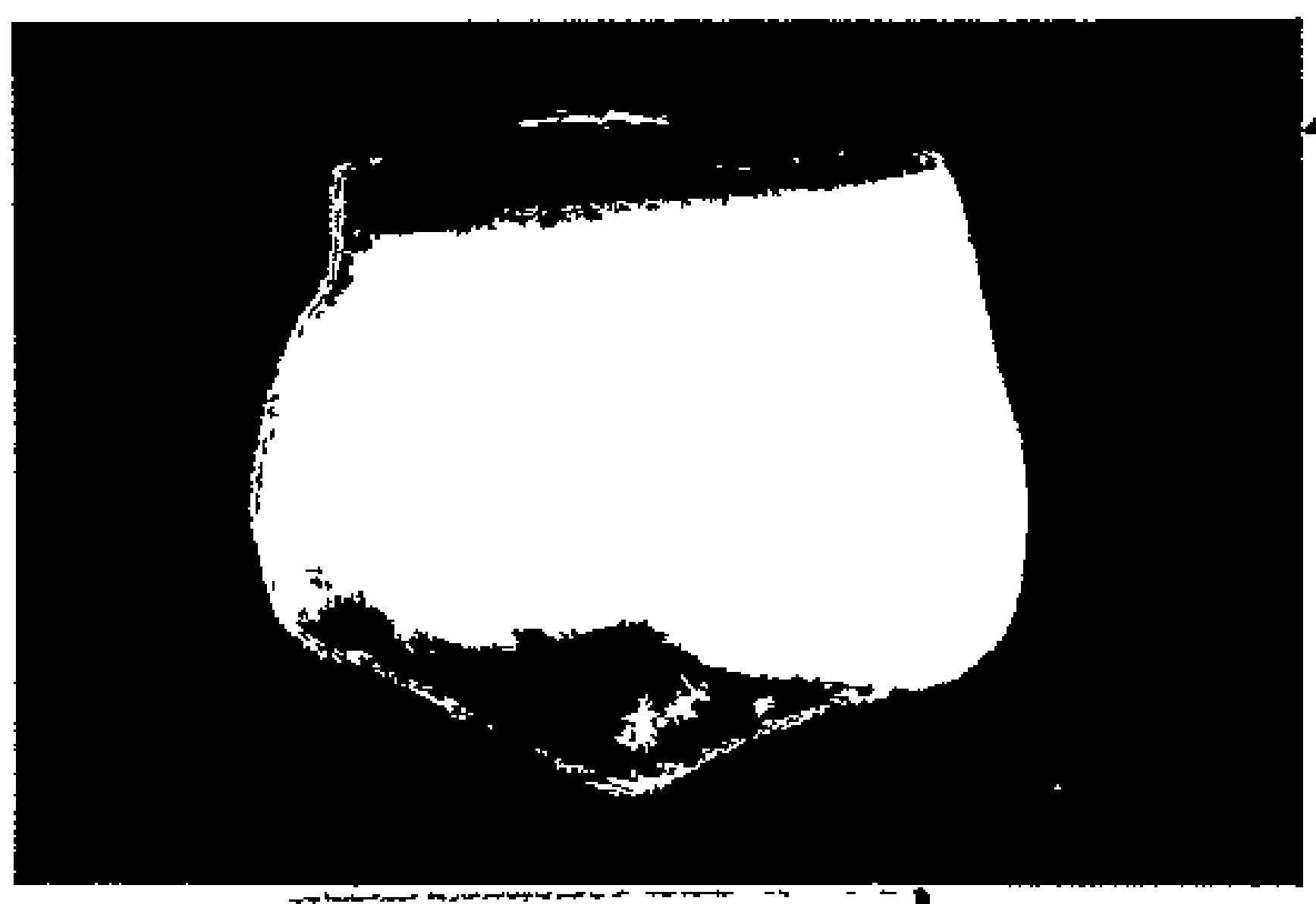


Summary

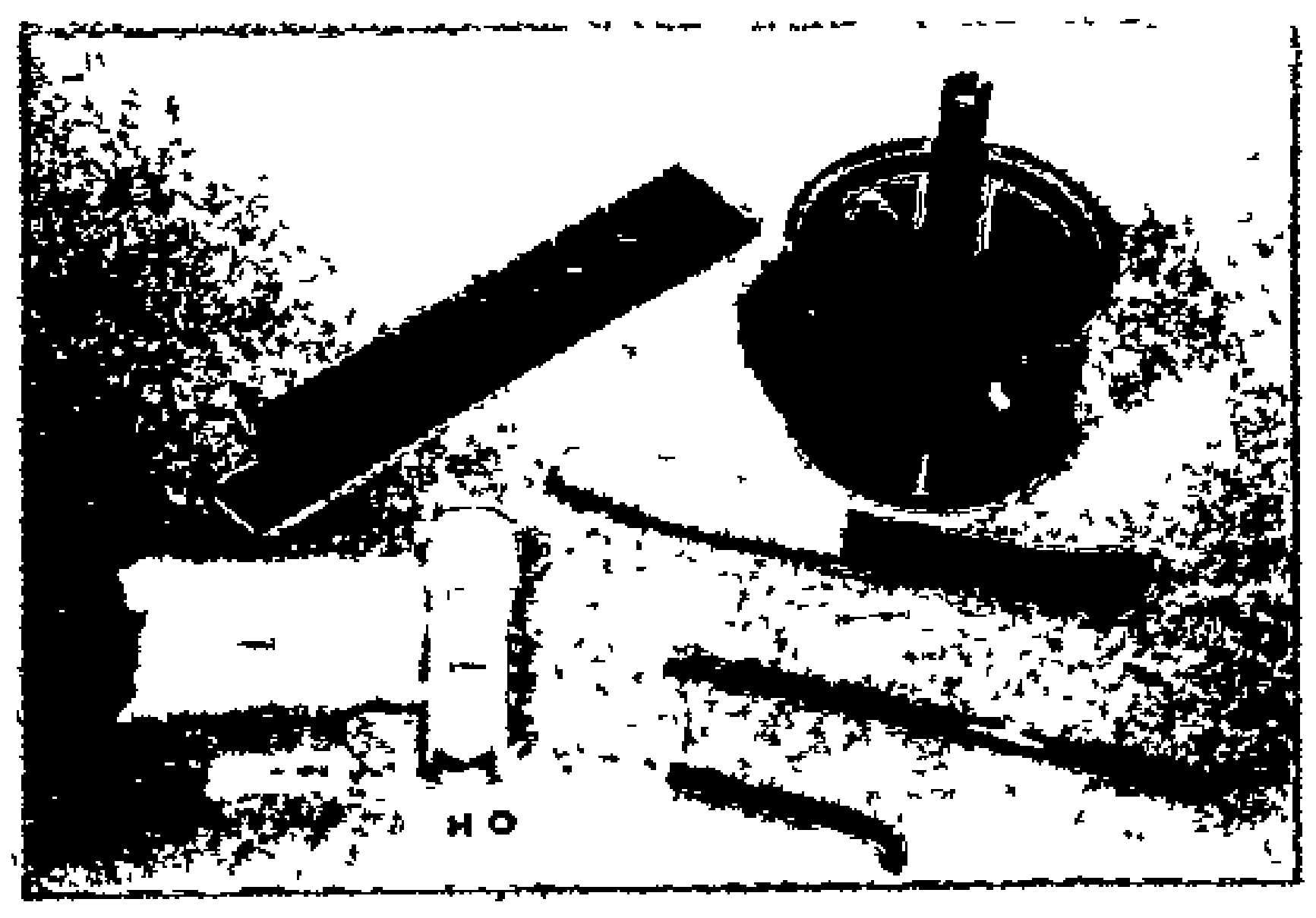


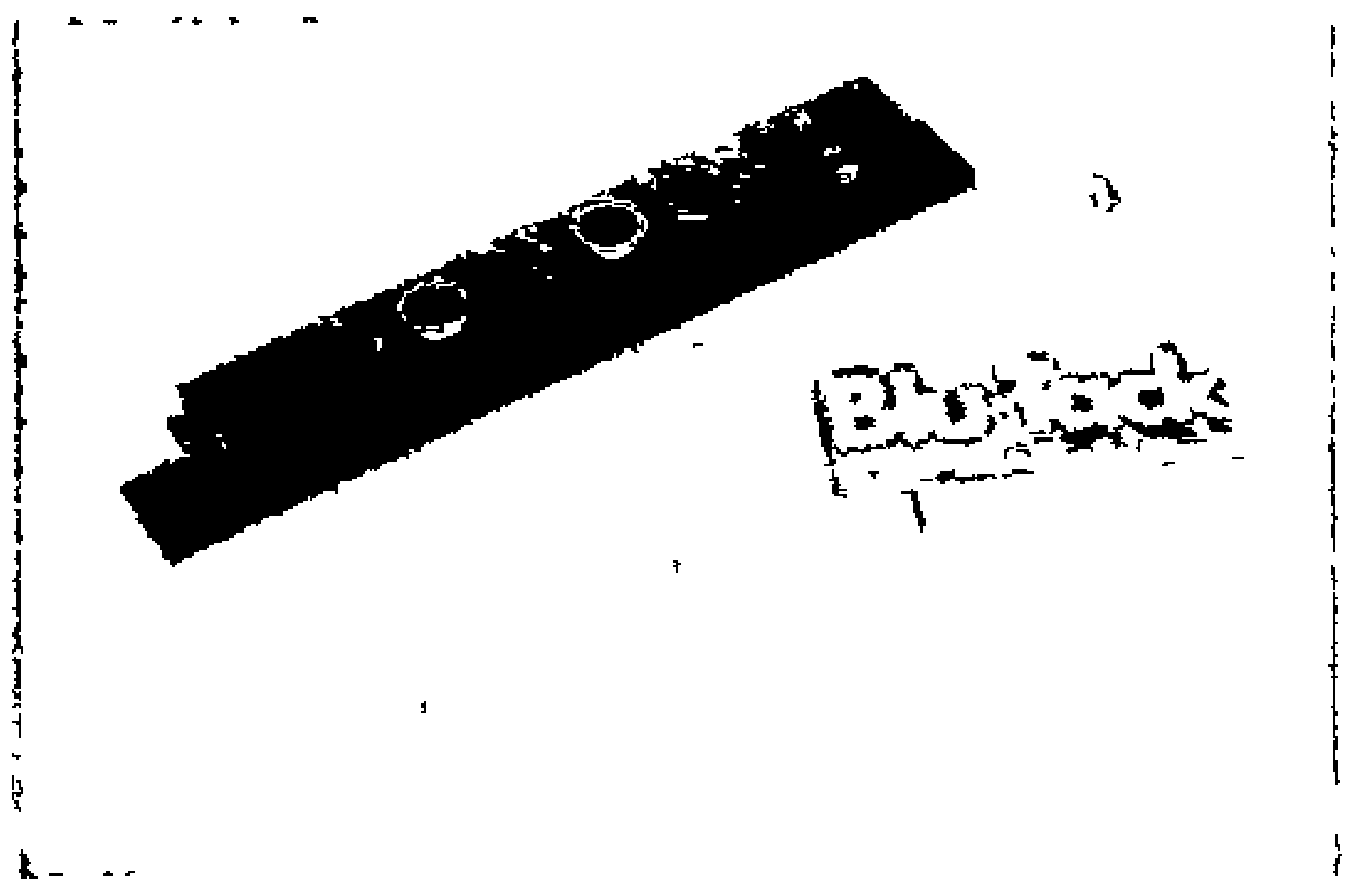
tooth





tooth crown





embedded crown

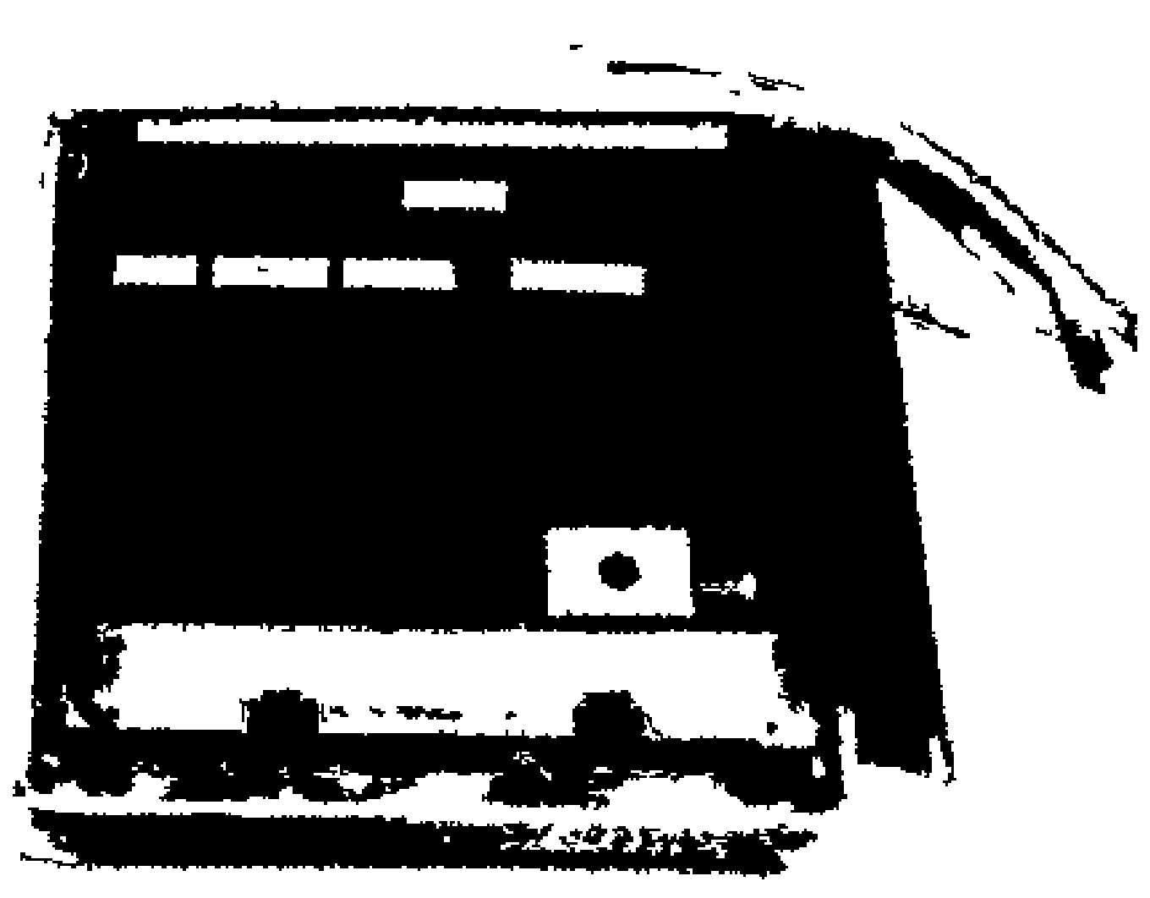
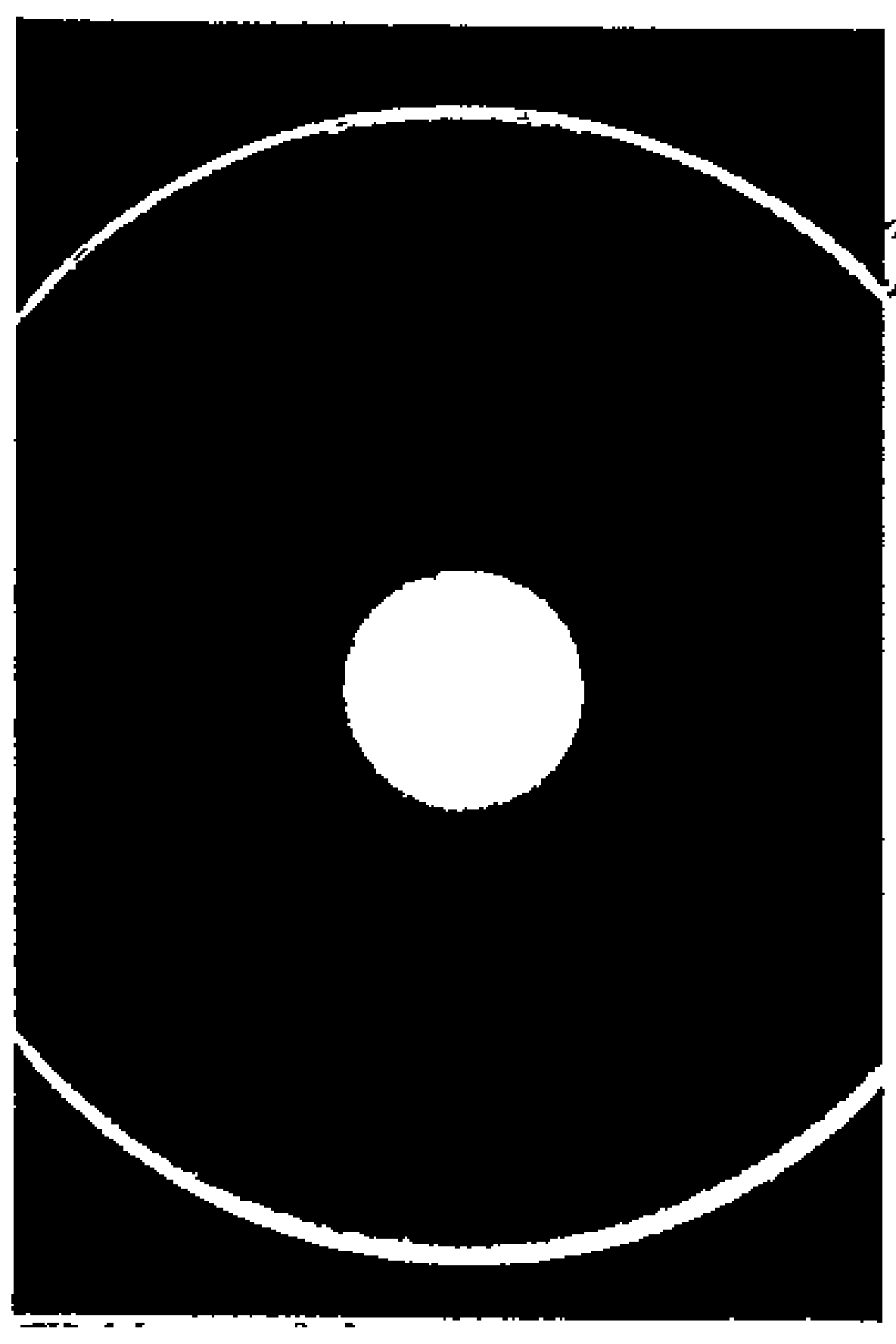


Figure 6a (cont.)

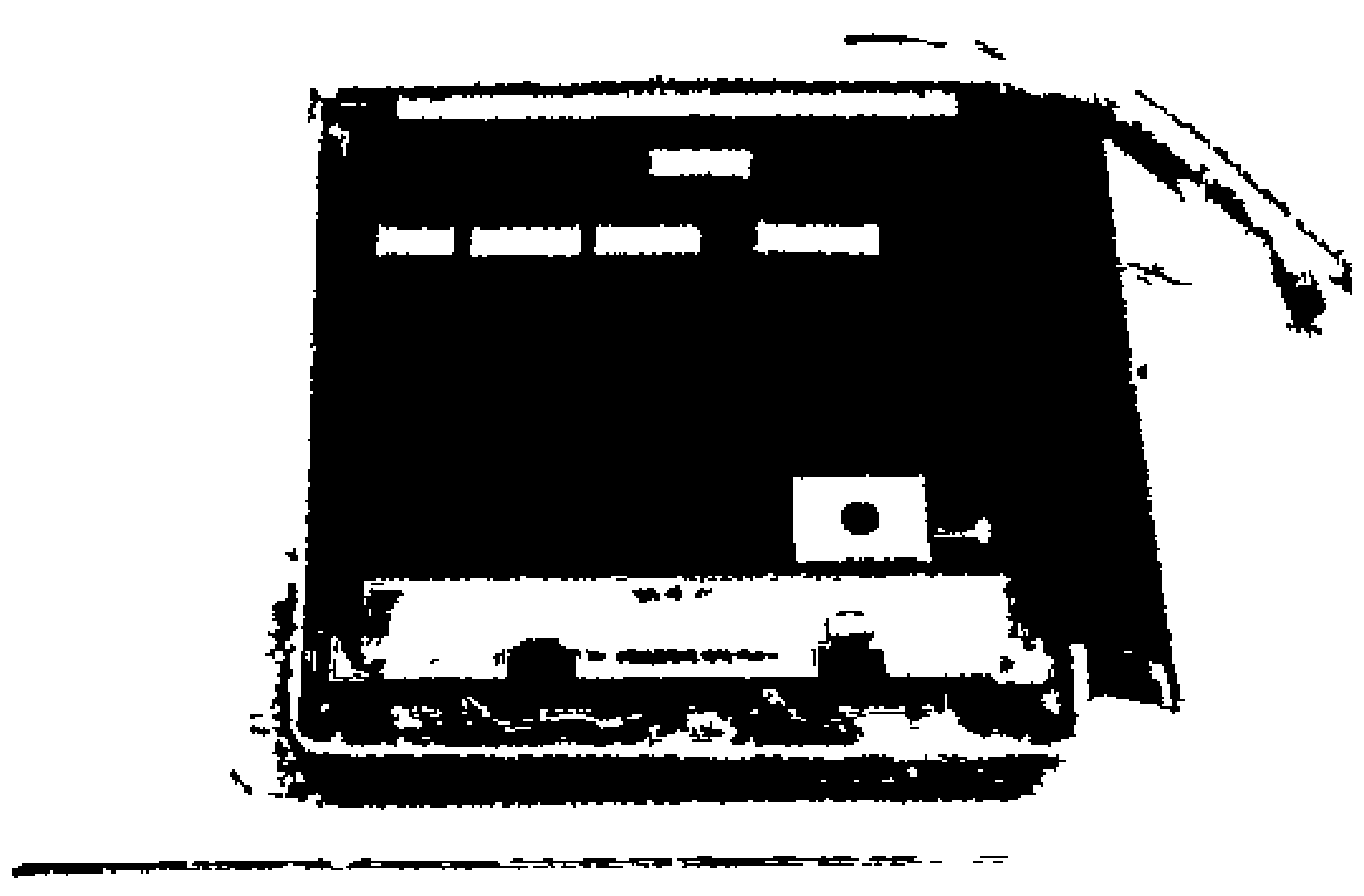
abraded embedded crown

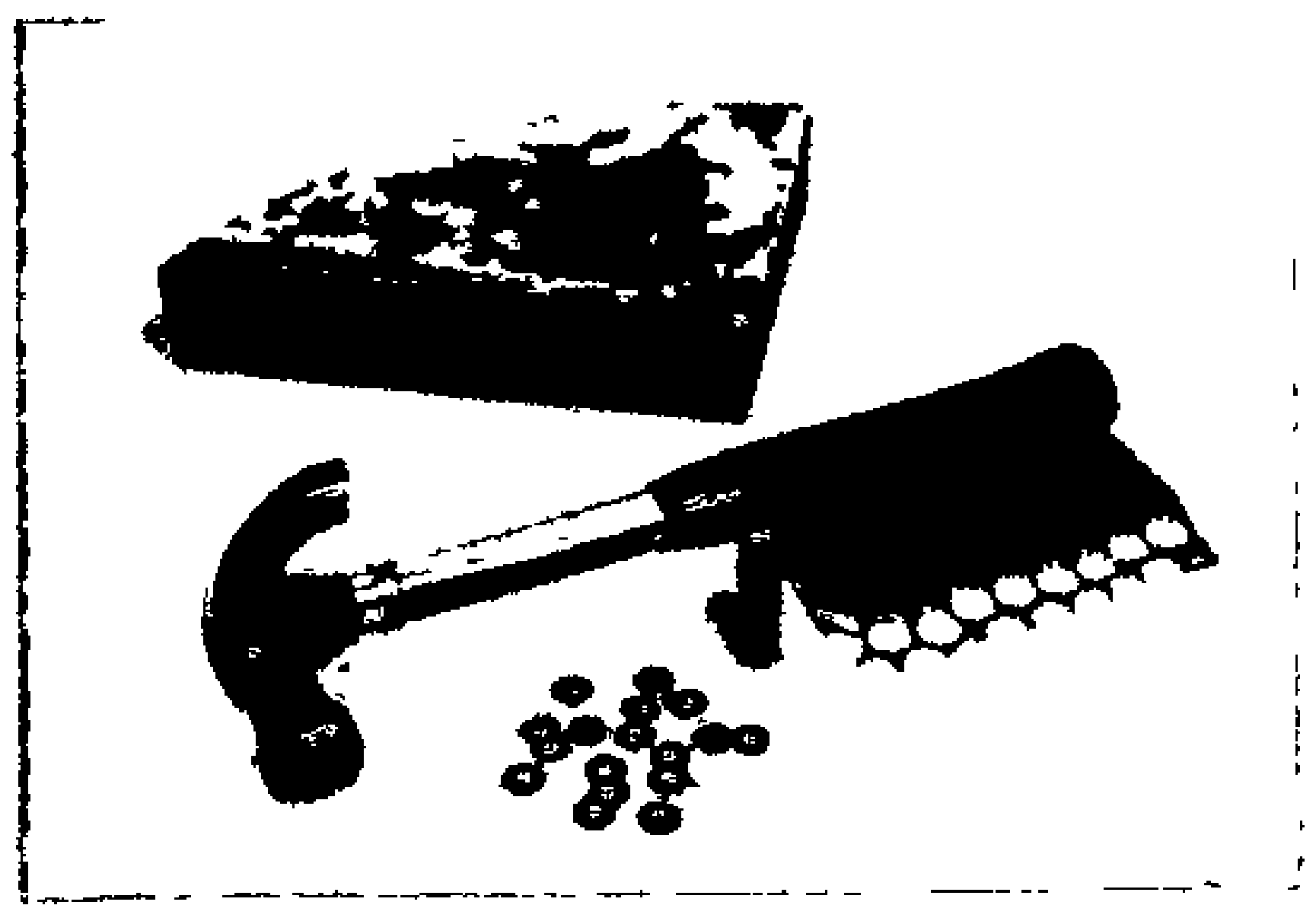


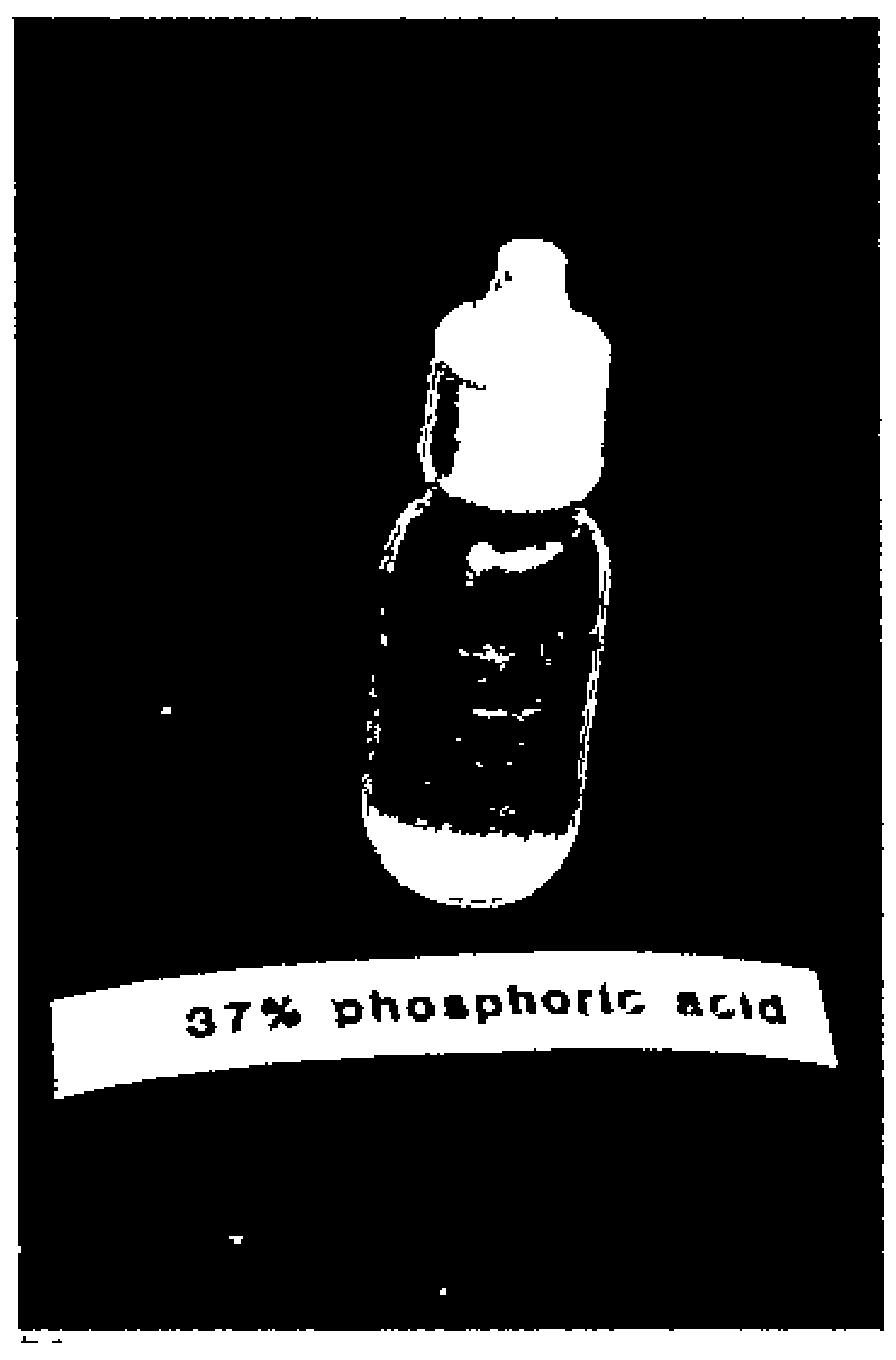
masked abraded embedded crown

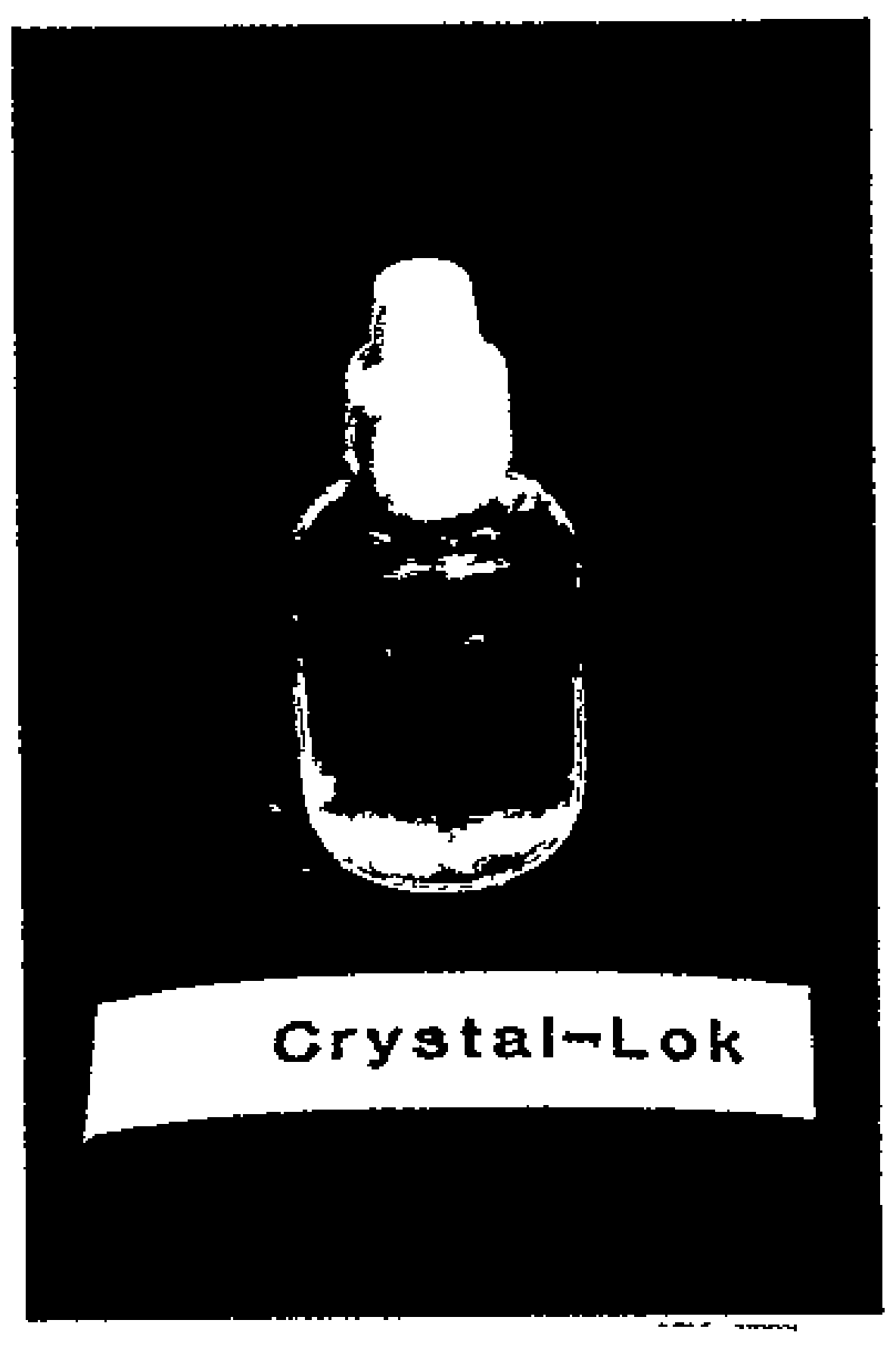
masked specimen

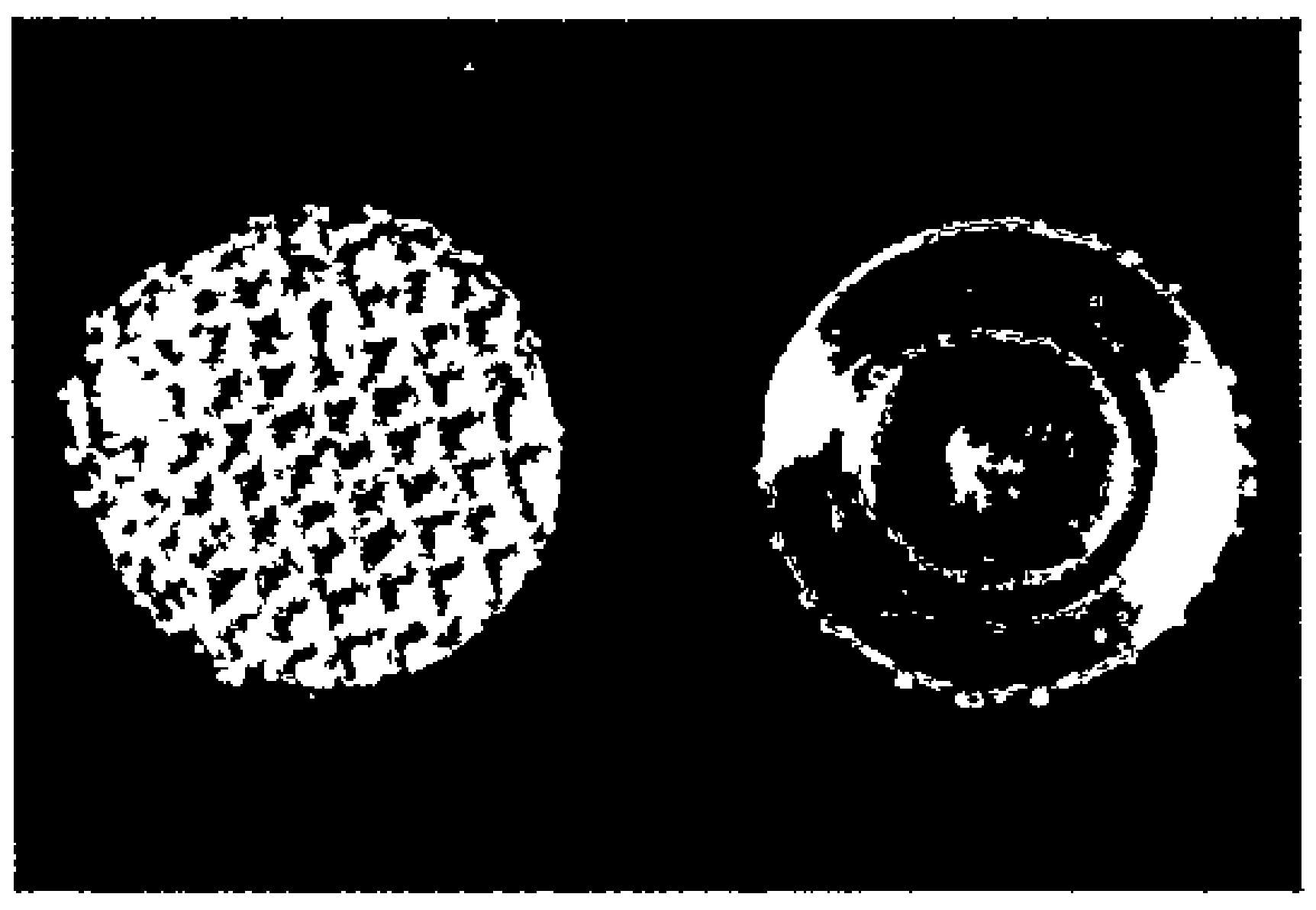
specimen

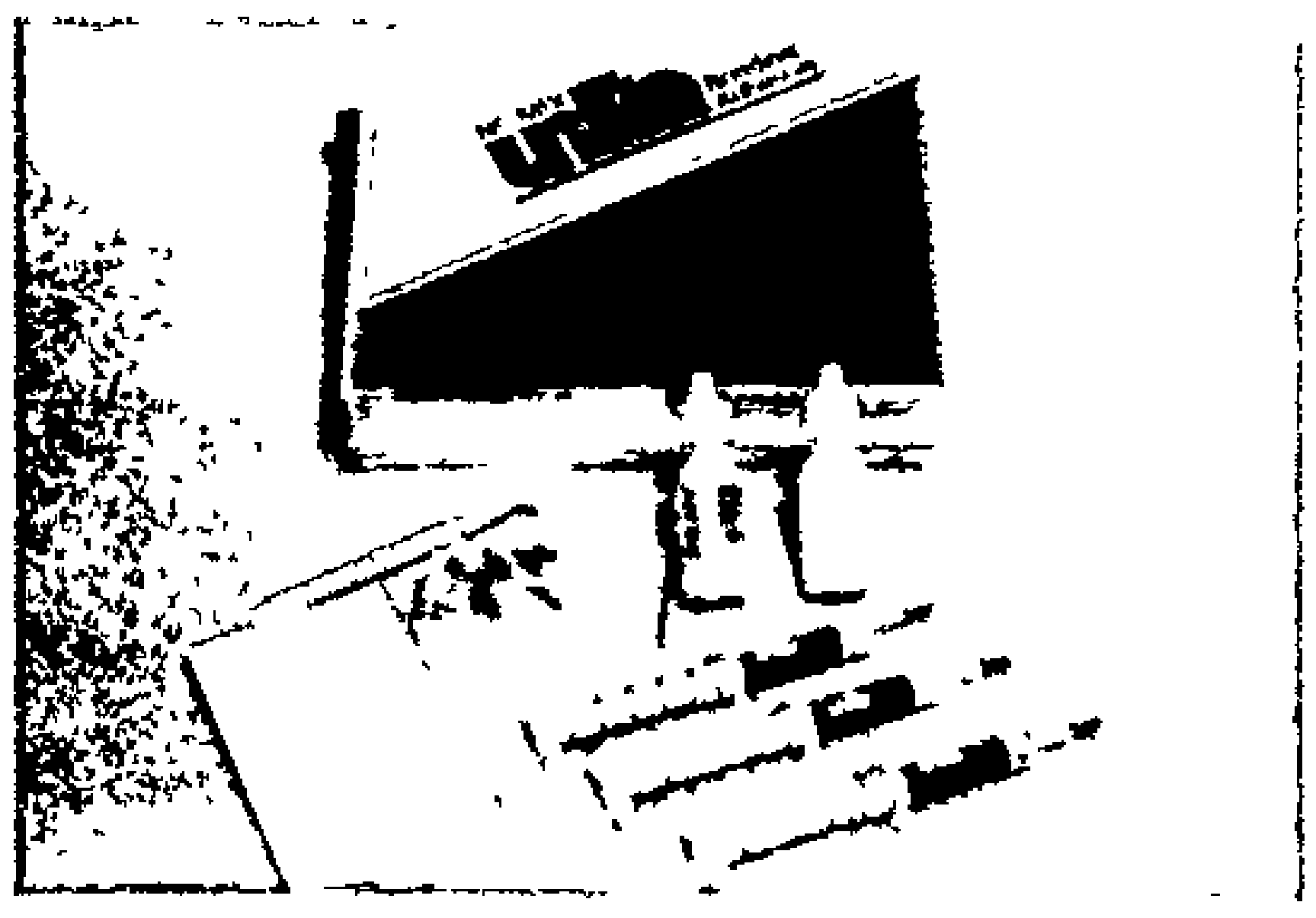






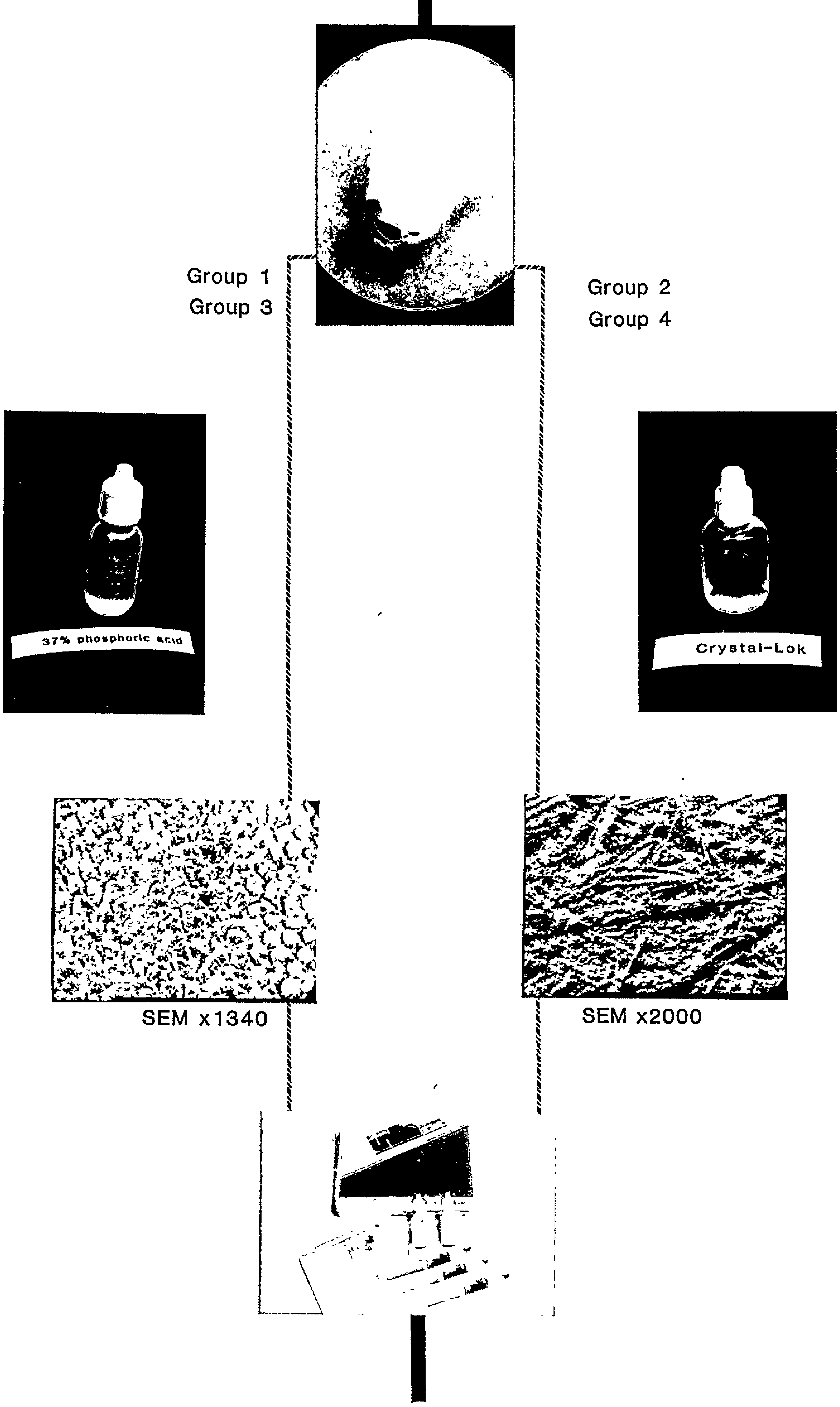






Major variation in specimen preparation

Figure 6b



Materials and Method [Fig. 6]

Immediately following extraction, human premolars and permanent molars were placed in fluoridated (1ppm F) tap water. Subsequently, using a water-cooled diamond disc in a straight handpiece, the roots were removed [Fig. 7], and mesiodistal crown widths reduced to enable the crown segments to be embedded in Vel-Mix* (dental stone) filled moulds. The crown segments were positioned, and then retained with a reusable adhesive#, on microscope slides, so that their buccal surfaces would, after embedding, be readily accessible to, and correctly oriented for abrading [Fig. 8]. The Vel-Mix cylinders in which the crown segments were embedded, were removed from the moulds after one hour, and placed into a 100 per cent humid atmosphere at room temperature, awaiting abrasion.

The abrasion procedure entailed:

1) the Vel-Mix cylinders being placed into a custom-made steel holder [Fig. 9]; this enabled production of visually flat enamel surfaces perpendicular to the cylinder long axes;

2) rubbing the cylinder/holder unit over continually wet silicon carbide paper, from grade 80 through 120, 240, 1000, held in a specially designed apparatus [Fig. 9];

3) inspection of the abraded surfaces, and rejection of any in which dentine had been exposed.

Each abraded surface was then washed with tap water and dried with oil-free compressed air [Fig. 10]. An annular self-adhesive vinyl@ mask, with a punched out central area, was placed over each, exposing an enamel area approximately 3.2 mm in diameter [Fig. 11].

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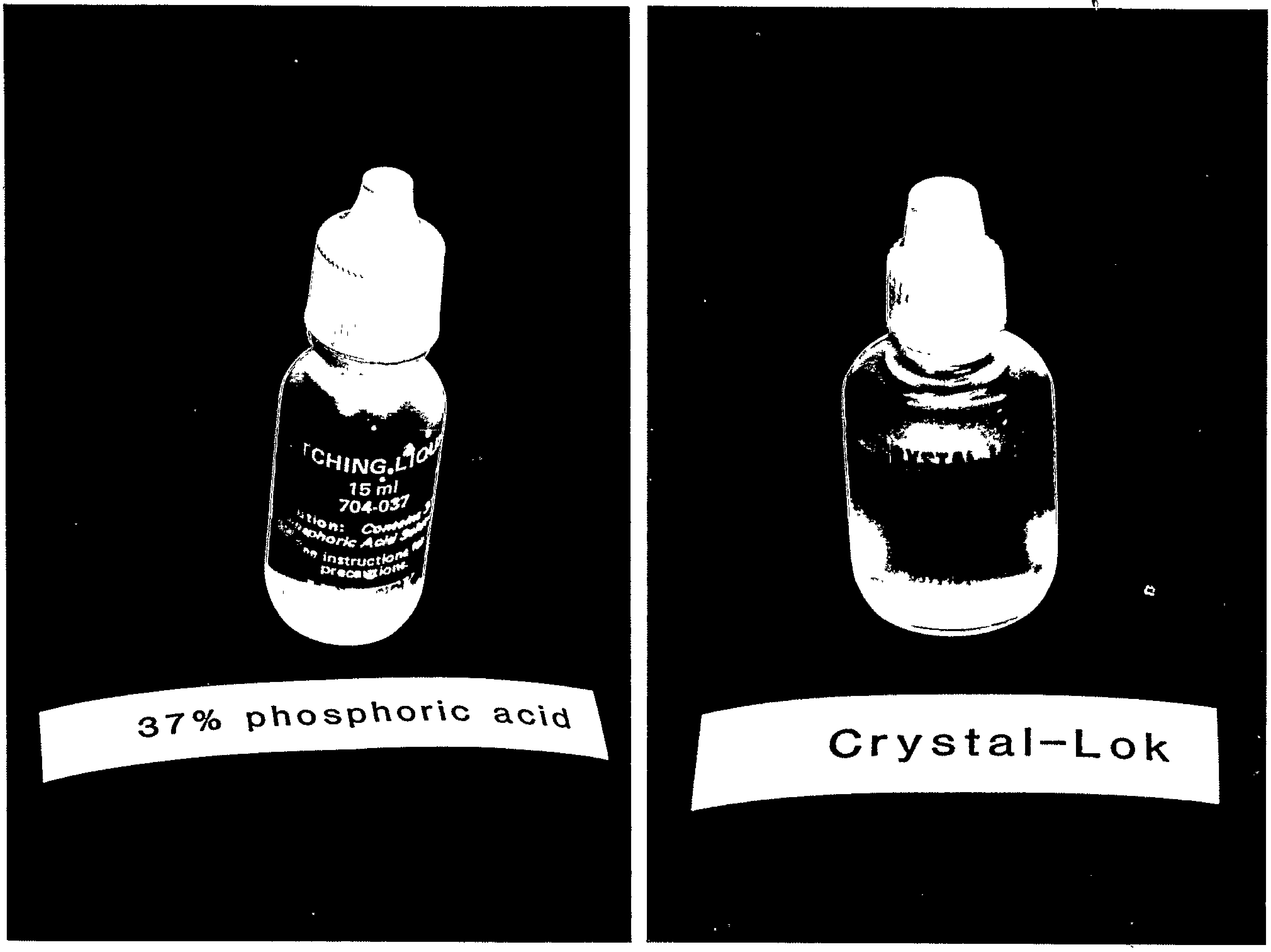
* Kerr, Sybron

\# Blu-Tack: Bostik, Emhart Aust. Pty. Ltd.

@ Con-tact: Acmil Aust. Pty. Ltd.



a) 37 per cent w/w phosphoric acid

b) Crystal-Lok

Figure 12. Enamel surface modifiers

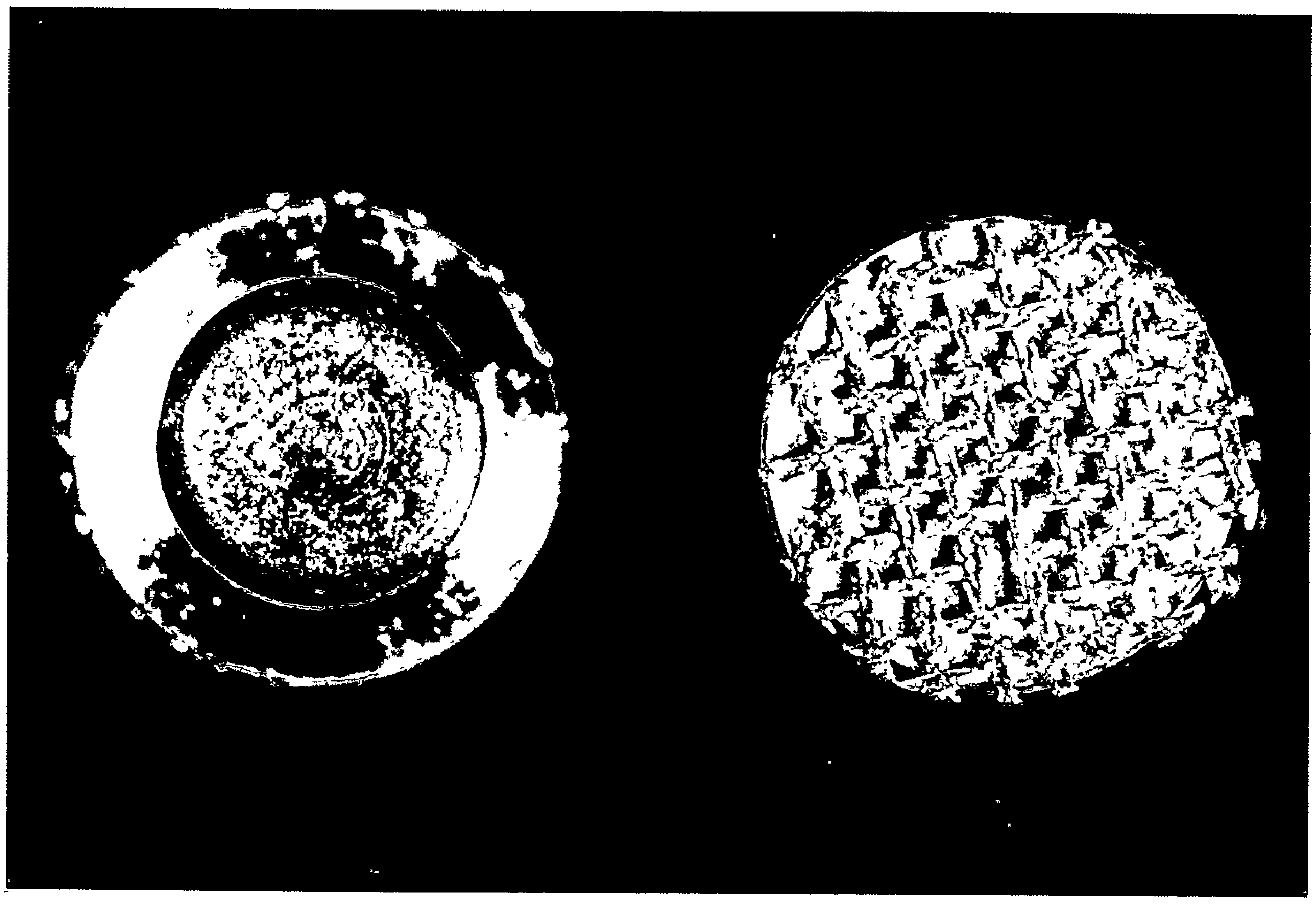


Figure 13. Lingual button with mesh base

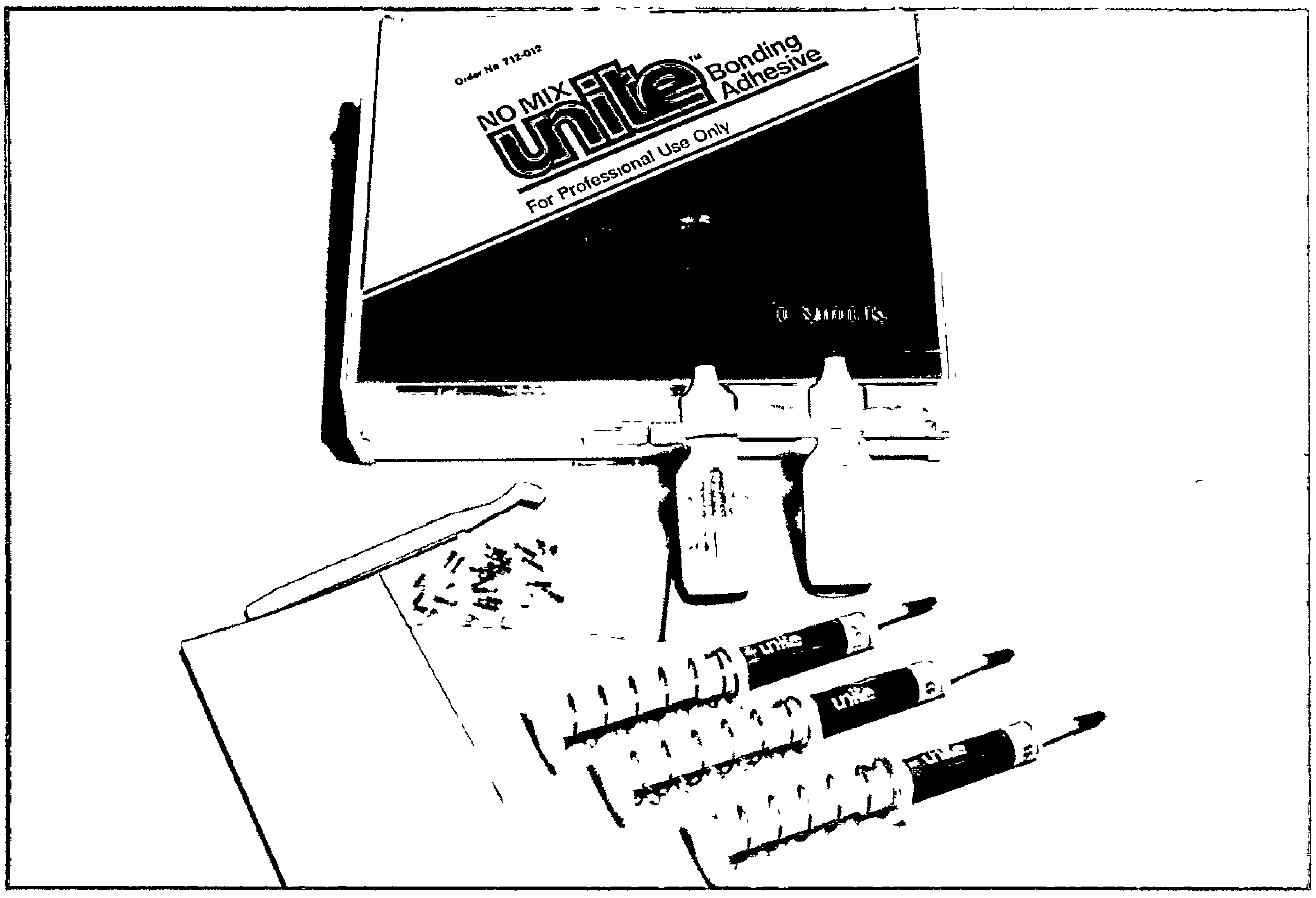


Figure 14. Unite bonding adhesive

To each of the following groups, twenty cylinders were allotted:

[Times listed refer to the period elapsed after polymerization initiation, and prior to testing]

Group 1: Acid-etch - 24 hours

The exposed enamel surface was modified with 37 per cent w/w phosphoric acid [Fig. 12a] for 60 seconds, washed with running tap water for 30 seconds, then dried with oil-free compressed air. To each surface a lingual button¢ [Fig. 13] was bonded using Unite bonding adhesive* [Fig. 14]. After 10 minutes polymerization on the bench, each specimen was stored in 100 per cent humidity until tested, 24 hours after polymerization initiation.

Group 2: Crystal-Lok - 24 hours

The procedure was similar to that in Group 1 with the exception of the enamel pretreatment [Fig. 6b] which, in this group was for 30 seconds with Crystal-Lok [Fig. 12b].

Group 3: Acid-etch - 10 minutes

Group 4: Crystal-Lok - 10 minutes

In these groups the cylinders were stored in 100 per cent humidity at $34^{o} \pm 2^{o}$ C for 24 hours prior to bonding. The Group 3 conditioner was the 37 per cent phosphoric acid, and the Group 4, Crystal-Lok. Tap water, at about 35^{o} C washed the conditioned enamel for 30 seconds, which was then dried with oil-free compressed air. One minute after the lingual bonding commenced, each specimen was stored at $34^{o} \pm 2^{o}$ C for 6 minutes, whereupon removal from the incubator and placement into the testing jig occurred.

¢ TP Laboratories, Inc.: 224-112: Batch 1732000
* Unitek Corp.: Batch 051383

Figure 17. Specimen; i.e. unmasked bonded abraded embedded enamel segment

Testing took place 10 minutes after the commencement of adhesive polymerization. A summary of the various steps in specimen production may be seen in Figure 15.

Shear testing was completed using a motor-driven Hounsfield tensometer# [Serial No. W5 617: Speed 1/8" per minute] in its compressive mode [Fig. 16a, b, c].

Each specimen [Fig. 17] was held in a specially made jig [Fig. 16b] during loading. Alignment of the shearing knife and specimen may be seen in Figure 16c. All testing was undertaken at $21^{\circ} \pm 1^{\circ}$ C, and 50 ± 5 per cent relative humidity.

Following shear testing, the site of fracture of each specimen was assessed with the aid of a Wild Photomakroskop M 400, magnification 6.3 to 32 times.

Testing apparatus used, and sites of bond fracture may be seen in Figure 18.

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125 lb beam: Group 1, Group 2 specimen no. 61, 62, 63
62½ lb beam: Groups 3, 4, & Group 2 specimen no. 64 to 80

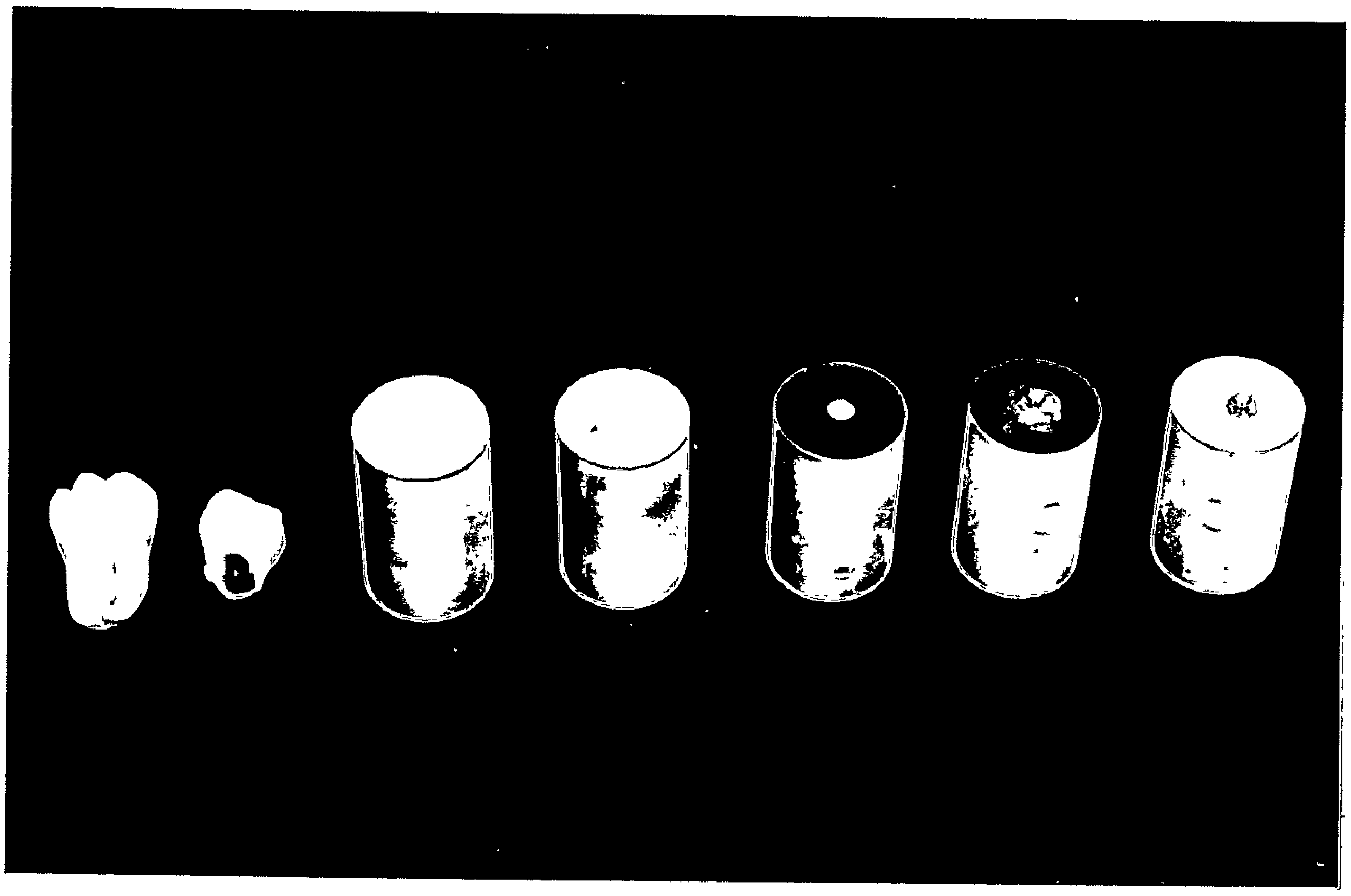
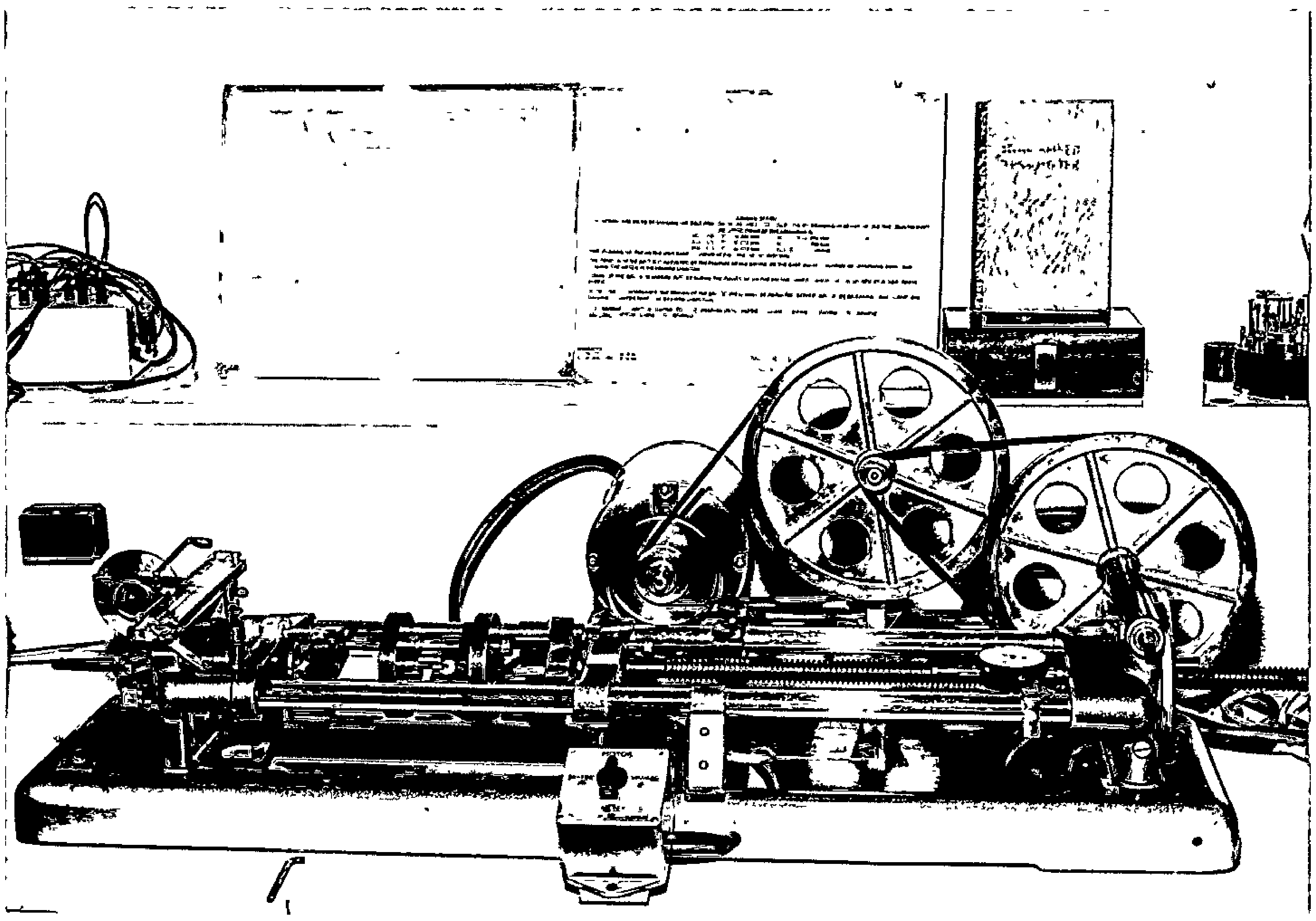


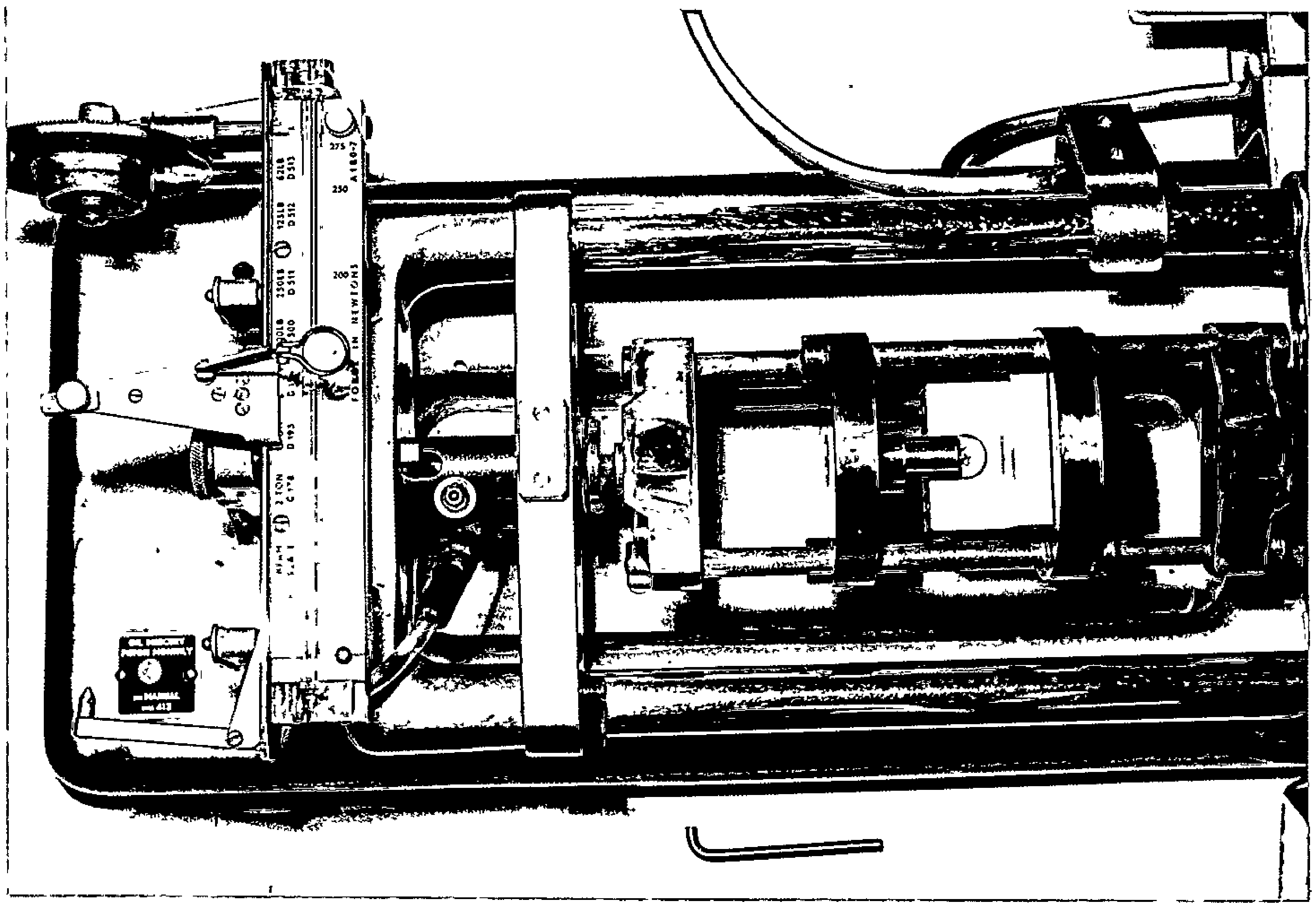
Figure 15. Various stages of specimen preparation



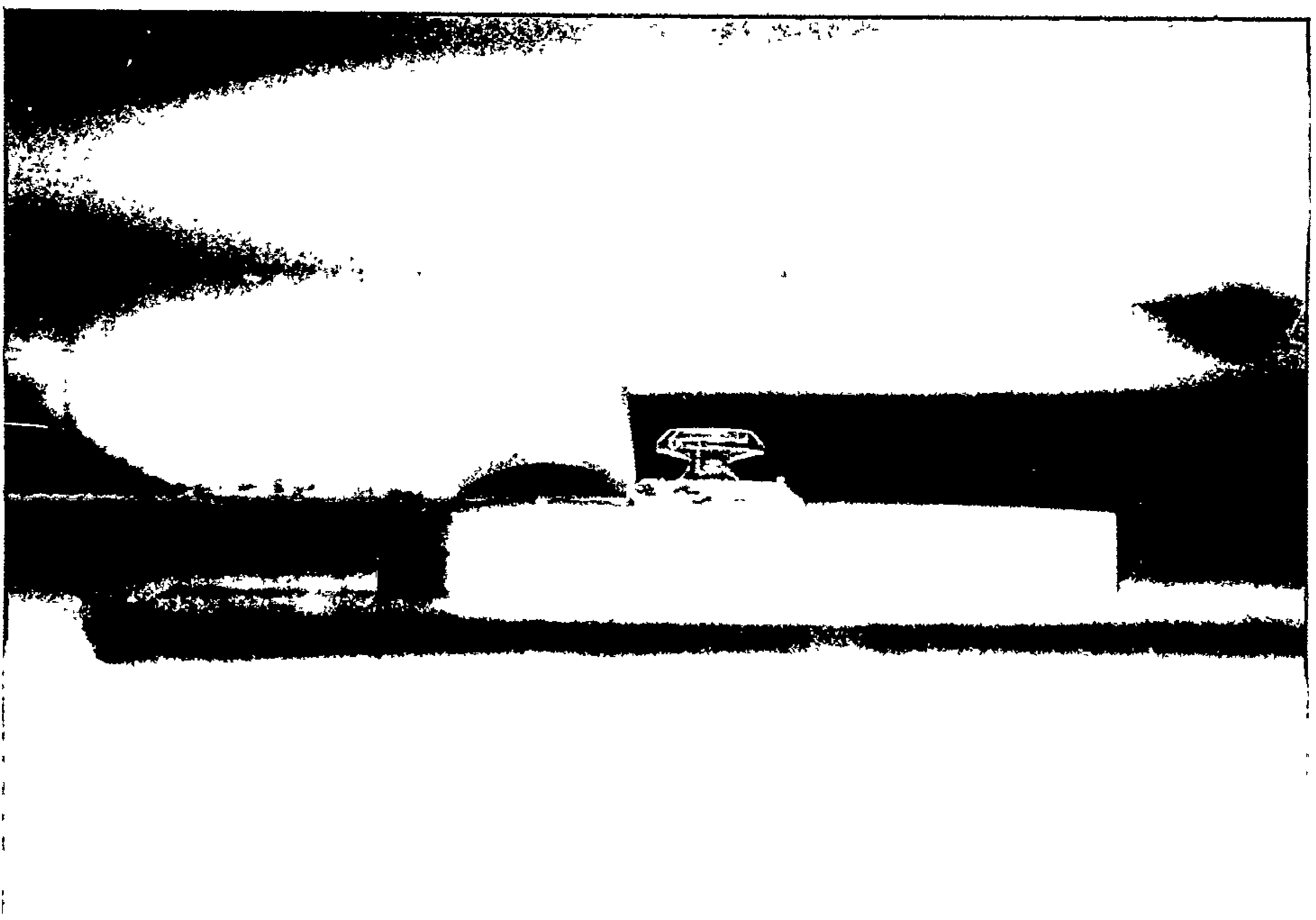
a) Hounsfield tensometer

Figure 16. Testing apparatus

Figure 16 continued



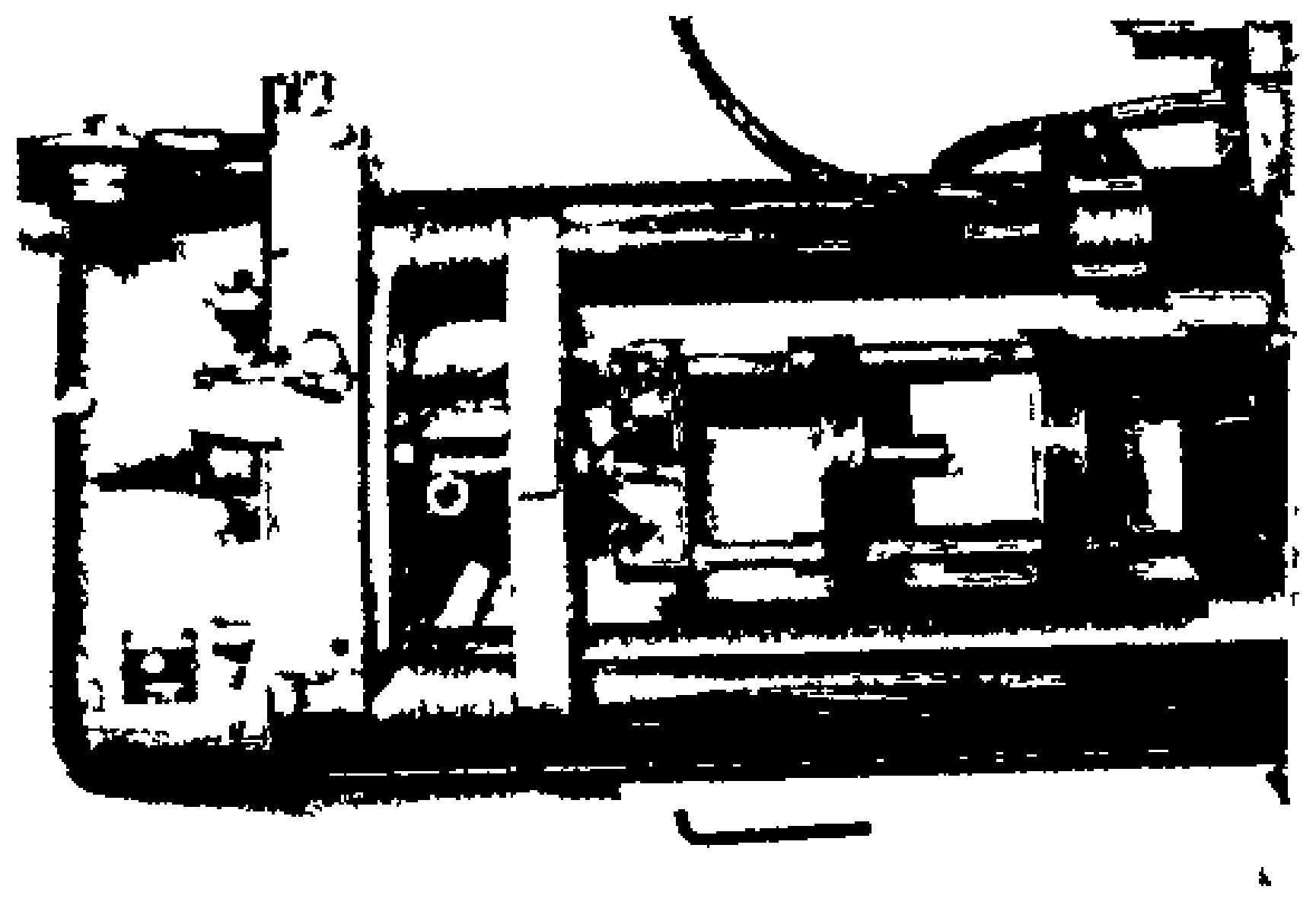
b) Custom-made jig with specimen in place



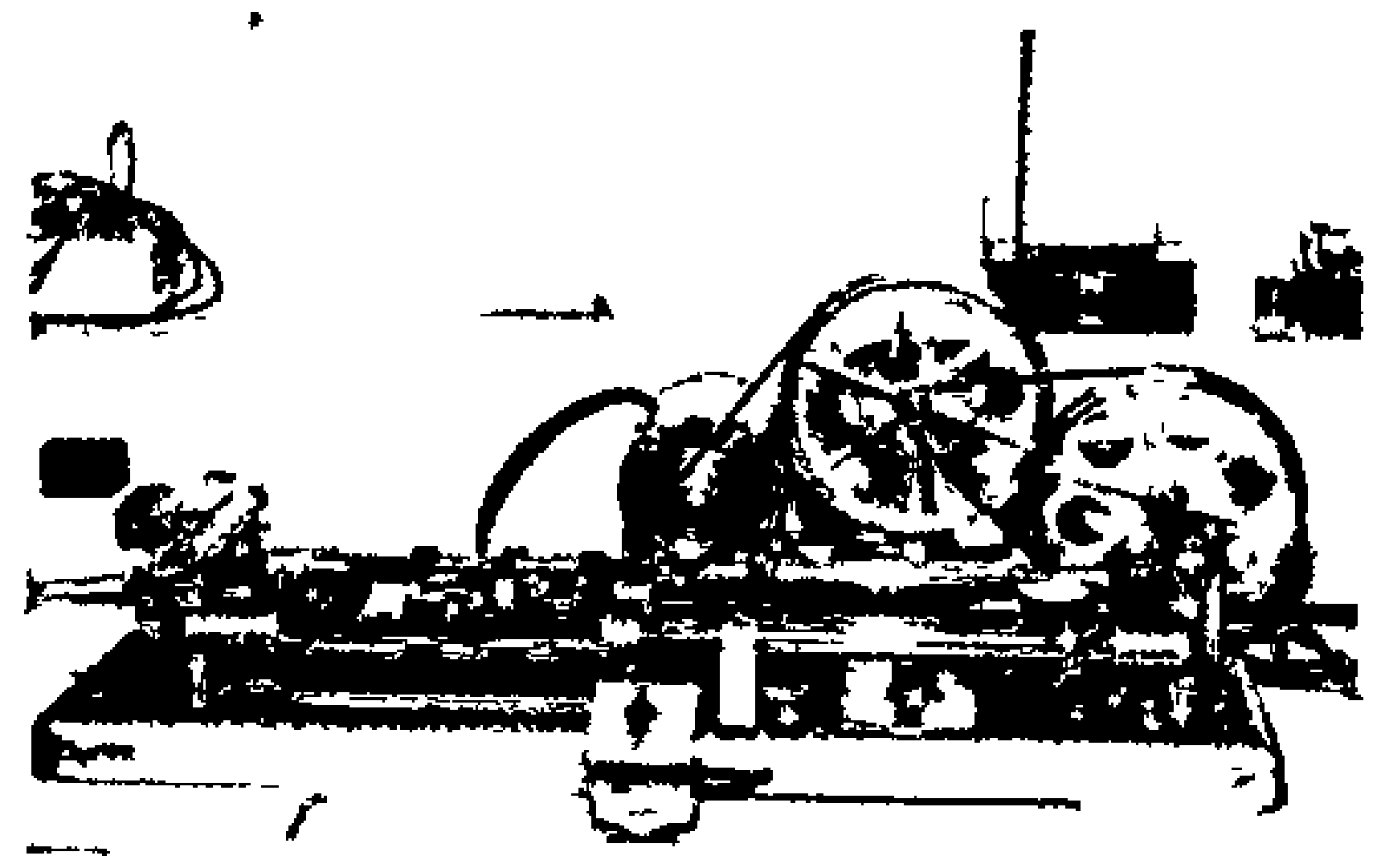
c) Alignment of shearing knife and orthodontic bonding unit

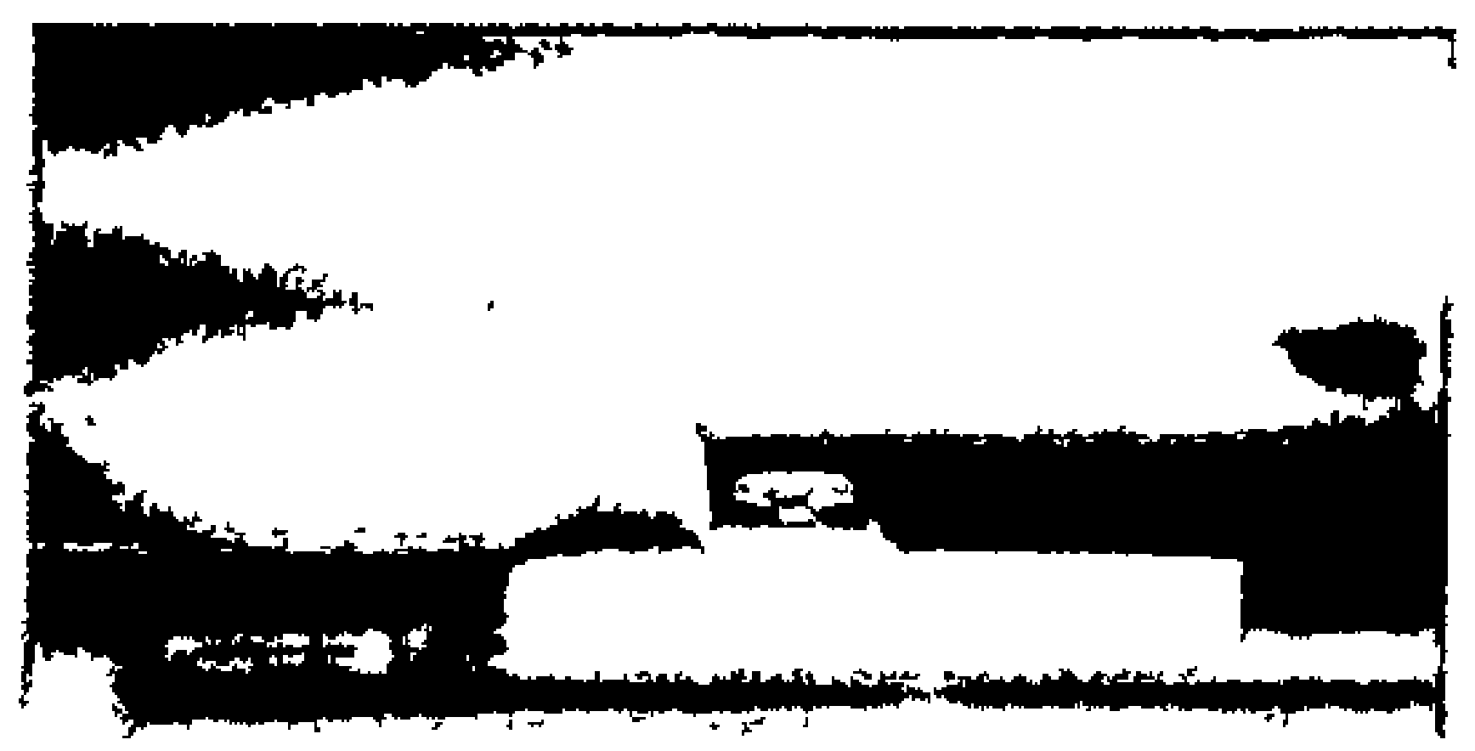
Figure 18

Shear testing apparatus and Fracture sites

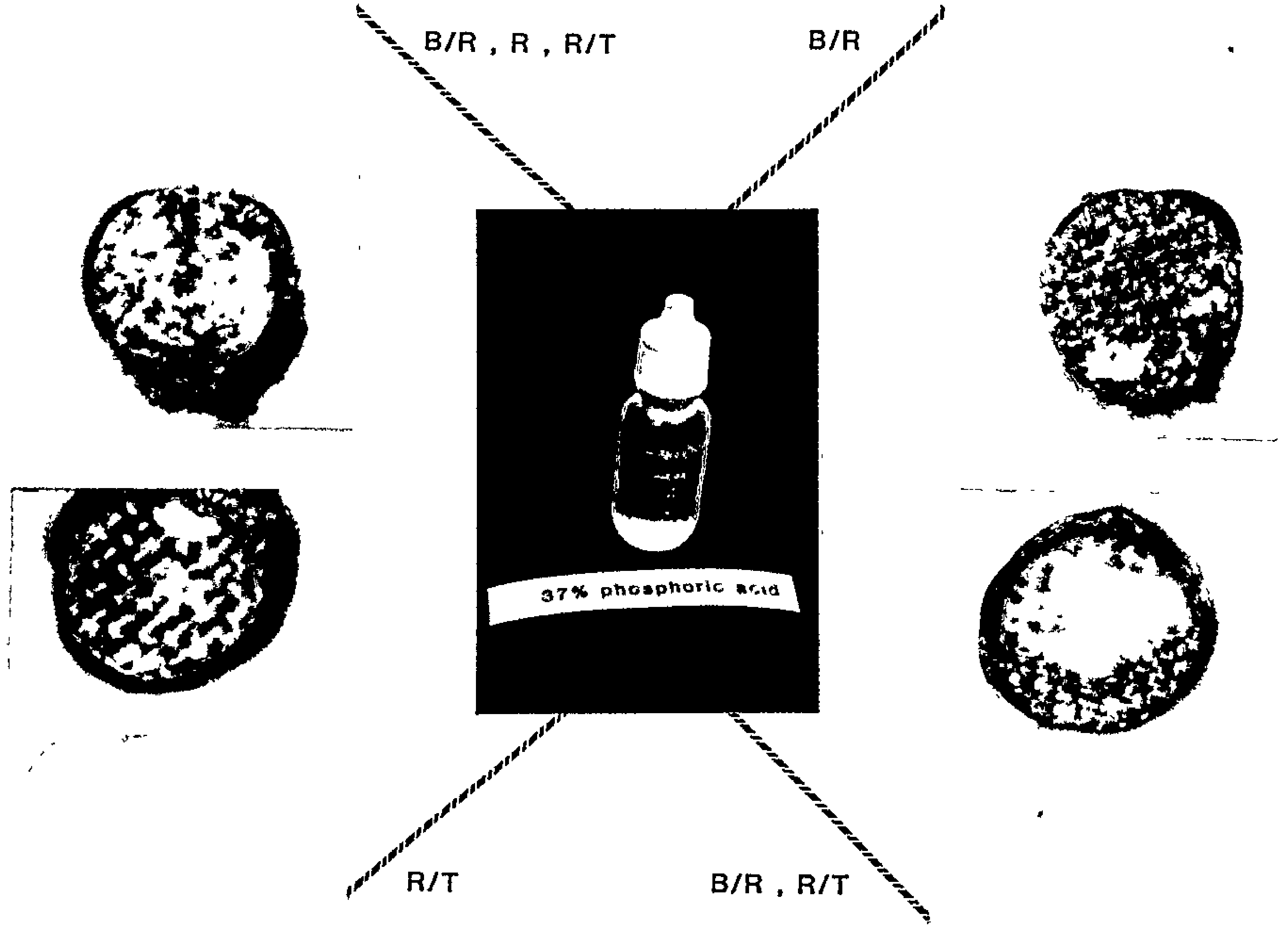


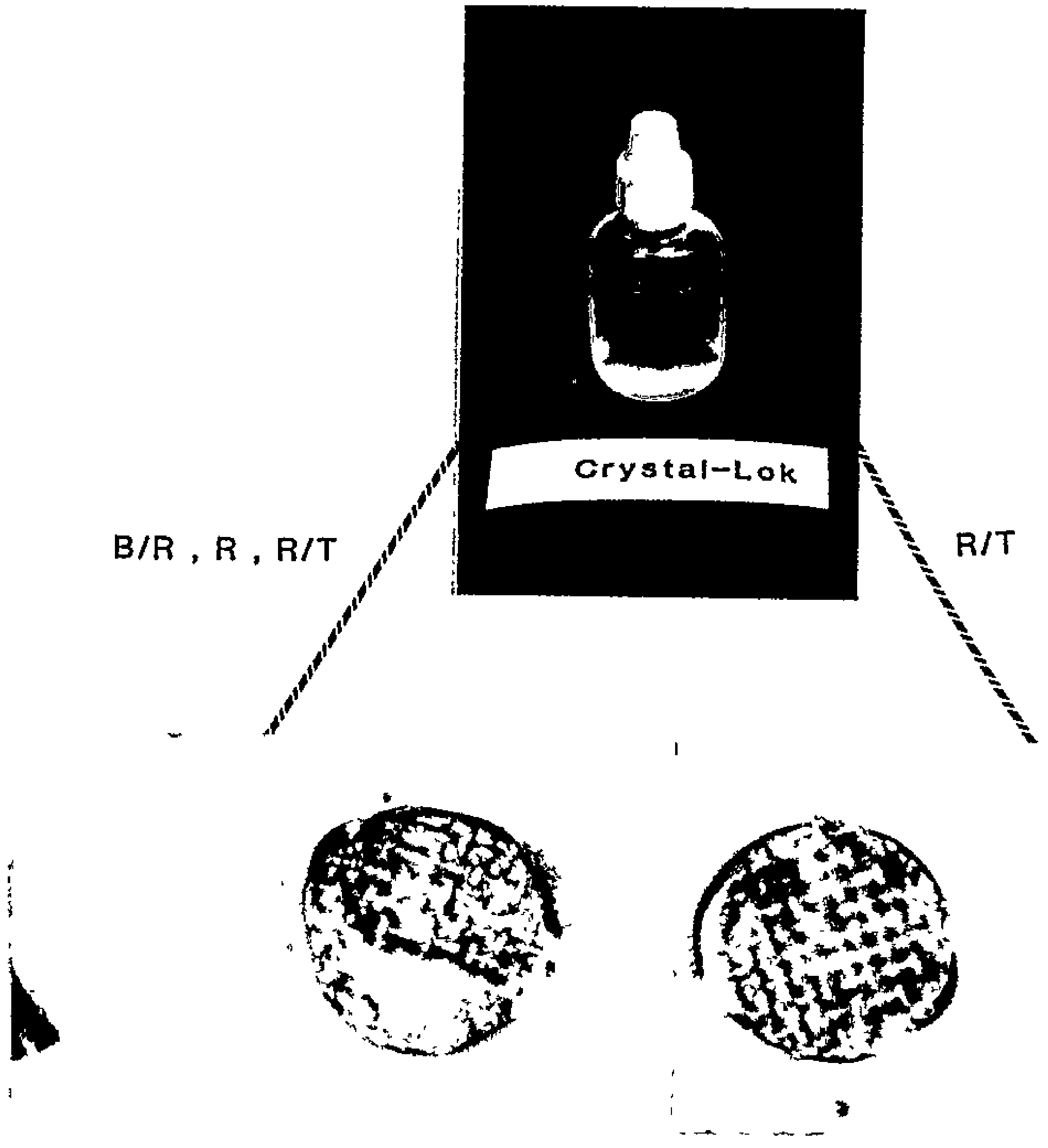
Jig





Jig and specimen aligned





		Number and sites of bond failure			
	n	BR [Fig. 16a]	RT [Fig. 16b]	BR/RT [Fig. 16c]	BR/R/RT [Fig. 16d]
Group 1: Acid-etch - 24 hours	20	0	8	10	2
Group 2: Crystal-Lok - 24 hours	19	0	19	1	0
Group 3: Acid-etch - 10 minutes	12	4	2	0	5
Group 4: Crystal-Lok - 10 minutes	19*	0	14	2	3

* one specimen used for SEM observation
BR = bracket-resin interface
RT = resin-tooth interface
R = within resin

Table 4. Number and sites of bond failure with different enamel treatments

	n	Mean shearing force at bond failure (N)	Standard deviation (N)	Approximate shear strength** (MPa)	Standard deviation (MPa)
Group 1: Acid-etch - 24 hours	20	162	24	20	3
Group 2: Crystal-Lok - 24 hours	19	101	21	13	3
Group 3: Acid-etch - 10 minutes	12*	78	14	10	2
Group 4: Crystal-Lok - 10 minutes	20	56	17	7	2

* specimen number reduced due to consistency of forces measured

**diameter of bonded area assumed to be 3.2 mm in diameter

N - newton

MPa - mega pascal

Group 1 is significantly greater than Group 2, $p < 0.001$

Group 3 is significantly greater than Group 4, $p < 0.001$

Table 3. Results of shear strength tests

Results

Results are tabulated in Table 3. Mean shearing force at bond failure was significantly greater for Group 1 (162 ± 24 N) than for Group 2 (101 ± 21 N), and for Group 3 (78 ± 14 N) than for Group 4 (56 ± 17 N).

Table 4 demonstrates fracture site distribution [Fig.18].

Figure 19. Scanning electron micrograph of abraded enamel
Magnification: 1000 x

Discussion

Many previous orthodontic bonding unit "shear" testing studies reported in the orthodontic literature have tested shear/peel rather than "pure" shear strengths (refer to Chapter 1). In this study, an attempt was made to measure shear strength forces more closely approximating "pure" shear strengths. This entailed abrading the enamel surface flat and smooth, as assessed by the naked eye [Fig. 10].

An attempt was made to minimise variables. However, many still existed. The extracted teeth were stored in fluoridated (1 ppm F) water and the abraded specimens in 100 per cent humidity so that the storage media would have minimal effect on enamel chemical and physical properties. However, composition variations within and between the enamel segments could not be controlled.

A syringe-packed, no-mix orthodontic bonding adhesive [Fig. 14] was used so that air incorporation into the set resin was minimised. However, handling of the material in accordance with manufacturer's instructions did not allow for constant proportioning of primer and bonding composite.

Only one bottle of each conditioning solution was used. Therefore, possible variation in composition between different bottles (Duff and El Motayam, 1975) did not occur.

One type of mesh-backed lingual button was bonded so that base type was constant (Reynolds and von Fraunhofer, 1976; Maijer and Smith, 1981). However, it was observed during this study that the weld spots varied in size and location, and the mesh-base in area. The effect of this latter variable was eliminated as far as possible by masking all but an area of enamel approximately 3.2 mm in diameter. Nevertheless, variation in the area bonded occurred due to slight variations in areas of exposed enamel, and occasional inexact positioning of the lingual button onto the unmasked area.

Even though the abraded enamel surfaces appeared smooth and glossy to the naked eye, scanning electron microscopy at magnifications of between 50 and 5000 times revealed grooves and surface irregularities [Fig. 19]. Thus, shearing forces observed in this study, although more closely approximating pure shearing forces than in most previous studies, were still approximations.

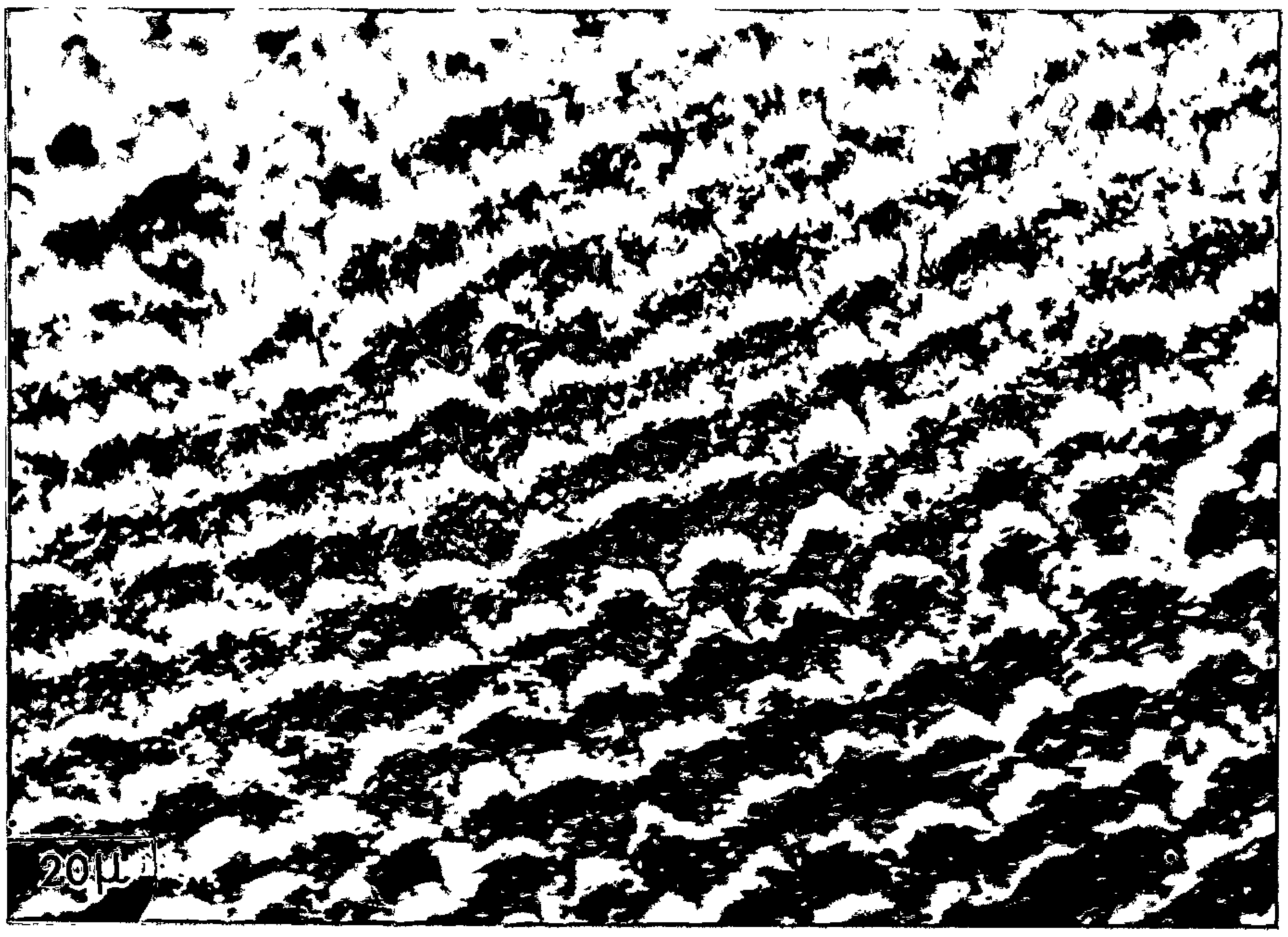
Manufacturer's instructions for the use of Unite bonding adhesive suggested that adequate adhesive-set will have occurred after 4 minutes, for archwire placement. In vitro at 21° ± 1° C, the bulk of the material was insufficiently cured (it was soft) for relevant testing to be undertaken at 10 minutes. The same situation occurred for specimins stored at 34° ± 2° C until just prior to testing at 4 minutes. Specimen storage at 34° ± 2° C for 6 minutes prior to testing at 10 minutes post-polymerization initiation produced what was considered to be a more appropriate degree of polymerization. These observations might indicate that the recommended 4 minutes should be extended.

Ultimate shearing forces of orthodontic bonding units demonstrated in this study were significantly greater for those created after enamel conditioning with 37 per cent phosphoric acid than with Crystal-Lok, at 10 minutes and 24 hours post-polymerization initiation. This is in contrast with Shaffer's (1984) claim that shear bond strengths for the two systems were essentially the same.

Fracture sites of the acid-etch specimens were distributed at various locations, whereas Crystal-Lok specimens fractured almost exclusively at the resin/tooth interface, in accordance with a claimed advantage of using this latter conditioner (Maijer and Smith, 1979; and Smith, 1979).

Evaluation of these results should include consideration of the following:

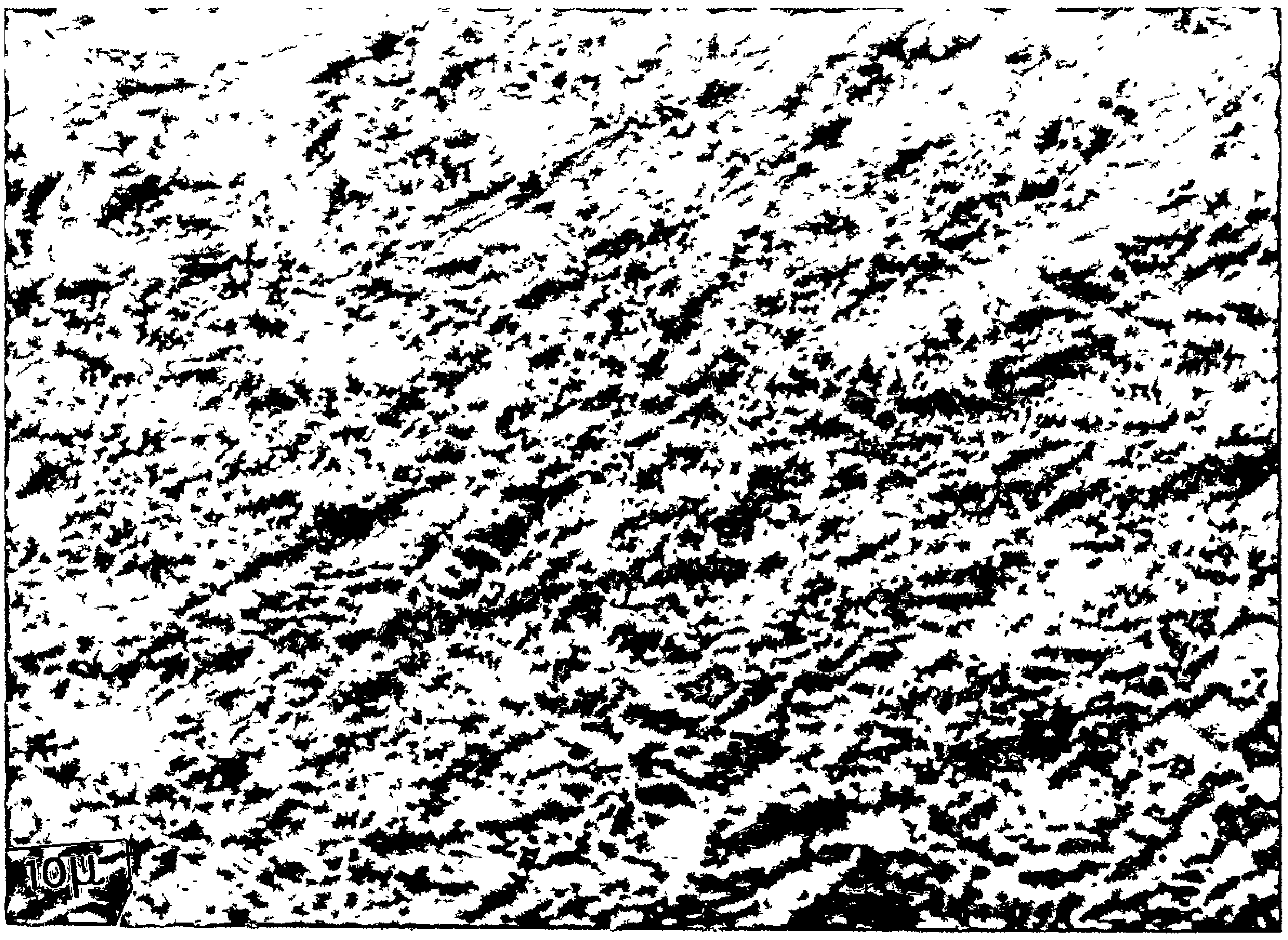
1. Many teeth used in this study were unerupted prior to extraction, therefore post-eruptive enamel maturation (Jenkins, 1978) would not have occurred, nor would any influence this process might have had on the physical and/or chemical behaviour of the enamel.



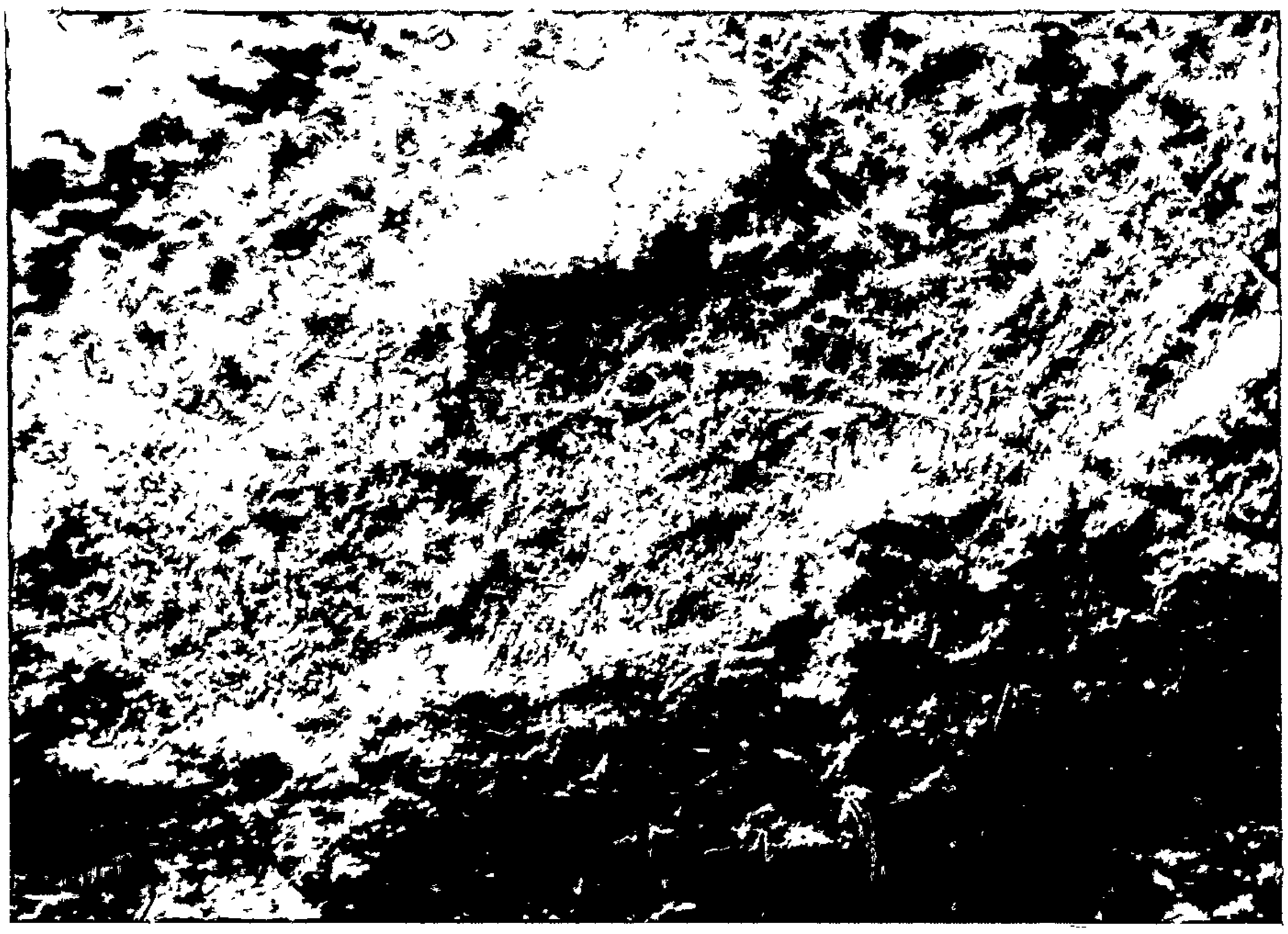
a. Magnifiaction: 1000 x

b. Magnification: 2000 x

Figure 21. Scanning electron micrographs of abraded enamel exhibiting type 2 acid-etch pattern



a. abraded enamel surface
Magnification: 2000 x



b. pumiced enamel surface
Magnification: 1000 x

Figure 20. Scanning electron micrographs of Crystal-Lok modified surfaces

2. In this study, scanning electron microscopy revealed differing surface features on unabraded but pumiced enamel when compared with abraded (as previously described) enamel following modification with Crystal-Lok. The latter exhibited greater crystal density, in agreement with the observation of Smith (1971), and more regular surface cover than did the former [Fig.20a, b]. The greater solubility of the abraded surface (Jenkins, 1978) might provide a partial explanation.

   The acid-etched abraded enamel viewed in this study (n=2) exhibited typical type 1 and type 2 [Fig.21] patterns described by Silverstone et al (1975), and Diedrich (1981). However, unlike the varying patterns on a single surface in those writers' studies, the two surfaces examined in this study each exhibited a single pattern over most of their etched area.

   These observations do not induce this author to refute the statement of Nathanson et al (1982) that "one may neither generalize that the enamel subsurface etches better than its outer surface nor claim that the opposite is true", but to hypothesize that there may be a difference in the response to conditioning of these different enamel layers.

3. The force system set up in this study was peculiar to the in vitro environment. Replication in vivo would be extremely unlikely.

   The results reported in this study are directly relevant to the system under which they were attained. Extrapolation to other systems, including in vivo should be made with caution. If this is considered, then it might be wise to use the relative strengths of the various groups rather than absolute values.

   It is evident from the literature that acid-etching of enamel with phosphoric acid in the optimum concentration range, 10-60 per cent w/w, causes alteration in surface morphology, composition, and physical properties to an indeterminate depth, at least 50-60 μm deep (Silverstone, 1975; and Diedrich, 1981), and that debonding results in

1) long-term clinical studies
    a) testing applicability to various appliance systems,
    b) indicating relative numbers of associated bond failures compared with acid-etch systems;
2) in vitro studies of
    a) bond strength tests
        i) tensile and shear/peel
        ii) over time,
    b) effects of Crystal-Lok on enamel.

Speculating: Crystal-Lok may have a major role in orthodontics even if it is proved to be inadequate when used in combination with conventional resins. New generation adhesives, such as the 4 META (4 - methacryloxethltrimellitic anhydride) or phosphate ester types (Yamashita, 1983), may be used with Crystal-Lok to achieve a reversible bond with, and minimal damage to, enamel surfaces, whilst forming stronger and/or more stable bonds with various attachments.

Summary

This study showed that,in vitro:

1) the shear bond strengths of orthodontic bonding units created following enamel modification with a 37 per cent w/w phosphoric acid were significantly greater than for those following Crystal-Lok, at 10 minutes and 24 hours;

2) the Crystal-Lok bonded specimens fractured almost exclusively at the resin-tooth interface;

3) unabraded but pumiced, and abraded enamel exhibited different surface features when modified with Crystal-Lok and viewed using scanning electron microscopy.

BIBIOGRAPHY

Adipranoto, S., Beech, D.R., and Hardwick, J.L. (1975)
Effect of pretreatment of enamel on bonding to composite restorative materials.
J. Dent. Res. : IADR Abst. L354: 53rd General Session: L89

Alexandre, P., Young, J., Sandrik, J.L., and Bowman, D. (1981)
Bond strength of three orthodontic adhesives.
Am. J. Orthod., 79: 653-660

Arana, E.M. (1974)
Clinical observations of enamel after an acid-etch procedure.
J. Am. Dent. Assoc., 89: 1102-1106

Bates, D., Retief, D.H., Jamison, H.C., and Denys, F.R. (1982)
Effects of acid etch parameters on enamel topography and composite resin-enamel bond strength.
Pediatric Dent., 4: 106-110

Brännström, M., and Nordenvall, K.J. (1977)
The effect of acid etching on enamel, dentine, and inner surface of resin restoration: A scanning electron microscopic investigation.
J. Dent. Res., 56: 917-923

Bruch, C.D. (1978)
Tension, compression, and shear.
Strength of materials for technology, Chapter 3.
John Wiley & Sons, Inc. : 53-56

Burapavong, V., Marshall, G.W., Apfel, D.A., and Perry, H.T. (1978)
Enamel surface characteristics on removal of bonded orthodontic brackets.
Am. J. Orthod., 74: 176-187

Chow, L.C., and Brown, W.E. (1973)
Phosphoric acid conditioning of teeth for pit and fissure sealants.
J. Dent. Res., 52: 1158

Council on dental materials, instruments, and equipment. (1982)
State of the art and science of bonding in orthodontic treatment.
J. Am. Dent. Assoc., 105: 844-850

Diedrich, P. (1981)
Enamel alteration from bracket bonding and debonding: A study with the scanning electron microscope.
Am. J. Orthod. 79: 500-522

Duff, E.J., and El Motayam, K.M. (1975)
Some etching solutions supplied with adhesive restorative dental materials.
Br. Dent. J., 139: 283-285

Fields, H.W. Jr. (1982)
Bonded resins in orthodontics.
Pediatric Dent., 4: 51-60

Fitzpatrick, D.A., and Way, D.C. (1977)
The effects of wear, acid etching and bond removal on human enamel.
Am. J. Orthod., 72: 671-681

Garberoglio, R., and Cozzani, G. (1979)
In vivo effect of oral environment on etched enamel: A scanning electron microscopic study.
J. Dent. Res., 58: 1859-1865

Gottlieb, E.W., Retief, D.H., and Jamison, H.C. (1982)
An optimal concentration of phosphoric acid as an etching agent. Part 1: Tensile bond strength studies.
J. Pros. Dent. 48: 48-51

Hirce, J.D., Sather, A.H., and Chao, E.Y.S. (1980)
The effect of topical fluorides, after acid etching enamel, on the bond strength of directly bonded orthodontic brackets.
Am. J. Orthod., 78: 444-452

Hormati, A.A., Fuller, J.L., and Deneby, G.E. (1980)
Effects of contamination and mechanical disturbance on the quality of acid-etched enamel.
J. Am. Dent. Assoc., 100: 34-38

Jendresen, M.D., Glantz, P., Baier, R.E., and Eick, J.D. (1981)
Microtopography and clinical adhesiveness of an acid etched tooth surface: An in vivo study.
Acta Odontol. Scand., 39: 47-53

Jenkins, G.N. (1978)
The physiology and biochemistry of the mouth.
Blackwell: 84, 173-174

Johnson, W.T. Jr., Hembree, J.H. Jr., and Weber, F.N. (1976)
Shear strength of orthodontic direct-bonding adhesives.
Am. J. Orthod., 70: 559-566

Jörgensen, K.D. (1975a)
The adaption of composite and non-composite resins to acid etched enamel surfaces.
In: Silverstone, L.M., and Dogon, I.L., editors
Proceedings of an international symposium on the acid etch technique.
St. Paul, Minnesota, North Central Publishing Co.: 93-99

Jörgensen, K.D. (1975b)
Contralateral symmetry of acid etched enamel surfaces.
Scand. J. Dent. Res., 83: 26-30

Jörgensen, K.D., and Shimokobe, H. (1975)
Adaption of resinous restorative materials to acid etched enamel surfaces.
Scand. J. Dent. Res., 83: 31-36

Keizer, S., ten Cate, J.M., and Arends, J. (1976)
Direct bonding of orthodontic brackets.
Am. J. Orthod., 69: 318-327

Köch, G. (1975)
Discussion of the paper given by L.M. Silverstone.
In: Silverstone, L.M., and Dogon, I.L., editors
Proceedings of an international symposium on the acid etch technique.
St. Paul, Minnesota, North Central Publishing Co.: 70-73

Kochavi, D., Gedalia, I., and Anaise, J. (1975)
Effect of conditioning with fluoride and phosphoric acid on enamel surfaces as evaluated by scanning electron microscopy and fluoride incorporation.
J. Dent. Res., 54: 304-309

Lee, H., Stoffey, D., Orlowski, J., Swartz, M.L., Ocumpaugh, D., and Neville, K. (1972)
Sealing of developmental pits and fissures: III. Effects of fluoride on adhesion of rigid and flexible sealers.
J. Dent. Res. 51: 191-201

Lee Brown, C.R., and Way, D.C. (1978)
Enamel loss during orthodontic bonding and subsequent loss during removal of filled and unfilled adhesives.
Am. J. Orthod., 74: 663-671

Lopez, J.I. (1980)
Retentive shear strengths of various bonding attachment bases.
Am. J. Orthod., 77: 669-678

Maijer, R., and Smith, D.C. (1979)
A new surface treatment for bonding.
J. Biomed. Materials Res., 13: 975-985

Maijer, R., and Smith, D.C. (1981)
Variables influencing the bond strength of metal orthodontic bracket bases.
Am. J. Orthod., 79: 20-34

Maijer, R., and Smith, D.C. (1984)
Preliminary clinical assessment of crystal bonding.
J. Dent. Res., 60: Special Issue: Abst. 1339: 319

Marshall, K. (1983)
Personal communication.

Mascia, V.E., and Chen, S-R. (1982)
Shearing strengths of recycled direct-bonding brackets.
Am. J. Orthod., 82: 211-216

Meurman, J.H., and Asikainen, M. (1976)
Re-hardening of acid-etched enamel.
Proc. Finn. Dent. Soc., 72: 120-126

Moin, K., and Dogon, I.L. (1978)
An evaluation of shear strength measurements of unfilled and filled resin combinations.
Am. J. Orthod., 74: 531-536

Nasr, Y.M. (1978)
The effect of time of topical application of fluorides on the hardness of the etched and un-etched enamel surfaces.
Egypt. Dent. J., 24: 393-418

Nathanson, D., Bodkin, J.L., and Evans, J.R. (1982)
S.E.M. of etching patterns in surface and subsurface enamel.
J. Pedodontics, 7: 11-17

Newman, G.V. (1969)
Adhesion and orthodontic plastic attachments.
Am. J. Orthod., 56: 573-588

Nygaard, V.K., and Simmelink, J.W. (1972)
S.E.M. and T.E.M. study of acid etched enamel.
J. Dent. Res., Special Issue: IADR Abst. 132: 50th General Session: 81

Pahlaven, A., Dennison, J.B., and Charbeneau, G.T. (1976)
Penetration of restorative resins into acid-etched human enamel.
J. Am. Dent. Assoc., 93: 1170-1176

Pus, M.D., and Way, D.C. (1980)
Enamel loss due to orthodontic bonding with filled and unfilled resins using various clean up techniques.
Am. J. Orthod., 79: 269-283

Reinhardt, K-J., and Vahl, J. (1979)
cited in: Diedrich, P. (1981)
Enamel alterations from bracket bonding: A study with the scanning electron microscope.
Am. J. Orthod., 79: 500-522

Retief, D.H. (1973)
Effect of conditioning the enamel surface with phosphoric acid.
J. Dent. Res., 52: 333-341

Retief, D.H. (1974)
A comparative study of three etching solutions.
J. Oral Rehab., 1: 381-390

Retief, D.H. (1975)
The use of 50 per cent phosphoric acid as an etching agent in orthodontics: a rational approach.
Am. J. Orthod., 68: 165-178

Reynolds, I.R. (1975)
A review of direct orthodontic bonding.
Br. J. Orthod., 2: 171-178

Reynolds, I.R., and von Fraunhofer, J.A. (1976)
Direct bonding of orthodontic attachments to teeth: the relation of adhesive bond strength to gauze mesh size.
Br. J. Orthod., 3: 91-95

Rouleau, B.D., Marshall, G.W. Jr., and Cooley, R.O. (1982)
Enamel surface evaluations after clinical treatment and removal of orthodontic brackets.
Am. J. Orthod., 81: 423-426

Shaffer, S.E. (1984)
Crystal-Lok bonding of orthodontic brackets to teeth.
J. Dent. Res., 63: Special Issue: Abst. 72: 178

Sharpe, A.N. (1967)
Influence of the crystal orientation in human enamel on its reactivity to acid as shown by high resolution microradiography.
Archs. Oral Biol., 12: 583-591

Shey, Z. and Brandt, S. (1982)
Enamel loss due to acid treatment for bonding.
J. Clin. Orthod., 16: 338-340

Silverstone, L.M. (1974)
Fissure sealants.
Caries Res., 8: 2-26

Silverstone, L.M. (1975)
The acid etch technique: In vitro studies with special reference to the enamel surface and the enamel-resin interface.
In: Silverstone, L.M., and Dogon, I.L., editors
Proceedings of an international symposium on the acid etch technique.
St. Paul, Minnesota, North Central Publishing Co. : 13-39, 78-92

Silverstone, L.M., Saxton, C.A., Dogon, I.L., and Fejerskov, O. (1975)
Variation in the pattern of acid etching of human dental enamel examined by scanning electron microscopy.
Caries Res. 9: 373-387

Smith, D.C. (1971)
The bonding of dental and orthopaedic cements to tissues.
In: Driessens, F.C., editor
Proceedings of an international symposium.
University of Nijmegan, The Netherlands: 235-247

Smith, D.C. (1975)
Approaches to adhesion to tooth structure.
In: Silverstone, L.M., and Dogon, I.L., editors
Proceedings of an international symposium on the acid etch technique.
St. Paul, Minnesota, North Central Publishing Co. : 119-138, 78-92

Smith, D.C., and Cartz, L. (1973)
Crystalline interface formed by polyacrylic acid and tooth enamel.
J. Dent. Res., 52: 1155

Smith, D.C., Lux, J., and Maijer, R. (1981)
Crystal bonding to enamel.
J. Dent. Res., 60: Special Issue A: Abst. 231: 368
and Dental Materials Group Microfilm

Smith, D.C., Maijer, R., Keyes, G., Bennett, G., and Peltoniemi, R. (1979)
Bonding to calcified tissues through crystal growth.
Transactions of the annual meeting of the Society of Biomaterials, 3: 136

Smith, R.S., Spinelli, J.A., and Tartakow, D.J. (1976)
Phosphoric acid penetration during direct bonding.
Am. J. Orthod., 70: 543-550

Soetopo, Beech, D.R., and Hardwick, J.L. (1978)
Mechanism of adhesion of polymers to acid-etched enamel.
J. Oral Rehab., 5: 69-80

Tavas, M.A., and Watts, D.C. (1984)
A visible light-activated direct bonding material: An in vitro comparative study.
Br. J. Orthod., 11: 33-37

Thanos, C.E., Munholland, T., and Caputo, A.A. (1979)
Adhesion of mesh-base direct-bonding brackets.
Am. J. Orthod., 75: 421-430

Voss, J.E., and Charbeneau, G.T. (1979)
A scanning electron microscope comparison of three methods of bonding resin to enamel rod ends and longitudinally cut enamel.
J. Am. Dent. Assoc., 98: 384-389

Yaeger, J.A. (1976)
Enamel.
In: Orban's oral histology and embryology. Chapter 3.
Editor: Bhaskar, S.N., 8th Edition, Mosby: 45-104

Yamashita, A. (1983)
Characteristics and bond strength of adhesive resins.
In: A dental adhesive and its clinical application, V. 2,
Tokyo, Japan, Quintessence Publishing Co. : 69-84

Young, K.C., Hussey, M., Gillespie, F.C., and Stephen, K.W. (1975)
In vitro studies of physical factors affecting adhesion of fissure sealant to enamel.
In: Silverstone, L.M., and Dogon, I.L., editors
Proceedings of an international symposium on the acid etch technique.
St. Paul, Minnesota, North Central Publishing Co.: 50-62

Results

Units: N = newton
MPa = mega pascal = 10^6 Pa

Group 1: Acid-etch - 24 hours

Specimen no.	Shear strength [x] (N)	$x - \overline{x}$	$(x - \overline{x})^2$
41	178	16	256
42	153	9	81
43	172	10	100
44	195	33	1089
45	200	38	1444
46	187	25	625
47	157	5	25
48	153	9	81
49	112	50	2500
50	182	20	400
51	147	15	225
52	158	4	16
53	163	1	1
54	175	13	169
55	182	20	400
56	153	9	81
57	108	54	2916
58	167	5	25
59	155	7	49
60	147	15	225
n = 20	Σ x 3244		$\Sigma(x-\overline{x})^2$ 10708
	n 20 ÷		
	$\overline{x}$ 162		

$$sd = \left(\frac{(x-\overline{x})^2}{n - 1}\right)^{\frac{1}{2}}$$

$$= \left(\frac{10708}{19}\right)^{\frac{1}{2}} = 24 \text{ N}$$

$\overline{x}_1 = 162 \pm 24$ N

Group 1: Acid-etch - 24 hours

Specimen no.	Shear strength [x'] (MPa)	$x' - \bar{x}'$	$(x' - \bar{x}')^2$
41	22	2	4
42	19	1	1
43	22	2	4
44	24	4	16
45	25	5	25
46	21	1	1
47	20	0	0
48	19	1	1
49	14	6	36
50	23	3	9
51	18	2	4
52	20	0	0
53	20	0	0
54	22	2	4
55	23	3	9
56	19	1	1
57	14	6	36
58	21	1	1
59	19	1	1
60	18	2	4
n = 20	$\Sigma x'$ 403		$\Sigma (x' - \bar{x}')^2$ 157

n 20 ÷

$\bar{x}'$ 20

sd = 3

$\bar{x}'_1 = 20 \pm 3$ MPa

Group 2: Crystal-Lok - 24 hours

Specimen no.	Shear strength [x] (N)	$x - \bar{x}$	$(x - \bar{x})^2$
61	87	13	169
62	130	29	841
63	92	9	81
64	86	15	225
65	58	43	1849
66	88	13	169
67	116	15	225
68	114	13	169
69	122	21	441
70	85	16	256
71	111	10	100
72	92	9	81
73	86	15	225
74	113	12	144
76	79	22	484
77	112	11	121
78	148	47	2209
79	92	9	81
80	114	13	169
n = 19	Σx 1925		$\Sigma(x-\bar{x})^2$ 8039
	n 19 ÷		
	$\bar{x}$ 101 N		sd = 21 N

$\bar{x}_2 = 101 \pm 21$ N

Group 2: Crystal-Lok - 24 hours

Specimen no.	Shear strength [x'] (MPa)	$x' - \bar{x}'$	$(x' - \bar{x}')^2$
61	11	2	4
62	16	3	9
63	12	1	1
64	11	2	4
65	7	6	36
66	11	2	4
67	15	2	4
68	14	1	1
69	15	2	4
70	11	2	4
71	14	1	1
72	12	1	1
73	11	2	2
74	14	1	1
76	10	3	3
77	14	1	1
78	19	6	36
79	12	1	1
80	14	1	1
n = 19	Σ x' 248		$\Sigma (x'-\bar{x}')^2$ 126
	n 19 ÷		
	$\bar{x}'$ 13		sd = 3

$\bar{x}'_2$ = 13 ± 3 MPa

Group 3: Acid-etch - 10 minutes

Specimen no.	Shear strength [x] (N)	$x - \bar{x}$	$(x - \bar{x})^2$
81	73	5	25
82	88	10	100
83	94	16	256
84	66	12	144
85	58	20	400
86	76	2	4
87	87	9	81
88	79	1	1
89	100	22	484
90	52	26	676
91	76	2	4
132A	84	6	36
$n = 12$	Σx 933		$\Sigma (x-\bar{x})^2$ 2211
	n 12 ÷		
	$\bar{x}$ 78		sd = 14

$\bar{x}_3 = 78 \pm 14$ N

Group 3: Acid-etch - 10 minutes

Specimen no.	Shear strength [x'] (MPa)	$x' - \bar{x}'$	$(x' - \bar{x}')^2$
81	9	1	1
82	11	1	1
83	12	2	4
84	8	2	4
85	7	3	9
86	10	0	0
87	11	1	1
88	10	0	0
89	13	3	9
90	7	3	9
91	10	0	0
132A	11	1	1
n = 12	$\Sigma\ x'$ 119		$\Sigma\ (x'-\bar{x}')^2$ 39
	n 12 ÷		
	$\bar{x}'$ 10		sd = 2

$\bar{x}'_3 = 10 \pm 2$ MPa

Group 4: Crystal-Lok - 10 minutes

Specimen no.	Shear strength [x] (N)	$x - \bar{x}$	$(x - \bar{x})^2$
101	79	13	169
102	40	16	256
103	60	4	16
104	43	13	169
105	74	18	324
107	39	17	289
108	67	11	121
110	71	15	225
120	35	21	441
121	50	6	36
122	38	18	324
123	26	30	900
124	32	24	576
125	46	10	100
126	68	12	144
127	84	28	784
128	84	28	784
129	60	4	16
130	65	9	81
131	60	4	16
$n =$ 20	Σx 1121		$\Sigma(x-\bar{x})^2$ 5771
	n 20 ÷		
	$\bar{x}$ 56		sd = 17

$\bar{x}_4 = 56 \pm 17$ N

Group 4: Crystal-Lok - 10 minutes

Specimen no.	Shear strength [x'] (MPa)	$x' - \bar{x}'$	$(x' - \bar{x}')^2$
101	10	3	9
102	5	2	4
103	8	1	1
104	5	2	4
105	9	2	4
107	5	2	4
108	8	1	1
110	9	2	4
120	4	3	9
121	6	1	1
122	5	2	4
123	3	4	16
124	4	3	9
125	6	1	1
126	9	2	2
127	11	4	16
128	11	4	16
129	8	1	1
130	8	1	1
131	8	1	1
$n = 20$	$\Sigma x'$ 137		$\Sigma(x'-\bar{x}')^2$ 110
	n 20 ÷		
	$\bar{x}'$ 7		sd = 2

$\bar{x}'_4 = 7 \pm 2$ MPa

Statistics

The statistical significance of a difference was used to compare Group 1 with Group 2, and Group 3 with Group 4. The significance ratio was determined, the p value obtained from a two-tailed t test table (Table III of R.A. Fisher and F. Yates, "Statistical tables for biological, agricultural, and medical research", published by Oliver & Boyd, Edinburgh).

Definitions

$$\text{Significance ratio} = \frac{\text{difference}}{\text{standard error of difference}} = t$$

$$\text{Standard error of difference} = [(SE_A)^2+(SE_B)^2]^{\frac{1}{2}}$$

$$\text{Standard error (SE)} = \frac{\text{Standard deviation (sd)}}{n}$$

$$\text{Degrees of freedom (df)} = (n_A-1) + (n_B-1)$$

Group 1 compared with Group 2

$$\text{significance ratio} = \frac{162 - 101}{\left(\frac{24^2}{20} + \frac{21^2}{19}\right)^{\frac{1}{2}}} = 8.5$$

df = 37, $p < 0.001$: this difference being significant at the level of 1 in 1000.

Group 3 compared with Group 4

$$\text{significance ratio} = \frac{78 - 56}{\left(\frac{14^2}{12} + \frac{17^2}{20}\right)^{\frac{1}{2}}} = 4$$

df = 30, $p < 0.001$: this difference being significant at level of 1 in 1000.