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DIRECT BONDING IN ORTHODONTICS AND THE ENAMEL SURFACE -

A SCANNING ELECTRON MICROSCOPE STUDY

A thesis embodying original work, submitted in partial fulfilment of the requirements for the Degree of Master of Dental Science in the Faculty of Dentistry, University of Sydney, December 1972.



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Dedication: To my parents, whose many sacrifices, made my
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I N T R O D U C T I O N

Despite many years of research, the perfect restoration or the "ideal" dental material has not yet been developed. If such a material were available it would have far reaching implications on dental practice as it exists today.

A utopian material, when used to restore carious teeth, should chemically bond with the adjoining tooth structure, should have physical and chemical properties similar to the tooth itself and should possess the same aesthetic qualities. None of these characteristics is totally present in any of the current restorative materials available to the dentist.

Of particular interest is the lack of adhesion between the material and the tooth. This lack of adhesion permits percolation of saliva, acids, micro-organisms, etc., along the tooth-restoration interface.

Hence an adhesive material can be seen to prevent such percolation and consequently minimise occurrence of recurrent caries. It would also lead to a revision of cavity designs, restoration of tooth structure damaged by trauma, erosion, attrition or other such causes. Such a material would provide a more serviceable restoration for the patient both physically and biologically.

In the field of orthodontics, the direct bonding of brackets and attachments to the buccal and lingual surfaces of teeth would remove the

trauma resulting from the fitting of full bands and permit better interproximal cleansing. The bands would no longer occupy valuable interproximal space and a more precise alignment of teeth could be achieved. Aesthetic values may also be enhanced, particularly by the use of plastic brackets and attachments.

Current research is endeavouring to produce such a material. Recently new bonding systems have been formulated, and marketed, which claim to have adhesive properties (both physical and chemical) of sufficient calibre to permit the direct fixation of orthodontic brackets and attachments to the tooth surface.

To date, the true test of any new dental product, destined for oral use, lies in a clinical test, because the exact minimum requirements for each of the physical and chemical properties have never been established. Although the investigations for this theses were carried out in vitro, the aim was to keep the investigations of the effects of the four direct bonding systems tested, upon the enamel surface (particularly the effects of the etching solutions), as clinically orientated as possible.

LITERATURE

REVIEW

HISTORICAL REVIEW OF ATTACHMENT RETENTION

PART I - CEMENTS AND CEMENTATION OF BANDS

Since the introduction of fixed appliance therapy in orthodontics, clinicians have been required to rigidly attach orthodontic attachments to teeth to be able to control the application of mechanical forces which effect movement of the teeth. Such attachments need to remain intact for the duration of treatment which may extend over a period of a few years.

Over the years this attachment placement has almost solely been achieved by the soldering or welding of attachments to a metallic band material encircling the tooth. For maximum possible mechanical retention it was required of the band to fit tightly onto the coronal portion of the tooth and burnished onto the tooth surface wherever possible.

Simultaneously it was recognised that such band fitting did not meet the entire demands of retention and that no matter how conscientious was the clinician in attempting to achieve "absolute" adaptation, this procedure alone did not effect an adequate marginal seal. Hence, due to percolation of oral fluids, food debris, plaque, etc. beneath bands, the enamel was susceptible to damage from the breakdown products of these materials as cleansing of such covered areas being virtually impossible.

To overcome these two failings, it was evident that a "luting" agent would be necessary to effect a marginal seal and also to enhance the

retentive properties of the system.

In 1871 Magill was credited with the first cementation of a plain band and it was in 1879 that the general introduction of cements occurred in the dental profession (Anderson, 1960).

During the development of orthodontics through the latter part of the 19th Century and now the majority of the 20th Century, orthodontists have used cements or luting agents for band retention that have been developed primarily for the retention of restorations and prostheses in restorative dentistry.

It may be questioned whether many cements used in other dental disciplines are suitable for orthodontic use.

In restorative procedures the functions of a cement as listed by Horn, 1965 are:-

1. Retention
2. Marginal seal
3. Insulation
4. Therapeutic

In orthodontic applications, the most important of the abovementioned factors are retention and marginal seal. The therapeutic and insulative properties of cements are of a secondary nature in that no thermal protection of the dental pulp and no palliative therapy for the dental pulp is necessitated. The only therapeutic consideration is one of

enhancing the integrity of the enamel surface or protection of it from attack.

The attack may originate from the acid itself or by penetration of injurious agents beneath the band material. Hence the functions of retention and marginal seal play a supportive role in protection also.

CEMENTS USED AS ORTHODONTIC LUTING AGENTS

1. METALLIC PHOSPHATE AND ZINC OXIDE - EUGENOL CEMENTS

These cements were first introduced to the dental profession in the latter half of the 19th Century. Such materials used today remain largely unchanged.

Shortly after zinc phosphate cements gained widespread use for temporary restorative procedures and for the cementations of crowns and bridges. Soon after their acceptance, zinc oxide-eugenol cements and copper phosphate (red and black) were introduced.

From this early stage of their development it was evident that the phosphate types were potentially injurious to the pulp tissues via the dentinal tubules.

However, this consideration was not relevant to their use in orthodontics due to the protection of the pulp by the intact enamel surface. These cements were preferred to the more palliative zinc-eugenol cements

for the reasons of better physical properties such as physical strength, film thickness and retention.

These cements, although they possess many desirable physical properties and handling characteristics, are unable to resist the demands of the oral environment (Smith 1971a). They lack any true adhesion to the tooth surface (Swartz and Phillips 1961) and, with the exception of the zinc oxide - eugenol cements, have poor sealing abilities (Norman et al 1963).

Wilson et al (1970) in a laboratory study showed that should there be any sustained drop in pH of the saliva, then the phosphate cements are highly soluble.

Norman, et al (1969) showed the interaction of solubility and abrasion to be the cause of in vivo disintegration of these cements.

Despite the fact that the zinc oxide-eugenol cements are less soluble than the phosphate cements in an acid environment (Phillips et al 1969), and that they are a considerably weaker cement (Skinner and Phillips 1967), they also, in time, will disintegrate to dissolution of eugenol.

Although the zinc phosphate cements have many shortcomings (Horn 1965), they have been, and still are, widely used because of their following properties:-

- a) Superior compressive strength (retention of bands)
(Swartz 1965);

- b) Ability to flow (film thickness when required)
(Horn 1965);
- c) Almost ideal handling characteristics
(Horn 1965); and
- d) Also due to the non-availability of any other or
any other superior cementing agent
(Fitzsimmons 1968).

An additional consideration also being that orthodontic treatment extends over a relatively short period and so its demands are perhaps less rigorous than the longer retentive period required of restorative procedures.

2. SILICATE CEMENTS

Silicate cements are not suitable as cementing agents due to their acidity (from the biologic standpoint) and in addition to that consideration not only are their handling characteristics unsuitable, particularly in relation to working time, but they do not extrude into a sufficiently thin film (Phillips 1963).

3. MODIFIED AND REINFORCED CEMENTS

Although improved manufacturing processes have enhanced the physical properties of the previously mentioned cements, some research workers sought greater improvements by the use of additives. Achievements

were made in these directions. However, an improvement in one property was usually gained at the expense of another.

(a) Zinc Oxide-Eugenol Cements.

Phillips et al, 1969 added rosin and synthetic resins to these cements but found no beneficial improvements in them for use as luting agents.

Recently a formula, substituting EBA (0-ethoxybenzoic acid) for a portion of the eugenol was advocated. This resulted in a material possessing physical properties approaching those of zinc phosphate. Unfortunately, there was an associated increase in solubility (Swartz 1965) and the film thickness doubled the film thickness value for zinc phosphate cements (Smith 1971b).

Further additives, viz: quartz or aluminium oxide, were used to reinforce the EBA which resulted in solubility decreases.

Smith (1971b) suggested that a good reason to persevere with these cements was their good manipulative qualities. However, these cements have not gained much acceptance as orthodontic cementing agents.

(b) Silico-Phosphate Cements.

These cements are hybrids of phosphate and silicate cements combining the translucency and strength of the silicate cements with

the setting time of the former. Most physical properties of these cements are a significant improvement over the zinc phosphate cements with the exception of film thickness (Phillips 1969). Although strength has been increased, their retentive ability is decreased due to the increased film thickness. However, film thickness is not as critical as it is in crown, inlay, etc. cementations.

4. OTHER CEMENTS

(a) Acrylic Cements

Phillips et al (1969) state that "although these cements demonstrate exceptionally good initial adaptations to tooth structures, this excellent adaptation dissipates as the resin absorbs water and as fluids penetrate along the resin - tooth interface". They go on to say that the relative insolubility of the acrylic cements is the only characteristic in which the resin is superior to other types of dental cements and that this factor is not sufficient criterion for their preference in cementing procedures over other types of dental cements.

(b) Zinc Polycarboxylate Cements

Smith (1968) developed a new type of cement comprising a powder and a liquid. The powder is a modified zinc oxide similar to that used in the phosphate and eugenol cements, while the liquid is a 40-50% solution of polyacrylic acid in water.

Smith (1968) states that the "setting reaction is a chemical one and that the cement possesses similar physical properties to the phosphate cements, with the exception of a low irritancy comparable to the zinc oxide eugenol cements and a very low solubility in water".

Although the claim is made that its solubility is less than that of zinc phosphate cements, no long term in vivo study results are yet available to enable conclusions to be drawn as to the clinical significance of such a property.

Another factor in its desirable attributes as an orthodontic luting agent as well as other clinical uses, is that Smith (1968, 1971a,b) claimed that this cement "could exhibit adhesion (see definition in later section on "adhesion") to the calcium and proteinaceous portions of tooth substance under suitable conditions". Smith believes that the adhesion arises from the ability of the polycarboxylate cements to form chelates with metal ions as well as complexes with proteins. They also are believed to bond chemically to metals and calcified substances.

Smith provides further evidence in a recent scanning electron microscope study which showed that the matrix of the set cement was intimately in contact with the enamel surface. The cement only slightly etched the tooth surface and that in some instances a profuse growth of a crystalline product occurred, which originated from the enamel surface and grew into the body of the cement (Smith 1972).

HISTORICAL REVIEW OF ATTACHMENT RETENTION

PART II - ATTACHMENT RETENTION BY DIRECT BONDING

Direct bonding is that process by which an orthodontic attachment is fixed through a chemical and/or physical means directly onto a tooth surface.

Research workers have, for some time, been endeavouring to find a chemical which adheres to tooth structure, which is physically and chemically similar to tooth structure, and which should also possess similar aesthetic qualities.

Two obvious advantages are improved aesthetics of such materials (c.f. stainless steel bands) and a saving of space (metal bands can occupy up to 4mms of total arch length in each fully banded arch). Other advantages may be easier maintenance of proper oral hygiene and hence reduced incidences of enamel decalcification and carious lesions.

The following is an outline of recent developments in research into the direct bonding of orthodontic attachments.

Following a report by Buonocore detailing how the adhesiveness of restorative resin to enamel could be markedly increased by etching of the enamel, other researchers began to investigate adhesive materials and their possible role in direct bonding in orthodontics.

Rose, et al 1955 and Sadler 1958 investigated the possibilities of

using materials that exhibit "adhesive" properties in dental and commercial uses respectively. Their investigations indicated that there was no known substance capable of forming a satisfactory bond to tooth structure under oral environmental conditions.

Bowen, in 1956, described gross experimental studies of one epoxy resin (Epon 828) used as a binder for fine particles of fused silicon dioxide and porcelain. He concluded that this material shows:-

1. Thermal expansion equal to that of tooth structure,
2. Adhesive properties,
3. Colour stability,
4. Apparent stability and insolubility in the oral environment.

He added that clinic investigations of epoxy resin systems were continuing and encouraging.

Swanson and Beck 1960 reported the testing of a modified cyanoacrylate (Eastman 910) accelerated with 1% acetone solution of phenyl ethyl ethanolamine, as a direct bonding adhesive. It was compared to acrylic resin materials. Results showed that "none of the materials tested produced a bond of practical usefulness under oral conditions". They did find that to achieve the maximum possible success the following conditions are important:-

1. The enamel surface must be clean, acid etched and dry;

2. Good contact between enamel and adherend
(def. in section on "adhesion").
3. Use of a waterproof adherend or a waterproof
coating to protect the adherend is desirable.

Further to their problems with the adherend - enamel relationships, no satisfactory attachment type or material was used.

Bowen (1965a) developed a method of determining bond strength and conducted a series of experiments testing the adhesive bonding of certain acrylic resins as influenced by a surface-active comonomer (NPG-GMA, the adduct of N-phenylglycine and glycidyl methacrylate) (1965b). He also tested the added effect of surface pretreatment in association with the surface-active comonomer (1965c) (1965d) and then varied the substrate (dentine, enamel and fluorapatite) and finally repeated the same experiments with more diversified substrates (1965e).

The most relevant results being:-

1. The surface-active comonomer, NPG-GMA improved the
water-resistant bonding between the resins tested
and tooth surfaces.
2. The mechanism for its improvement in bond strengths
may be primarily by interaction with the mineral
phase rather than with the organic phase of the
tooth structure.

If this is the case it may be that the effectiveness of pretreatments which can dissolve away mineral (apatite) would be interpreted as being due to modification of the mineral surface rather than to an increase in the amount of exposed organic matter.

Mitchell 1967 in attempting to eliminate the use of the orthodontic band tested an Epoxy-polyamide resin, two general purpose adhesives and two phosphates (Zn and Cu) cements using a 24 carat gold based, patch-like 'M' bracket designed to protect the adhesive. Although bonds survived under the 'M' bracket due to the sealing effects of the burnishing of the gold base, over the adhesive, onto the tooth surface, the bonds were unable to maintain integrity in water. These bonding systems were considered not suitable for use in a moist environment such as the oral cavity without the protection of the burnished gold.

Gwinnett and Matsui 1967, in studying enamel adhesives, cited the efforts of other research workers (Gwinnett and Buonocore 1965) who indicated that satisfactory bonding can be achieved after etching the enamel surfaces. Their in vivo and in vitro studies have shown that several materials bond with surfaces so treated; for example, Eastman 910 monomer and silaceous filler, epoxy resin, and several methacrylate resin restorative materials.

Takeuchi and Kizu 1966, and Takeuchi et al 1966, demonstrated the potential of a mixture of an alkyl cyanoacrylate and methyl methacrylate to seal the pits and fissures of untreated human teeth. However, these workers did not specify the homologue of alkyl cyanoacrylate used, nor did they discuss the means by which the material was retained.

Gwinnett and Buonocore 1965 reported on the relationship of an adhesive (Eastman 910) containing methyl-2-cyanoacrylate and treated enamel surfaces. Gwinnett and Matsui 1967 investigated similar relationships using two cyanoacrylates, a methyl methacrylate, a glycidyl dimethacrylate, and four commercial dental restorative resins. Penetration of the adhesive into the enamel together with the bulk of the adhesive showed theoretical protective properties for the enamel against attack by injurious agents.

Cueto and Buonocore 1967 reported encouraging results for the methyl-2-cyanoacrylate system adhesive in the sealing of pits and fissures as a means of caries prevention.

This early work led to the development of an adhesive acrylic (a derivative of "Bowen's" resin) resin polymerized by ultraviolet light, being used as a pit and fissure sealant (Buonocore 1971).

Buonocore's development of this adhesive system led to its use for the attachment of clear, plastic orthodontic brackets to teeth (Cohl et al 1972).

Newman (1965) published a "Progress Report" on his research into the use of epoxy adhesives for orthodontic attachments. He chose to experiment with an epoxy adhesive for the following reasons:-

1. They are free of solvents and hence no solvent evaporation occurs on setting;

2. They are solids;
3. They have shear strength and rigidity;
4. They show excellent wettability of surfaces;
5. They are resistant to breakdown by oral fluids.

Not all epoxy resins exhibit these properties, and so he chose a "relatively innocuous flexibilising polyamide-polyamine agent" to cure the formulation to fulfill the above requirements. The epoxy adhesive tested is a reaction product of bisphenol A and epichlorhydrin. To this mixture was added the polyamide curing agent. The polyamide resin formulated is of the thermosetting type and the setting reaction exothermic. He used cold-cure acrylic resin, plexiglas and Lexan polycarbonate attachments. The tooth surfaces were used in an etched and non-etched state.

The results showed both advantages and disadvantages for bonding attachments to tooth surfaces. The advantages of this formulation over conventional anime-cured epoxies are increased flexibility of the joint, reduction in irritation potential, low toxicity and reduced sensitivity to damage from moisture in the oral cavity.

However, despite his success with clinical trials the predominant disadvantage was the lengthy setting (gelling) time (15-30 minutes), and the fact that complete curing took approximately four days. He considered these factors to be clinically inconvenient.

The acrylic resin attachments provided better bonds strengths than did the Plexiglas and the polycarbonate attachments. He also recognised

the need to use fillers to achieve a compromise in thermal expansion between the adhesive and the adherends. He also recognised the role of surface etching in increasing bond strength.

Newman in recognising the above difficulties of the epoxy resins, turned his attention to acrylic adhesives together with two colleagues (Newman et al 1968). Their reasons for investigating adhesive systems containing homo and copolymers of methyl methacrylate included:-

1. Rapid setting times (which can be easily varied);
2. Flexibility of physical properties by alteration to composition;
3. Ease in mixing and placement;
4. Asset of in situ polymerization;
5. Acceptance by clinicians in restorative dentistry.

Tooth surfaces were pretreated with 85% phosphoric acid, and Lexan polycarbonate attachments were used.

Pretreated surfaces showed increased wettability by the adhesive (lower contact angles) and hence higher bond strengths. Another factor is shrinkage of the adhesive during setting. This must be kept as low as possible without reducing the mechanical properties of the set adhesive, so that bond strength is not impaired. Newman et al found that the optimum molecular weight for the polymer additives utilised in the fast setting acrylic system is approximately 20,000.

Certain fillers improved bond strengths further and it was reported

that water immersion did lessen bond strengths but that the stronger the initial adhesive bond the less the effect.

They concluded by stating: "on the basis of the present in vitro study and concurrent clinical investigations by Newman that reliable, fastsetting acrylic adhesive systems are attainable and that further investigation will produce a practical system which will have value in orthodontics".

Retief and Dreyer (1967), also foreseeing the desirability of direct bonding of orthodontic attachments, and encouraged by the success of Bowen 1956, Newman 1965, Phillips 1966 and Mitchell 1967, sought to develop an epoxy adhesive system that would be suitable for intra-oral use in orthodontics.

Similarly to Newman 1965, they recognised the advantages of etching the enamel surface and did so as described by Gwinnett and Buonocore 1965. Unlike Newman 1965, however, these authors chose a metallic attachment as the other adherend in their system.

The brackets were welded to a piece of orthodontic band material which in turn was welded to an additional base of fine stainless-steel gauze, this increased the surface area of the adherend.

Curing time was controlled by temperature variation, (temp cure time) and also by the use of catalysts (phenol gave the best results). The need for maintenance of a dry field during initial stages of cure soon became apparent. Initial results indicated justification for clinical

trials and the results of the trials were reported three years later (Retief et al 1970). The formulation accepted as worthwhile for clinical testing consisted of the epoxy resin and thixotropic agent in the first part, and the curing agent (reactive hardener) mixed in the ratio of 100 parts to 30 parts respectively. The original bracket design was dropped due to its bulk and a new bracket with undercuts in its base was used. The undercut area being necessitated due to the lack of adhesion between epoxy resins and stainless steel. They found this formulation, unlike that used by Newman 1965 did not adhere to brackets made of polycarbonate.

After a spell of failures, technical and clinical procedures were reassessed and much better retention results were achieved. The improvements are reported to be due to:-

1. Adequate surface preparation of the enamel surface;
2. The development of an optimum preheat schedule and use of catalysts to provide optimal curing rates;
3. Cleansing of phosphoric acid from the etched surface;
4. Increased maintenance of dryness of the field;
5. Improvements in cleansing of the bracket bonding surface and its mechanical design.

Dijkman and Retief 1972 reported the results of further clinical trials. They had reverted to the original bulky bracket design and were isolating the teeth with rubber dam during bracket placement. Failures, expressed as a percentage of total brackets placed compared favourably with other reports (Miura et al 1971 and Mizrahi and Smith 1971). Although they

expressed their satisfaction with their results they admit the concept of direct bonding had not become an accepted clinical procedure.

As previously mentioned Smith 1968 developed a new dental cement, viz, the polycarboxylate group of cements. Smith has presented evidence of the ability of these cements to adhere to tooth and metallic surfaces (Smith 1968, 1971a and 1971b). As a result of the development of this cement and its early testing by Williams 1967, Mizrahi and Smith 1969 felt that the cement, being superior in adhesion to enamel to that of existing cements, warranted testing in relation to direct cementation of orthodontic brackets to the enamel surface. Their in vitro study used orthodontic lingual buttons as attachments and compared the performance of a few conventional cements with some of the polycarboxylate cements in tensile strength tests.

The polycarboxylate cements did prove superior and results were of such an order (78 kg/sq. cm. to 29 kg/sq. cm. of conventional cements) it was recommended that further testing of an attachment suitable for clinical use be undertaken.

Manning 1971, developed a patch-base of band material burnished onto the tooth surface (to minimise film thickness of the adhesive) to which could be welded or soldered an orthodontic attachment. In testing this system with conventional and polycarboxylate cements Manning found the polycarboxylate group of cements to have strengths (in both tension and shear) capable of justifying clinical testing of his technique of direct bonding of orthodontic attachments using a polycarboxylate cement as the adhesive.

Proffit 1972 described a direct bonding technique (developed by post-graduate students at the University of Kentucky, Lexington, Kentucky, U.S.A.) using a specially designed metallic bracket, an etched tooth surface and an acrylic resin direct filling material. The self-curing acrylic resin is a copolymer of methylmethacrylate powder mixed with methyl methacrylate monomer which is activated by the catalyst p-toluene sulphinic acid. Clinical success is claimed by Proffit for the technique. This technique, as does that of Manning 1971, Mitchell 1967 and Retief and Dreyer 1967, suffer from a decrease in aesthetic values due to the use of metallic attachments in comparison to the plastic attachments of Newman 1965 and Newman et al 1968, Cohl et al 1972 and Muira 1971, although they are considered to be an improvement over the conventional circumferential stainless steel band.

Muira et al 1971 reported the development of direct bonding system using Lexan polycarbonate brackets. The adhesive consists of the monomer (methyl methacrylate), the polymer (polymethyl methacrylate) and the catalyst (tri-n-butyl borane derivative, TBB). They recognised the aspect of adhesive behaviour tending to breakdown under the prolonged influence of moisture in the oral cavity. To combat this the etched tooth surface is coated with methacryloxypropyl tri-methoxysilane as they believe this chemical reacts chemically with calcium ions at the enamel surface and it increases the surface wettability of the adhesive and so has a two-fold effect in increasing bond strength.

The authors claim superior results with their system according to clinical trials but offer scant scientific evidence, for the claims of chemical adhesion. Physically, through testing of bond strengths, the system compares most favourably with other direct bonding systems.

THEORY OF ADHESION

The problem of developing a bonding system for the placement and retention of orthodontic attachments directly onto tooth surfaces are those of the phenomena of adhesion and the behaviour of adhesives in the rigorous environment of the oral cavity.

What then, is adhesion?

Adhesion is the joining together of two dissimilar materials (Parker and Taylor, 1966), and can further be defined as the molecular attraction exerted between the surfaces of bodies in contact or the attraction between molecules. The material added to produce the adhesion is known as "adhesive" and that to which it is applied is called the "adherend". The "interface" is the zone between the interacting substances (Retief 1970a).

Cohesion is that phenomenon attributed to the interaction of molecular forces acting between molecules of the same kind.

The forces involved can be divided into chemical (intra-molecular attractive) forces and physical (inter-molecular attractive) forces. All these forces are due to electromagnetic interactions produced by continual fluctuations in the distribution of electrons within the molecules (de Bruyne 1962).

In the case of adhesion to tooth structure, atoms or molecules on the surfaces of the tooth and those of the adhesive attract each other.

When the distance between the two is within the limit of attraction, electrostatic force results and a stable condition of energy is attained. Adhesive strength occurring at this distance is due to Van der Waal's forces. Further stability is attained if the distance is again shortened due to the forces of hydrogen bonds, and if further shortening of the inter-molecular or interatomic distance occurs then a stabilised condition results, due to a chemical bond force and consequently a change in substance, i.e. a third substance is formed. Matsui (1964) believes that the ideal adhesion should result in chemical combination.

Intermolecular Force	Distance between Atoms
Van der Waal's	about $4\text{\AA}$
hydrogen bond	3.2 $3.6\text{\AA}$
chemical bond	about 1.5 $2.0\text{\AA}$

Table 1 shows the distances between the particles when the attractive forces mentioned above will function.

It should be remembered that not all these forces necessarily occur in any one adhesive system and that other forces of inter-molecular and interatomic interaction are known to exist and contribute to adhesive strength. A brief outline of all the forces that might be involved in adhesion will be described.

A. CHEMICAL FORCES

There are three types of chemical bonds and these constitute the primary bond.

1. Electrovalent (ionic) Bond

When electrons are transferred from one valency orbit of one atom to another, positively and negatively charged ions result, and the resultant attractive forces are due to an electrostatic attraction. (See Fig. 1).

2. Co-valent Bond

This bond is formed by the sharing of electrons of the valency orbits, and a shared pair of electrons constitute a covalent bond. A purely covalent or non-polar bond is formed by the equal sharing of electron pairs by similar atoms, e.g. Cl_2 (Parker and Taylor 1966). Such a bond has no ionic character. (See Fig. 2a).

If the electron pairs are shared by dissimilar atoms, that is, those which have different degrees of electro-negativity, they will be displaced closer towards the more electro-negative atom. Such bonds are ionic in character, and hence will have a polar characteristic due to the unequal sharing of the electron pairs, e.g. C Cl_4 (Retief 1970). (See Fig. 2b).

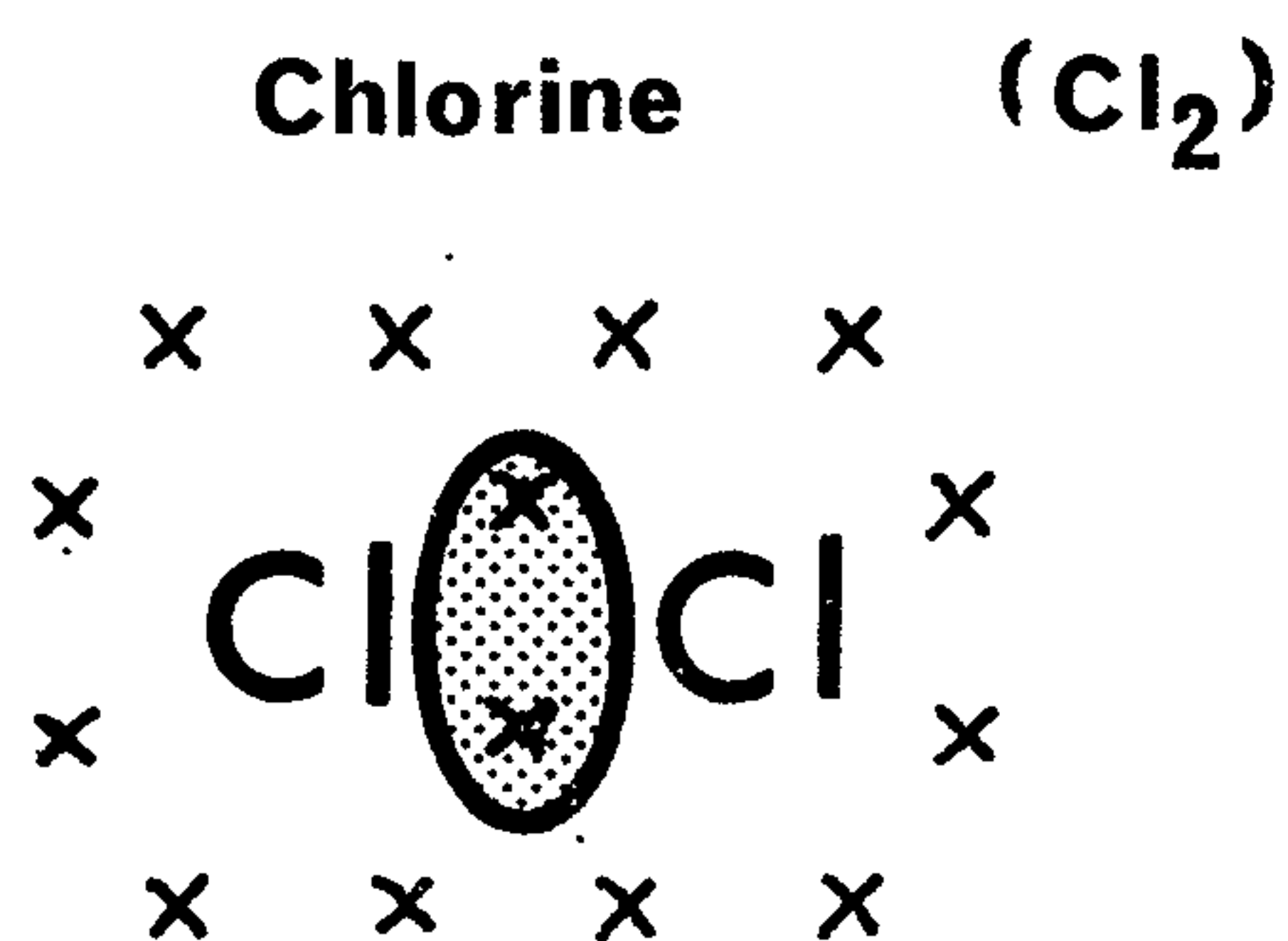


Fig. 2a An example of a pure covalent bond

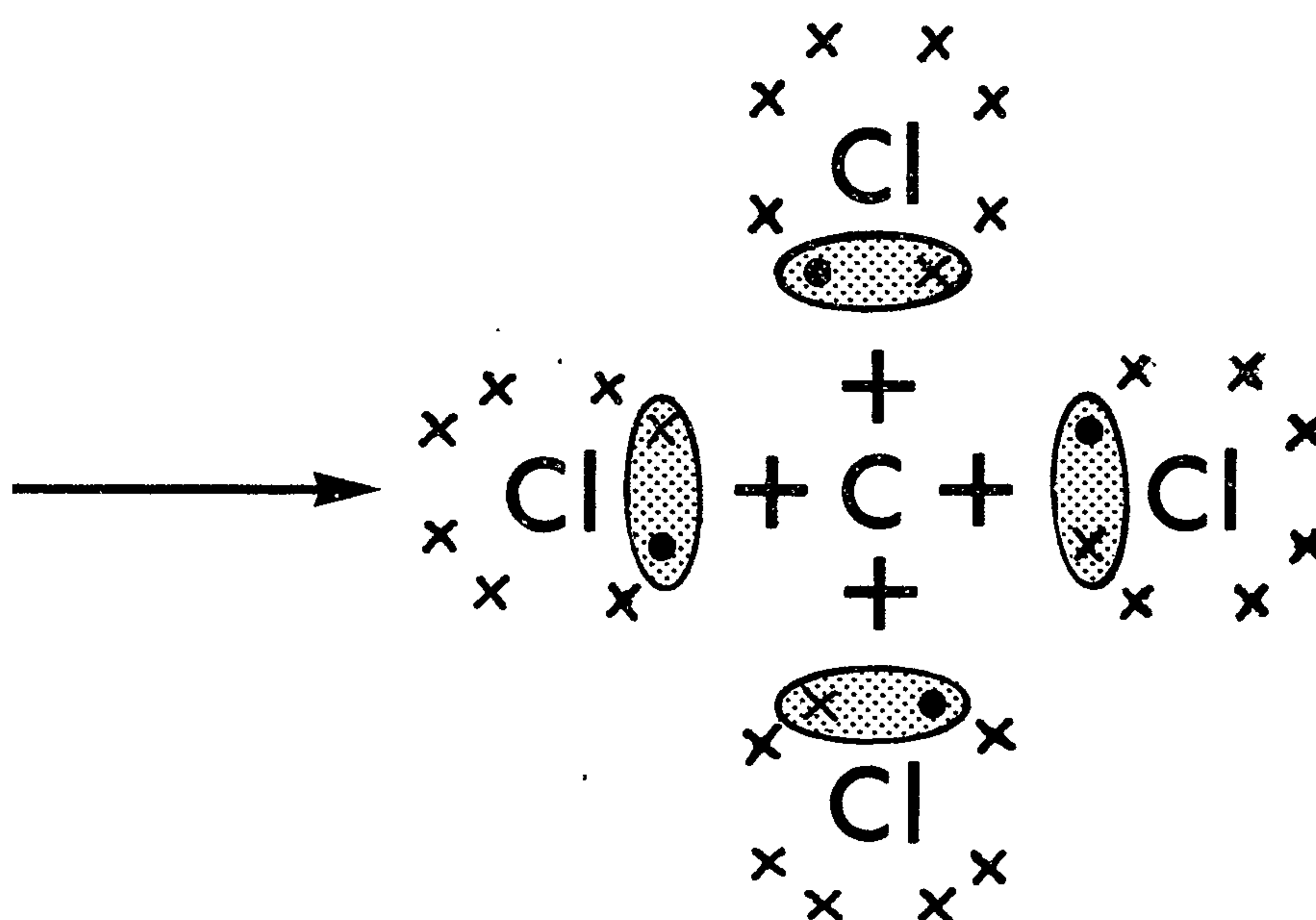
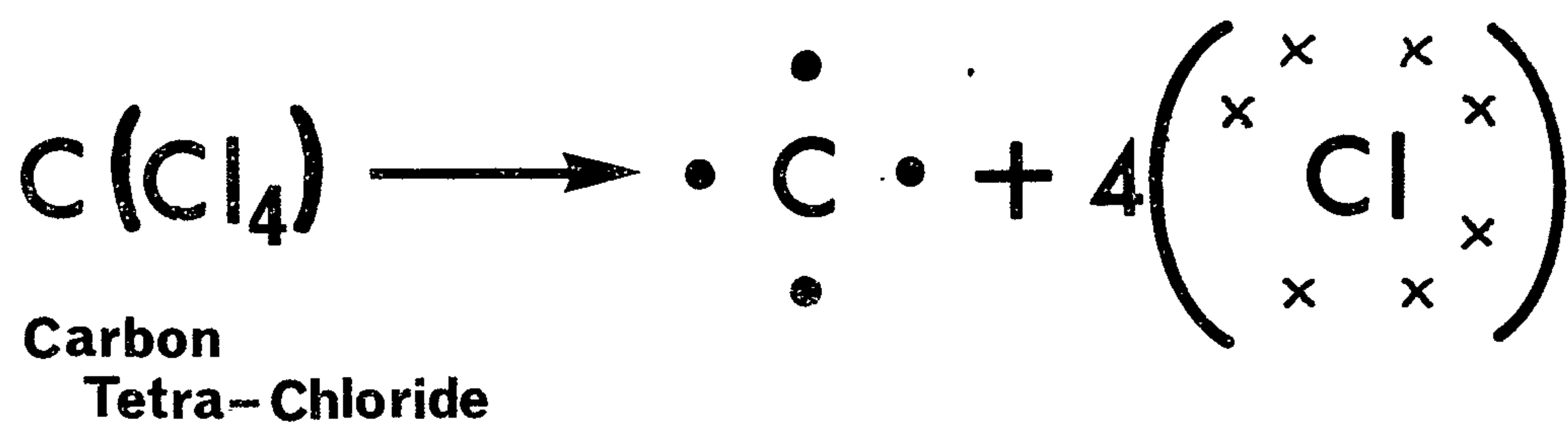


Fig. 2b An example of a shared covalent bond

It can be seen that the ionic character of polar covalent bonds varies as it is dependent on the electro-negativity of the atoms between which the bonds are formed. The displacement of the shared electron pair towards the most electro-negative atom and the degree of displacement is reflected by the dipole moment.

Covalent bonds are commonly found in organic compounds and permanent dipoles are found in such polar organic compounds and these are important in adhesion. (Retief 1970).

3. Metallic Bonds

The free valence electrons of metals can move about the metal space lattice to forming an electron cloud. This movement causes a regular array of positive ions in the core of the crystal. The "clouds" and the "cores" provide the forces which bond metal atoms together. As a result, metallic surfaces will have some free electron deficient sites available for bonding.

B. PHYSICAL FORCES

1. Van der Waal's Forces

Eley (1961) states these forces of molecular attraction are due to three main factors:-

- (a) the Keesom forces;
- (b) the Debye forces;
- (c) the London forces

(a) The Keesom Forces

These forces occur when the molecules are so orientated that an electrostatic attraction results between permanent dipoles in neighbouring molecules of polar compounds. The arrangement is one of a head-to-tail or lowest energy configuration, i.e. an orientation effect. Rotation into such configuration only occurs in molecules of low polarity in liquids (does not occur in non-polar substances). (See Fig. 3a).

(b) The Debye Forces

This induction effect arises by one molecule possessing a dipole, inducing a dipole in another molecule capable of being polarised and so the two molecules then attract one another. This again will not occur in non-polar substances. These forces are less important than the Keesom and London forces in adhesion (Retief 1970) (See Fig. 3b)

(c) London Forces - dispersion effect

These are not dependent on the existence of permanent dipoles. Slight displacement of the electrons or nuclei in an atom or molecule is constantly occurring; it is instantaneous and at random, and results in the formation of a dipole which at any one instant induces another dipole



Fig. 3a Diagrammatic representation of Keesom forces – Orientation Effect

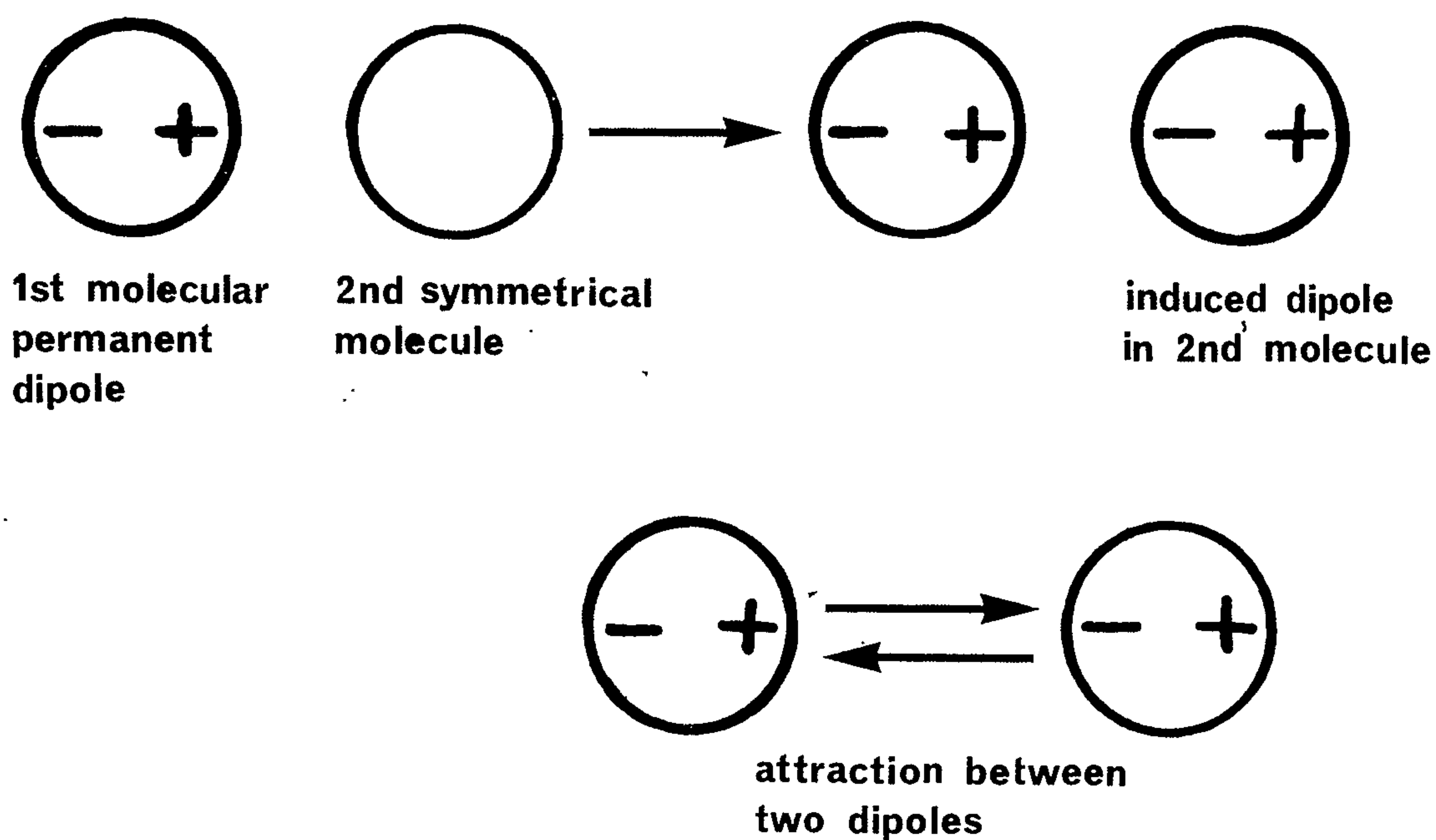


Fig. 3b Diagrammatic representation of Debye forces – Induction Effect

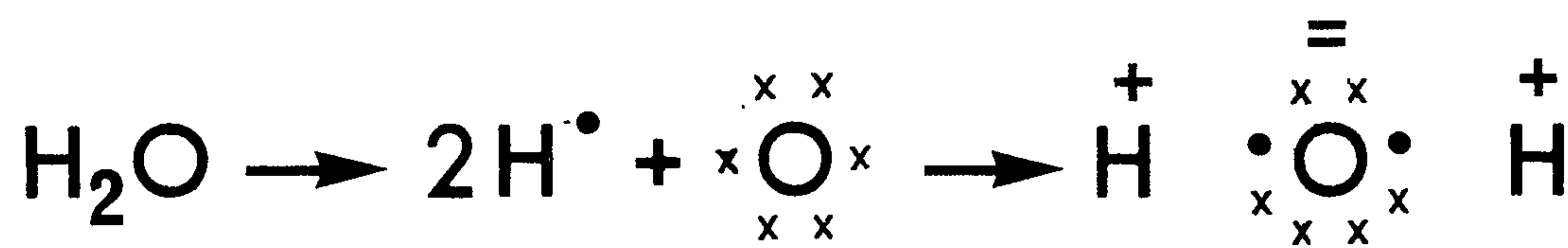


Fig. 4a

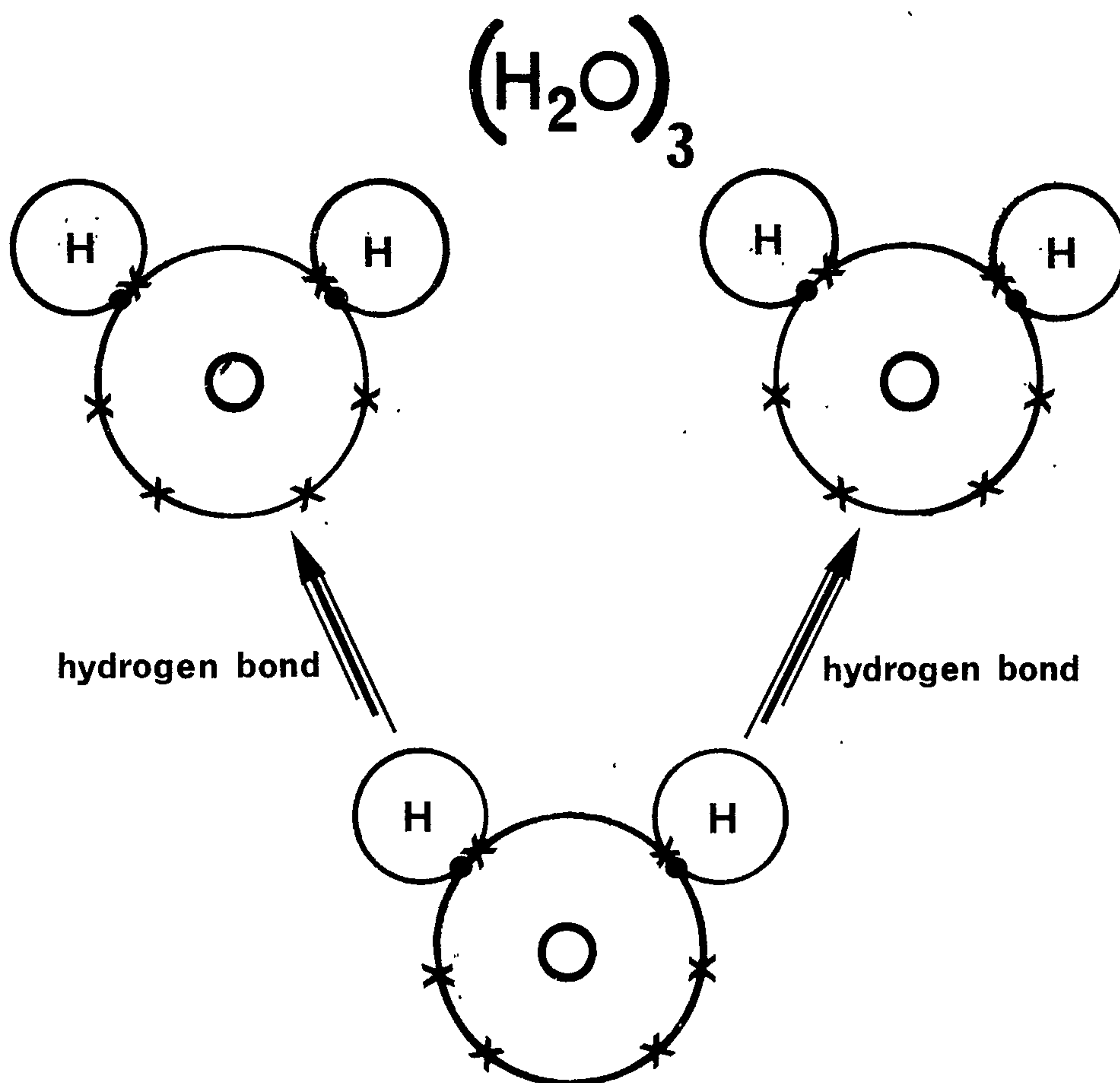


Fig. 4b Hydrogen bonding in the associated water molecule

in a neighbouring molecule.

According to Retief 1970a, the Keesom and London forces are by far the most important in adhesion.

2. Hydrogen Bond

Buonocore 1963 and Retief 1970a both state that this bond can be regarded as a special type of dipole - dipole interaction. Such bonding is found in the water molecule. The O-H bond is highly polar; the electron distribution around the hydrogen atom is distorted by the electronegativity of the oxygen atom so that there is a nett positive charge on the two hydrogen atoms. (See Fig. 4a). Since the hydrogen atom has no core or intact inner shell of electrons, the proton is partially bared.

In liquid water, this poorly shielded proton is surrounded by similar molecules and so there is a very strong attraction between these projecting unshared electrons and the poorly shielded proton of an adjacent water molecule. Hence the dipole-dipole attraction. (See Fig. 4b).

The requirements for this interaction are a highly electronegative atom (which must be small for close proximity of the atom) bonded to a hydrogen atom. Experimentally, only F, O and N atoms and some CN compounds exhibit such bonding.

SUMMARY:

1. The physical forces of attraction result in the physical absorption of the adhesive onto the adherend. This is a rapid reversible process. All the forces are dependent on separation between the interacting molecules - it specifically being the inverse sixth power of the distance. The London forces will always provide adhesion provided that intimate contact at the molecular level is achieved between any two substances regardless of their chemical nature.
2. Chemisorption is preceded by physical absorption and the absorbed molecules are held to the surface by bonds which may be covalent, ionic or metallic. The nature of the adherend will affect the reaction and the process can provide strong forces which are not easily reversed.
3. Parker and Taylor 1966 state "that polar molecules exhibit differing 'attraction potentials' and that this phenomenon is dependent upon the square of the dipole moment, and inversely proportional to the cube of the distance of separation between them. So, within limits, an abundance of polar groups is conducive to good adhesion". They add that good cohesive forces of London are desirable, i.e. a high molecular weight. However, high molecular weight is significant too, in that if too high the adhesive will be viscous and so have a poor wettability factor and, if too low, it will be weak in cohesion. A balance between the two is essential.

INFLUENCES OF SURFACE PHENOMENA ON ADHESION

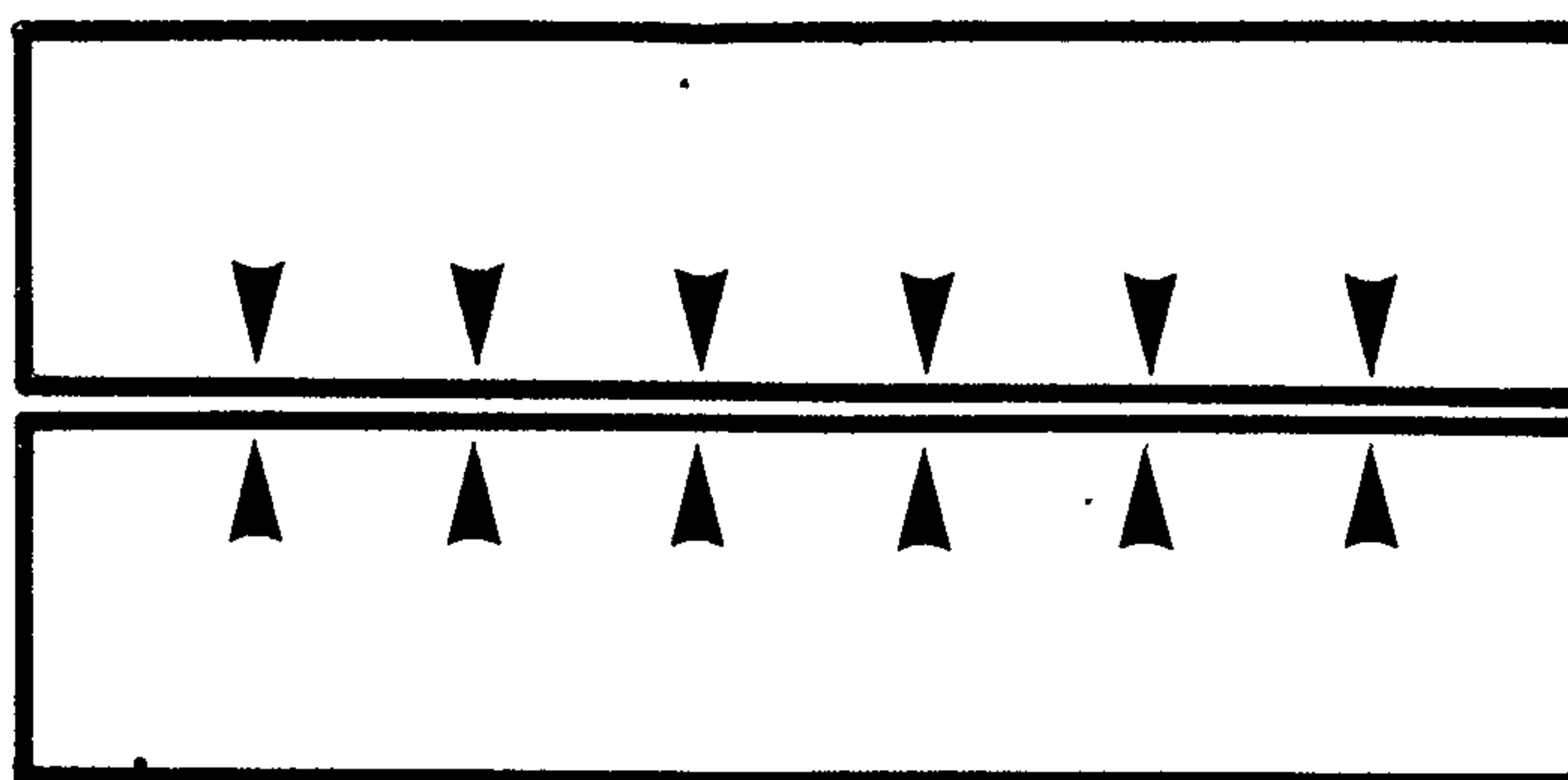
1. Surface Contact

If two solid surfaces, naturally smooth at an atomic level, were brought together they will adhere spontaneously (Retief 1970a). All attempts to separate them would result in a cohesive failure in the bulk of one of the solids (Parker and Taylor 1966). This adhesion exists only at short distances of separation ($1-2\text{\AA}$) and is entirely due to physical forces of attraction. Chemisorption may follow. However, Baier 1970 states that the physical forces will suffice to cause the above-mentioned failure. (See Fig. 5a). Retief (1970a) adds that even slight contamination (a mono-layer of this film oxide) will greatly reduce this solid adhesion. Retief is supported by Fowkes (1964) who states "that the simple rule that a low-energy liquid will wet and strongly adhere to a high-energy solid only holds if the intermolecular forces in the solid and liquid can interact".

In practice atomic smoothness cannot be achieved and so the physical molecular attractive forces only act at points of microscopic contact at most. These forces will be relatively widely spaced and so poor adhesion results as contact areas are a minute fraction of the total surface area. (See Fig. 5b).

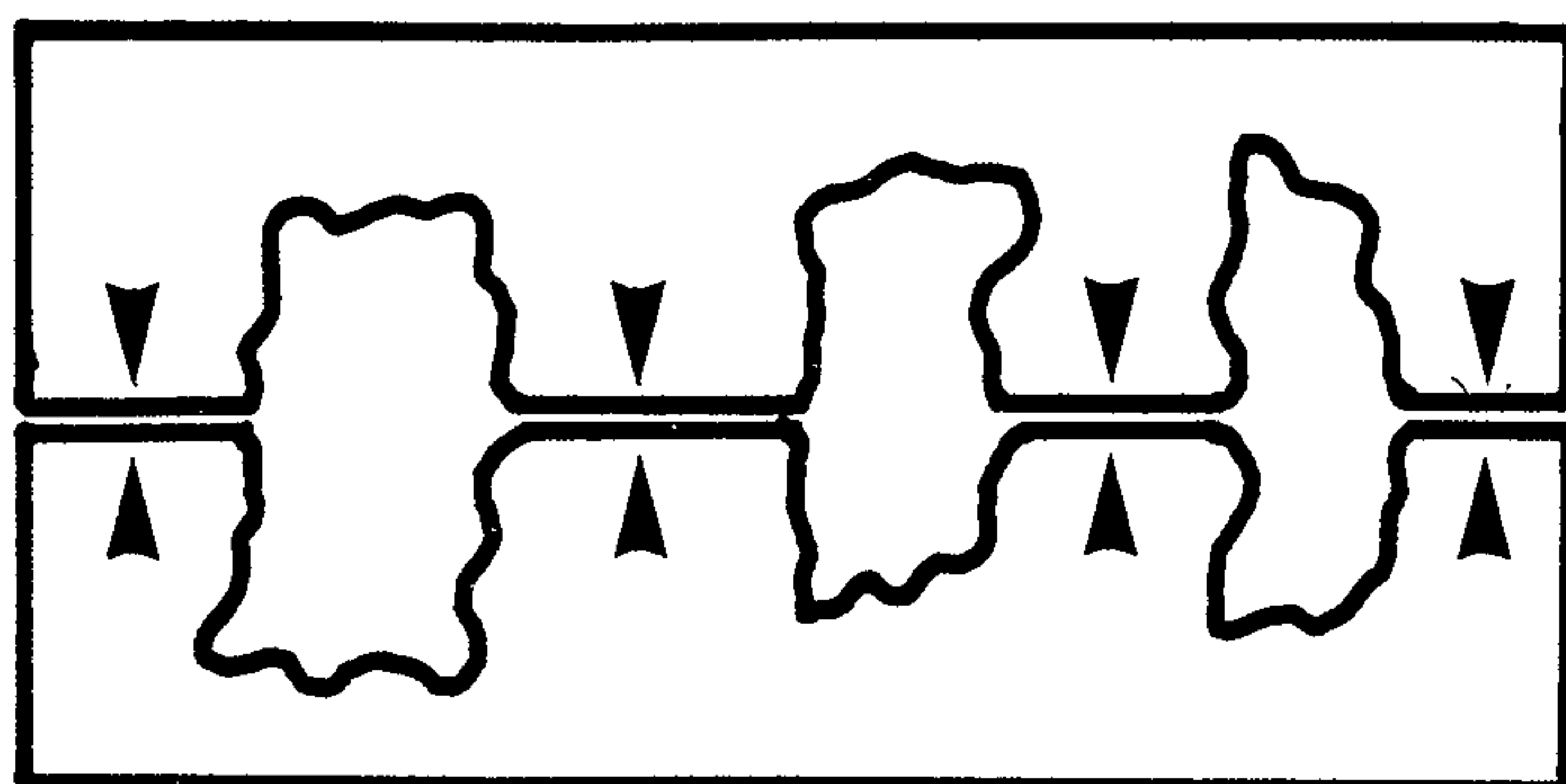
An adhesion functions to fill the surface irregularities and so establish close contact between the two adherends. Hence the previously mentioned forces will be supplemented by those acting

a.



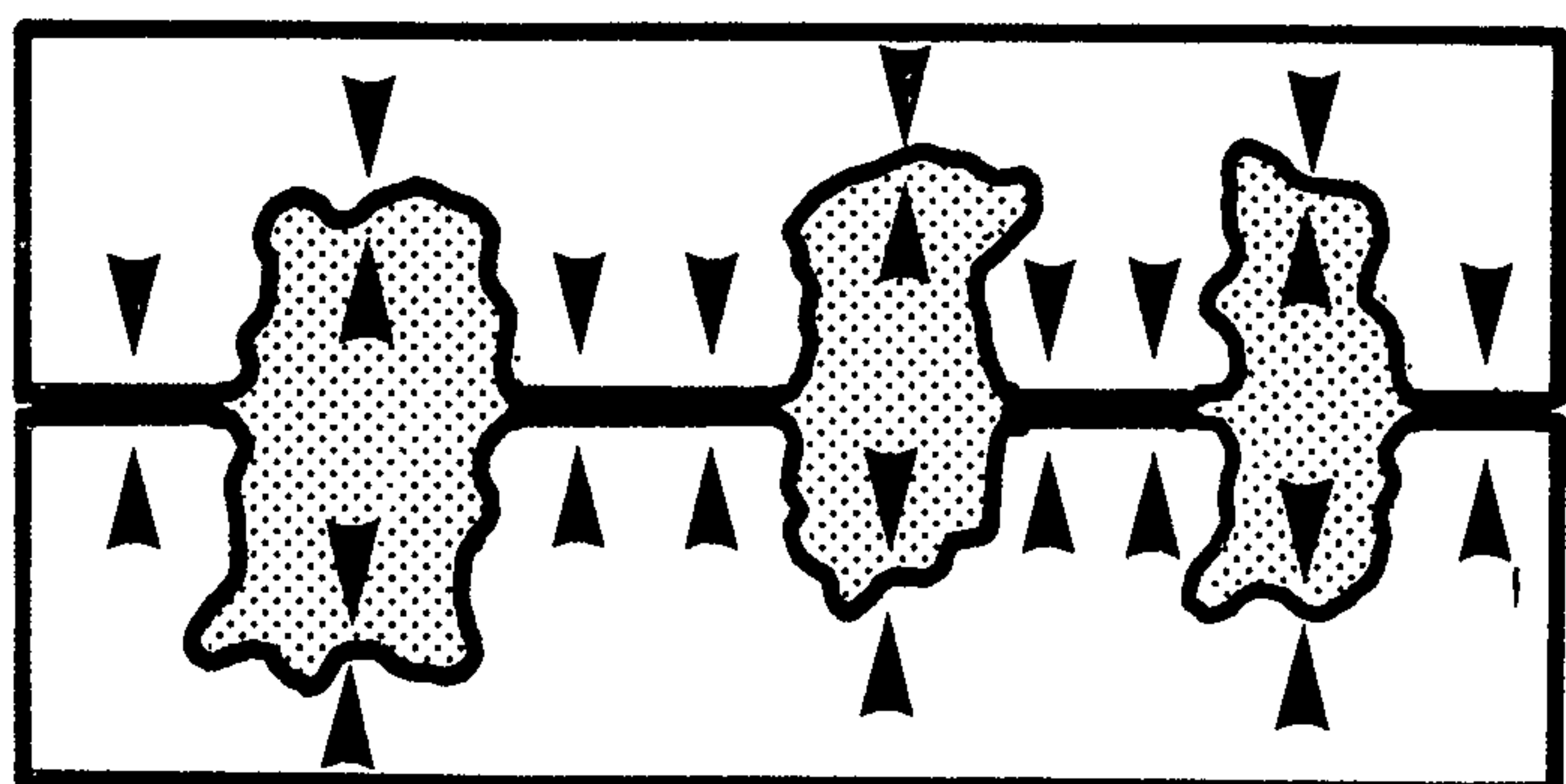
Anatomically smooth surfaces

b.



Rough surfaces

c.



Rough surfaces with adhesive

Fig. 5

a. Adhesion between anatomically smooth surfaces

b. Adhesion between rough surfaces

c. Adhesion with adhesive between rough surfaces

Between the adhesives and the adherends. Molecular closeness is maintained by use of adhesives which solidify on setting. (See Fig. 5c).

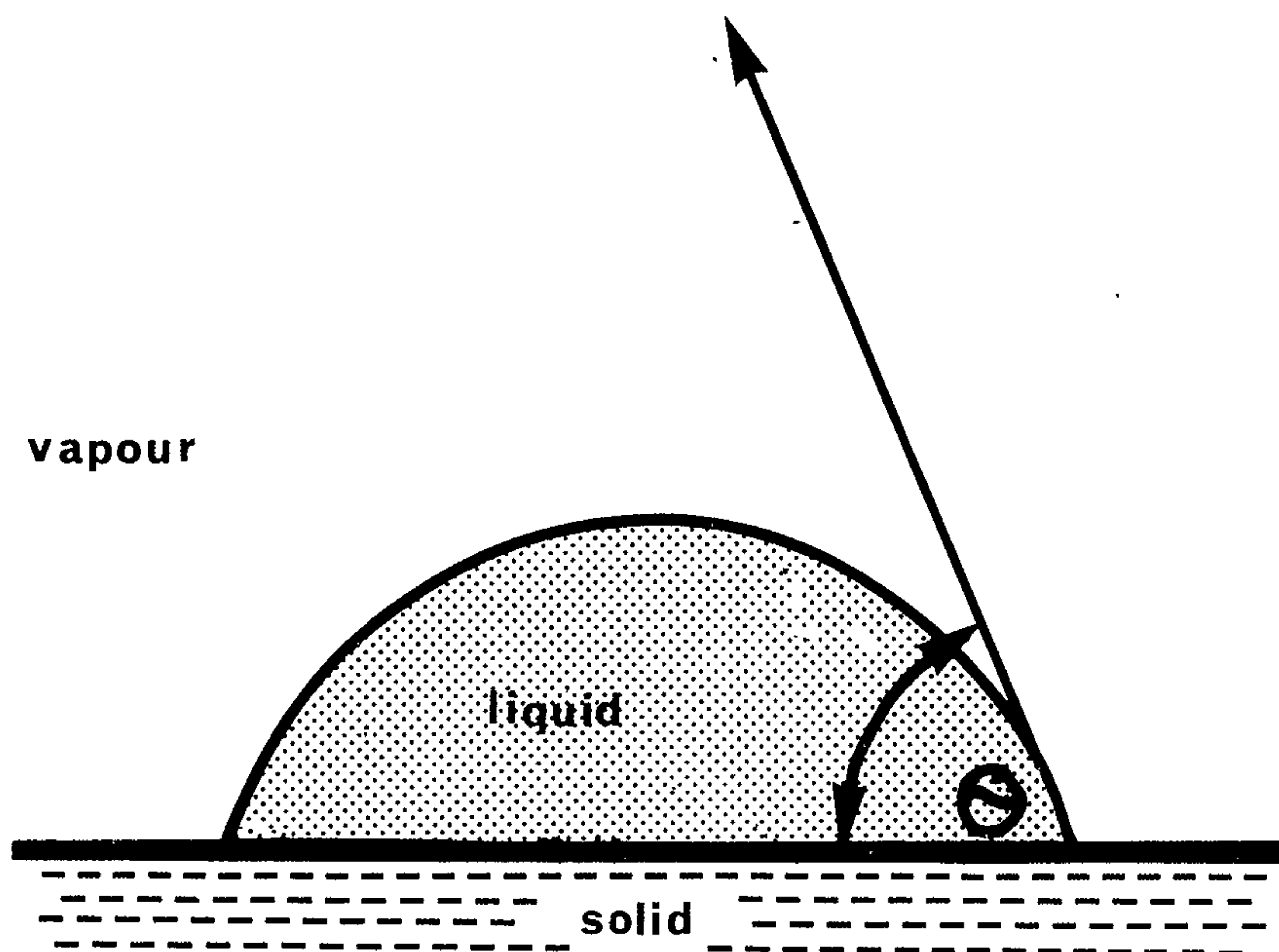
2. Surface Wetting

The desirability of intimate contact between the adhesive and adherend(s) is established. In other words, it is desirable for the adhesive to completely "wet" the adherend surface(s). Also reduction of surface irregularities tends to avoid incomplete wetting due to air entrapment and also tends to reduce thickness variations in the adhesive (Retief 1970).

Basically, wetting of a surface occurs because the attractive forces between the adhesive and the adherend are greater than the cohesive forces between the molecules of the adhesive (the phenomena of surface tension).

It then becomes apparent that it would be desirable to have prior knowledge of the degree to which a particular adhesive is going to wet a particular adherend.

Zisman 1961 explains the concept of the Contact Angle (θ) (See Fig. 6) between a drop of the liquid and a plane solid surface as expressed by Young in 1805.



Contact Angle (θ)

Fig. 6 The CONTACT ANGLE, θ , is the one formed between the surface of the adhesive drop and the surface of the adherend upon which it is resting. The diagram gives a diagrammatic scheme for the drop of liquid in equilibrium with the solid surface and the surrounding atmosphere saturated with the liquid vapour.

The degree of wetting depends on the contact angle at which the adhesive meets the surface of the adherend. It increases as the angle decreases. The contact angle is small if the attraction between the molecules of the adhesive and that of the adherend is greater than the attractive forces between the molecules of the adhesive. If this angle is small the adhesive will wet the adherend surfaces, and the molecular forces of attraction will operate along the entire interface and strong adhesion will result. If it is large the adhesion will be poor.

Fig. 7 gives a diagrammatic presentation of the effect of the contact on wetting and adhesion.

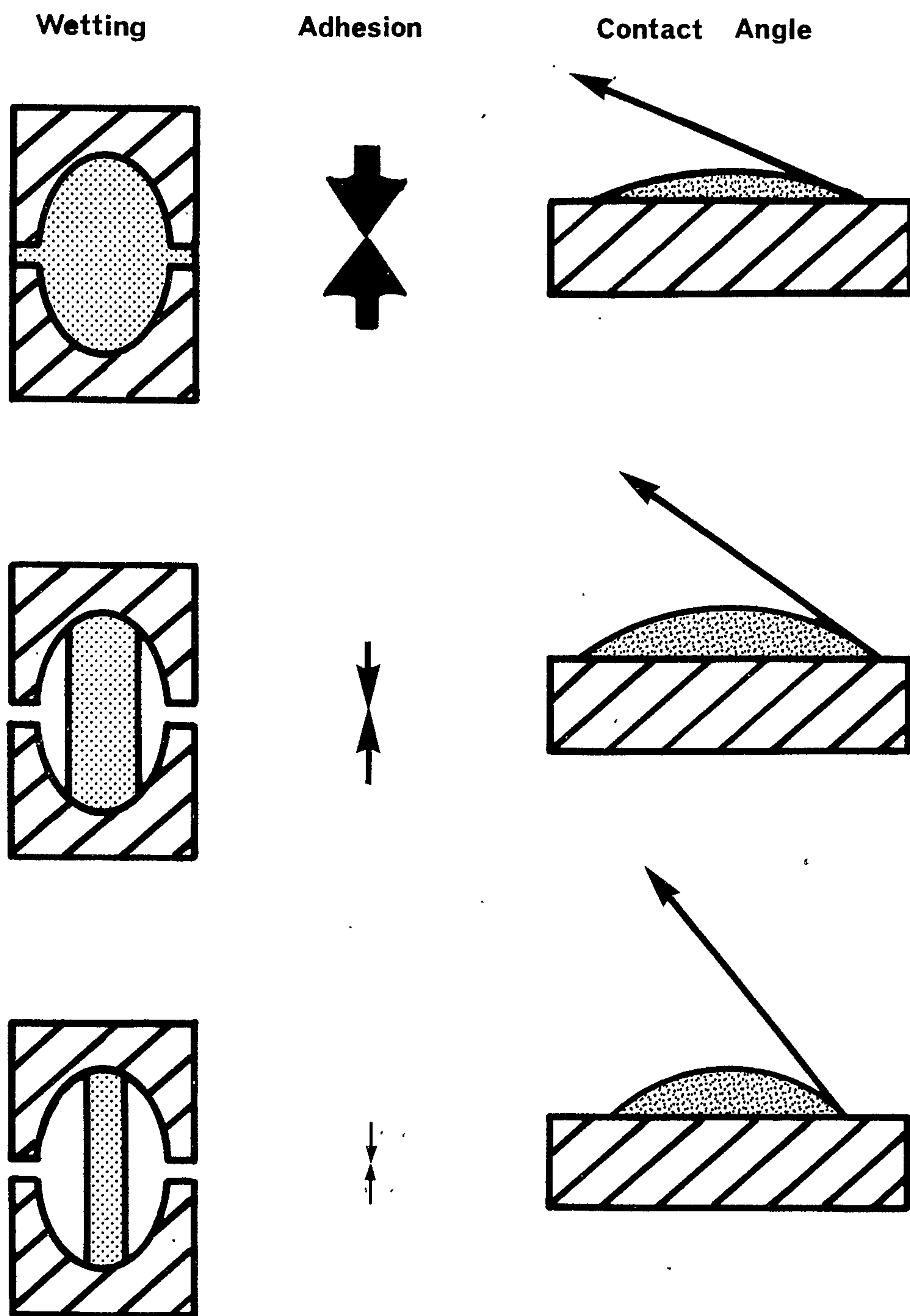


Fig. 7 The effect of the contact angle on wetting and adhesion.

Where,

γ_{sv} = free energy (surface tension) of the interface
between the solid and the saturated vapour.

γ_{lv} = free energy (surface tension) of the interface
between the liquid and the saturated vapour.

γ_{sl} = free energy (surface tension) of the interface
between the solid and the liquid.

Baier (1970) states "for small drops (not distorted by gravity) θ is independent of the volume of the liquid drop and temperature variations do not play a major role".

Young's (1805) concept enunciates that the three surface tensions, γ_{sv}^0 , γ_{sl} and γ_{lv}^0 , existing at the phase boundaries of a drop of liquid at rest on a solid surface must form a system in static equilibrium. (See Fig. 8).

If the forces acting along the line of the solid to liquid interface are resolved, the following expression is obtained:-

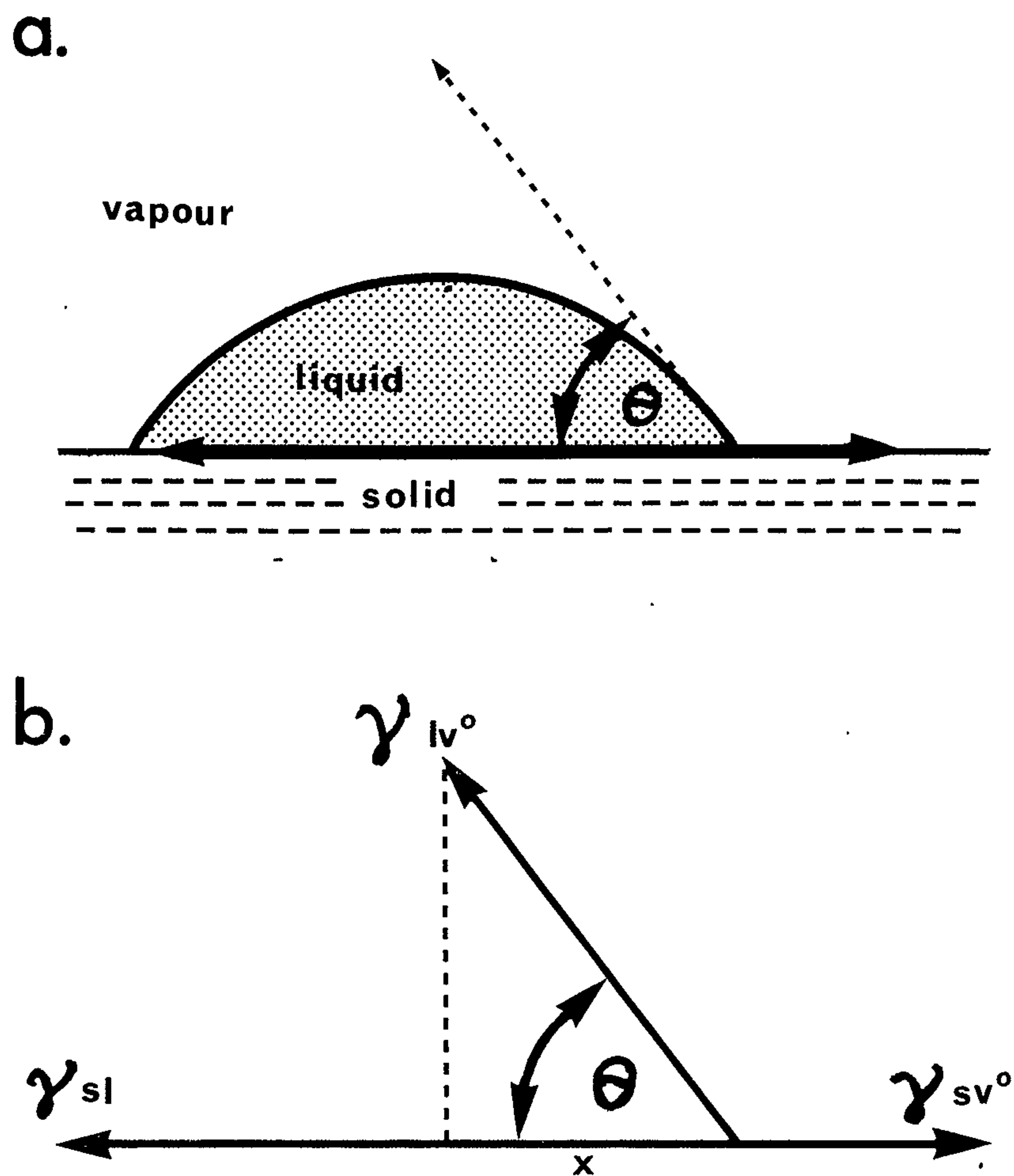


Fig. 8

a. The surface tensions at the phase boundaries of a liquid at rest on a solid surface.

b. Resolution of forces at the point where the phases meet.

$$\gamma_{sl} + x = \gamma_{sv}^0 \text{ ----- (1)}$$

$$\cos \theta = \frac{x}{\gamma_{lv}^0} \text{ where } \theta = \text{contact angle}$$

$$\therefore x = \gamma_{lv}^0 \cos \theta$$

By substituting x in (1)

$$\gamma_{sl} + \gamma_{lv}^0 \cos \theta = \gamma_{sv}^0$$

$$\text{or } \gamma_{sv}^0 - \gamma_{sl} = \gamma_{lv}^0 \cos \theta \text{ ----- (2)}$$

$$\text{and } \cos \theta = \frac{\gamma_{sv}^0 - \gamma_{sl}}{\gamma_{lv}^0} \text{ ----- (3)}$$

Hence the cosine of the contact angle formed between a drop of liquid and the plane solid surface upon which it rests, at equilibrium, has a definite relationship to the liquid and solid surface tension when in contact with the vapour.

The free energy of a surface expressed in ergs/cm^2 is dimensionally the same as the surface tension expressed in dynes/cm .

Dupre (1869) showed that W_A , the reversible work necessary to separate a liquid from a solid, (i.e. the force of adhesion), is related to the decrease in free energy when the two surfaces come together to form an interface. Dupre's equation expressed the relationship when considering the free surface energy of a solid in a vacuum.

Zisman (1963) came to realise that the solid surface was covered

by an absorbed vapour of the liquid and hence defined a new quantity W_A^* as "the reversible work of adhesion to pull the liquid off the surface leaving the equilibrium absorbed film".

$$\therefore W_A^* = \gamma_{sv}^0 + \gamma_{lv}^0 - \gamma_{sl} \text{ -----(4)}$$

where γ_{sv}^0 = the free surface energy of the solid
in equilibrium with the vapour.

By eliminating γ_{sl} from equations (3) and (4) a new expression is achieved:-

$$W_A^* = \gamma_{lv}^0 (1 + \cos \theta) \text{ -----(5)}$$

Experimentally γ_{lv}^0 and θ can be determined and W_A^* calculated.

Zisman 1963 showed that W_A^* is always less than W_A and the free energy change in a system of wetting is always positive.

The specific reversible work of cohesion (W_C) of the liquid is calculated by applying equation (5) to a liquid - liquid interface made up of two layers of the same liquid.

$$\therefore W_C = 2\gamma_{lv}^0 (\theta = 0^\circ; \cos \theta = 1 \text{ -----(6)})$$

According to Zisman (1961) and 1963, Cooper and Nutta (1915) set out the conditions for spreading of a liquid on a solid surface.

For spreading to occur $S > 0$

For non-spreading $S < 0$

Where,

$$S = \gamma_s^0 - (\gamma_{lv}^0 + \gamma_{sl}) \text{ -----(7)}$$

In a system where an organic solid is spreading on an organic solid γ_{sl} is negligibly small in comparison to γ_{lv}^0 .

$\therefore$ for spreading to occur $\gamma_s^0 > \gamma_{lv}^0$.

Thus in systems where the specific surface free energy of the liquid is less than that of the solid, spread should occur.

From equation (5) it can be seen that any system having

$$\theta = 0^\circ, \text{ i.e., } \cos \theta = 1$$

$$W_A^* > 2 \gamma_{lv}^0.$$

This value is greater than the tensile strength of common adhesives (Retief 1970).

When $\theta = 0^\circ$, the adhesive strength at the solid/liquid interface will be much greater than the tensile or shear strength of the bulk phase (Baier 1970). This is expressed by Retief (1970a) as a cohesive failure in the adhesive and not bond failure at the adhesive/adherend interface should such a system be subjected to stresses that will rupture the bond.

Glantz (1969) stated that when $\theta = 0^\circ$, the liquid is said to completely wet the solid, and that it will then spread freely over the surface at a rate depending on the viscosity and the surface roughness.

De Bruyne (1962) is more specific on the influence of surface roughness and believes wettability of an adhesive to be related to the shape of the surface irregularities. (See Fig. 9).

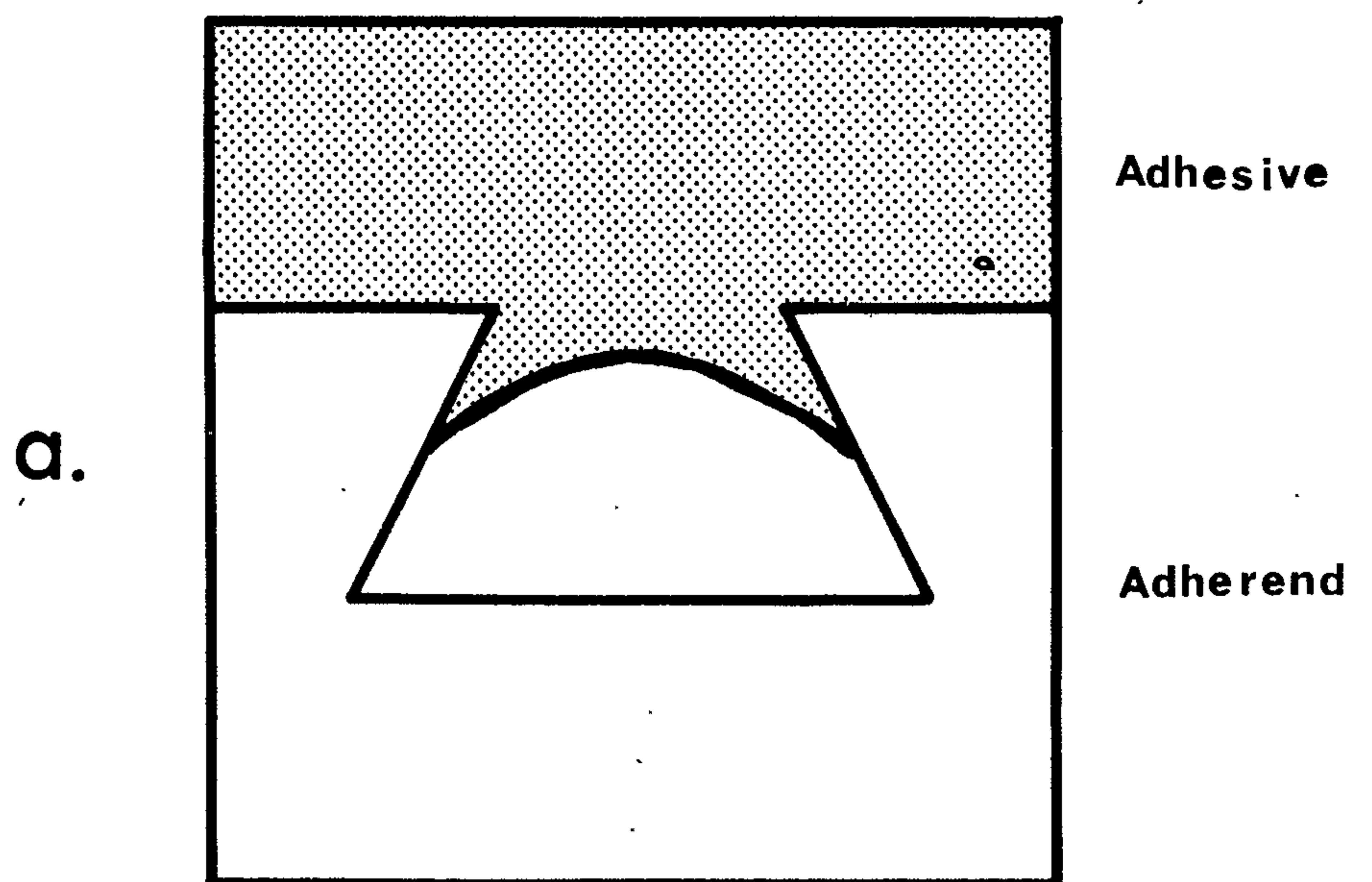
Huntsberger (1966) said the wetting rate is directly proportional to the viscosity of the liquid. He continues by stating that maximum rate or degree of wetting are not necessarily associated with zero contact angles. His experimental evidence shows that even though an adhesive may have $\theta = 0^\circ$, under practical use insufficient time for complete wetting is available and so inferior bonds may result.

Manning (1971) cites Buonocore (1971) as stating that even though an adhesive may have zero contact angle some micro-pores of the surface may not be wetted and hence he distinguishes between "wetting" and "spreading" of the adhesive over the adherend surface.

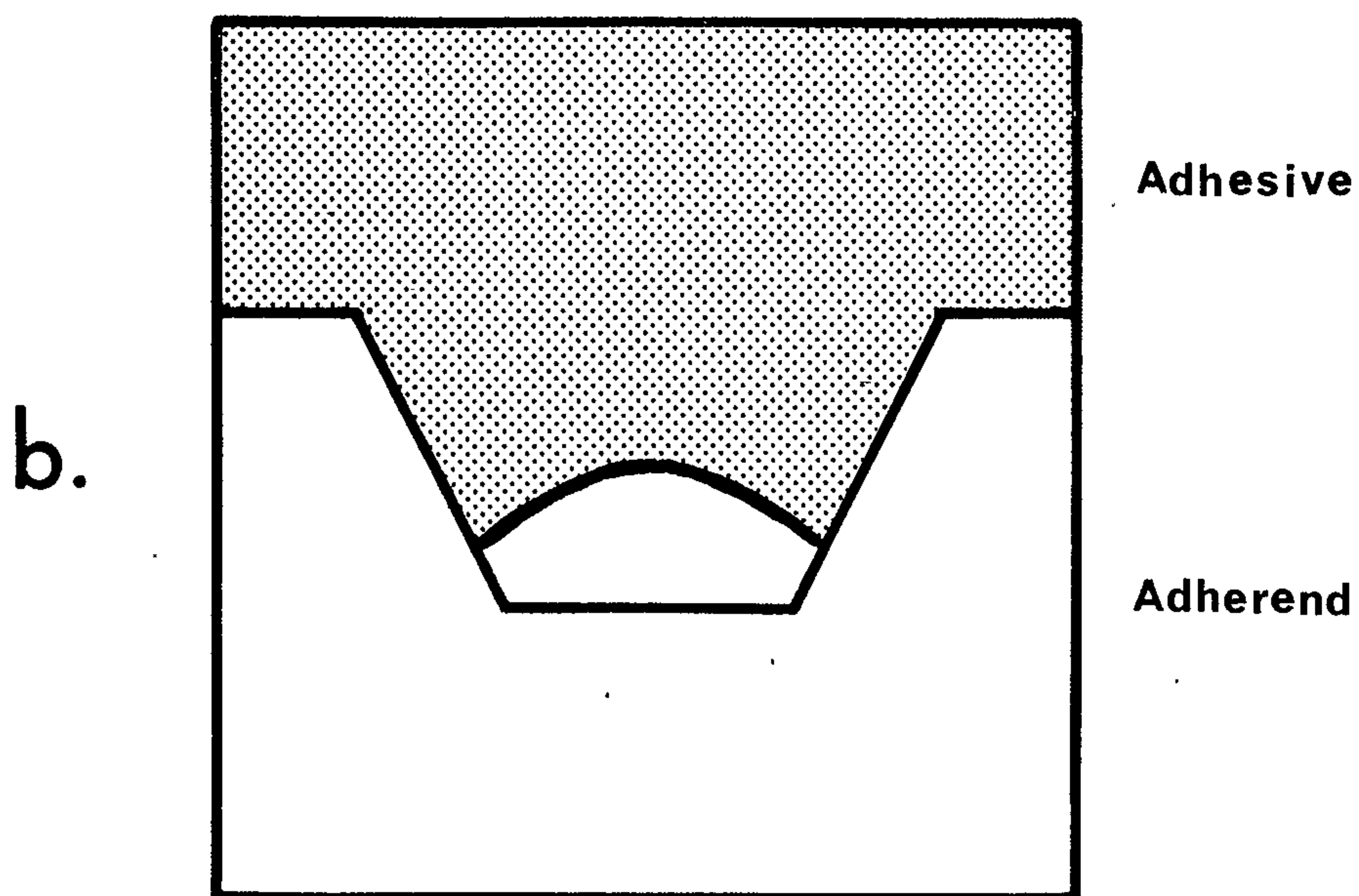
Zisman (1961) states that every liquid must wet every solid to some extent and consequently there must be some degree of adhesion between every liquid and solid.

3. The Critical Surface Tension of Wetting (γ_c)

Zisman and his co-workers (Glantz 1969) while investigating aspects



"INK BOTTLE PIT" - poor penetration
of the adhesive



"FLOWER POT PIT" - better penetration
of the adhesive

Fig. 9 Diagrammatic representation of the
types of depressions found on
adherend surfaces.

of wetting found a rectilinear relationship between $\cos \theta$ and surface tension γ_{lv}^0 for homologous series of organic liquids. Parker and Taylor (1966) defined the "critical surface tension" of a smooth solid as "the surface tension a liquid must have in order to just spread out on the solid". In practice, the spreading will occur if the liquid surface tension is less than, or equals, the critical surface tension of the solid.

Taylor (1951) pointed out that for every system where complete wetting of the solid (spreading of the liquid) occurs '(i.e., $\theta = 0^\circ$), the work of adhesion W_A^* will be equal to or greater than twice the surface tension of the liquid.

γ_c can be precisely defined as "the value of critical surface tension of wetting, for each homologous series that occurs at the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight line plot of $\cos \theta$ vs. γ_{lv}^0 ". Non-homologous series also showed close relationships.

As a result of this research Zisman (1962) concluded that the reversible work of adhesion (W_A^*) generally increases in the same order as do the values of the critical surface tension (γ_c). Hence γ_c is a useful index of wettability and adhesion.

4. Changes in Wettability

(a) High Energy Surfaces

Zisman (1964) stated "a high energy surface seldom retains its hydrophilic properties for any considerable length of

time". He believed this to be due to its high energy surface attraction and being covered by low energy substances in its neighbourhood. Baier (1970) points out that the above resultant decrease in surface energy will be caused by only a monolayer of absorbed molecules due to the highly localised nature of the forces:

(b) "Autophobicity"

Hare and Zisman (1955) described this phenomenon as being the inability of a liquid to spread because of its own absorbed monolayer. This results when the molecules of a pure liquid absorb onto a high energy surface in such a way as to have a surface film whose critical surface tension of wetting is less than the surface tension of the liquid itself.

Most non-polar liquids do not exhibit autophobic properties and those polar liquids which are not autophobic are those whose surface tensions are less than the γ_c of their own monolayers Baier (1970).

(c) Advancing and receding contact angles

Zisman (1962) pointed out that when observing the θ of a liquid boundary, which was advancing over a clean dry surface for the first time (θ_a), it was invariably higher than that when the boundary was receding over the previously wetted surface (θ_r): The reason being that the micropores and cracks in the surface of the solid became filled with the fluid and remained there, so assisting spread of the liquid

on the second application. Zisman says that if the surface is clean and smooth the difference between θ_a and θ_r should not be significant.

Theoretically, if "autophobicity" does not occur, a second application of the same liquid will more easily wet the same solid, if liquid from the first application has remained in the micropores.

(d) Influence of Water

The presence of a monolayer of water (perhaps derived from high humidity) will convert a high energy surface into a lower one. Hence the absorbed layers of physically bound moisture reduce the spreadability of organic fluids.

This absorbed monolayer does not affect the spreadability of water itself because the critical surface tension of water is lower than the critical surface tension of the absorbed film.

(e) Roughness of the solid surface

Wenzel (1936) found that small and large irregularities in the surface of the solid influenced the contact angle values.

He expressed his findings by the following equation:-

$$R = \frac{R_1}{R_2} = \frac{\cos \theta_1}{\cos \theta_2}$$

Where,

R = roughness factor

R_1 = true, or total area of the solid

R_2 = area of ideally plane solid

θ_1 = contact angle between liquid and "rough" surface

θ_2 = contact angle between the same liquid and the ideally plane solid.

Zisman (1962) and Glantz (1969) both agree that Wenzel's equation is important because surfaces having $R = 1$ are rarely encountered.

The equation further shows that if the contact angle is less than 90° (as with most organic liquids contacting polished surfaces) a roughened surface will decrease the contact angle. The converse applies if the contact angle on a smooth surface is greater than 90° . The two authors differ in the interpretation practically, as Zisman believes that the increase in roughness only appears to increase spreadability, whereas Glantz believes that it actually does increase wettability (c.f. to Buonocore's, 1970 differentiation between "spreadability" and "wettability").

Parker and Taylor (1966) state that a highly polished surface is undesirable for bonding because little adhesive becomes contained by the surface and so some degree of roughening should be provided. They point out, however, that

excessive roughening will decrease bond strength.

Retief 1970 and De Bruyne 1962 claim that the shape of surface irregularities are important because the adhesive may tend to trap small pockets of air and lead to incomplete wetting.

(See Figs. 9-10). As the viscosity of the adhesive increases, more air becomes trapped, resulting in poor contact and lower adhesion values (Parker and Taylor 1966).

Zisman (1969) states that the adhesive must wet, penetrate and fill every micropore of the surface for maximum adhesion to occur. Buonocore (1971) points out that adhesives possessing high surface tensions will fill capillaries better than those of lower values.

Zisman (1969) supports Parker and Taylor (1966) on some surface roughness being desirable for bonding but points out that a regular pattern of roughness may facilitate crack propagation along lines of air pockets when the bond is subject to stress.

Manning (1971) cites Bowen (1971) as conceding that in the practical situation it would seem impossible to obtain intimate contact between an adhesive and the substrate if there were water, polishing materials, fractured or loose substrate material or other debris at the bottom of microscopic pits on a rough surface.

Hence, wettability of an adhesive on an adherend surface

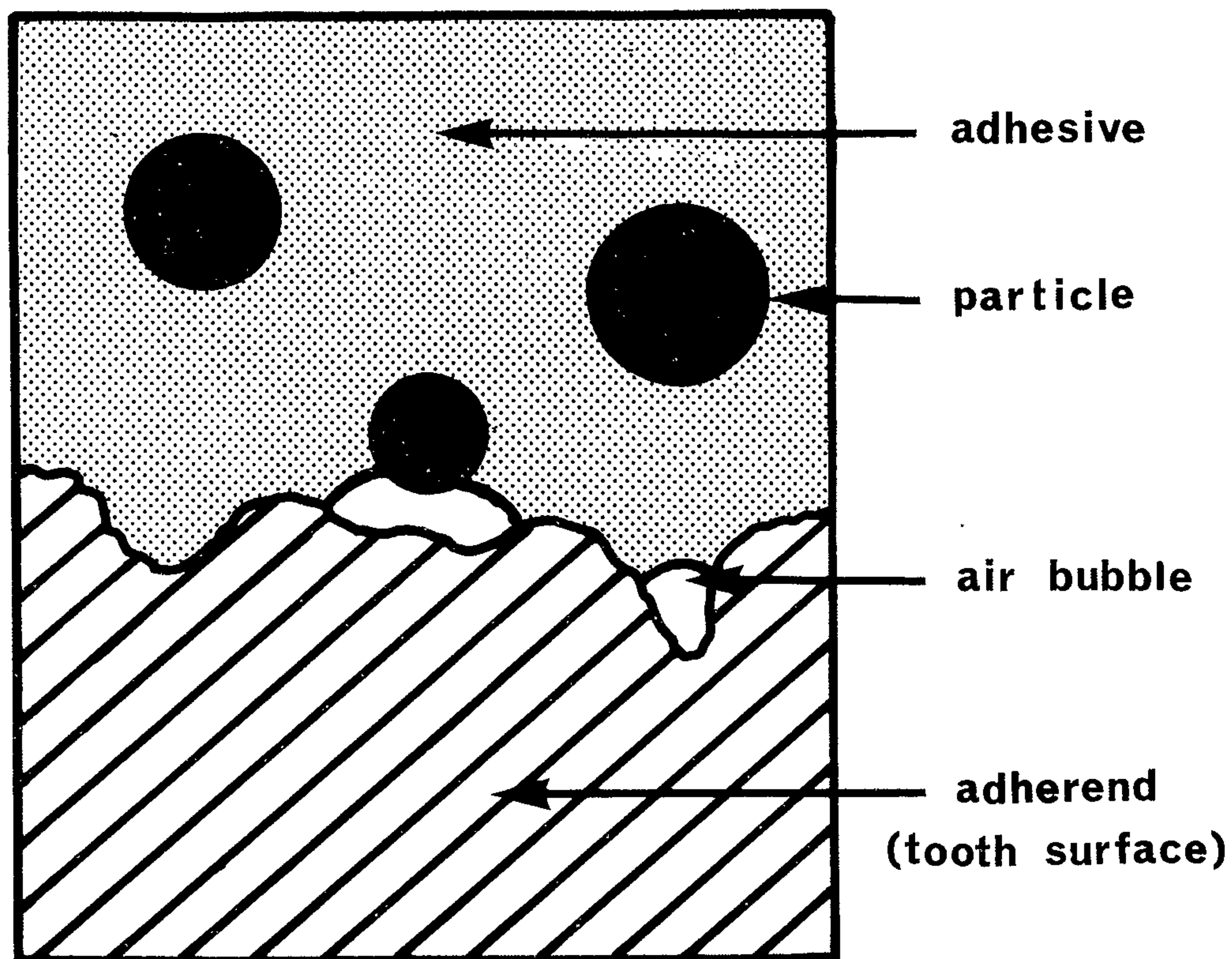


Fig.10 Adhesion to a rough tooth surface.

appears to be related to surface roughness. However, the nature of the roughness, the trapping of air pockets and the viscosity of the adhesive will all influence intimate contact between the adhesive and the adherend.

OTHER FACTORS INFLUENCING ADHESION AND BOND STRENGTHS

Previous discussion has mentioned the roles of surface contact (wettability), nature of adhesion (physical or chemical) and the cohesive strength of the adhesive as important factors in adhesion. These are not the only considerations, and hence the following include the main additional factors influencing the adhesive bond strength.

1. THERMAL EXPANSION

Zisman (1969) states that the most common cause of internal stresses in adhesive bonds is the difference in coefficients of thermal expansion between the adhesive and the adherend(s). Ideally, the coefficients of thermal expansion should be the same for both adhesive and the adherend(s) to avoid inducing stresses at the adhesive and the adherend(s). Practically, in the mouth, this is difficult to achieve. Efforts to match coefficients of thermal expansion have involved the use of large concentrations of inorganic fillers, preferably those with negative coefficients of expansion (Buonocore 1970). Unfortunately, any dramatic improvement in tending to equalise the thermal coefficients of expansion for an adhesive and the enamel usually is achieved to the detriment of another property of the adhesive.

Newman 1969 cites the following values for coefficient of thermal expansion:-

1.	Enamel	= 5.3×10^{-6} in./in./°F
2.	Acrylic resin	= 40×10^{-6} in./in./°F

3. Epoxy resin (unfilled) = 38×10^{-6} in./in./°F
4. Epoxy resin (filled) = 7.1×10^{-6} in./in./°F
5. Polycarbonate = 39×10^{-6} in./in./°F

He adds that even though the three partners of the adhesive system may have their physical properties matched, a superior bond need not result.

Bowen (1956) suggests that because of the low thermal coefficient of expansion of filled epoxy resins they possess one outstanding adhesive quality in comparison to other materials, e.g., acrylic resins.

Peterson et al (1966) showed that a temperature range of 10°C to 50°C is realistic in terms of extremes that could be tolerated in the oral cavity by the average patient. Greater extremes, however, may exist at certain times.

So it can readily be appreciated that if there is a large variation in coefficients of thermal expansion between that of the adhesive and the adherent(s) then a weakened joint structure will result from temperature variations within the system.

2. FLAWS IN THE SURFACE OF THE ADHEREND AND IN THE ADHEREND

Some considerations, particularly those relating to surface roughness, have been considered.

Other flaws such as air bubbles and discontinuities due to surface

contamination or pores, give rise to stress concentrations in the bond when subjected to a load (Buonocore 1963). These breaks, or cracks, may be considered as initiation points from which larger, disastrous fractures through the adhesive, may be propagated under relatively light loads as a result of stress concentrations.

Godfrey (1972) suggests the need for further investigation into the possibilities of reducing air bubbles, or pockets, both within the adhesive and on the surface of the adherend by some physical means, e.g. a "securing effect", obtained by using, say, a brush and suitable wetting agent.

3. VOLUMETRIC CHANGES IN THE ADHESIVE

Buonocore 1963 states that most adhesives undergo shrinkage on hardening or polymerization which induces internal stresses in the material. These stresses are believed to act tangentially to the adhesive interface. The thicker the adhesive the greater these stresses which tend to pull the adhesive away from the adherend.

According to Newman et al 1968, acrylic monomers exhibit very high shrinkage during setting to polymer: The volumetric decrease being in the order of 20%. To minimise shrinkage these workers experimented with low molecular weight polymers ($\approx 10,000 - 20,000$). They stress the minimisation of shrinkage in order to prevent formation of voids, bubbles, weak boundary layers and unfavourable stress distributions.

Parker and Taylor (1966) point out that highly crystalline polymers

are poor adhesives because of the large volume changes involved. Also, in the case of solvent adhesives, the change of state just by the loss or evaporation of the solvent is enough to cause some volume change. The resultant stresses will weaken the bond.

Swelling of the adhesive because of absorption of fluids can endanger adhesion Buonocore 1963. Hence the presence of moisture in the mouth could influence the adhesive bond initially and for the duration of the bond. The resins (particularly the acrylics) are prone to water absorption, resulting in expansion (Phillips et al 1969).

4. FLEXIBILITY OF THE ADHESIVE

Smith (1971b) states that an adhesive should be mechanically strong and it should possess some flexibility to minimise stress concentrations in the bond. He also says that a high value of tensile strength relative to compressive strength usually indicates a material which is more resilient and tougher than one whose respective strengths were oppositely related.

Newman 1969 states that joint flexibility helps to avoid impact fracture.

To increase joint flexibility, Patrick 1961 has suggested the use of a "rubbery" liner between the tooth structure and the restorative material. Lee et al 1971 states that, if a dental restoration is to be called "truly adhesive", then it must maintain adhesion in spite of the induction of stresses caused by thermal and dimensional changes.

The type of stress to which the joint is exposed, the rate and speed at which the stresses are applied, the temperature changes to which the joint is exposed, and the chemical stresses to which the bond may be subjected, will all affect bond strength (Patrick 1961).

5. FILM THICKNESS OF THE ADHESIVE

Buonocore (1963) states "that the adhesive industry generally recognises that thick adhesive layers give weaker joints than thin ones". He postulates three reasons for this:-

1. Increased likelihood of imperfections.
2. They are more likely to undergo lateral deformation under stress.
3. There are greater volumetric changes due to shrinkage during setting and, in the mouth, increased amounts of imbibition of water.

A thick layer can be thought of as a number of thin layers and so a summation of stresses increases the risk of joint failure.
(See Fig. 11).

Retief 1970 supports this thesis in stating that if there is any significant volumetric or thermal changes in the adhesive relative to the adherend during, or subsequent to, bond formation, then the thinner the film the better. He points out, however, that for any adhesive, there is an optimal value of film thickness. If the film

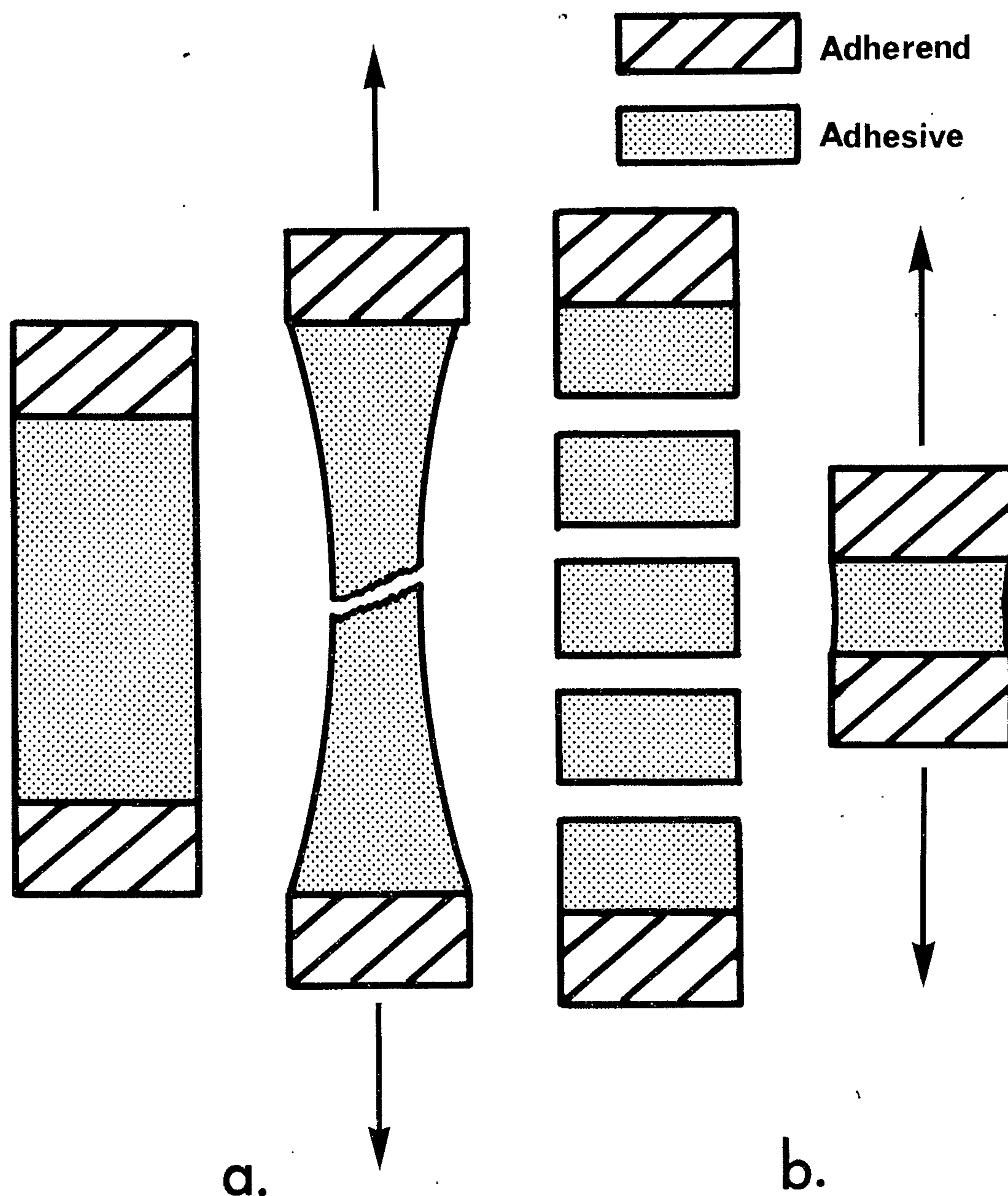


Fig. 11 Thickness of adhesive layer.

- a.** Cylindrical rod of ductile material in tension, with shear type of break at the point of reduced diameter.
- b.** Same cylinder cross-sectioned with one segment placed under the same tension as in (a); greater resistance to rupture can be attributed to the ability of the thin layer to resist lateral deformation better than the thick layer.

should be any thinner, insufficient material becomes available to cover the whole joint and the bond will fail as a result of "joint starvation". (See Fig. 12).

Zisman (1969) confirmed by experiments that thinner adhesive layers give greater bond strengths, but this only occurs whenever the bond failure is a cohesive failure of the adhesive.

Very few of the dental adhesive materials have known film thicknesses for optimal adhesion. Generally it is recommended that in the case of an orthodontic attachment, the bonding surface of this adherend should be adapted as closely as possible to the surface of the enamel before adhesive placement.

Mizrahi and Smith (1969) found that a seating pressure of 13.3 mgms/cms² gave an optimal film thickness of 15 microns for the direct attachment of an orthodontic "button" to an enamel surface using polycarboxylate cements.

Other researchers, Newman 1969, Muira et al 1971, Proffit 1972, do not suggest any specific seating pressure and merely recommend firm hand pressure. It should be realised that the pressure determined by Mizrahi and Smith 1969 as being optimal is difficult to achieve clinically for orthodontic attachments due to both patient comfort and difficulty of the operator to sustain such pressure throughout the setting reaction of the cement (Manning 1971).

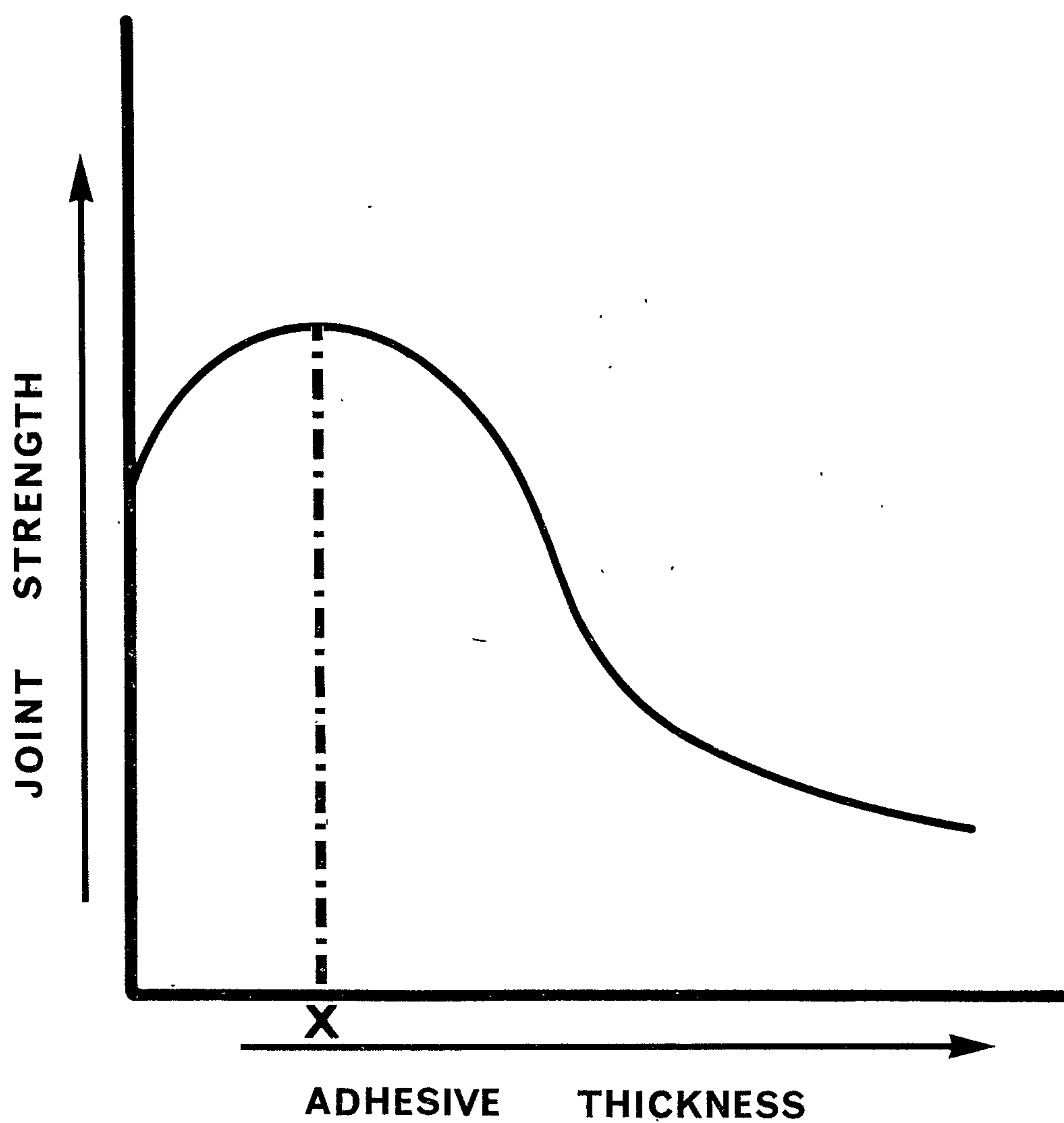


Fig. 12 The effect of adhesive thickness on the joint strength; where 'X' represents the optimal adhesive thickness.

So any optimal thickness must be achieved by an optimal pressure for any given adhesive.

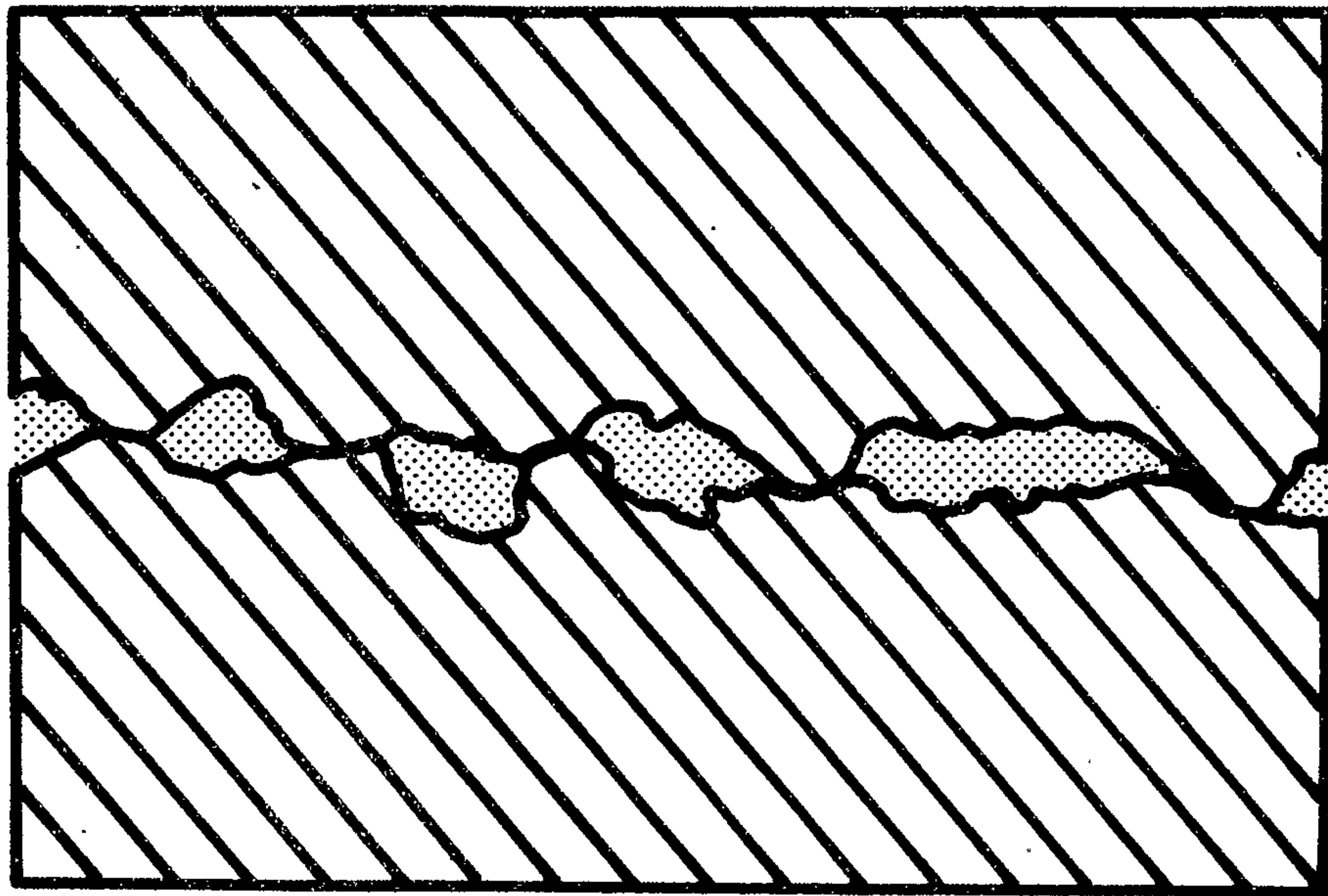
Too much pressure could be applied and Zisman (1963) pointed out that if the applied pressure were too great, solid-solid contact of the adherend surfaces could result in the development of elastic strains at the base of each surface pit and so tend to weaken the bond strength of the joint. (See Fig. 13). Similarly, any elastic deformation of the adherends occurring during bond formation would have similar effect upon removal of the load.

6. OTHER PHYSICAL AND CHEMICAL FACTORS

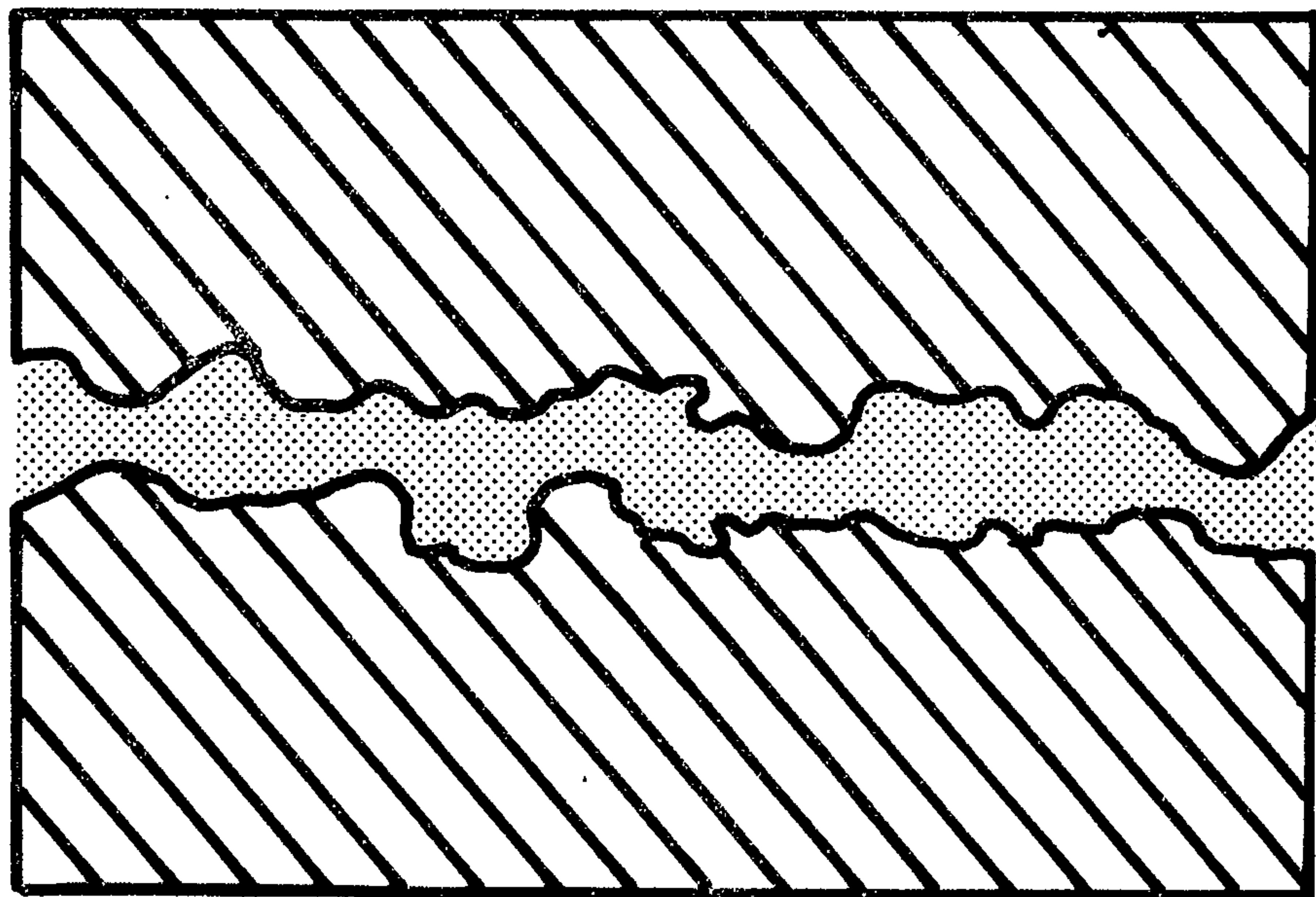
Buonocore (1963) points out that the strengths of polymeric materials, in practice, are far below calculated theoretical values because they are not oriented or crystallised ideally and also contain imperfections. Hence under load, the mechanical stresses are not distributed evenly, which results in stress concentrations in the bond that initiate early failure.

Fowkes (1964) supports this practical situation. He says that practical tensile strengths are always lower than theoretical values since failures are not the result of rupture of physical bonds at the molecular level but are of crack initiation.

Specific chemical and physical influences found in the oral environment are to be discussed later.



a.



b.

Fig. 13 a: Discontinuity of adhesive layer caused by contact between projections on both surfaces, results in a weak joint. Regions of discontinuity may act as initiation points for propagation of fractures under stress.

b: Stronger adhesive joint due to a slightly thicker and continuous adhesive layer.

SOME MATERIALS FOR WHICH ADHESION TO TOOTH
STRUCTURE HAS BEEN CLAIMED

Following the review of aspects of adhesion, it will be appreciated at this stage that a material exhibiting initial adhesion to tooth structure may succumb to the rigorous nature of the oral environment. Such a development would result in bond failure by disintegration of the adhesive and/or the adhesive joint after a relatively short period of time. It is also recognised that the adhesive joint is predominantly a mechanical interlocking of the adhesive in and about the adherend (a polished and/or etched enamel surface). For this reason Zisman (1969) states that it may be necessary to obtain either chemical reaction between the adhesive and adherend, or use a chemically reactive intermediary in order to prolong joint life.

The following is a list of some dental materials - some used routinely for dental (and in particular orthodontic) procedures, for which adhesion to tooth structure has been claimed:-

1. PHOSPHATE CEMENTS

Smith (1971a) and Phillips et al (1969) state that the zinc phosphate cements do not exhibit any adhesion to the tooth's surface and any apparent adhesion exhibited by this cement is a result of mechanical retention between the cement and surface irregularities.

In some instances, clinicians have used copper phosphate in preference to zinc phosphate cement, believing it to be superior

and possessing some adhesive properties. Swartz (1965) could not find any reason for it to be superior to the zinc phosphate cements. Phillips et al (1969) say: "the opinion that this cement is somewhat superior to other cements in its ability to retain appliances undoubtedly stems from the acidic characteristics of the cement rather than the physical properties. The tooth is more apt to be etched by the cement (because of its lower pH value) possibly providing greater mechanical retention".

Ware (1971) obtained the opinions of a number of orthodontists who used the phosphate cements clinically. He found that the majority considered bands that were cemented with the copper phosphate (both red and black) were relatively easy to remove, cf. zinc phosphate and silico-phosphate cements.

From clinical experience Godfrey (1972) found that bands recemented with black copper cement were relatively difficult to remove (cf. cementations with zinc phosphate cements). He believed this may have been due to an increased mechanical retention of the cement because of previous enamel decalcification caused by the oral environment due to loss of cement seal or, alternatively, due to an acid pre-conditioning prior to recementation, caused by the original cementation. Fitzsimmons (1968) found phosphate cementations did cause such minor etching of the enamel surface.

2. ZINC OXIDE-EUGENOL CEMENTS

The excellent sealing properties of this cement have been well

documented (Phillips et al 1969, Smith 1971b).

According to Smith (1971b) the ability of these cements to minimise leakage may be due to chemical bonding to the tooth surface through a chelation mechanism. However, their low strength and their continued loss of eugenol through fluid extraction leads to a poor durability in the mouth.

3. RESINS

(a) Acrylic Resin

Glantz (1969) states that the free surface energy of enamel is partially due to Van der Waal's dispersion forces, polar forces and/or hydrogen bonds. As acrylic monomer is a polar substance, it would be reasonable to assume that under suitable conditions there would be some physical adhesion, at least initially. Such adhesion may not occur due to the presence of the firmly bound monolayer of water on the enamel surface.

Other investigators believe that as well as a physical adhesion, there may be some chemical adhesion between the acrylic monomer and the enamel surface (Buonocore et al 1968).

Newman (1969) believes that there is a possibility of a reaction occurring between the hydroxyl groups present on the enamel surface and some polymeric adhesive compounds.

Uy and Chang (1966) state that the protein constituent of the tooth's surface is expected to contribute an appreciable polar force which adds to the total surface energy. Buonocore et al (1968) treated enamel surfaces with 50% phosphoric acid for one minute and they found that the subsequent decalcification exposed proteinaceous "tags" on the etched enamel surface. The acrylic was then able to wet the etched surface better and microscopic studies following demineralisation showed an intimate contact between the acrylic and the "tags", but these investigations did not state whether it was a chemical or physical union.

They believed that chemical bonding between enamel and the self-curing resin may be indicated by the failure of radioisotope and dye materials to penetrate the bond.

One considerable problem with resins adhesives is their tendency to imbibe water. Another is that, as polymerisation takes place, shrinkage occurs and the stresses set up at the resin/tooth interface probably become released with time and any bond (not mechanical interlocking) which existed initially, is lost after a short time.

Miura et al (1971) claimed no such shrinkage occurred at the acrylic/tooth interface during polymerisation. Although it may be conjecture on their part to claim no polymerisation shrinkage at the interface, there is some hope for an acceptable resin system in the future (Manning 1971).

(b) Epoxy Resins

There is no evidence in the literature that these resin bonding systems give any superior chemical or physical adhesion to any of the other resin systems (Manning 1971).

In fact Retief (1967) and Retief et al (1970) are the only workers who have persisted with the use of an epoxy resin direct bonding system for orthodontic clinical use.

Epoxy resins do give the lowest cure shrinkage (excluding the use of fillers) of any resins and also have a low coefficient of thermal expansion (Newman 1965).

It is one of the strongest resin systems and this is enhanced by mechanical retention in the surface roughness of etched enamel. Lee and Swartz (1970) found that although the epoxies are more resistant to water diffusion than the acrylics, and capable of bonding to moist surfaces, adhesion to smooth enamel surfaces is lost within 24 hours immersion in tap water. They concluded from this that the water disrupted the bond either along the adhesive interface or via the enamel "tubules". They also used heat-cured epoxies which were more water resistant but less practical. These epoxies were attached to the surfaces of the teeth by means of a silane intermediary which is, theoretically, capable of bonding chemically to the enamel surface and to the resin.

According to these investigations, the bond energy of this system was four times that of the self-curing system with no silane treatment.

To date, the long curing cycle and possible irritancy of some catalyst systems have limited their use (Newman 1965). In fact, it is interesting to note that Newman, discouraged by his research with these systems, then developed and now uses an acrylic resin system for bonding plastic orthodontic attachments to teeth (Newman et al 1968 and Newman 1969).

(c) Cyanoacrylates

Cueto and Buonocore (1967), Buonocore (1970b), Takeuchi and Kizu (1966) and Takeuchi et al (1966) have all met with some success when using cyanoacrylate pit and fissure sealer for the prevention of caries.

It is not known if such materials actually bond to the tooth surface or if they are merely retained by mechanical retention. Cueto and Buonocore (1967) who etched the enamel surfaces with 50% phosphoric acid obtained similar results to Takeuchi et al (1966) who applied the material directly to the teeth. These findings could lend support to theories of chemical and/or physical bonding.

Newman (1969) found cyanoacrylates to be unsuccessful resin systems when used for bonding attachments to the surface of teeth because of problems of manipulation and hydrolysis. He

also claimed they form brittle bonds.

Cohl et al (1972) are using the adhesive reported by Buonocore (1970) to bond clear polycarbonate plastic attachments to teeth for orthodontic purposes.

(d) Polyurethanes

Galligan et al (1970) reported that certain types of polyurethane resins, formed in situ, have the property of adhering "with considerable force" to freshly cut human dentine or enamel and were able to maintain this adhesion in the aqueous environment of the mouth.

These resins are formed by the condensation of a polyglycol with a large molecular excess of a di-isocyanate.

This isocyanate group is capable of reacting quickly with hydroxyl; amino-and carboxyl-groups to form relatively stable urethane linkages (Buonocore 1970a).

These authors believe the polyurethanes to have the potential to become complete restorative materials, but to date their use is restricted to that of linings or intermediaries for acrylic restorations.

Mixed results in regard to adhesion were found by both authors. However, they did find that the amount of isocyanate in the mixture was critical to obtain adhesion for tooth

structure. Newman (1969) found these materials, as for the cyanoacrylates, had problems with manipulation and were capable of being hydrolysed.

(e) Polycarboxylate Cements

The liquid component is basically a 40-50% water solution of polymerised acrylic acid. The powder is a modified zinc oxide similar to those already used in other dental cements.

Smith (1968, 1971a and b) claimed that these cements "could exhibit chemical adhesion to the calcium and proteinaceous portions of tooth substance under suitable conditions".

Smith believes that the adhesion arises from the ability of these cements to form chelates with metal ions as well as complexes with proteins. They are also believed to bond chemically to metals and calcified substances.

Smith provides further evidence in a recent scanning electron microscope study which showed that the matrix of the set cement was intimately in contact with the enamel surface.

The cement only slightly etched the tooth surface. In some instances a profuse growth of a crystalline product occurred and it originated from the enamel surface and grew into the body of the cement (Smith 1972).

Beech (1972) has shown that the adhesion of polycarboxylate cements to enamel is due to the formation of ionic bonds.

These bonds arise from the ionisation of the carboxyl groups

of polyacrylic acid through interaction with the calcium ions in the enamel.

Smith (1968) states that the cement is hydrophilic and excessive drying of the tooth's surface should be avoided. It is interesting to note at this stage that all the resin systems discussed are hydrophilic to some degree when applied to the tooth's surface. Therefore, the water molecules should be attracted, to some degree, from the tooth's surface by the polar bonds of the resin molecule. However, once the resin has polymerized, any polar bonds remaining will continue to attract water which can only help to cause disruption of the bond (Buonocore et al 1968).

Once set, the zinc salt of the polycarboxylic acid possesses a very low solubility of 0.05%.

As already mentioned, Smith claims these cements will adhere to proteinaceous material. However, if a film of saliva or other proteinaceous material covers the enamel surface, it will act as a separating medium.

These cements are used in the direct bonding of metallic orthodontic attachments to tooth surfaces as well as for conventional band cementations (Mizrahi and Smith 1969, Smith 1971, Manning 1971 and Mizrahi 1972).

THE NATURE OF THE SURFACE ENAMEL

The use of satisfactory adhesive materials must take into account the physical and chemical properties of the dental hard tissues to which it must adhere. These properties of enamel and dentine will determine the adhesive qualities of tooth surfaces.

Buonocore (1970a) states "enamel and dentine are qualitatively similar but quantitatively quite different. Both may require different adhesives and methods of surface preparation and different techniques of application". As a consequence of the above, and in considering that the orthodontic adhesives contact only enamel surfaces, only the properties of enamel will be discussed.

It should be remembered at this stage that one of the major problems lies in the difference in tooth structure, not only from one tooth to another but even in adjacent areas of the same tooth, i.e. the heterogeneity of enamel, a factor which appears to be characteristic of this tissue. (Spiers 1971). The orthodontic use of adhesives concerns the outermost enamel and to assist in its definition the discussion will predominantly be concerned with the surface zone that comprises the outermost 100 microns as suggested by Spiers 1971 and in particular only the anatomy as seen in surface views will be described in detail.

In unerupted teeth, differences between surface and subsurface enamel are attributable to processes associated with the cessation of amelogenesis and the longer exposure of the last formed enamel to tissue fluid. In erupted teeth, there are, in addition, acquired differences resulting

from the dynamic state at the interface between the enamel surface and the oral fluid environment.

1. PHYSICAL AND CHEMICAL PROPERTIES

(a) General

Enamel is that tissue which forms the protective covering of variable thickness over the entire surface of the tooth crown. It is the hardest tissue found in the human body and its specific function is to form a resistant covering of the teeth, rendering them suitable for mastication. Its hardness results from its high content of mineral salts (predominantly a reduced form of hydroxyapatite) and their crystalline arrangement determined by the process of enamel development: amelogenesis.

It consists of an inorganic phase, and an organic phase, and water. The inorganic content of the enamel amounts to 95-97% by weight, the remainder consisting of organic matter and water. The actual organic content is extremely small, being only 0.4 - 0.8% of the total weight. The organic matter consists predominantly of soluble protein, peptides, insoluble protein, citrates and carbohydrates. The inorganic content of mature enamel is predominantly hydroxyapatite, with a Ca:P ratio of a little more than 2:1 by weight.

Scott and Symons (1964) point out that considerable evidence has accumulated which indicates that the surface layer of enamel differs from the rest of enamel in certain physical

and chemical characteristics. The surface enamel is highly radio-opaque, harder and less soluble compared with sub-surface enamel. It can contain up to ten times the quantity of fluoride and a much higher concentration of carbohydrate. They add that some of these differences are found in unerupted teeth and concur with Spiers (1971) in that likely further accentuation may exist by post-eruptive absorption from the saliva.

(b) Degree of Mineralisation

Weidman et al (1967) found that the specific gravity of small particles dissected out from enamel sections, gradually increased from 2.86 near the dentine-enamel junction to 3.01 at the surface of unabraded cusps. Their results are supported by the measurements of Angmar et al (1963). Little and Brudevold (1958) determined the Ca/P ratios by weight in successive layers of enamel and their results showed that these were unrelated to enamel depth and age of the teeth. There was no evidence that the concentrations of calcium or phosphate were significantly increased at the enamel surface. Weatherell et al (1971) were unable to find a high degree of correlation between the density patterns in enamel and the percentages of calcium or phosphorus. They did note large variations in the calcium and phosphorus concentrations but a constancy in the Ca/P ratios in particles of enamel.

They studied numerous minute sections of tooth enamel and found that the gradient of density values, over the tooth

surface is by no means regular or comparable. Variations existed between cervical, cuspal and mid-coronal enamel. Density fell from the surface to the interior and the density gradients were by no means smooth. They state that as yet it is not possible to interpret the changes in density solely in terms of chemical composition. This is not surprising as density is a composite parameter dependant upon, among other things, the amount of mineral, organic matter, water and space/unit volume. Their results did show, however, that density values did not correlate closely with percentages of calcium, phosphorous, or protein. Sharp fluctuations, however, did appear to be associated with local disturbances in chemical composition. They added that the general patterns of density roughly follow that of enamel development and presumably arise from changes occurring in the mineralising environment.

There now appears to be less reason to suggest an abrupt fall in the degree of mineralisation on penetrating the subsurface enamel as was inferred from some of the earlier radio-graphic studies (Darling 1956 and Lyon and Darling 1957).

More recent studies (Frank and Brendel 1966 and Frazier 1967) using more sophisticated methods have confirmed that there is a very gradual increase in mineralisation towards the surface with no evidence for a discrete hypermineralised surface layer. However, Gwinnett (1967) and others, reporting on evidence from microradiographs, maintain that the superficial

layer is distinctly denser than subsurface enamel. This phenomenon may, however, only be present in old teeth.

Ripa et al (1966) showed a gradual increase in negative birefringence towards the enamel surface (although their micro-radiographic evidence failed to support this finding) whereas Houwink (1970) reports a marked increase. The increase in birefringence has been ascribed to an increase in the degree of mineralisation or to a more regular arrangement of crystallites near the surface.

According to Spiers (1971) Koulourides (1966) found that a surface zone, about 100 microns in thickness, was harder than the rest of the enamel. This correlates with the variations in density reported above, if these are gradual and small in magnitude. Hence, another explanation is needed, e.g. the possibility that the arrangement of the surface crystallites could be responsible.

However, Spiers (1971) points out that "even the concept of a discrete layer which is harder than subsurface enamel, is not proven". Again attention is directed to the fact of density (and even more so, hardness) being of composite parameters, and in this realisation it is likely that several factors contribute to the variations which are found.

(c) Protein

Coolidge (1951) demonstrated that surface enamel nitrogen

was ten times greater than that of subsurface enamel. The results were attributed to a surface membrane persisting on the teeth. This was shown to be present after decalcification of the teeth in mineral acids. Spiers (1959) cites Brudevold as having shown a definite nitrogen pattern throughout the enamel; the greatest concentration being at the DEJ and at the enamel surface, overall concentration increased with the age of the tooth.

Weidman and Eyre (1971) reported low surface values and their findings vary from those reported previously by Brudevold, but Weidman and Eyre measured only protein released by acid dissolution in the outer enamel as distinct from the surface layer. They may have also removed more of the organic surface integument or used different areas of tooth surfaces. By acid etching, they found the amount of protein was 0.05% expressed as amino-acids/weight enamel. It was found that all of the protein found in the outer enamel was acid soluble (this is significant in using acids to etch surfaces for bonding procedures as it assures penetration of the acids into all aspects of the enamel surface). Once again great variations were noted from tooth to tooth.

(d) Chloride and Sodium

It seems to be generally agreed that there is a steady decline in the chloride content from the surface to the inner enamel (Besic et al 1969). In investigating chloride distribution of enamel, Soremark and Gron (1966) found a lack of

correlation between chloride distribution pattern and that for sodium, which is evenly distributed at least through the outer half of the enamel thickness. They suggested that chloride might be firmly bound to, or incorporated in, apatite thus precluding a stoichiometric relationship between sodium and chloride.

(e) Carbonate

Weatherell and Hiller (1968) confirmed the results of others by showing that carbonate increases in concentration from the enamel surface towards the middle region and then more gradually towards the DEF. Brudevold and Soremark (1967) showed a decrease in surface carbonate with age. Worn surfaces have higher carbonate levels than unabraded surfaces due to higher internal concentrations (as mentioned above) and that this finding was distinct from the age findings.

(f) Citrate

Gedalia et al (1969) found that citrate levels varied on different surfaces of erupted teeth and increased with age in erupted molar teeth.

Brudevold et al (1960) and Nikiforuk and Grainger (1965) have shown more citrate on the outer third of the enamel thickness than in the middle zone. They found there was a trend towards less surface citrate in those teeth with the high fluoride levels but the degree of correlation was not statistically significant. That inconclusive result agreed

with the more recent findings of Gedalia et al (1969).

(g) Trace Elements

(i) Zinc

Brudevold, et al (1963) showed levels of up to 1,000-2,000 ppm but, unlike fluoride, there appears to be no appreciable post-eruptive uptake. Enamel exposed to zinc has decreased solubility in acids (Brudevold and Soremark 1967).

(ii) Lead

Similar levels are reported for lead. Brudevold and Steadman (1956) reported that enamel surfaces possess greater concentrations of lead than subsurface enamel and that it increases with age.

(iii) Copper

According to Brudevold and Stedman (1955) the concentration of copper in surface layers is greater than in subsurface enamel. Their evidence suggests that surface copper is incorporated in the enamel prior to eruption and does not accumulate post-eruptively with age.

Spiers (1959) confirms the above but adds the reservation that in teeth from amalgam free mouths, the difference in surface and subsurface levels was less marked.

(iv) Tin

Brudevold and Stedman (1956b) concluded that tin is not present in higher concentrations in surface enamel than subsurface enamel. However, they claimed a post-eruptive accumulation occurred in the surface. Spiers (1959) showed that tin was found in much higher concentrations in surface enamel but only in mouths containing amalgam restorations.

(v) Iron

Brudevold and Soremark (1967) point out that this mineral also accumulates in the outermost portion of the enamel. Concentrations varying from 200-280 ppm and from 120-220 ppm have been reported in surface and subsurface enamel respectively by Torrelli (1957) as cited by the above authors.

Brudevold and Soremark (1967) also report that levels show geographic variations and that the levels detected seem to be related to the degree of iron ingested. They also found fluoride levels closely correlated with those of iron.

(vi) Strontium

Stedman et al (1958) showed that strontium concentration is usually lower in the outermost parts of enamel than in the deeper parts. Great variations in levels in teeth of individual and geographic locations are

documented. Spiers (1959) using spectrographic techniques found no such lower outer levels. Brudevold and Soremark (1967) found no correlation between fluoride uptake and strontium levels although this had been reported in the literature.

(vii) Magnesium

Layer analyses of intact enamel have shown increasing concentrations from the surface inwards; the concentration increasing to threefold in the innermost portions (0.11% to 0.30% dry weight). (Brudevold and Soremark 1967). They obtained similar levels in erupted and unerupted teeth, which suggests that the uptake of magnesium is primarily a pre-eruptive process. Age effects on magnesium in enamel are unknown.

(viii) Others

Other elements including Al, Mn, Si, Ni, Au and V are normally present in low concentrations and are therefore less likely to affect the physical properties of the enamel.

(h) Fluoride

Spiers (1971) states "in the last ten years it has been repeatedly confirmed that the fluoride concentration in enamel falls exceptionally from the surface inwards' towards a plateau in the middle third of the enamel".

There is an increasing uptake of fluoride by enamel as the unerupted tooth matures and upon eruption an increase in surface fluoride in permanent teeth with age (Brudevold and Soremark 1967). This was not found to be so by Weatherell in early experiments. However, later work by Hallsworth and Weatherell (1969) has shown that labial surfaces of incisors, upon which their earlier studies were made, are often abraded, particularly in older teeth and that these consequently have lower fluoride values. It was found that any post-eruptive uptake of fluoride did not compensate for the loss resulting from attrition.

Little et al (1967) considered that high surface fluoride levels, found particularly in old teeth, were due to its accumulation in visually-intact but discoloured areas. They found that when teeth were carefully selected before analysis, to exclude as far as is practical such regions, less steep gradients were obtained. Spiers (1971) questions the meaning of such selection procedures. His misgivings are supported by Weatherell et al (1971) who stated "opaque and pigmented areas are indeed so common that their composition and properties must be considered if the behaviour of the tissue as an integrated whole is to be understood".

This again, adds support to the heterogenous nature of the surface enamel and indeed of all enamel.

Little et al (1971) also claim that the fluoride accumulated

in surface enamel is organically bound, stable and requires drastic measures for its release. If their results (which were considerably higher than those most frequently accepted in the literature) are substantiated, it may be that fluoride figures in the literature will require the prefix "inorganic" attached to them.

Brudevold and Soremark (1967) list the three possible mechanisms of fluoride uptake as:-

1. Diffusion into and exchange with anions, in the tightly held water adjacent to the crystal;
2. Migration into the body of the crystal and incorporation in the interior lattice structure;
3. Fixation in the surface of the hydroxyapatite by replacing hydroxyl or bicarbonate ions.

It is doubtful that the third mechanism actually occurs in the lifetime of the tooth and it is about the first mechanism that Little et al (1971) make their claim, which has not yet been substantiated.

As distinct from the mechanism of uptake, the deposition of fluoride in enamel occurs in three stages (Brudevold et al 1956a).

1. Low concentrations are incorporated in the apatite crystals during their formation;
2. A post development and pre-eruptive uptake of fluoride occurs in the external enamel which is in contact with tissue fluids; and
3. After eruption and throughout life, the surface enamel continues to take up fluoride from the oral environment.

Analyses of enamel from a great number of human teeth have shown that the pre-eruptive uptake of fluoride by surface enamel increases markedly with increase of fluoride in the drinking water (Brudevold et al 1960). It was also shown that the more fluoride-saturated the surface enamel is at the time of eruption, the less tendency it has to accumulate additional amounts. The post-eruptive acquisition of fluoride by the enamel is mostly due to direct contact of drinking water. It may also be gained by topical applications, and surface uptake from fluoride tablet mastication, dent-rifices, floss and other aids containing fluoride (Brudevold and Soremark 1967).

Fluoride is acquired at depths of up to 80 microns from the surface in unerupted teeth, but is restricted to about 15 microns in erupted teeth. Some loss of surface fluoride occurs in vivo after topical application and, despite this

rapid and variable loss of fluoride, there is some evidence of fluoride retention several months or even years after treatment (Spiers 1971).

Fluoride in surface enamel is known in some way, still controversially argued to increase resistance to carious attack. The optimal fluoride levels are not known and no levels of fluoride concentration have been discussed due to analytical variations resulting from variations in section thickness and location, of different methods resulting in possible misinterpretation of experimental results. Consequently, only general concepts of fluoride surface chemistry have been considered.

(i) Water

Brudevold et al (1960) deduced that there was less water in surface enamel since both radiodensity and organic content were found to be higher in surface than subsurface enamel. However, the lack of a suitable method has prevented the accurate measurement of the water content. Usual methods were to simply heat the enamel to 100°C for several hours and then determine the weight difference between the initial and final samples. Such determinations resulted in estimations of water content as slightly above 2% by weight of total enamel. Little, Cueto and Rowley (1962a) showed that fully mineralised enamel contains a greater concentration of water than was earlier indicated, since appreciable amounts are firmly bound and will be released only after heating to temperatures

considerably in excess of 100°C .

Brudevold and Soremark (1967) claim that "loosely and firmly bound water" accounts for roughly 4.0% by weight of the enamel surface. Only 25% of the water is "loosely bound" and associated with the organic phase, whereas the remainder is "firmly bound" to the mineral phase. Carestrom et al (1963) have confirmed experimentally that there is less loosely bound water in surface enamel. Dibdin (1972) suggests that the water in enamel behaves in a normal way, with the loosely bound water being easily removable at room temperature merely by lowering the humidity, while the other less mobile species, probably apatite hydroxyls and some "strongly bound" water are left in the tissue. He suggests there may be "an activated diffusion of water from stronger to weaker bonding sites", under such conditions. This seems consistent with the finding of Poole (1971) that at humidities less than a few per cent there is a slow effusion of water vapour from enamel, perhaps from "some inner pore system".

Poole et al (1963) showed that there is a relatively free flow of water through human enamel, probably involving the loosely bound fraction. Bergman and Siljestr nd (1963) found the velocity of flow of water through intact mature enamel, in vitro, to be approximately $4\text{mm}^3/\text{cm}^2/24\text{ hr}$, which they suggest permits the passage of significant amounts of water. Other fluids may also diffuse through the enamel but certain ionic exchanges are impeded (Poole et al 1963).

"Water in enamel thus appears to act as an ion exchanger but because of many uncontrolled variables, e.g. lamellae or cracks which greatly facilitate the "normal" fluid movements, it has not been possible to characterise this behaviour in detail", (Brudevold and Soremark 1967).

2. SOLUBILITY OF THE ENAMEL SURFACE

Spiers (1959) believed that the link between solubility and chemical composition was uncertain. In a more recent review he (Spiers 1971) states that many reports still appear in the literature in which attempts are made to relate surface fluoride levels, hardness values and caries incidence to solubility. He further expresses no surprise that better correlation results have not been obtained considering the "sledge hammer" techniques used.

It appears that the two predominant tests of solubility are:-

1. Rate of dissolution in acid
2. Rate of penetration by acid (as judged microscopically).

These two tests probably depend upon different structural features and properties of enamel.

Brudevold and McGann (1968) state that most enamel solubility tests are not concerned with determination of actual solubility, but with measurements of amounts of enamel dissolved after a

shorter period of acid exposure than that required for equilibrium. These techniques are used on the basis that the caries process suggests that mineral dissolution is governed by rate-determining factors rather than by equilibrium solubility.

The force or energy which causes dissolution is a function of the degree of saturation of the solution. The more undersaturated the solution, the greater is the tendency or driving force for dissolution to occur. Hence dissolution is initially rapid in an acid buffer, and tapers off as saturation or equilibrium is neared. However, the rate at which dissolution occurs in a system (e.g. amount of enamel dissolved in a fixed period) is determined not only by the state of saturation of the solution, but by factors such as particle size, solid-solution rates, viscosity of the buffer, specific ion effects, agitation and temperature.

Acid demineralisation seems to be diffusion controlled. Gray (1962) found the initial rate of dissolution was a function of the hydrogen ion concentration at the solid-solution interface. In the case of buffers, he also found it to be a function of the concentration of undissociated acid and its dissociation constant that would determine the supply of hydrogen ions at the reaction site. The mechanism by which equilibrium, in the case of acid dissolution of enamel (predominantly hydroxyapatite) is obtained is not clear.

Brudevold and McGann (1968) note that the solubility product of enamel is not fixed.

Apart from the influences of altering solid-solution ratios, lower pH values of the acids, time of exposure, etc., other influences are involved. It is known that the surface composition of hydroxyapatite, (and it can hence be assumed the composition of the solid surface enamel exposed to the acid), may vary considerably by ionic exchange processes, (Brudevold and McGann 1968). McGann (1966) showed the importance of such compositional variations, particularly the exchange of hydrogen for calcium, on the solubility of apatite.

Basically then two factors will influence dissolution of the enamel:-

1. Its actual solubility, which determines the driving force for dissolution; and
2. Conditions which control diffusion of hydrogen ions to the enamel, of reaction products away from the enamel and those conditions which thus determine the rate of the process (Brudevold and McGann, 1968).

Many agents are reported to have a reducing effect upon enamel solubility, particularly on surface enamel. Such

agents are, among others, NaF , SnF_2 , SnF_4 , SnCl_2 , ZrF_4 , $\text{Pb}(\text{NO}_3)_2$, PbF_2 , and FeF_4 . Again, the exact mechanism by which such agents reduce enamel solubility is not clear but Brudevold and McGann (1968) offer three possible mechanisms:-

1. By incorporation into the apatite lattice of ionic species and formation of a more stable lattice structure, deposition of F as fluorapatite is the only known example of this mechanism.
2. By deposition of inorganic precipitates, involving a decomposition of the enamel apatite and formation of relatively insoluble calcium or phosphate compounds.
3. By formation of organic films or monolayers on the enamel surface, leaving the apatite crystals intact. Precipitates and films probably retard dissolution by forming diffusion barriers at the surface of the enamel. They conclude this point by commenting that no decrease in enamel solubility obtained by such deposits has been demonstrated.

The conclusions reached by these authors, as a result of their experiments, tend to support those of Spiers (1971) mentioned above.

Their views, however, are not entirely shared by Gray and Francis (1963) who argue that the composition of surface enamel should not alter the initial rate of dissolution but could alter the solubility rate as equilibrium is attained.

3. SURFACE INTEGUMENTS

Spiers (1971) asks: "Are any of the surface integuments, which collectively may only be a few microns in thickness, an integral part of surface enamel, and if so, to what extent are they responsible for some of the characteristic properties of the outer enamel?".

Meckel (1965) describes the existence and nature of the following organic films on teeth:-

- (i) Primary enamel cuticle (Nasmyth's membrane);
- (ii) Subsurface cuticle;
- (iii) Surface cuticle;
- (iv) Stained pellicle;
- (v) Plaque

It is generally agreed that Nasmyth's membrane is lost during or soon after eruption. The remaining organic films form subsequent to this occurrence in a roughly layered arrangement, i.e. they are acquired and very likely of salivary origin. Meckel's findings have subsequently been verified by Armstrong and Hayward (1968). They showed the subsurface cuticle to be continuous with the acquired cuticle and pellicle and postulate that it could be merely extensions of them into porous surface defects. Hoffman et al (1969) suggest that the "surface skin" of enamel may actually be an integral part of the matrix which remains unmineralised at the completion of amelogenesis. Spiers (1971) suggests it is

difficult to differentiate between contributions made by inorganic and organic components of surface enamel towards the observed increase in acid resistance of the surface.

Meckel (1965) mentions the insolubility of these films and adds that such films can act as diffusion barriers against acids and by such action claims a significant reducing effect on the solubility rate of enamel. Gwinnett and Matsui (1967) support such claims by stating, "the acquisition of a thick organic cuticle and continued maturation involving changes in the surface chemistry of the tooth with age, probably protect the surface from dissolution".

Dawes (1968) concluded from his experiments on naturally and artificially abraded surfaces that resistance to acid-etching is more attributable to outer enamel proper than to the pellicle covering.

Nonetheless, in the use of adhesive materials, it is generally held that it is desirable to remove the firmly adhering organic cuticle by pumicing of the tooth surface, before etching so that the acid will have the maximum effect in a given time. (Buonocore et al 1968, Newman 1969, Newman and Facq 1971, Retief et al 1970, Takeuchi et al 1966, Miura 1971b, Profitt 1972). These authors claim reduced bond strenghts due to reduced etching of enamel surface if the organic films are not removed and hence such reduction supports Meckel's (1965) claim of the films affording some degree of protection to the enamel from acid attack.

PHYSICAL AND CHEMICAL PROPERTIES RELATIVE TO ADHESION

Both the inorganic and organic components of enamel may play a role in the adhesive processes. Retief (1970) states that although enamel is essentially inorganic, the relatively small organic component may be important in securing adhesion. Buonocore et al (1968) studied dye and radio-isotope penetration at the enamel-adhesive interface. In finding a lack of penetration they concluded that such a failure of penetration could be indicative of a chemical union between the adhesive and the enamel surface forming a relatively impermeable interface which would also contribute to the enhanced bonding. They did not state which phase of the enamel was involved but suspected that the chemical bond, as distinct from the mechanical interlocking ^{a/ much} may be attributed to the organic phase of the enamel surface. However, Buonocore (1970) clarifies the relativity of importance by stating that the organic matter of enamel is limited in amount and so bonding to enamel will probably occur through its inorganic phase.

The complexity of the problem is made clear by the following statement by Retief (1970) "it is difficult to describe the mechanism of adhesion to the heterogenous surfaces of enamel and dentine".

Posner (1961) stated that hydrogen bonding can contribute to the ^{b/} adhesion between enamel apatite surfaces and filling materials. Schwartz and Galligan (1965) showed by means of infra-red measurements that liquids which wet hydroxyapatite might also form hydrogen bonds with the mineral.

Glantz (1969) proved that, in addition to Van der Waal's dispersion

forces, polar forces and hydrogen bonds play a part in the bonding to enamel surfaces. It is generally accepted, however, that although the polar Keesom forces and hydrogen bonding will enhance adhesion, and that covalent bonding between the adhesive and the enamel surface will markedly increase it provided the adhesive wets the surface enamel completely, the physical Van der Waal's dispersion forces (London forces) will be strong enough to provide adequate adhesion..

Glantz (1969) studied the wettability of enamel and dentine. He determined the contact angles of six liquids on ground but otherwise untreated surfaces and on a synthetic hydroxyapatite surface. He found that the means of the critical surface tension, γ_c , of enamel to be 46.1 dynes/cm whereas the synthetic hydroxyapatite surface had a high energy surface (72.6 dynes/cm). However, to remain uncontaminated these crystals had to be stored in a vacuum. His results suggest that the enamel surfaces are covered with a low energy organic film. He explained the mechanism of the formation of the low energy surfaces of enamel by presuming that at least some part of the organic phase is mobile and exists in the form of a gel (i.e., thixotropic). If the high energy hydroxyapatite crystals are exposed during treatment of the surfaces, the gel part of the low energy organic phase will cover the high energy phase as a result of an energetic difference.

Zisman (1966) found that a high energy surface such as a clean tooth surface is a powerful absorber of contaminants. Hence it will be extremely difficult to keep a tooth surface, so prepared, free from contamination.

According to Buonocore (1970b), enamel undergoes a variety of ionic ✓ substitutions, confined largely to the outermost layers, as a result of exposure to a variety of chemical agents derived from food and drink (Brudevold et al 1960). It has already been mentioned that ✓ there is a free flow of water through enamel and that it acts as an important diffusion mediator of molecules and ions through the enamel. ✓

As a result Zisman (1961) stated that enamel possesses a fully reacted, low energy surface not ideally suited for bonding. ✓

It has been noted previously that water accounts for 4.0% by weight of the enamel and will reduce the surface energy of a solid. Zisman (1966) points out that hydrophilic solid surfaces (e.g. clean tooth surfaces) are always found coated with a film of absorbed water.

As previously mentioned, tooth surfaces can only be dried out by pro- ✓ longed heating at high temperatures in vacuo and that the absorption energy of one monolayer of water on the hydroxyapatite surface is extremely high (18-21 kilo calories/mole). Consequently, a tooth sur- ✓ face in vivo cannot be dried out and hence the presence of at least a monolayer of water on the hydroxyapatite surface must be accepted (Retief 1970). This is supported by Zisman (1966a) who stated "hydro- philic solid surfaces are always found coated with a film of absorbed water". He added that unless this water is removed prior to applying the adhesive, or unless there is some chemical within the adhesive the film of water, it will seriously interfere with bonding. ✓

Retief (1970) concurs with Zisman and adds that as the water actually

functions as a liquid adhesive, a dental adhesive must compete with it and must do so over long periods because of the exchange processes that take place in the tooth.

WATER REMOVAL

According to Zisman (1966a) the residual, firmly bound water present on the clean enamel surface cannot be removed (as mentioned above) and consequently further research is required into its influence on liquid "spreadability" and "wettability" and adhesion.

There are two methods available for effective removal of the loosely bound water layer from the enamel surface:-

(i) Compressed Air

This method has been recognised for some time. However it is not entirely satisfactory due to the subjective judgement of whether a surface is "dry". Zisman (1966a) has noted in some situations that the water displaced physically by the compressed air can seep back within a short period of time. This replacement could come from within the tooth itself or from the oral environment by direct wetting or condensation. Newman (1969) said investigations were being carried out into the effect(s) the capillary movements of the internal enamel fluid has on an adhesive joint.

Compressed air is the most commonly used technique of

drying tooth surfaces. Most advocates of direct bonding systems (Buonocore et al 1966, Newman 1969, Miura 1971) use compressed air for drying tooth surfaces but only use cotton roll isolation for its maintenance. Dijkman and Retief (1972) employ rubber dam procedures to enhance and maintain simple, clinically possible levels of dryness.

(ii) Water Displacement Chemicals

If a drop of such agent is placed on a film of water (such as on the surface of clean enamel) then a lowering of the surface tension of the water film occurs in that area.

✓ Because this agent is more attracted than water to the surface of the enamel, there is a stronger tendency for it to spread out onto the enamel surface. Zisman (1966b) investigated the displacement of water from a tooth surface by surface chemical methods. He says "if an appropriate amount of high boiling polar-non-polar compound absorbs from solution to remain on the bare solid surface after the water has been displaced, the residual hydrophobic monomolecular film will keep the water permanently displaced".

"Obviously, for subsequent adhesion, this film must not be of the low energy type which would interfere with the adhesive bond". Manning 1971.

In his experiments (Zisman 1966b) found butanol effectively displaced the loosely bound water fraction due to formation of hydrogen bonds between the hydroxyl groups of the butanol

molecules and the adjacent water molecules. This inter-molecular bonding leads to a cloud of water molecules accompanying each butanol molecule as it advances over the moist tooth surface. Unfortunately, the butanol will evaporate and the water will return.

It seems a hydrophilic adhesive capable of displacing water would be ideal. In such a situation, according to Buonocore (1970a) and Smith (1968) the forces of attraction between the enamel and the adhesive must be greater than either phase for water, and if chemical bonding takes place, it must be resistant to hydrolysis.

Further to the above, it should be remembered that the presence of water in the oral environment can be the precursor of chemical activity at the adhesive/adherend interface which will eventually dislodge the bond. In addition many adhesive materials will absorb water, leading to swelling and dimensional changes in their bulk. This will tend to result in stress concentrations at the interface which will have an adverse effect on the bond strength (Retief 1970).

IONIC EFFECTS

A review of ionic constituents of the outer enamel surface has been made, largely from more extensive reviews by Spiers (1959 and 1971). Newman (1969), Glantz (1969), and Brudevold and Soremark (1967) state

that the outer enamel surface undergoes a variety of ionic substitutions ✓ as a result of exposure to a variety of chemical agents derived from food and drink. It has also been mentioned that significant quantities ✓ of water pass through intact mature enamel and that the loosely bound fraction of the water in enamel serves the important function of mediating diffusion of molecules and ions through the enamel.

Brudevold and Soremark (1967) believe that the electrical asymmetry of the hydroxyapatite crystal sets up a powerful electrical field which ✓ pulls charged ions and water molecules towards it. Deakins (1942) has shown that the process of mineralisation in the enamel involves the displacement of water by minerals. According to this concept, the nearly complete displacement of loosely bound water from the outer enamel surface is the result of its particularly high content of mineral.

Analysis of layered samples of enamel by Brudevold and Soremark (1967) and others (see earlier section) shows concentrations of F, Pb, Zn, Sn, Fe, Cl, Al, Si, Sr, Mg, Mn, Si, Ni, Ti and Cu in the enamel surface. Other minerals exist and all are of varying importance to its structure and integrity and their concentrations vary within individual teeth, between teeth of the same mouth, and according to the nature of the intra-oral and extra-oral environment of the individuals. The levels of F are of particular importance.

Zisman (1961) believes the presence of metallic ions has almost left the outer enamel surface relatively inert and almost fully reacted. ✓ Investigations into the relative effects of these ions on the surface energy and resistance to acid attack are most complex.

However, the internal ingestion and the topical applications of fluoride are recommended preventive procedures in the field of dental health. As absorption of F ions into the outer enamel surface affects the properties of surface energy and its resistance to acid attack, it, above all other ions found in the outer enamel surface, is worthy of further consideration.

Glantz (1969) found that aqueous solutions of certain metal fluorides have an obvious free surface energy-decreasing effect on enamel surfaces. Stannous fluoride (SnF_2) solutions reduced the polar forces, hydrogen bonds and Van der Waal's dispersion forces of untreated enamel. Other aqueous metal fluoride solutions to have similar effects were those of silver, cobalt and, to some extent, nickel. Brudevold and McGann (1968) reported similar effects with NaF , SnF_4 , ZrF_4 , PbF_2 and FeF_4 .

Mulholland and de Shazer (1968) believed the presence of fluoride in hydrofluoric acid to be beneficial in adhesive bonding because of the increased wettability of tooth surface when compared with hydrochloric acid pretreatment. According to Glantz (1969), however, the reason for a tooth's surface becoming hydrophilic immediately following application of 10% hydrofluoric acid was because it was such a powerful solvent for practically all known non-polymeric organic substances.

Gwinnett et al (1972) showed by experimentation that to obtain maximum adhesion (bonding strength) in the clinical application of adhesives to enamel, the adhesives should be applied to the acid-conditioned enamel surface directly and not following a topical fluoride treatment.

Their experiments showed a decreased penetration of resin into surfaces which had received topical fluoride. They observed a decreased number and length of "tags" of adhesive which accompanied decreased bond strength. They concluded that the decrease in bond strength could be due to either:-

1. Reaction products being left on the surface, or ✓
2. Surface chemical changes at the molecular level. ✓

Both could have significantly altered the wetting characteristics of the surface. They do recommend topical fluoride application, after bonding procedures are completed, to enhance protection of the enamel surfaces not covered (protected) by the adhesives.

In clinical use of adhesives opinion differs as to the influence of fluoride on bond strength and integrity of the bond. Craig (1972) in using pit and fissure sealants at the University of Sydney, Department of Preventive Dentistry, found that insufficient etching occurred (i.e. failure to provide a good bonding surface) when the acid was exposed to teeth that experience the uptake of fluoride either by ingested and/or topical techniques. He found it necessary to increase etching time from the recommended 60 secs. to 2½ minutes. ✓

Similarly, most authors (Buonocore 1970b, Retief et al 1970, Miura 1971 and Profitt 1972) recommended increased acid exposure time to provide adequate etching of the enamel surface, when the teeth have a history of fluoride uptake. They also recommended the use of a non-fluoridated

pumice paste to clean the enamel surface prior to etching.

Newman (1968 and 1969), however, recommends the use of a fluoridated prophylaxis paste for initial cleansing of the enamel surface. He does advocate increased exposure times for fluoridated teeth and even adds 1% sodium monofluorophosphate to the etching acid solution. This is done for caries reducing effects and not for reasons of surface energy increase, etc., but the need for doing so has not been scientifically proven as yet.

MEANS OF INCREASING SURFACE ENERGY OF ENAMEL

It has been shown by Buonocore (1955) that the fully reacted, relatively-inert, outer enamel surface (as later described by Zisman 1961) must be mechanically or chemically removed and/or altered in order to increase the resistance of the bonding of water to enamel and to increase the bond strength of adhesive to the enamel. It has been mentioned that this can be achieved, to a limited degree by removal of organic films and drying the tooth surface. There are two commonly used techniques:-

1. MECHANICAL REMOVAL

Uy and Chang (1966) showed an increase in surface energy by mechanically polishing the enamel surface of a tooth. However, the immediate problem is one of "how much", i.e. what depth of the enamel should be removed. This is still not known because, as Helmecke (1967) stated, "more information about the ultra-structure of the outermost layer is required". Apart from

structural considerations, other problems encountered include:-

- (a) The concentration of ions found in the outer layer. Such concentrations will vary from time to time depending on the tooth's environment and its age.
- (b) The effects of particular ions found in the outer layer on the surface energy of the enamel.
- (c) The nature of the inherent and/or acquired organic films covering the enamel surface.
- (d) The mineral concentration of the surface enamel.
- (e) The water content and its physiological role in surface enamel.
- (f) The ability of the enamel surface to "recover" from such treatment.

Uy and Chang (1966) also showed that following the initial increase in surface energy after cleaning, there was a subsequent decrease in it and that this decrease was related to the time stored in the atmosphere. They and Zisman (1966b) believed the reduction in surface energy was due to absorption of organic films and/or water, originating from the atmosphere, the tooth

itself or both. They both stressed the importance of applying the adhesive as soon as possible after polishing.

2. ACID ETCHING OF THE ENAMEL SURFACE

Phosphoric acid has been used by some investigators to etch, or remove, the outermost layer of enamel (Buonocore 1955 and 1970b, Miura et al 1971, Newman 1969, Profitt 1972, Retief et al 1970). Ohswa (1972) extensively studied the effects of fifteen soluble acids each at seven different molar concentrations, on the solubility of enamel as measured by the release of Ca^{++} ions from treated crushed enamel pellets and on the relation of such solubility to adhesion, and also observed their effects upon the surface microscopically.

According to these authors the increased surface energy of the enamel surface (hence the increased bond strength) could be due to one, or a combination of the following:-

- (a) Removal of the outermost layer to expose a more reactive surface.
- (b) Increased surface roughness, which promotes wetting of the adhesive.
- (c) Increased surface energy, due to the deposition of highly reactive polar groups (phosphoric groups in the case of phosphoric acid) on the "new" surface of the tooth.

- (d) An increase in surface area due to the acid etching.
- (e) An exposing of the organic material of enamel which may serve as a network in, about, and to, which the resins can penetrate.
- (f) Creation of spaces in depth along interprismatic and within intraprismatic areas into which the resins can penetrate.

Mention of initial surface cleansing by abrasive agents before acid etching has already been made earlier in this review. Such cleansing will remove the firmly adhering organic cuticle(s).

Newman and Sharpe (1966) found that the contact angles for water on these surfaces were in excess of 50° . Uy and Chang (1966) found a decrease in surface energy of enamel after polishing. The decrease, followed an initial increase was found to be due to atmospheric contamination of the enamel surface and that the decrease was closely correlated to the time of atmospheric storage after pumicing.

Newman and Sharpe (1966) applied phosphoric acid of 85% to the pumiced surface of the enamel and found the new value for the contact angle to be zero. These authors also noted that the original hydrophobic condition of the enamel surface could be restored again by pumicing. Consequently, it would appear that a

low energy film was introduced to the enamel surface, either via the polishing medium, or from the tooth itself.

Newman (1969) noted that without polishing, after acid treatment in vivo, the enamel surface, with time, returned to its original condition. He concluded this effect was the result of acquiring a smooth, tightly adhering pellicle of salivary origin.

Lenz and Muhlemann (1963) found that the rapid disappearance of the prism end-structure of the etched enamel surfaces when exposed to a salivary environment, was not due to repair by a process of enamel remineralisation. They found that the smooth surface of the previously etched enamel was brought about by the deposition of a salivary pellicle. Abrasion could also have helped such a surface transformation. Monus and Grenoble (1971) found that when a surface etched with 50% phosphoric acid for one minute is left to stand in vivo, it will return to normal in 96 hours. They believe this remineralisation process to be due to the deposition of calcium phosphate of salivary origin and also claimed that enamel had a 'natural repair mechanism'.

Nonetheless, it is usually recommended that surfaces so treated be pumiced after adhesive removal, so that a "smooth" surface similar to the original surface is present.

Ever since Buonocore (1955) detailed the effects and benefits of acid etching of enamel surfaces as a means of enhancing adhesion, using 85% phosphoric acid, this acid has generally been the one

of choice by most research works and clinicians. Its use has not always been recommended at that strength or with the same time of exposure. In fact, Buonocore now recommends 50% phosphoric acid with 7% zinc oxide as an attenuating agent (Buonocore et al 1968) as exposure of this solution results in adequate etching. Newman and Facq (1971) also added 1% sodium monofluorophosphate to the above solution to "inhibit decalcification and caries".

Miura et al (1971) recommended the use of 65% phosphoric acid solution for 30 seconds. In their study they found that one week of normal tooth brushing restored the enamel surface and concluded that the damage caused by such etching was negligible.

Retief et al (1970) use 50% phosphoric acid solution for one minute to etch the enamel. These workers found that after such treatment the enamel was restored to the original surface after one week in vivo. They felt that such changes could be due to remineralisation.

Profitt (1972) recommended the use of "any suitable phosphate cement liquid" for a period of time "from one minute but not more than four" depending upon the fluoride exposure history of the patient.

Ohsawa (1972) recently reported his studies on adhesion to the enamel in pre-treatment for a pit and fissure sealant. The adhesive consisted of Ethyl-2-cyanoacrylate and Polymethylmethacrylate. He used fourteen acids and ethylene diamine tetra-acetic acid (EDTA), a chelating agent at different molar concentrations at constant

exposure times (30 seconds) and measured the adhesion of the adhesive to the treated compressed enamel tablets. He found:-

- (i) Calcium dissolution increased to a maximum as molar concentration of the acid increased but then decreased despite increased molarity of the acid (Maleic Acid & EDTA did not).
- (ii) Similar effects with adhesion in relation to acid strengths.
- (iii) Different acids could have the same adhesion and different solubility effects, and the opposite could also occur. He suggests that there might be some treating agent which will give good adhesion with only a slight amount of enamel dissolution. He found 2.0 Mol pyruvic acid to give the most satisfactory adhesion commensurate with a reasonable calcium dissolution.

See Tables 2 and 3 for all his results. It is particularly interesting to note the high calcium dissolution figures for the various concentrations of phosphoric acid (it should be noted that phosphoric acid did give good adhesion results). It can only be presumed that similar results would be obtained with other adhesives.

ACIDS	ACID CONCENTRATION (molar)						
	0.1	1.0	2.0	3.0	4.0	5.0	6.0
Acetic	95	160	190	135	95	65	60
Acrylic	135	175	180	190	140	140	75
Malonic	290	460	610	560	550	520	300
Glycolic	315	365	390	405	390	385	355
Lactic	195	275	315	365	300	295	205
Pyruvic	155	420	440	355	260	155	135
Levulinic	65	100	135	105	65	65	30
Phosphoric	420	570	690	900	840	810	480
	0.1	0.5	1.0	1.5	2.0	2.5	3.0
	245	665	690	690	700	700	700
	175	190	205	225	345	195	190
	165	295	310	320	320	315	260
	105	255	330	345	285	215	140
Formic	0.5	1.0	2.0	4.0	6.0	8.0	10.0
	320	415	530	555	505	415	400
Hydrochloric	0.05	0.1	0.5	1.0	1.5	2.0	2.5
	630	680	1,380	1,400	1,380	1,230	1,150
E.D.T.A.	0.01	0.05	0.1	0.15	0.2	0.25	0.3
	55	90	100	105	110	110	245

Table 2. CALCIUM DISSOLUTION FROM ENAMEL TABLETS (ppm)
from: Ohsawa, 1972

ACIDS	ACID CONCENTRATION (molar)						
	0.1	1.0	2.0	3.0	4.0	5.0	6.0
Acetic	20.5	23.5	31.0	29.5	24.0	23.5	19.0
Acrylic	23.0	31.5	33.0	45.5	36.5	32.5	22.5
Malonic	39.0	59.5	61.0	60.0	50.0	47.5	40.5
Glycolic	28.5	35.5	50.5	67.0	48.0	43.5	32.5
Lactic	34.5	57.5	66.5	72.0	61.0	53.5	44.5
Pyruvic	47.5	89.0	109.5	108.0	91.0	71.5	58.5
Levulinic	12.5	20.5	28.0	24.0	20.0	16.5	14.5
Phosphoric	39.5	60.0	75.0	90.0	81.5	78.5	69.5
Maleic Tartaric Malic Citric	0.1	0.5	1.0	1.5	2.0	2.5	3.0
	38.0	59.0	62.0	64.5	72.0	61.0	52.5
	25.0	33.5	38.0	39.0	46.0	41.5	36.5
	37.5	40.5	56.0	59.0	60.0	53.0	44.5
	37.0	60.0	69.5	76.0	71.5	56.5	55.5
Formic	0.5	1.0	2.0	4.0	6.0	8.0	10.0
	52.5	59.5	71.5	76.5	61.5	52.5	47.5
Hydrochloric	0.05	0.1	0.5	1.0	1.5	2.0	2.5
	39.0	45.0	46.0	49.5	49.5	48.0	47.0
E.D.T.A.	0.01	0.05	0.1	0.15	0.2	0.25	0.3
	11.0	13.5	15.5	16.0	18.0	18.0	22.0

N.B. Adhesion of non-treated enamel = 8.0kg/cm^2

Table 3. ADHESION OF ENAMEL PRETREATED BY ACID SOLUTIONS (kg/cm^2)
From: Ohsawa, 1972

OTHER METHODS OF INCREASING SURFACE ENERGY

The two most commonly used techniques:-

- (a) mechanical removal, and
- (b) acid etching/ have been discussed

Other methods of less common use are:-

1. SURFACE ACTIVE COMONOMERS

The previous methods discussed involved removal of surface structure. These agents are actually added to it and by bonding to the existing surface provide a new surface to the adherend for bonding with the adhesive which is more suited for such bonding. (Buonocore 1970). To be more effective, the bonds between the two surfaces must be more resistant to destruction than the adhesive alone.

Compounds that might be useful in altering the surface should preferably have on one end of the molecule one or more polar groups that are capable of forming a strong bond to tooth structure and at the other end one or more non-polar groups capable of copolymerizing with the adhesive or material to be used in restoration (Buonocore 1970).

An example of a comonomer synthesised by Bowen (1965) is a compound which is an adduct of N-phenyl glycine and glycidylemethacrylate.

The N-phenyl glycine portion may be considered to form a chelate ring with calcium, and the methacrylate residue in turn would copolymerize with self-curing resins. The comonomer reacts with the inorganic phase of the enamel and is possibly no thicker than a monolayer. Testing showed greater bond strengths when used as compared to surfaces without it on both acid-etched and smooth-polished enamel surfaces.

In oral conditions, the reactive group of the surface active comonomer should be capable of successfully competing with water for bonding sites on the enamel surface. The greater this capability the longer the bond will survive, (Buonocore 1970).

Other intermediaries used are the silane derivatives which are thought to be capable of bonding to tooth structure chemically and to the resin. (Miura et al 1971 and Lee and Swartz 1970).

2. CAVITY LINING MATERIALS

These materials are deposited from solutions of volatile solvents in the form of thin, visible films over the tooth surface. They are predominantly natural or synthetic resins (Swartz and Philips 1960). No such commercial film-forming materials, however, will remain bonded to enamel or dentine in the presence of water, for any appreciable period of time (Buonocore et al 1962); nor will they prevent leakage. Profitt (1972) advocates the use of such a material (cavity varnish) on the enamel surface before placement of the adhesive.

Recently (Galligan et al, 1968) investigated certain polymers or prepolymers such as the polyisocyanates as lining materials. The isocyanate group is capable of reacting quickly with hydroxyl, amino and carboxyl groups to form relatively stable urethane linkages. The presence of protein in enamel provides a substrate for reaction with isocyanates to form a chemically bound polymeric surface over hard tissues.

Because of their physical and chemical properties, the isocyanate prepolymers would best be employed as comparatively thick coatings perhaps up to 100 microns to which resin adhesives may be bonded. Buonocore (1970a) points out that the great disadvantage of these materials is their high reactivity with water.

ENAMEL SURFACE MICROANATOMY AND ADHESION

PART I "NORMAL" ENAMEL

Until the early part of the 1950's knowledge of the historical structure of enamel and the various theories regarding its disintegration in caries, had been derived almost entirely from the study of ground and decalcified sections cut perpendicular to the enamel surface. Such studies have been made with the use of optical microscopes. Consequently, even less was known about the micro-structure and properties of the outer enamel surface, largely due to the lack of adequate techniques for surface studies. Sectioning methods are difficult to employ because of the curvature of the tooth surfaces and the inability to observe details accurately on the surfaces of ground sections by transmitted light.

Some observations have been made with reflection type microscopes but the method is of limited value, again mainly due to the contoured nature of surface enamel. Chase (1926) and Eisenberg (1938) were prominent among early researchers into surface structure using optical microscopical techniques.

Gerould (1944) was among the early developers of replica techniques which enabled indirect examination of enamel surfaces by optical microscopy (using both transmitted and reflected light) and, as Gerould found, also by electron microscopy.

The electron microscope has been used extensively in studies of enamel

surface structure following the early work of Gerould and also two early extensive studies by Scott and Wychoff (1949) and Scott et al (1949). Some years later the scanning electron microscope was developed and found most suitable for direct examination of enamel surfaces largely due to its optical microscope-type characteristics, and its tremendous depth of field, thus removing the early problems of enamel surface curvatures at high resolutions in the optical microscope. Some of these studies will be discussed later.

The characteristic appearance of the surface topography of enamel in deciduous and young permanent teeth has been described as a series of concentric, alternating ridges and grooves that encircle the coronal aspects of the teeth. These are referred to as the imbrication lines of Pickerill and the perikymata, respectively. The grooved perikymata represent the site of the surface enamel immediately overlaying the striae of Retzius. The imbrication lines are narrow convex bands that represent the surface terminal extensions of these striae (Provenza 1964).

It was Pickerill who first showed the correspondence of perikymata to the striae of Retzius after precise photomicrography of a ground section in the region of its outer surface. As mentioned above, it is his name that is used in conjunction with the convexities between perikymata.

Hinrichsen and Engel (1966) state that the morphology of the striae of Retzius may change with formative factors of various types and severity. They found that the striae of Retzius are caused by

alteration in the rod width resulting from displacement of the rod during formation. No altered mineralisation was found in the striae of Retzius but due to extension into the displaced region, the crystals of the striae exist at an angle to the remaining crystals of the rod.

Scott et al (1949) demonstrated, by means of optical and electron microscopy of metal - shadowed collodion replicas, the minute structure of perikymata. They found in recently-erupted teeth pronounced, alternating concavities and convexities, perikymata and imbrication lines of Pickerill respectively. The concavities were further characterised by clearly visible rod ends and the convexities by their smoothness. They demonstrated that with age there was more rapid wear on buccal and lingual surfaces than on proximal surfaces and that wear was more pronounced on anterior than on posterior teeth. Such wear was indicated by a gradual loss of structural detail until the surface was flat and uncharacterised. They also found that where pronounced patterns did remain on older teeth, a cuticle was present. This occurrence was predominantly on the proximal surfaces of posterior teeth emphasising the lack of functional abrasion to these surfaces.

They suggested that perikymata have a long, gently sloping wall and a short steep wall, the latter being nearer to the cemento-enamel junction. The walls of the perikymata form a 'V' shaped trough on the middle third of the surface but the sharp angulation decreases as they approach the occlusal or incisal edge. Pickerill (1913) suggested that the perikymata represented an overlapping of enamel 'sheets', but Scott et al were unable to support this hypothesis.

The previously mentioned pattern of concavities which were thought to be ends of enamel rods were noted to be approximately six microns in diameter and to exist in greater numbers on more recently erupted teeth than older teeth. They also noted numerous "crack-like" structures on the enamel surfaces and postulated that they may be surface manifestations of lamellae but were unable to prove this on their replica studies. However, Scott and Whychoff (1949) were able to show that the inference was correct.

Gustafson and Gustafson (1967) agree that lamellae are surface manifestations of an enamel tuft or tufts. Normally enamel tufts do not reach the surface; only abnormally long ones do so. In addition, however, cracks may occur during the formation, or after the eruption of teeth. These may be filled secondarily either by ingrowing epithelium or by salivary deposits, and hence can become continuous with the substance of the enamel cuticle.

As well as finding perikymata, rod ends and cracks, they noted the presence of "patches of material seen superimposed upon all other detail". They stated "these patches appear to be either the remains of an additional layer which once has covered the surface, or some stratification of the surface itself.

Hoffman (1972) using a scanning electron microscope studied surface topography of extracted, sound third molar teeth. He found two distinct topographies at specific sites, one blending into the other. The first was characterised by a continuous smoothly flowing, undulating pattern of perikymata - imbrication lines.

The second, he described as "a discontinuous, overlapping pattern in which the convex portions resembled parallel concentric ridges or bands with sharply delineated terminal borders".

Examination of erupted teeth showed both patterns to be present over the entire surface with the overlapped junctions being confined to the cervical third of the crown and the undulating patterns in the occlusal two thirds.

Boyde 1971, in observing the enamel surfaces of enucleated teeth with the aid of the scanning electron microscope, found zones containing enamel rod-end pits in the troughs of the perikymata. These zones alternated with others in which pits were absent or poorly marked, and in which true surface zone enamel had developed at the crests of the perikymata (imbrication lines).

He observed prism sheath 'cracks' in these pits and felt they were indicative of the loss of the difference in rates of growth of the floors and walls of the pits that characterise the development of the bulk of enamel. Developmentally, the pits are caused and occupied by Tomes' processes of the ameloblasts.

Normally enamel formation slows down gradually so that the ameloblasts lose their Tome's processes before they finally cease secreting.

Boyde says that this causes a flat formative front and the enamel crystallites are all orientated perpendicular to the surface, thus determining the development of a layer of true, surface-zone, prismless enamel. He presumes that, whatever the causative factors are in the

development of the striae of Retzius, they also cause the early cessation of activity on the part of the particular ameloblasts which should then be ceasing to secrete. Consequently the enamel surface still contains the pits in the regions in which the total thickness of enamel is slightly deficient viz, the perikymata troughs. He considers that various types of pitted and defective surfaces constitute micro-stagnation areas and that these coincide with certain regions of the surface where caries incidence is greatest.

The spread of carious process seems to be facilitated via the striae of Retzius which reach the enamel surface at the troughs of the perikymata in which the pits previously described exist. The perikymata are considered to be the termination of the lines of Retzius at the surface of the enamel. The width between the striae of Retzius diminishes as the line approaches the enamel surface due to a reduction in height of the prism segments present between the striae of Retzius. Consequently, very often, at the surface the individual segments lose their identity forming a non-prismatic or prismless layer, Johnson (1967).

Ripa et al (1966) made a study of the outer layer of enamel on longitudinal, undecalcified sections, prepared from twenty eight erupted and forty impacted permanent teeth. The sections were examined by means of polarised light and phase contract microscopy and micro-radiography.

A layer of apparently prismless enamel was found on all the deciduous teeth. This layer averaged about 30 microns in thickness and often

showed parallel laminations with the crystallites orientated with their c-axis almost perpendicular to the enamel surface.

In permanent teeth, the two types of prismless layers observed were:-

1. The surface parallel lamination, and
2. The "onion"-type layer.

The formation of a prismless layer has been traced back to amelogenesis and has been explained as the result of reduced functional activity during the terminal stages of it. This, together with the loss of the staggered or step-like arrangements of adjacent ameloblasts, would result in a linear secretory activity of these cells which give a laminated appearance of the outer enamel. They believe that the surface laminations represent narrowly spaced incremental lines similar to either the cross-striations, or the striae of Retzius. The fact that the prismless layer is also found in unerupted teeth shows that this layer is not acquired post-eruptively.

The onion-type layer appearance of some prismless enamel is due to the presence of striae of Retzius which emerge on the enamel surface. This type was not seen in the deciduous teeth because the striae in these teeth do not generally converge on the surface but run parallel to it.

It was also found that the prismless layer was not present over the entire surface, particularly on the buccal and lingual aspects, and

this could be due to abrasive and/or masticatory forces exerted on these surfaces.

In another study of the ultrastructure of the prismless enamel of permanent human premolar teeth by different techniques, Gwinnett showed that the crystallites in this prismless enamel surface were arranged parallel to each other with the c-axis perpendicular to the enamel surface (Gwinnett 1967). He also noted that they are probably more closely packed and uniformly arranged than in the subsurface enamel, where, within a prism, a considerable but ordered variation exists in the orientation of the crystallites relative to prism axis.

Gustafson and Gustafson (1967) examined surface layers of enamel and noted that the width between Retzius lines diminishes as the lines approach the enamel surface due to a reduction in height of the prism segments present between the Retzius lines. They observed that at the surface, frequently, the individual segments lose their identity and so form a "non-prismatic zone".

Other variations detected by these authors include:-

1. Sometimes, the cross-striations may be accentuated and so the distinction between individual prisms can become evident.
2. Sometimes also, the final prism segments can deviate at an angle which results in a smoother enamel surface.

3. Surfaces were also observed that appeared flat and without perikymata, and not due to wear. Such surfaces did not seem to be associated with anything unusual in the internal structure of the enamel.

These authors also noted the occurrence of some defects of mineralisation in which two Retzius lines meet, so producing an unusually marked depression on the surface of enamel. More severe and complex disturbances and variations in the structure of surface layer(s) of enamel occurred, and they were found to exist in both mature and developing enamel.

Another important finding made by the Gustafsons was that in some sections the surface may present a homogeneous surface layer which was highly negatively birefringent and hard to distinguish from the enamel cuticle.

These findings of Gustafson and Gustafson substantiate those of Gwinnett (1967) Ripa et al (1966) and Miyoshi et al (1972) on the occurrence of a distinct "prismless" zone in the outermost part of enamel.

Within the prismless layer, crystallites are orientated approximately perpendicular to the surface, (Gwinnett (1967) and Ripa et al (1966), and Miyoshi et al (1972) and, as mentioned previously, such findings were supported by Frank and Brendel (1966).

The crystallites are probably more closely packed and uniformly arranged

than in the subsurface enamel, where, within a prism, a considerable but ordered variation exists in the orientation of the crystallites relative to the prism axis.

Sharpe (1967) in studying the effects of acid on enamel crystals as influenced by the crystal orientation reported differential rates of acid dissolution within crystals. He found the crystallite was attacked primarily along the c-axis when this was standing perpendicular to the surface. He concluded that the different appearances of etched surfaces (one-surface cut parallel to prism direction and one surface cut perpendicular to prism direction), when exposed to acids, was due to the above-postulated direction of attack and the crystallite orientation in the respective surfaces. So it might seem that prismless zones would be preferentially attacked by acids.

Poole and Johnson (1967) and Poole (1971), in similar experiments using scanning electron microscopy, found differing results to those of Sharpe. They admit "our own results are at first sight, entirely in agreement with the foregoing" (Sharpe 1967) and agree that "the mean direction of the crystallites does have a role in determining relative rates of dissolution". Some evidence indicates that the differential dissolution of enamel is not simply a function of crystalline orientation, e.g. loss of prism cores irrespective of the orientation of crystallites relative to the direction of attack.

Two differences in the experiments by Sharpe, and by Poole and Johnson, however, could explain some of the interpretations:-

1. The explanations of surface orientations given by both authors are not sufficiently clear for one to be able to ascertain as to whether they are the same or not.
2. Sharpe used the model of prism structure as postulated by Meckel et al (1965), and Poole and Brookes (1961). These authors postulate a less variable and stylised packing of the prism and arrangements of the crystallites within the prism than the model used by Poole and Johnson, viz; that of Johnson (1967a).

Poole and Johnson felt that as a result of these variations, it was not easy to explain, on the basis of crystallite orientation, the finding that relatively large areas showed a uniform etching pattern. From this sort of contradictory evidence they concluded "that crystallite orientation relative to direction of attack is not the only factor involved in the differential dissolution of enamel.

Other facts could be:-

1. The involvement of quantitative or qualitative difference in the distribution of organic material;
2. Sites adjacent to diffusion pathways especially at prism peripheries slowly accumulate trace elements, e.g. fluorine, which contribute to resistance.
3. Darling (1956) showed a surface zone (approximately 30 microns

thick) that often remains relatively intact over early carious lesions with extensive subsurface decalcification. This phenomenon can partly be explained in terms of diffusion kinetics of the carious process (Gray 1966). However, there is a great deal of evidence to show that other factors, notably difference in chemical composition, are also involved (Isaac et al 1954). Similarly, it was observed that natural tooth surfaces were much less affected by the etching agents than deeper enamel cut transversely to the prisms. The presence of an organic cuticle afforded some of the protection to the outer enamel. However, the higher organic content of surface enamel is believed to provide some protection too (Meckel 1965 and Leach and Saxton 1966).

From the work of Sharpe (1967) it might seem that prismless zones would be preferentially attacked by acids. However, Poole and Johnson (1967) and Poole (1967), in their experiments, failed to substantiate this claim. Boyde (1965) further points out that "the prismless area of the surface is widely held to possess caries-resistant characteristics". Innes and Schroff (1966) suggest that the prismless area is more resistant to attack by weak organic acids than the region where the prisms reach the surface. They also suggest that the greater the percentage of the tooth covered by areas where the prisms reach the surface (i.e. the less prismless areas) the more susceptible the tooth will be to carious attack (acid attack). Mention has been made of the existence of rod ends in the perikymata and that acid attack is initiated in these areas initially. Rods do reach the surface at the imbrication lines also. However, if the imbrication lines are not prismless, the prisms

(rods) are very often bent over so that their crystallite a-axis is presented to the surface rather than their c-axis being perpendicular to it as is the case in true prismless zones. Consequently, the acid attack is initially less effective at these sites. This is in accordance with the findings of Sharpe (1967), and Poole and Johnson (1967).

If acid attack is prolonged greater effects upon the enamel, than have been outlined above, will occur. Consequently, subsurface and, indeed, even deep enamel structures could be involved. It is beyond the scope of this review and of its purpose to discuss in detail the numerous changes that have occurred in the last fifty or so years in the concepts of internal enamel ultrastructural morphology. The enamel is composed of highly mineralised prismatic structures called enamel prisms or rods. Cross-sectional prism outlines were first described as "hexagonal", (Retzius 1837), then later as "fish scale" (Orban 1962) and "arcade" (Provenza 1964). They are now being described as "keyhole" in cross sectional form (Meckel et al 1965). The head of the keyhole has a diameter of about 5 microns and the height from head to tail is about 9 microns. The heads were found to be orientated towards the occlusal surface and the tails orientated toward the cervical border. Such a close-packed structure should have great strength because of the interlocking of heads and tails of adjacent prisms. These authors found a good deal of variation in the cross-sectional outlines of the enamel prisms.

The rods are made up of submicroscopic structures; the enamel crystallites.

Results from X-ray diffraction studies by Frank and Nalbandian (1967) indicated that crystallites in dental enamel are elongated crystalline structures having the approximate dimensions of $410\text{\AA} \times 1600\text{\AA}$.

The long-axes of the crystallites appear to be orientated along the long-axis of the prism in the front half of the head-end of the prism cross-section. Moving towards the tail of the prism, cross-section shows a gradual change in the direction of the crystallites until the crystallites within the tail of the prism cross-section are lying with their long-axes nearly perpendicular to the long-axis of the prism. The crystallites in the tail region of the prism cross-section also appear to lie with their long-axes fanning out towards the tail from the midline drawn from the head to tail of the prism.

In cross-section, when the section is cut perpendicular to the long-axes of the prisms, the junctions between adjacent prisms are apparent only because of sudden changes in the orientation of the enamel crystallites. Where the front half of the head-end of the prism structure abuts against the tail area of the adjacent prism there is an abrupt demarcation. There, the small cross-sections of the crystallites which are observed in the head of the prism are immediately adjacent to the long lath-like side view of the crystallites in the tail of the adjoining prism. Further down the head of the prism, where the long axes of the crystallites are observed to be inclined closer to the plane of the section, the junction with the tail of the next adjacent prism is marked by a discontinuity in direction of the long-axes of the crystallites that resembles a herringbone pattern.

It is considered that the change in direction of the crystallites must approach 90° at all the junctions of prism borders, and that the apparent differences seen within a section are caused by the different projections of the three-dimensional crystallites on the micrograph. No differences in the density of the enamel structure were observed between prism borders and the body of the prism, nor between the head and tail regions of the prism cross-sections, according to the authors (Meckel et al 1965).

Interprismatic substance (IPS), once thought to be a cementing substance (Orban 1962) binding prisms together, is now considered non-existent by some investigators including Meckel et al (1965), and Hoffman and Gross (1967).

Poole and Brooks (1961), Sharpe (1967), Gwinnett (1967) and Ripa et al (1966) all agree that prism sheaths, which were thought to surround and delineate enamel rods from other enamel rods or from interprismatic substance, (Frank and Nalbandian 1967), do not exist and in fact are artifacts. This group of authors explain the separation that exists between prisms as being due to crystallite orientation around prism peripheries.

In summarising a review of his own, Spiers (1971) wrote, "At present, it is impossible to relate with any degree of confidence these experimental findings to the structural features of surface enamel. There is little doubt that differences in properties exist over the crown of any one tooth, that they are mostly confined to the superficial enamel and that their cause is multifactorial". That statement highlights the

nature of the heterogeneity of surface enamel structurally and chemically and summarises the immense difficulties involved with the study of surface enamel.

PART II ETCHED ENAMEL

The clinical use of direct bonding of orthodontic attachments to the labial or buccal enamel surfaces of teeth requires etching of those surfaces by an acidic solvent prior to their placement. The purpose of such treatment is to remove the majority of reacted inorganic deposits, and to increase the surface area of the enamel, and to enlarge existing micropores in the tissue, and/or create new ones which by capillarity entrap the adhesive sealant (Gwinnett and Buonocore 1972). The attributes of such conditioning were first recognised by Buonocore in 1955, and he used 85% phosphoric acid for that purpose. The common adhesive systems all use inorganic acids (mostly phosphoric acid) at different strengths and are used for differing times of exposure on the enamel surface (Buonocore 1970b, Miura 1971, Newman 1969, Profitt 1972 and Retief et al 1970). According to these authors, the increased surface energy of the etched enamel surface (and consequently the increased bond strength) could be due to one, or a combination of the following:-

- (a) Removal of the outermost layer to expose a more reactive surface;
- (b) Increases surface roughness which promotes wetting of the adhesive;
- (c) Increased surface energy due to the deposition of highly reactive polar groups on the "new" surface of the tooth;
- (d) An increase in surface area due to the acid etching;

- (e) An exposing of the organic material of enamel which may serve as a network in, about, and to, which the resins can penetrate or adhere;
- (f) Creation of spaces in depth along interprismatic areas into which the resins can penetrate.

It can be appreciated that the morphological changes produced are of immense importance. However, Eich et al (1972) point out that although some roughness is warranted, too much roughness will act as a barrier to the flow of the liquid adhesive and the bond will be of a lesser strength due to incorporation of air pockets (see earlier section). Hence there should be some "ideal roughness" that produces optimum wetting because of capillary pressure and yet is not so rough that air entrapment at the interface is produced. They add "the exact topographic nature of this ideal roughness has not been established". Even if it were, it would be impossible to achieve clinically due the heterogeneity of tooth structure and the subjective interpretations of it by operators at the macroscopic level of observation of which the human eye is capable.

Poole and Johnson (1967) studied the effects of different demineralising agents (two organic acids, one inorganic acid and a chelating agent) on human enamel surfaces by using a scanning electron microscope. Essentially they found similar etching patterns were produced by all the acids, viz. that the etching defects were in the centre of the exposed prisms. However, the natural surfaces etched with EDTA (ethylene diamine tetra-acetic acid) showed greater differential loss of structure than similar surfaces etched with organic or inorganic

acids. In such cases, the tissue lost being apparently that around the prism margins. Muller and Schait (1957) and Muhlemann (1960) had previously noted the striking difference between the effects of EDTA and acids. Poole and Johnson (1967) also noted that the effects of both the acid and EDTA seemed to be independant of the direction of attack.

Gwinnett (1971) studied the histologic changes in labial enamel surfaces of human incisors when etched with eight different acids (two organic and six inorganic) for two minutes. He noted similar changes to those mentioned above, viz. an extensive loss of prism-core material while the peripheral zone remained relatively intact (the most common). The opposite effect also occurred and, as well, he observed surface areas which were pitted or smooth and relatively featureless without any clear prism delineation. He believed the observed topographical features recorded were related to intrinsic differences in enamel, either chemical, or histological, or both. From the point of view of adhesion, Gwinnett does not believe it important whether prism peripheries or cores are dissolved. However, he points out that the time needed to achieve histologically meritorious changes with chelating agents such as EDTA do not make their clinical use practical, particularly when acids produce a "good adhesive surface" in a much shorter time (30 seconds to 3 minutes).

The depth of etch is important, as too little will not adequately assist adhesion, whereas too much may actually weaken the adhesive bond as well as cause permanent and irreparable damage to the surface.

Gwinnett (1971) suggests that etch-depths of 25 microns or less are most suitable. In his experiments only the hydrochloric acids produced etched surfaces of depths greater than 25 microns. It is interesting to note that the 85% phosphoric acid, used in his experiments, was reported to produce less etching (less than 5 microns) than did the weaker solutions of 50% and 10% of the same acid (greater than 5 microns but less than 25 microns). This was in accordance with the findings of Gwinnett and Buonocore (1965).

Sharpe (1967) suggested that the presence of organic matrix on the external surfaces of crystallites might protect them against acid and thus inhibit lateral spread. It may be that organic matter is more soluble in EDTA than in acid and this protective effect is useless against EDTA attack.

Poole (1971), in support of the above findings, postulates that perhaps because of the size of the EDTA anion, it can only penetrate readily at the junctional site. In these regions, pores are probably larger and certainly more irregular than in the centre of prism where crystallites are generally parallel and closely packed. However, if etching is carried out with EDTA at its natural pH (4.0) the pattern of dissolution of the central part of the prism is similar to that found with organic and inorganic acids. Conversely, the etching patterns of EDTA at pH 7.0 (loss of prism peripheries) could be achieved by the use of 88 per cent lactic acid and if ionization of acids was inhibited by preparation in nonaqueous solvents, the same manifestations occurred.

Johnson et al (1971) found a relationship between the time of exposure

and the concentration of the demineralising solution with the etching pattern produced. The variable results with EDTA solutions were similar to those described above as were most findings of acid-etching solutions. However, short term applications of acids produced narrow clefts, apparently at prism junctions as well as central core dissolution. The clefts were similar in appearance, size and distribution to those produced by dilute neutral EDTA. They noted that "as the depth of the concavities in the prism cores increased, the peripheral channels apparently became confluent with them, eventually producing the classical honeycombe appearance".

The possible role of crystal orientation in determining the differential etching effects has been discussed. Johnson et al (1971) however, claim that the fact that the same structural sites in enamel are attacked with any given agent, irrespective of which crystal face of the enamel crystallite is exposed, indicates that differential solubility of individual crystals cannot play a dominant role in determining etching patterns. They concede, however, that crystal orientation might be important if the relative surface areas of crystal groups of differing orientation are considered in relation to the depth of penetration of the demineralising agent between the crystals.

Johnson et al (1971) also suggest the following could influence etching patterns:-

- (a) Difference, if any, in the chemical composition between the central and peripheral parts of the enamel prisms;

- (b) The increased porosity of prism junction could affect the types of ionic diffusion in these areas;
- (c) The organic, or ionic (especially fluoride) composition of crystallite surfaces;
- (d) The difference in size of electric charges exhibited by the different demineralising radicals.

Other physical and chemical properties of the substrate and the demineralising agents, that could affect etching patterns have been mentioned in the section "Enamel Solubility".

Newman (1969) using a 50% phosphoric acid solution for one minute found the depth of etch to be 5-15 microns. However, he claimed that the inclusion of attenuating agents in the acid, such as zinc oxide and sodium fluoride, limited the etching to approximately 10 microns. Buonocore et al (1968) were able to demonstrate tag-like projections of adhesive, approximately 10-25 microns in length, formed in the "grooves" formed on the enamel surface. They used the same time interval as Newman, and the same etching solution without the sodium fluoride (50% phosphoric acid and 7% by weight).

Miura et al (1971) recommends the use of a 65% phosphoric acid solution for 30 seconds. They concluded that the effects on the enamel surface so caused were clinically negligible.

Retief (1971), as cited by Manning (1971), using a 50% phosphoric acid solution for one minute demonstrated an etching effect of 50 microns in depth.

Smith (1972) claims that the effects of etching solutions are far greater than those currently reported in the literature and believes the effects could go as deep as 100 microns.

Manning (1971) says "although it would be difficult to estimate the quantitative amount of enamel removed, it would be reasonable to state that this method of enamel preparation, plus the pumicing of the tooth surface prior to and subsequent to bonding, is far more destructive than the single polishing technique before bonding as advocated by Smith (1971 a and b). That may be so. However, no evidence is available to suggest that the loss of the tooth structure which occurs as a result of direct bonding procedures, is clinically significant.

ORIGINAL

WORK

PURPOSE AND SCOPE OF THE INVESTIGATION

The purpose of the investigation was to observe, primarily with the aid of a scanning electron microscope, and secondly with the naked eye, the effects, in vitro, of four direct bonding systems, and in particular their etching solutions, on the enamel surface of human tooth enamel surfaces.

The observations of these effects, produced by the four direct bonding systems, received for testing, were to be undertaken at the following stages of tooth adhesive preparations:-

- (a) Pumiced enamel surface;
- (b) Etched enamel surface;
- (c) Enamel surface after bulk removal
of the adhesive and the attachment; and
- (d) The enamel surface after it had been
"scaled" of any obvious remnants of
adhesive and then re-pumiced.

In addition to the above experiments other tests were to include:-

- (a) Examination, by scanning electron
microscopy, of adhesive surface, at the
enamel interface, after the enamel had
been dissolved away from it.

- (d) Examination, by scanning electron microscope, of the effects of the etching solutions of the four products, at different times of exposure, on the enamel surface.

MATERIALS AND METHODS

TEETH USED THROUGHOUT TESTING PROCEDURES

The heterogeneous nature of tooth structure is well established (Spiers, 1971). Consequently it is known that not only do qualitative and quantitative differences in composition and structure occur in teeth of different persons but there are similar differences in teeth from the same individual and indeed they also occur from one area to another within the same tooth.

The direct bonding systems in clinical use today, predominantly require their attachments to be centrally placed on the buccal or labial surfaces of tooth crowns. The attachments are small and it was found in pilot investigations that surface preparation, bonding procedures, and sample handling was made extremely difficult when the crown was divided into parts in an attempt to provide numbers of samples from the same tooth so that more accurate comparisons could be made between samples. It was also found that the sectioning procedures caused a rupturing of the adhesive joint due to vibrations of the cutting disk in the small sections, which in effect ruined half of the experiments.

Random selection of buccal tooth crown surfaces was considered. However, this was considered to be taking steps toward the opposite extreme and that such selection would make future possible comparisons somewhat limited, due to the surface variabilities that would have been encountered.

As four products were to be tested, it was decided to use "sets" of extracted premolar teeth from young orthodontic patients. Such selection was a compromise based on the two previous alternatives and provided a method by which limited, yet valuable, comparisons could be made between the effects encountered from use of the four adhesive systems tested.

The patients were selected from those attending for treatment at the Orthodontic Clinic, Department of Preventive Dentistry, University of Sydney and also from three private, orthodontic practices in the suburbs of Sydney.

When the decision to extract four premolars had been made, the patient was given a letter and a small screw-capped bottle containing physiological saline, in which the teeth were to be placed after extraction. The letter, addressed to the patient's dentist, outlined the desire to preserve the teeth, the scope of the research for which they were intended and requested:-

- a) That the teeth should be extracted carefully to avoid all possible damage to the labial (buccal) surface.
- b) That the teeth be washed in tap water and placed in the bottle of saline solution provided, immediately following extraction.
- c) That a brief fluoride exposure history be written on the plain label glued to the bottle, as well as the patient's age.

Arrangements were made to collect the bottles as soon after the last extraction(s), as possible. After collection, the details required on the labels were checked with the dentist concerned.

The teeth were cleaned of any soft tissue remaining on the roots. Their buccal surfaces were then examined under a light microscope (Stereomicroscope II, Carl Zeiss, 7082 Oberkochen, Postfach 35-36, West Germany), at 20 X magnification for cracking and crazing damage that may have resulted from the extraction procedure or any other cause. Any teeth so affected were rejected and consequently so was the entire set to which it belonged. It should be pointed out that some damage could be expected to escape detection at such magnification.

After this examination the teeth were placed in a new, sterile and sealable bottle containing a 50% Ethyl Alcohol solution as according to Boyde, 1972. This solution according to Boyde, should preserve the integrity of the tooth surfaces and inhibit bacterial activity on them. The previous data was recorded on the bottles and they were then stored at a controlled room temperature (21°C) until required for use.

All teeth were extracted from young adolescent patients whose average age was about $12\frac{1}{2}$ years. The patients selected had lived in the Sydney metropolitan area all their lives. The reticulated water supply of Sydney has contained 1ppm Fluoride since 30th June, 1968 (Flynn 1972).

They were further selected as not having had regular topical applications of fluoride. Many, however, had used a dentrifice containing

fluoride but this variable had to be accepted due to the availability of patients, which was limited. All the extracted teeth had fully erupted and no impacted or surgically removed teeth were accepted.

As far as tooth age was concerned, it closely represented the tooth age that would be involved in the clinical use of direct bonding systems.

Fluoride uptake by the enamel surface was standardised within reasonable limits. All teeth could have been expected to have experienced at least a post-development, pre-eruptive uptake of fluoride in their enamel surfaces (Craig 1972).

MATERIALS USED IN TESTING

Four direct bonding systems were used. However, only two systems were used specifically as directed by the manufacturer. The other two systems were used with modifications which will be detailed later.

PRODUCT A (see Plate 4)

"ORTHOMITE" - DIRECT BONDING SYSTEM, which was obtained from:-

ROCKY MOUNTAINS DENTAL PRODUCTS COMPANY,
POST OFFICE BOX 17085,
DENVER,
COLORADO, U.S.A.

This system contained:-

- (a) A number of Lexan-polycarbonate brackets,
- (b) A dappen glass, a press, a cap opener and a brush,
- (c) A bottle containing 5 mls. of 65% phosphoric acid (labelled A),
- (d) A bottle containing 5 mls. of a silane coupling agent (labelled B),
- (e) A bottle containing 2.5 gms. of polymethyl methacrylate powder, and
- (f) 10 glass vials (container C) in each of which was about 1 ml. of the monomer liquid and contained within the cap was a sealed capsule of the "Orthomite" catalyst.

PRODUCT B (see Plate 5)

"O.I.S. ADHESIVE SYSTEM", which was obtained from:-

ORTHO INTERNATIONAL SERVICES INC.,
POST OFFICE BOX 2074,
WILMINGTON,
DELAWARE, U.S.A. 19899

This kit contained:-

- (a) A number of polycarbonate brackets,
- (b) A bottle containing 10 mls. of 50% phosphoric acid, 7% (by weight) of zinc oxide and 1% sodium fluoride,
- (c) A bottle containing 5.3 gms. of powdered polymethylmethacrylate containing 3% sodium monofluorophosphate,
- (d) A bottle containing 15 mls. of methyl methacrylate monomer, and
- (e) An eye-dropper, a sand-paper filter, a powder dispenser and some soft, white wax.

PRODUCT C (see Plate 6)

CAULK "NUVA-SEAL" PIT AND FISSURE SEALANT SYSTEM, which was obtained from:-

L. D. CAULK CO.,
DIVISION OF THE DENTISTS SUPPLY CO.,
MILFORD,
DELAWARE, U.S.A.

This systems, as used by Cohl et al, 1972 consisted of:-

- (a) 40 bottles of methacrylate liquid
- (b) 2 bottles of liquid initiator
- (c) 2 bottles, containing 10 mls. each, of 50%
phosphoric acid with 7% zinc oxide by weight.
- (d) A number of brushes and brush stems
- (e) Two bottles of brush cleaning fluid (chloroform)
- (f) A separate container in which was stored the ultra-violet light "activating gun" used to activate the setting reaction by directing a beam of ultra-violet light onto the initiated resin.

The adhesive is a relatively stable, thick liquid containing as the ingredients, 3 parts by weight of the reaction product of bisphenol A and glycidyl methacrylate, and 1 part by weight, of methyl methacrylate monomer. (Bowen's resin - Bowen 1965a). By the addition of one drop of 2.0% of Benzoin Methyl Ether (the initiator), just prior to use, an ultra-violet light sensitive composition is formed. The ultra-violet light is a high intensity source of $8,400 \text{ microwatts/cm}^2$ of radiation, in the region of $3,600^{\circ}\text{A}$ wavelength, at a distance of 18 inches. Part of the light source is transmitted via a plastic rod onto the adhesive on the tooth surface. The nozzle is held approximately

1-2 mms above the tooth surface (i.e. just above the bracket being "cemented" onto the tooth surface).

The brackets used were the same as those used in the system designated "Product A". The adhesive system is actually a pit and fissure sealant (Buonocore, 1971) and modified for use as a direct bonding system with polycarbonate brackets as reported by Cohl et al 1972.

PRODUCT D (see Plate 7)

This system was made up from results of research into direct bonding as reported by Profitt, 1972 and Ohsawa, 1972 and as discussed in earlier sections.

Three main agents were incorporated in this new system, viz:-

- (a) The adhesive: the restorative methyl methacrylate resin, SEVITRON SIMPLIFIED and some stainless steel brackets which were obtained from:-

UNITEK CORPORATION,
95 ROYAL OAKS DRIVE,
MONROVIA,
CALIFORNIA, U.S.A. 91016

- (b) The etching solution: a 40.4% (2 mol.) solution of pyruvic acid. This acid was used in preference to the recommended "any suitable phosphoric cement liquid" for two reasons:-

1. 3 different solutions of phosphoric acid were already being used in conjunction with the other systems, and
2. Ohsawa, 1972 found a 2.0 mol. (40.4%) solution of pyruvic acid gave the maximum adhesion for the minimal loss of mineral from his enamel samples of all the acids (at different strengths) tested.

In the remainder of this report the adhesive systems shall be referred to as "Products A, B, C or D" as listed above.

EXPERIMENTAL PROCEDURE

1. INITIAL TOOTH PREPARATION

Prior to the use of the teeth in the actual experiments, each tooth was removed from its container and the crown was partially sectioned mesio-distally from the occlusal surface towards the root area. The cut was made, as closely as possible, parallel to the buccal surface of each tooth, to a point some 1-2 mms below the level of cemento-enamel junction. The bucco-coronal portion of the crown was approximately 2-3 mms thick and remained intact with the tooth (see Fig. 14). Cuts were made by use of a Gillings-Hamco machine; the diamond disk used for cutting being water cooled during the procedure.

The buccal surfaces of the teeth were then carefully "cleaned and polished" by using a bristle brush (ASH Junior Apline, wheel-shaped brush for straight handpieces - Amalgamated Dental Company, London, U.K.) in a conventional handpiece and a fine pumice (Prophylaxis pumice, XXX Fine, produced by Ainsworth Dental Company, Sydney, Australia) mixed with water, for 10 seconds, using light hand pressure.

The teeth were then thoroughly washed in tap water and dried by compressed air at 20 p.s.i.

The teeth were then arranged on sheets of Red Wax ("Investo" Bite and Boxing Wax, Investo Manufacturing Company Pty. Ltd., Neutral

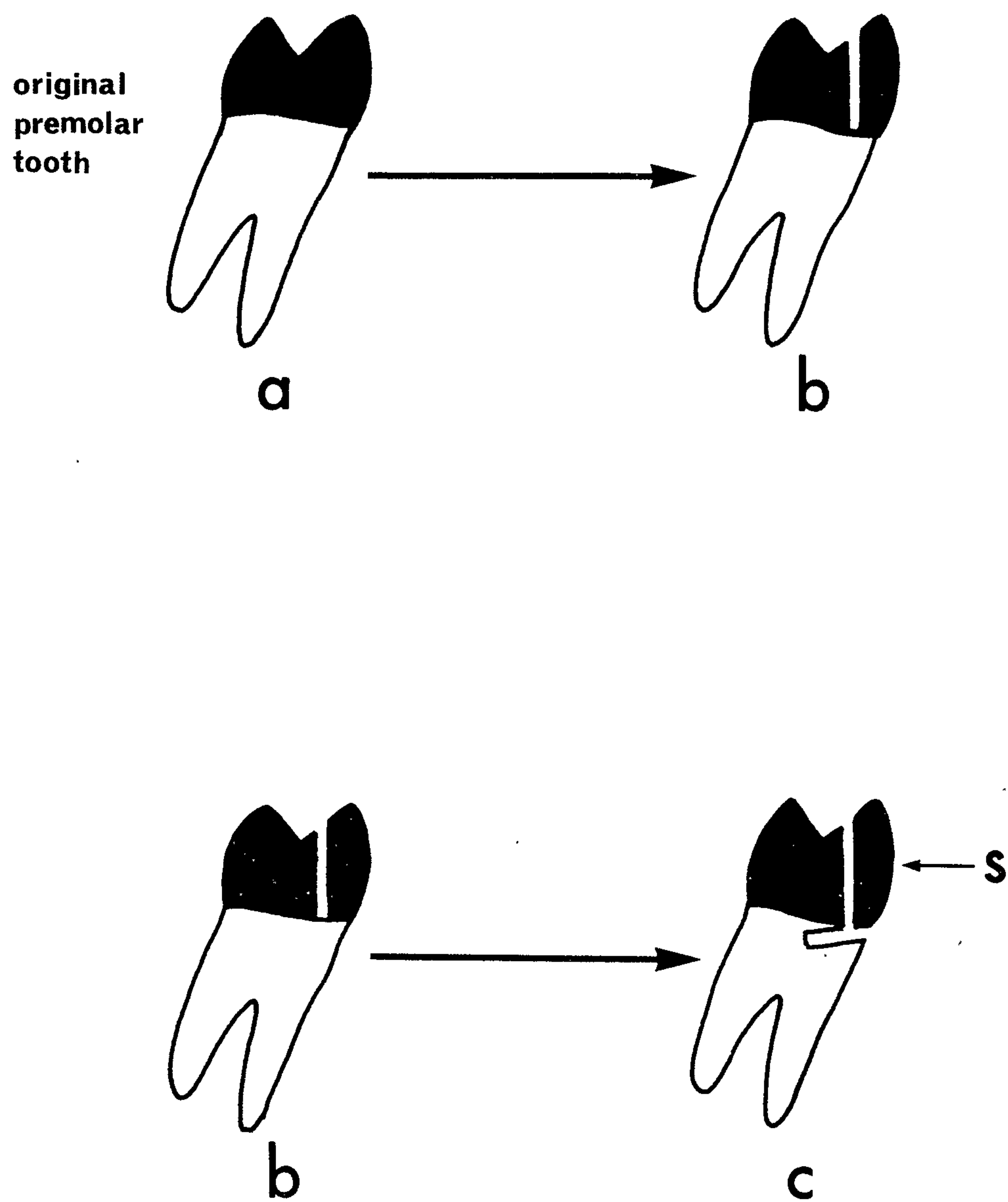


Fig. 14 Preparation of tooth specimen (S)

b. shows site of initial sectioning procedure

c. shows site of second sectioning procedure

Bay, N.S.W., Australia) as detailed in Table 4, with the buccal surface uppermost.

The arrangement of samples, as shown in Table 4, was chosen for the following reasons:-

- (i) It provided an ordered arrangement of the premolar teeth, for testing. This arrangement removed any location bias and so not necessarily the same tooth (location) was continually photographed in the scanning electron microscope.
- (ii) It provided actual sets to be distributed evenly (one tooth each) to the four products and yet each product in each experiment had a complete "set" as far as location was concerned.
- (iii) It allowed a comparison, within actual tooth sets, of the effects of the different products in each experiment, e.g. one could compare Experiments IA2, IB2, IC2 and ID2 for product effects.
- (iv) It allowed a comparison to be made between tooth sets in the same experiment, e.g. IA1, IA2, IA3 and IA4. This gave a comparison of the effects of substance (tooth enamel) variation and so enabled assessment of typical or atypical appearances in the hope that a trend might emerge, in these effects. If a

trend in appearance was observed, then that appearance was taken as representative of the effects of that product in the particular experiment being examined. This reduced the number of specimens photographed and so conserved valuable time on the scanning microscope.

Further, typical surface appearances could then be used for comparison with typical surface appearances of teeth treated with other products in the same experiment.

Experiment No.	Tooth Set No.		PRODUCTS							
			A		B		C		D	
	Actual	Expt.	Wax Sheet A1		B1		C1		D1	
I	(1)	1	UL		UR		LL		LR	
	(2)	2	UR		LL		LR		UL	
	(3)	3	LL		LR		UL		UR	
	(4)	4	LR		UL		UR		LL	
Wax Sheet										
			AII		BII		CII		DII	
II	(5)	1	UR		LL		LR		UL	
	(6)	2	LL		LR		UL		UR	
	(7)	3	LR		UL		UR		LL	
	(8)	4	UL		UR		LL		LR	
Wax Sheet										
			AIII		BIII		CIII		DIII	
III	(9)	1	LL		LR		UL		UR	
	(10)	2	LR		UL		UR		LL	
	(11)	3	UL		UR		LL		LR	
	(12)	4	UR		LL		LR		UL	
Wax Sheet										
			AIV		BIV		CIV		DIV	
IV	(13)	1	LR		UL		UR		LL	
	(14)	2	UL		UR		LL		LR	
	(15)	3	UR		LL		LR		UL	
	(16)	4	LL		LR		UL		UR	
Wax Sheet										
No product variation										
V	(17)	1	UL		UR		LL		LR	
	(18)	2	UR		LL		LR		UL	
	(19)	3	LL		LR		UL		UR	
	(20)	4	LR		UL		UR		LL	
Wax Sheet										
			AVI		BVI		CVI		DVI	
VI	Sets		UR	1.	LL	1.	LR	1	UL	1
	arranged as		LL	2.	LR	2.	UL	2.	UR	2.
	for products		LR	3.	UL	3.	UR	3.	LL	3.
	and not between		UL	4.	UR	4.	LL	4.	LR	4.
	products		(21)		(22)		(23)		(24)	

TABLE 4. ARRANGEMENT OF TOOTH SAMPLES

2. THE EXPERIMENTS (Classification)

The Experiments as listed and coded in Table 4 were:-

a) EXPERIMENT I - Etched Enamel Surfaces

These surfaces were those treated with the etching solutions of the four products for the manufacturer's recommended exposure times. Hence, sample IA1 was that tooth treated with the etching solution from Product A for the recommended exposure time (in this case 30 seconds), the tooth set being No. 1, which happened to be the upper left premolar (see Table 4) of that set.

The variability of the effects of the four agents could be assessed by comparison of samples IA1, IB1, IC1 and ID1. Tooth surface effects could be assessed by comparing samples IA1, IA2, IA3 and IA4. These types of comparison could be made in each Experiment.

b) EXPERIMENT II - The Adhesive Surface

This surface was that of the adhesive at the adhesive-enamel interface. This surface was obtained by dissolution in acid, of the attached enamel.

c) EXPERIMENT III - The "Removal" Surface

This surface was that of the enamel after the bulk removal of the adhesive and the attachment.

d) EXPERIMENT IV - The Repolished Surface

This surface was that of the enamel after it had been repolished by prophylaxis with a pumice powder-water slurry (the same procedure described for Experiment V) following bracket and adhesive removal.

e) EXPERIMENT V - The Original Polished Surface

This surface was the original pumiced surface of the teeth before any bonding procedures were instigated.

f) EXPERIMENT VI - The Multiple Etched Surfaces

These surfaces were those that had been etched with the four different etching agents, for four different exposure times (viz. 30 seconds, 1 minute, 2 minutes and 3 minutes).

3. BRACKET PREPARATION

With the exception of Product D, all systems used polycarbonate brackets which had to be trimmed, adapted and contoured to "fit" the buccal surfaces of the sample teeth. Product D used a pre-formed stainless steel bracket, which required no adjustment.

The brackets used are shown in Plate 8.

In Product A, only trimming of the edges was generally required¹/₄ although contouring was required for a few brackets.

Product C used the same brackets as for Product A.

The brackets of Product B had a larger and flatter base and consequently required more extensive contouring and trimming.

All contouring was achieved by use of ASH., Howe pattern pliers (Amalgamated Dental Company, London, U.K.) and the trimming by use of Pin and Ligature Cutting pliers No. 150 (Dentaurum Company, Pforzheim, West Germany).

The bracket bases of Product B were slightly roughened by the use of a heatless stone, No. 769 (obtained from Busch and Company, 525 Engelshirchen, Bez. Cologne, West Germany).

Product D required no preparation of its surface and no direction in this matter was available at the time of experimentation for Product C.

It should be pointed out at this stage that this interface (bracket-adhesive) was of minor importance in these Experiments. Actual bracket placement merely allowed correct procedure to be followed and facilitated handling of the systems and the specimens.

After each bracket was selected and prepared where necessary, it was placed on a sheet of paper, in a position corresponding to that of the tooth on the wax sheets, for which it had been adapted. This procedure facilitated easy relocation of each bracket onto its correct tooth when required and minimised the risk of surface contamination which may have occurred if they had been stored on the wax sheets together with the teeth.

4. FINAL PREPARATION OF TOOTH SURFACES PRIOR TO BONDING

Once the pumiced, washed and dried teeth had been arranged according to Table 4, on the wax sheets, chloroform (used as a degreasing agent) was applied for 20 seconds with a cotton pledget. The teeth were washed with distilled water and again dried with compressed air at 20 p.s.i. This procedure was followed by a further 20 seconds with a cotton pledget washed in 70-80% alcohol and again dried by compressed air at 20 p.s.i. as according to Manning, 1971.

The above procedure standardised surface preparation in all Experiments and so removed what would have been another variable factor in procedure between the products.

5. ATTACHMENT BONDING PROCEDURES

All procedures described below were commenced at the conclusion of the final preparation of the "clean" tooth surface and followed each manufacturer's detailed instructions which were provided with their product. The instructions were all directed at clinical use of the products. As this study was a laboratory exercise, the instructions required minor, insignificant deletions and modifications. However, this in vitro study was clinically orientated and so all procedures from the instructions that could be practically undertaken in the laboratory, were, in fact, carried out.

The timing of all etching periods and mixing procedures (where applicable) was achieved by the use of an electric, alarm-type timing device which was calibrated in seconds and minutes.

(Gralab Universal Timer, Model 167, manufactured by: Dimco-Gray Company, Daytona, Ohio, U.S.A.). The timer was set to the recommended exposure and released simultaneously with the commencement of etching (or mixing). When the alarm sounded, at the expiration of the etching time, the tooth was immediately and thoroughly rinsed in tap water. It was then rinsed in distilled water and dried by blasting with compressed air at 20 p.s.i.

PRODUCT A. (See Plates 4 and 8)

- (a) A cotton pledget was saturated with Solution A from the kit (65% phosphoric acid and 7% zinc oxide by weight) and applied to the relevant enamel surfaces by means of a pair

of dental tweezers light hand pressure and an agitating action being used, for 45 seconds.

- (b) The tooth surface was washed and dried as detailed earlier.
- (c) A new cotton pledget was then saturated with Solution B from the kit (the methacryloxypropyl tri methoxysilane) and was then quickly applied to the dry, etched buccal tooth surface. The drenched area was immediately blasted by compressed air at 20 p.s.i. to facilitate spread of the solution and to minimise its thickness over the enamel.
- (d) The press was then used to rupture the capsule within the vial (container C). Visual inspection verified whether rupture of the capsule had occurred or not. If it had occurred, the vial was shaken, vigourously but briefly, to mix the released catalyst with the monomer liquid (methyl methacrylate).

If initial rupture had failed, the puncture process was repeated until the capsule had ruptured. The vial lid was then removed with the opener provided.

- (e) A small amount of the powder (polymethylmethacrylate) was dispensed into the dappen dish.
- (f) The adhesive was mixed and applied by use of a "brush-on" technique (Healon, 1952). The brush was dipped into the

mixed liquids, in container C, and then lightly into the powder. A bead of mixed adhesive, so formed on the brush tip, was immediately applied to the enamel surface.

- (g) The bracket, adapted previously for use on the particular tooth, was then placed onto the adhesive, on the tooth surface, and held with moderate finger pressure, by use of dental tweezers, in the desired position, until the adhesive had set (usually less than 2 minutes).
- (h) The brush was wiped clean, on tissue paper, between successive applications, to minimise contamination of the liquid mix in the vial (container C).

PRODUCT B (see Plates 5 and 8)

- (a) The etching solution (50% phosphoric acid, 1% sodium fluoride and 7% zinc oxide by weight) was applied to the relevant enamel surfaces, by the same method as for the etching solution in Product A.

However, it was applied for 60 seconds.

- (b) Essentially, the bonding procedure was the same as that for Product A except in the mixing of the adhesive.
- (c) The adhesive was prepared by dispensing two, level full,

scoops (the scoop was provided in the kit) of the resin powder (polymethyl methacrylate and 3% sodium monofluorophosphate) onto a new, clean, chilled glass mixing slab. The powder was formed into a "crater-shape" to prevent the liquid flowing over the glass slab, as the liquid has a low viscosity, a low contact angle on glass and hence a high degree of wettability on it. The eye-dropper (provided in the kit) was then used to dispense seven drops of the methyl methacrylate liquid, into the centre of the powder. The "crater-shaped" heap of powder helped to contain the liquid. The mixture was quickly spatulated for 20 seconds into its final consistency. This was a free-flowing slurry which was still firm enough to permit adequate control during bonding.

- (d) The adhesive was then quickly applied to the tooth surface and the bracket placed in position in the same manner as for Product A.
- (e) Only two brackets were placed with each mix due to the short setting time of approximately 60 seconds.

PRODUCT C (see Plates 6a, 6b and 8)

- (a) The etching solution (50% phosphoric acid and 7% zinc oxide by weight) was applied to the relevant enamel surfaces in the same manner as for Product A. However, like Product B, it too was applied for 60 seconds. The teeth were washed

and dried as described earlier.

- (b) The ultra-violet light "gun" was connected to the power supply and allowed to "warm up" for 10 minutes, with the light switch closed, before it was used.
- (c) A fresh bottle of adhesive liquid (Bowen's resin in methyl methacrylate) was opened and one drop of initiator (benzoin methyl ether) was added to the adhesive liquid. The cap was replaced. Then the bottle was shaken to mix the two solutions.

The adhesive liquid was then ready for use.

- (d) When the ultra-violet light "gun" was functioning, some of the adhesive was applied to the tooth surface and some to the bracket base surface with the brush provided. The bracket was then placed on the tooth and held in position with dental tweezers.
- (e) The ultra violet light "gun" was then held in position over the bracket. Its flat, nozzle tip was held some 1-2 mms above the level of the adhesive so that the light was directed onto it. The light shone on the adhesive at slightly varying angulations for two minutes. This was a longer period than that recommended by Buonocore (1971) in its use for pit and fissure sealing. However, due to the requirement of the light to pass through the clear plastic bracket, a

longer exposure time was considered desirable for thorough setting of the adhesive.

PRODUCT D (see Plates 7 and 8)

- (a) The etching solution (40.4% pyruvic acid) was applied, by the same means as described for Products A, B & C for 30 seconds (Ohsawa 1972). The teeth were washed and dried as also described earlier after the 30 second application of the pyruvic acid.
- (b) The intermediary coupling agent (a varnish consistency of glycerophosphoric acid dimethacrylate in liquid methyl methacrylate) was briefly applied to the tooth surface by means of a saturated cotton wool pledget held in dental tweezers. The varnished tooth surface was immediately blasted with compressed air, in the same manner and for the same reasons as the coupling agent used in Product A.
- (c) A brush technique (Nealon 1952) was again used to prepare the Sevitron Simplified adhesive mixture. It was applied to the tooth surface and also to the bracket base to ensure complete filling of the undercut bracket base by the adhesive.
- (d) Then the bracket was placed in the desired position and held in that position on the tooth surface with moderate finger pressure, by means of dental tweezers, until the adhesive had set. (usually between 1 and 2 minutes).

Plates 9, 10, 11 and 12 show the bonded brackets, of Products A, B, C and D (in situ). Excess of adhesive was minimised by performing trials with each product. Some very slight excess, however, did occur on some samples but was considered irrelevant in these experiments.

In clinical use, excess must be removed as it could: interfere with archwire placement, cause irritation to gingival tissues or hinder oral hygiene measures.

None of the preparations was sealed with wax or varnishes etc., after completion of the bonding procedures as the teeth were kept dry for 30 minutes. Such procedures do assist in the maintenance of the dry oral field, in vivo, however, the manufacturers of Product B were the only manufacturers to advocate such a procedure (wax to cover the adhesive - bracket area when used in vivo- was provided with the kit). The manufacturers of the other products merely advocated the continued maintenance of a dry oral field (by use of cotton-wool rolls and suction equipment, in vivo) until the set of the adhesive is complete. Retief et al (1970) advocate the use of rubber dam, in vivo, to assist in dry, oral field maintenance.

6. THE EXPERIMENTS (Description)

All tooth surfaces had been pumiced, washed, cleaned and dried as described earlier.

The teeth of Experiment V were then sectioned horizontally at about the level of the cemento-enamel junction (see Fig. 14b) in the Gillings-Hamco sectioning machine. The buccal coronal segment was washed in tap water, rinsed in distilled water and dried with compressed air. It was then carefully placed, with the buccal surface uppermost, in a clean sterile pill bottle for storage. The bottle was labelled according to the specimen classification (see Table 4) and it was stored in a cardboard container until the specimen was required for mounting prior to coating the specimens for examination in the scanning electron microscope.

A typical specimen is shown in Plate 13. This specimen size was found to be most suitable for scanning electron microscopy as it permitted nine samples to be processed at once in the vacuum coating machine. If whole teeth had been processed only three teeth could have been treated at any one time in the machine.

A description of the coating procedure will be detailed later.

All specimens for Experiments I, II, III and IV were then individually etched with their respective etching solutions, for the recommended time of exposure, washed and dried, as already described.

The brackets were then bonded to the allocated surfaces for all these teeth, as already described, with the exception of the specimens of Experiment V. Plate 19 shows an etched specimen.

The wax sheets, with the teeth of Experiment II, III and IV on them, were then immersed in a glass beaker of distilled water. The beaker was sealed to prevent evaporation and the samples were left in the beaker for 14 days. Although this figure for time of water immersion was arbitrarily chosen, it coincided with that period of time for which Miura, et al (1971), detected a loss of bond strength. It also exceeded the period of time which Rose et al (1955), Sadler (1958), and Swanson and Beck (1960), found to be sufficient for total failure of the bonds, of their tested materials, to occur.

On expiration of this period of 14 days, the samples were removed from the water and dried by compressed air.

With the exception of the specimens of Experiment II all the brackets (and adhesive) were removed, according to the manufacturer's instructions, where applicable (no such instructions were available for Product C).

The brackets of Products A and C were removed with pin and ligature cutters whereas those of Products B and D were removed with conventional band removing pliers (Pattern No. 347. The Dentaureum Company Pforzheim, West Germany), although this procedure (Products B and D) was altered later (see discussion section).

The teeth of Experiment III were sectioned horizontally, washed and dried (both gently) and the specimens so produced were stored in their respective, labelled bottles.

The teeth of Experiment IV were then washed and dried. Any visible adhesive remnants were washed with chloroform (to assist removal) and then removed by means of a sickle-shaped Morse scaler (The Amalgamated Dental Company, London, U.K.). The surfaces were then pumiced for 10 seconds (as described earlier), horizontally sectioned, washed, rinsed, dried and placed in their respective bottles for storage.

The samples of Experiment II were dried with compressed air and a small piece of plastic tubing (3 mms long and 3-4 mms in diameter) was placed over and around the bracket and held in position on the enamel surface by a few beads of sticky wax. (Ainsworth Dental Company, Sydney, Australia). The placement of the tubing is shown in Plate 14a.

Self-curing acrylic resin (de Trey's Rapid Repair Material - The Amalgamated Dental Company, London, U.K.) was mixed and poured into each piece of tubing, about the bracket, until the tubing was full (see Plate 14b). This procedure provided a base for the adhesive sample which was suitable for handling for scanning electron microscopy mounting procedures. It also prevented acid dissolution of the stainless steel bracket of Product D at a later

stage of the specimen preparation. When the resin had set, the plastic tubing was cut along its length and carefully removed. The cylindrical block of resin formed by the procedure is shown in Plate 14C. The tooth was sectioned vertically, close to the outer buccal enamel and then horizontally beneath the bonded area. Then the acrylic block and the attached tooth structure was placed in a solution of concentrated hydrochloric acid in a glass beaker. Each specimen being placed in a separate labelled beaker. The samples actually floated with the enamel surface downwards and so possible damage to the adhesive surface could not occur as the adhesive surface did not contact the sides of bottom of the glass beaker. After complete dissolution of the tooth structure had occurred, the specimens were washed, rinsed and stored (as described earlier for other preparations) in their respective bottles. An example of such a specimen is shown in Plate 14d; the adhesive surface being the large concave, uppermost one.

The first four specimens (VIA1, VIB1, VIC1 and VID1) of Experiment VI were etched with their respective etching solutions for 30 seconds (i.e. specimen VIA1 with the etching solution of Product A for 30 seconds, specimen VIB1 with the etching solution of Product B for 30 seconds etc.). The next four specimens (VIA2, VIB2, VIC2 and VID2) for 1 minute, the next four specimens (VIA3, VIB3, VIC3 and VID3) for 2 minutes and the last four specimens (VIA4, VIB4, VIC4 and VID4) for 3 minutes with the respective etching solutions. At the expiration of each exposure, (only one tooth was treated at a time) the specimen was washed, dried and stored

in its respective bottle. The vertical and horizontal sectioning was completed before these etching experiments were performed, as handling of the specimens in this experiment was easier due to lack of any bonding procedures.

All specimens were now ready for processing for scanning electron microscopy.

The specimens were individually mounted on one end of a small aluminium cylinder ($\frac{3}{8}$ " long x $\frac{3}{8}$ " diameter) by means of a double-sided adhesive tape, with the surface to be examined uppermost. The specimen code was written on a small piece of single-sided adhesive tape. This was then placed on the bottom of the cylinder for identification of the specimen, e.g. specimen IVC3 was that specimen from tooth set No. 15 - the lower right premolar - which had been repolished, following the removal of the bracket and adhesive of Product C and it was the third tooth used for Product C in that experiment (see Table 4).

The specimens (9 in each load) were then coated with a thin film of gold (approximately 500°A in thickness) in the DYNAVAC high vacuum coating machine (Dynavac High Vacuum Pty. Ltd. Burwood, Victoria, Australia). The purpose of the coating was to provide electrical conductivity at the enamel surface of each specimen. The machine used for this purpose is shown in Plate 15.

A mounted and coated specimen is shown in Plate 16.

All specimens were examined in a scanning electron microscope (Model J.S.M.U.3, Japan Electron Optics Laboratory Co. Ltd., Marunouchi, Chiyoda-mu, Tokyo, Japan). The scanning electron microscope is shown in Plate 17.

The scanning electron microscope was operated at 10KV and specimens were examined by the mode of secondary electron emission. All specimens were examined. Specimens taken as representative or selected for other reasons (see section on "Results") were photographed. Such selection procedures conserved time on the machine, as to take photographs of all specimens at the selected and constant magnifications would have been beyond the scope of this project, the time limits available on use of the machine, and a waste of photographic film. All photographs were taken with the photographic attachment (SMU3-CSI) using FX-120 film (Kodak A/Asia Pty. Ltd. Sydney, Australia), at f11 and a scanning speed of 50 seconds/frame.

Prior to any photography, all specimens were examined initially on the television screen for area location and then on the cathode ray tube at a scanning speed of 2.5 seconds/frame for final area location and focusing, etc.

Where possible the area selected for photography was close to the middle portion of the tooth crown.

In Experiments I to V inclusive, the specimens were examined at magnification ranging from 65 to 10,000 x and those areas of the

specimens selected for photography were photographed at magnification of 3,000X, 1,000X, 300X, 100X and 65X, in that order. By reducing magnification on subsequent photographs focus was maintained without inbetween adjustments, although checks were made on some occasions.

In Experiment VI, the magnifications chosen were 2,000x, 1,000x, 500x and 100x original size. These exposures were chosen merely to reduce the number taken and it was considered they also provided a better range than the previous magnifications used.

Some other microphotographs were taken of isolated and interesting features, throughout examination of the specimens, at various levels of magnification.

RESULTS

The results of the experiments are presented in the following order: V, I, II, III, IV and VI. Experiment V is presented first, out of chronological order, as it represents the surface appearance of the teeth prior to any bonding procedures.

Experiment V - Polished Enamel

The appearance, by visual examination, of these surfaces was one of a relatively smooth and shiny surface. The "relative smoothness" being the result of the pumicing procedure. This procedure smoothed and flattened the lines of imbrication and perikymata. These features were clearly more prominent before the surfaces examined were polished.

Plate 13 shows such a surface. This specimen was rejected for further testing due to the fractures present in the enamel (see adjacent to the coronal midline of the specimen). Direct forcep trauma is evident at the region of the cemento-enamel junction.

Plate 18 shows the pumiced enamel surface of one tooth specimen at:-

- a) 65 X,
- b) 100 X,
- c) 300 X, and
- d) 1,000 X

original size. This specimen (and its microphotographs) was chosen as

being representative of pumiced (polished) tooth surfaces.

Plate 18a shows a smooth enamel surface. In the upper part of the microphotograph, part of a large surface pit is visible.

Plate 18b shows a smooth surface upon which are small particles of debris. These particles may have been pumice particles which adhered to the tooth surface strongly enough to resist the cleansing procedures. As the magnification increases, (18c then 18d) the smoothness of the specimen decreases, until in Plate 18d, there are clearly visible scratch marks. These scratch marks have been caused by the abrasive action of the pumice particles and/or the brush bristles. In parts the surface also appears very smooth and in others quite pitted. Some of the pits appear to be partially or totally filled with particles of debris while other particles of debris are situated on the smooth areas. The lines of imbrication and perikymata are not visible on this sample and, in fact, their appearance was greatly reduced in prominence, if present at all; on most specimens.

The microphotographs shown in Plate 18 were chosen as being representative of the samples examined in Experiment V. No product variation was to be expected in this experiment as all the surfaces were treated in the same manner as described in the section on sample preparation. Only very minor surface variations were encountered.

Experiment I - Etched Enamel Surfaces

Plate 19 shows the buccal enamel surface of an etched tooth of a

tested specimen. When this specimen is compared to the specimen shown in Plate 13, it is readily apparent that the etching process has caused a change in appearance. The etched specimen is a whiter colour and appears opaque compared to the darker, shiny specimen of polished enamel.

Plates 20, 21 and 22 are the microphotographs at magnifications of 100 X, 300 X and 1,000 X original size, respectively, of the effects of acid etching upon the enamel surface. The subdivisions of the plates, labelled a, b, c and d, represent the typical surface view of the effects of the etching solutions of Products A, B, C and D, respectively, on tooth structure from the same mouth, at a particular magnification.

Specimens which exhibit tooth surface differences in effects of the same etching solution (e.g. IA1, IA2, IA3 and IA4) were examined but only one was photographed as similar appearances were found for each sample. In fact, Experiment IA1, IB1, IC1 and ID1 (Set 1) was chosen for presentation as this set was considered to offer the most satisfactory compromise in relation to the choice of the set which was most typical of all the four sets in all product reactions.

Similar selection procedures were used in all experiments.

The samples were not moved between photographs (i.e. between adjustments in magnifications) so that Plate 22a is a microphotograph of the area centrally located on Plate 21a (and 20a), at a higher magnification. Similarly Plate 21a is the area centrally located on Plate 20a, at a higher magnification.

Plate 20 shows the effects of the etching solutions used for the recommended exposure times on buccal premolar surfaces from the same mouth and viewed at 100 X original size. In Plate 20a (Experiment IAI) the lines of imbrication and the perikymata are more prominent and closer together due to the microphotograph being taken closer to the cemento-enamel junction, where such surface characteristics are found, than the other microphotographs which are of Experiments IBI, ICI and IDI.

Most etching activity has occurred, in all samples, in the pitted areas - the perikymata. Very little change is observed at this magnification 100 X original size) on the smoother lines of imbrication. Where these areas have been affected, it has been predominantly in, or about, scratch marks. Some areas of apparently unaffected enamel are present in all specimens.

Plate 21 shows the same surfaces at the higher magnification of 300 X original size. Very slight etching is shown in Plate 21d (Experiment IDI) - minor enlargement of rod end pits has occurred in the region of the perikymata whereas the lines of imbrication are even less affected. Plate 21a (Experiment IAI) shows a greater degree of etching effects than the previous specimen, although, it too, is only lightly etched. The relatively unaffected areas of the imbrication lines are somewhat narrower than in the previous specimen.

Plate 21b (Experiment IBI) shows yet a greater degree of etching although some areas (bottom left and top left) are unaffected and appear to be like an amorphous crust on the external surface. This feature appears

to be a prismless layer and, in fact, it covered almost the entire surface of this specimen. Certain areas appeared to be more selectively affected than others. This specimen (IBI) was the most heavily etched of all the samples of the IB series (IBI, IB2, IB3 and IB4). However, the appearance of the other product specimens (IAI, ICI and IDI) justified the selection of this tooth set for the representation of Experiment I.

Plate 21c shows the most severe etching of all the samples. However, its severity is only relative to the other specimens. It cannot be considered an outright example of severe etching. It, too, shows areas of unaffected enamel and the etching of the imbrication lines is slight.

Plate 22 accentuates the features seen in Plate 21. Plate 22c shows the prism etching patterns most commonly observed (the initial stages of prism core type of acid dissolution and the initial stages of prism periphery type of acid dissolution) as well as the sponge-like appearance of etched prismless enamel. These features were observed only in the perikymata. The other three Plates (21a, 21b and 21d) do not show much else but acid dissolution of the featureless surface layer.

Experiment II - The Adhesive Surface

Plates 23, 24 and 25 show the adhesive surfaces of Experiments IIAI, IIBI, IICI and IIDI. They were prepared by the method previously described and chosen as representative of the specimens of the tooth sets of the samples of Experiment II. These microphotographs show the ability of the adhesives to flow into the etched tooth surfaces and

consequently are negative reproductions of the etched tooth surfaces except for those areas where air bubbles, voids, etc., existed, the occurrence and problems of which have already been discussed.

Plate 23 shows the appearance of the adhesive surfaces at 100 X original size. The dark, smooth areas represent the unetched portions of the enamel surface and largely correspond to the convex regions of the tooth surface: the imbrication lines which appear as the deeper concavities in these microphotographs. Such regions are most apparent in Plates 23a and 23b. The spindle-like ridges of adhesive represent the adhesive that had flowed into the grooves originated by the abrasive pumicing process and enhanced in dimensions by the etching solutions. Their presence in all specimens, especially in Plates 23a and 23d (Experiment IIAI and IIDI), indicates that the original etch was only slight. Although very few such features are present on Plate 23b (Experiment IIBI) this microphotograph was taken on a more gingivally sited section of the specimen than the others, and its generally smoother surface indicates that the initial acid etching was poor and/or that there was less penetration of the adhesive.

Plates 24 and 25 show the same surfaces at higher magnifications. These microphotographs show the acrylic adhesives are able to flow into the minute spaces in and about the enamel surface produced by the dissolution effect of the etching solutions.

Some appreciation of the contribution of mechanical interlocking between the adhesive and the etched tooth surface, toward bond strength can be made by observing the trabeculated appearance of these surfaces.

Experiment III

Plate 26 shows the appearance of typical buccal enamel surfaces following the removal of the brackets and the adhesive.

The specimens a and c (Products A and C) had their attachments removed with pin and ligature cutters whereas the samples b and d (Products B and D) had their attachments removed with conventional band removing pliers.

- (a) Product A - On removal, the adhesive joint predominantly fractured at the enamel-adhesive interface, with minor areas (estimated to be less than 10%) visible where failure occurred within the adhesive (cohesive failure of the adhesive). No bond failure was observed at the polycarbonate bracket base-adhesive interface. The excess adhesive existing around the bracket base fractured cohesively in close proximity to the bracket base periphery. However, this failure did not occur around the entire periphery of the bracket base. Some areas of excess fractured at the enamel-adhesive interface also. The adhesive remnants (less than 10%) on the bracket-base site were difficult to detect due to the transparency of the adhesive.
- (b) Product B - Fracture on removal of this adhesive-bracket system occurred almost entirely at the adhesive-enamel interface. Only very small amounts of adhesive remained. The opaque, white colour of the adhesive, which did little for the bonded appearance of the system when in situ, made detection of the adhesive

remnants easier than in the other systems with the possible exception of Product C.

It was found that the sharp jaw of the band-removing pliers tended to gouge the enamel surface and so pin and ligature cutters were then used. No such damage occurred by this method. On testing one sample, the entire buccal enamel lifted away from the dentine at the level of the dentino-enamel junction. This "disaster" was considered to have been due to a weakening of the tooth structure as a result of the extraction procedure rather than due to an exceptional bond between the adhesive and enamel. Another consideration was that it may have been due to dehydration by the preserving fluid (50% Ethyl Alcohol). Boyde (1972) claims dehydration would not have occurred.

(d) Product C - In all cases the bond failure was entirely at the bracket base-adhesive interface. The adhesive-enamel bond seemed to be unaffected. Possible reasons for this occurrence include:-

(i) Lack of roughening of the bracket base surface, and/or,

(ii) A poor bond between the two as a result of incompatibility between the two products, or incomplete polymerisation of the adhesive due to failure of the ultra-violet light transmission (penetration or alteration in its wavelength) through the polycarbonate bracket, and/or,

(iii) A much stronger bond was formed with the enamel due to

the larger surface area of that bond or other influences.

These brackets were very easily removed.

- (d) Product D - It should be pointed out that this bracket base was so manufactured as to provide mechanically retentive areas and to increase its surface area.

Consequently, the adhesive was much thicker than for other products tested. The predominant failure type was a cohesive failure of the adhesive with some failure (less than half) occurring at the enamel-adhesive interface and also the adhesive-bracket interface.

Plate 27 shows the surface views at 100 X original size. Small amounts of residual adhesive can be seen on microphotographs a and b (Products A and B, i.e. Experiments IIIAI and IIIBI). These acrylic remnants were still firmly attached to the enamel surface and were predominantly situated in the rougher pitted regions of the perikymata. Plate 27c (Experiment IIICI) shows the surface of the adhesive at the adhesive-bracket base interface where the bond failure occurred. It is mostly smooth. However, polymerisation shrinkage voids can be clearly seen. These voids were mostly located directly beneath the bracket proper, whereas the adhesive beneath the smooth, constant-thickness, peripheral regions of the bracket base showed far less evidence of such polymerisation shrinkage. These findings indicate that the bracket itself could cause refractive changes in the ultra-violet light passing through it and/or alter the wavelength of the ultra-violet light. Either effect

would affect polymerisation. Plate 27d (Experiment IIIDI) shows an area of adhesive failure at the enamel-adhesive interface and a cohesive failure of the adhesive. The adhesive failure found in these samples left a very clean surface, whereas the bulk of the remaining adhesive was quite difficult to scale off the tooth surface. Applications of chloroform assisted its removal with a Morse scaler.

Plate 28 shows up the microscopic spicules of adhesive remaining attached to the tooth surface in Samples a, b and d. They can be seen even more graphically in Plate 29, especially in Plate 29a.

Plate 28c shows the polymerisation shrinkage and cracks at a higher magnification than in Plate 27c.

Experiment IV - The Repolished Enamel Surface

Plates 30, 31 and 32 show the repolished enamel surface. The polishing procedure has already been described.

It is evident, at each magnification, that no significant differences occurred in the polished enamel surfaces of the teeth, each having been subjected to a different bonding procedure. This is particularly so for the Specimens a, b and c (Products A, B and C). The slightly smoother surface of Specimen d in each plate indicates that the etching effect of the 30 second application of the 40.4% pyruvic acid may be minimal in consideration of bonding requirements and hence the surface was "recovered" more easily than in the other specimens.

Plate 30 shows that the previously prominent surface features: the imbrication lines and the perikymata are again evident, even if somewhat flattened and less prominent. Plate 30c shows two areas of adhesive left on the surface (bottom right and top right corners). Similar areas were found on all samples to various extents. Such gross areas remain because of the difficulty in seeing and feeling these thin adhesive areas before, during, and after cleaning procedures.

Plates 31 and 32 show similar surface appearances to those found at the same magnifications in Experiment V. However, these samples are slightly rougher, more pitted and more deeply scratched. Adhesive can be seen remaining in these surface pits with other debris particles. Similar remnants can also be seen lying on the enamel surface.

Further improvements in the smoothness of the enamel surface could be gained by application of an even finer prophylactic paste, with a rubber cup, to the surface. Such observations were made, but no photographic evidence is available for presentation.

Experiment VI - Product A (Etched Enamel)

Plates 33 and 34 show the appearance of buccal enamel surfaces of four premolar teeth, from the same mouth, etched with the same acid (Product A - 65% phosphoric acid, containing 7% of zinc oxide by weight) and etched for different periods of time.

Plate 33a = 30 second exposure

Plate 33b = 60 second exposure

Plate 33c = 120 second exposure

Plate 33d = 180 second exposure

The magnification shown in Plate 33 is 100 X original size, and that in Plate 34 is 1,000 X original size. Increasing surface roughness is clearly visible as the exposure time increases. A crack is visible, in Plate 33a, in the enamel surface. A crack of such size should have been detected under the light microscope, but it is of no consequence to this experiment. The surfaces shown in Plates 34b and 34c most closely resemble the surface shown in Plate 1, which Gwinnett, 1967 considered to be "a good bonding surface". Plate 34c shows typical acid dissolution patterns of the enamel prisms. Both prism-core-type of loss and prism-periphery-type of loss are visible, as well as projections of etched prismless enamel. The specimens 33a and 34a did not appear an opaque, white colour after etching, and so would have needed to have been re-etched according to Miura, et al (1972). The other specimens' surfaces all appeared as white, opaque surfaces after etching. Gross enamel loss is seen in Plates 33d and 34d. Such destruction is unnecessary and may even weaken adhesive bond strengths. The specimens shown in Plates 33c and 34c were shown as the surface with the most desirable appearance for bonding procedures due to the overall surface etching due to its nature of etch and its continuity over the entire surface. All these surfaces returned to the appearance of the specimens showed in Experiment IV when polished with the pumice-water slurry, although the 180 seconds specimen was slightly rougher.

Experiment VI - Product B (Etched Enamel)

Plates 35 and 36 show the appearance of buccal enamel surfaces of four premolar teeth, from the same mouth, etched with the same acid (Product B - 50% phosphoric acid, containing 7% of zinc oxide by weight and 1% sodium fluoride) and etched for different periods of time. The etching times were the same as for Experiment VIA.

These tooth surfaces were not typical of all the teeth tested in that they had a thick prismless crust of enamel over their entire surfaces. As the acid exposure time increases, there is an increasing loss of this layer (the decreasing amounts of smooth, dark surface), until in Plates 35d and 36d (particularly the latter) most of this crust has been dissolved away to leave a prism-end-etched pattern commonly found after acid etching. In Plate 36d, "islands" of unaffected enamel remain (near the top of the microphotograph) while Plate 35d shows the unusual surface appearance at a lower magnification. Although most of the surface crust has been lost, the underlying etched enamel does not appear to be irreversibly damaged. On polishing, this was found to be true, although minute porosities did exist. The porous nature of the etched enamel can be seen by observing the pores found within the etched prisms. Their size is extremely small as the enamel prism is only 5-6 microns in width.

It was suspected that this tooth set (Set 22, i.e. Experiment VIB1, VIB2, VIB3 and VIB4) could have been subjected to regular applications of topical fluoride. If this was so, it was not recorded and could not be substantiated.

Experiment VI - Product C (Etched Enamel)

Plates 37 and 38 show the appearance of buccal enamel surfaces of four premolar teeth, from the same mouth, etched with the same acid (Product D - 50% phosphoric acid, containing 7% by weight of zinc oxide), and etched for different periods of time. The etching times were the same as for Experiments VI A and VI B.

Plate 37 shows the increasing roughness of the etched enamel as the time increases, from a state of very slight etching; Plate 37a, to an obvious rough surface (even at this magnification) in Plate 37d. Plate 38 shows the increase more graphically.

Plate 38c represents a "classical" acid-etched surface, which shows the etching pattern of prism core dissolution. Such a surface should be a good surface for bonding procedures. However, once again the 180 seconds exposure shown in Plate 38d shows gross destruction of the enamel surface. Such severe etching is undesirable from the aspects of adhesion and surface recovery.

Experiment VI - Product D (Etched Enamel)

Plates 39 and 40 show the appearance of buccal enamel surfaces of four premolar teeth, from the same mouth, etched with the same acid (Product D - 40.4% pyruvic acid) and etched for different periods of time. The etching times were the same as for Experiment VI A, VI B and VI C.

Plate 38 shows that it was not until the 180 seconds exposure (Plate 39d) that any marked degree of surface roughness was apparent. In fact, the surface scratches left from the pumicing procedures are still clearly visible (indicating the minimal etching that had occurred) and they can also be seen faintly in Plate 39d.

Plate 40 shows an initial enamel loss pattern similar to Experiment VI B, A prismless crust which was quite thin in this specimen, is etched away to expose a good bonding surface after a 180 seconds exposure seen in Plate 40d. In this plate can be seen the 3 types of etched surface described by Gwinnett (1967).

DISCUSSION OF THE RESULTS

EXPERIMENT I - The Etched Enamel Surface (recommended etching times)

Plate 19 shows the microscopic appearance of an etched tooth specimen. In comparing its appearance to that of a polished tooth surface, shown in Plate 13, two features are of interest, viz:-

- a) The surface of the polished tooth presents a shiny appearance, whereas that surface of the etched tooth appears whiter, duller and more opaque. This appearance change is a result of the etching process which has roughened the tooth surface, and so less light reflected from it.

In clinical use, Muira et al 1971, Proffit 1972 and Buonocore 1971 use this decreased surface reflectivity of light as a test for successful etching. If such surface changes do not occur after etching and drying of the tooth surface, they all recommend that the process be repeated until such changes do occur. If such changes do not occur, and this occurrence is not detected by the operator, then a poor adhesive bond will result. It should be pointed out that this crude assessment of etching must be made when the surface is dry. Moisture (saliva, water, etc.) present on the surface tends to provide good reflection of light and so makes etching assessment difficult, if not impossible.

At present this subjective form of assessment of the etching

process is the only one available to the clinician (at this stage).

- b) These two plates clarify the sorting procedures used to select acceptable teeth, and, hence, tooth "sets" for testing. Plate 19 shows an example of a specimen accepted for testing. It shows no sign of actual damage due to extraction procedures, whereas the specimen shown in Plate 13 (a reject) clearly shows such damage.

Perhaps the first overall assessment of the effects of etching by the etching solutions of all four products is one of tremendous variation. This variation is seen in different areas of the same tooth, in different teeth from the same mouth, in different teeth from different mouths and, consequently, it is difficult to distinguish between the effects of the different etching solutions and the effects of tooth structure variation.

The etched specimens shown in Plates 20, 21 and 22 are the microphotographs showing the effects of the four etching solutions upon buccal enamel surfaces of teeth from the same mouth (see Table 4). The etching times were those recommended by the manufacturers, for each product.

The etching patterns produced in all cases are considered to show minimal effects on the surfaces, in relation to the surface changes suggested by Gwinnett (1971) as being conducive to good bonding. Plate 20 shows large areas of unaffected enamel. Those areas most

affected are the perikymata (concavities) and the base of the sloping walls of the imbrication lines (ridges) of the surfaces. Hoffman (1972) reported two types of surface patterns or morphology, viz:-

- a) A surface "characterised by a continuous, smooth flowing, undulating pattern, found mostly in the occlusal two-thirds of the enamel", and
- b) A surface described as a "discontinuous, overlapping pattern, in which the convex portions resembled parallel concentric ridges or bands with sharply delineated terminal borders". This type, he found predominantly in the cervical region of the enamel.

In all samples examined, the perikymata-imbrication line patterns observed were almost exclusively those of the undulating type (see Plate 20). The almost total dominance of this pattern probably resulted from two experimental procedures, viz:-

- a) The pumicing of the tooth surface. This process did cause some smoothing of the enamel surface, even when viewed with the naked eye.
- b) The microphotographs were usually taken of areas centrally located on the tooth surface (or adhesive surface) where such patterns are found almost exclusively according to Hoffman (1972).

Acid etching activity (perikymata and base of the slopes of the imbrication lines) seen in Plate 20 is not in accordance with the findings of Hoffman (1972). He reported most activity on the slopes and crests of the imbrication lines. There was generally very little etching of the crests of these features except where they had been scratched by the pumicing process.

Gwinnett (1967) reported the occurrence of prismless enamel in permanent teeth and large areas of such enamel are shown, especially in Plate 21b. Such enamel is seen to be highly resistant to acid attack, and its surface crust appears to be removed by penetration of the acid through minute pores in its surface, from which the acid undermines adjacent areas and so its disintegration spreads. Plate 21c shows the "honeycomb" appearance which was anticipated to occur on all surfaces. Plate 22c shows such a surface at a higher magnification and clearly shows the preferential dissolution of enamel prism cores reported by Poole and Johnson (1967), Sharpe (1967) and Hoffman et al (1969); due to acid demineralisation.

The etched enamel shown in Plates 21a, 22a 21d and 22d is of the prismless type reported by Gwinnett (1967). The etching solutions of Product A has caused a slightly greater degree of etching than that of Product D. However, again, most of the effects are observed in the perikymata regions. This is also in contrast to the findings of Hoffman (1972)

It should be remembered that the microphotographs show only small areas of tooth structure. At 100X magnification, 1 cm^2 on the plate represents 0.001 cm^2 of tooth structure and at 1,000X magnification 1 cm^2 on

the plate represents 0.0001 cm^2 of tooth structure. The size can also be gauged knowing that one etched enamel prism is approximately 5 microns in diameter. So although microphotographs are presented as representative of the experiment, this was not the case for all specimens in each series of each experiment. This consideration is mentioned because the specimen shown to represent the effects of Product C (viz. 20c, 21c and 22c) in Experiment ICI was in fact etched more severely than the specimens examined in Experiment IC2, IC3 and IC4. However, Experiments IAI, IBI, ICI and IDI were presented as being the most representative of the four sets tested in Experiment I. Also the severest portions of etching in Experiment ICI were found in the perikymata and not on the imbrication lines (perikymata region as photographed for Plate 22c).

Consequently, although Plate 21c shows the most severe etching of all the samples presented, its severity is still considered to be one of relativity when compared to the other specimens. It too, showed areas of unaffected enamel and the etching of the imbrication lines was slight (see Plate 20c). In Plate 22c, the perikymata regions show etching patterns of the three types reported by Gwinnett (1971) (see Plate).

If such patterns had been observed more generally, then that surface would have been considered a "good" bonding surface.

Although the optimal surface appearance is not known (Gwinnett, 1971) there should be some "ideal roughness" that produces optimal wetting and so provides maximal bond strength for a particular adhesive (Eich

et al, 1972). By comparison with microphotographs presented by Gwinnett (1971), Hoffman (1972), Johnson et al (1971), Miura et al (1971), Newman and Facq (1971) and Gwinnett and Buonocore (1972), the microphotographic evidence presented in Plates 20, 21 and 22 indicates that the surfaces were insufficiently etched by all etching solutions tested. Product C was considered to be the most active and Product D the least active in regard to etching effects of these samples.

EXPERIMENT II - The Adhesive Surfaces

Plates 23, 24 and 25 show the appearance of the adhesive surfaces at the enamel-adhesive interface. These plates support the evidence presented in Experiment I but in a "negative" form, i.e. these microphotographs are almost complete negatives of surfaces treated in the manner described in Experiment I. They are incomplete negatives as it must be considered that some voids, air pockets etc. did occur during placement of the adhesive and there was probably some dimensional changes during polymerisation (not so according to Muira et al 1971 but admitted by Newman 1969), imbibition of water during immersion in the water and release of stresses (Buonocore 1963). Voids etc. could not be detected or their location described as no replica of the original surface was available for comparison. It can only be presumed that they must inevitably occur.

The high magnification microphotographs (Plates 24 and 25) show the commendable attributes of all the adhesives, in relation to their abilities to wet the etched surfaces and flow into the "trabeculated, honeycomb porosities" of the etched surfaces.

This ability of each adhesive to flow into these minute spaces must provide a great deal of mechanical interlocking of the adhesive and the adherend (the etched enamel surface). This mechanical interlocking, in turn, must make a considerable contribution to the overall bond strength of the adhesive-adherend joint.

The good wetting and spreading properties of the adhesives on the etched enamel surface provides good surface contact between the adhesive and the adherent, and so must provide favourable conditions for physical and chemical (if any) adhesion to occur between them.

The apices of the adhesive projections (which were those parts at the bottom of the enamel pits, fissures, etc. are relatively smooth when examined at magnifications greater than 3,000X original size. However, most projections seen in Plate 25 are sharply defined, this suggests that the voids and air pockets, if and where they exist, were probably extremely small.

The adhesive surfaces were not examined in transverse section, but the appearance observed in these surface views are in accordance with the evidence presented by Buonocore et al (1968) and Gwinnett and Matsui (1967) in their descriptions of the relationship of adhesives to etched enamel surfaces and the presence of penetrating "tags of adhesive".

EXPERIMENT III

Plates 26, 27, 28 and 29 show the macroscopic and microscopic effects of bracket removal. The procedure and results have already been

described.

Mention has been made of the fact that the band-removing pliers caused a gouging of the enamel surface. When the jaw of the pliers was placed on the cervical aspect of the bracket (Product B), with the padded jaw on the occlusal surface, and pressure applied, the plastic bracket merely collapsed and the bonds failed to rupture. Hence the lower jaw was placed against the tooth beneath the adhesive and when pressure was applied the adhesive and bracket were removed. However, it was almost impossible to avoid the cervico-incisal gouging that occurred. Hence this technique was discarded, and pin and ligature cutters used to conduct the remaining "removals" for Products B and D.

No damage was detected, using this method, when the surfaces were observed visually by the naked eye, or beneath the light microscope, or with the aid of the scanning electron microscope.

The bond failure site (adhesive-bracket base interface) in all specimens of Product C was disappointing and unexpected. Further testing with a roughened surface on the bracket base provided a much stronger bond (in comparison to the above, which were easily removed) but some samples still ruptured at this interface. This site of bond failure could be advantageous, clinically, as the enamel surface remains protected by the adhesive if the bracket is lost.

This would not be the case for the other products where the etched surface would be exposed to attack following bond failure, from the oral environment.

Plate 41 shows the boundary of the adhesive and uncovered, hence unprotected, etched enamel adjacent to it. Such surfaces were observed adjacent to the brackets and adhesives of all products. Such areas would be most retentive of plaque, materia alba etc. and very difficult to clean, in vivo, due to archwire location. The retention of such materials could cause decalcification if left unattended, and so one of the supposed advantages of direct bonding would be lost. Monus and Grenoble (1972), and Lenz and Muhlemann (1963), all claim the enamel surface remineralises, in vivo, under such conditions, also acquiring a new organic surface integument, Meckel 1965) within a few days. However, no research has been reported on this specific situation.

The findings of the above authors are of plain, etched surfaces. It should be noted, however, that Muira et al (1971) reported no such decalcification occurring in their long term clinical study. Retief et al (1970) claims that patients' mouths with directly bonded attachments were cleaner than those with conventional full band techniques.

At a microscopic level the bond failure was observed to be predominantly a cohesive one of the adhesive or an adhesive failure at the enamel-adhesive interface (except for Product C). Microscopically, especially at higher magnifications the above failures were noted, and in addition to them, cohesive failure of some enamel projections was observed also. This latter failure was very close to the level of the original enamel surface and never along the base plane of the etched porosities. Also at the high-powered microscopic levels it was noted that there were considerable amounts of adhesive remaining in the enamel

porosities. Gwinnett and Matsui (1967) claim these adhesive remnants provide considerable protection to the enamel surface following bulk adhesive removal both before and after surface repolishing.

EXPERIMENTS I - The Original Polished Surface and

II - The Repolished Surface

The original polished surface is shown in Plates 13 and 18 while the repolished surface is shown in Plates 30, 31 and 32. These two surfaces are to be discussed together for ease of comparison.

The original surface, through the process of pumicing, has lost a lot of the original detail that it can only be presumed it had, according to the studies and reports of Boyde (1971), Eisenberg (1938), Gerould (1944), Gustafson and Gustafson (1967), Gwinnett (1967), Hoffman and Gross (1967), Hoffman et al (1969), Innes and Schroff (1966), Meckel, et al (1965), Orban (1962), Provenza (1964), Scott and Symons (1964) and Scott and Wychoff (1949), as no observations of the enamel surface were made prior to the original polishing procedure at microscopic levels.

The appearance of the polished enamel surface most closely resembles that described by Scott et al (1949) for aged teeth. The surface was an almost smooth and featureless structure. The imbrication lines had been almost flattened and numerous scratch marks and particles of debris were observed both upon the surface and within the rod end pits and other surface defects.

The repolished surface appeared very similar to the original polished

surface, particularly at lower levels of magnification.

Macroscopically, no difference could be observed other than the repolished surface being slightly smoother. Microscopically, especially at higher magnifications, the surface was slightly rougher. Further research into the long term effects of this rough surface and the loss of enamel from the surface may be justified. However, even further polishing with a finer prophylactic paste was observed to offer further improvement in surface texture. However, no photographic evidence is available to substantiate this observation.

Muira et al (1971) claim that normal toothbrushing will improve surface smoothness within one week, after one application of pumice following bracket-adhesive removal. Monus and Grenoble (1971) claim spontaneous remineralisation will occur, in vivo, so restoring a smooth tooth surface within three days. The application of the second, finer paste would be a conservative prophylactic procedure, as it would appear to enhance total surface recovery.

The adhesives, with the exception of Product B, were difficult to see on the tooth surface unless in considerable bulk. The adhesive of Product B is an opaque, white colour and while it may detract from its aesthetic value, it did make its detection a lot easier, especially when compared to the transparent adhesives used in other systems. Chloroform applications assisted gross removal procedures.

Some areas of adhesive were not detected during the cleaning procedure and remained attached following polishing. The clinical significance

of such adhesive retention on the tooth surface is not known.

The repolished surface appearance indicated good enamel recovery had occurred after polishing, following bonding procedures although the recovery was not absolute.

EXPERIMENT VI - Etched Enamel Surfaces (at various exposure times)

In consideration of the results and discussion of the tests in Experiment I only small additions need be made to them in discussion of the results of Experiment VI.

It was felt that as a result of the evidence observed in Experiment I that the recommended etching periods for all the acidic etching solutions were inadequate. Such exposure times failed to produce etched surfaces most favourable for the provision of the maximum possible bond strengths, as according to the guidelines of good bonding surface appearances reported by Gwinnett (1971) and others. It must be remembered that the teeth used had undergone, at least a post-formation, pre-eruption uptake of fluoride in their surface enamel (Craig 1972).

The most desirable surface changes caused by each etching solution occurred at the following exposures:-

- a) Product A - 2 minutes (+ or - $\frac{1}{2}$ minute)
- b) Product B - 2 minutes (+ or - $\frac{1}{2}$ minute)
- c) Product C - 2 minutes (+ or - $\frac{1}{2}$ minute) , and
- d) Product D - 3 minutes

The results are shown in Plates 33 to 40 inclusively.

It is difficult to make comparisons between the products, as single tooth sets were used for each product. However, the results do clearly show up, once again, the heterogeneity of the tissue concerned.

The surfaces chosen as most desirable (see Plates 33c and 34c, 35c and 36c, 37c and 38c, 39d and 40d as evidence of the surfaces deemed "good bonding surfaces" for Products A, B, c and D respectively) were repolished (but no bonding procedures were used on them) and examined again in the scanning electron microscope. These surfaces showed equal recovery to an original-likeness, as did those of Experiment IV. No photographic evidence is presented.

Exposures longer than those recommended above, were deemed to be unnecessarily long in duration, as the surface became very rough indeed. This rougher surface did not recover as easily on polishing as did the other specimens. It is doubtful whether any significant increase in bond strength and durability would be achieved. It could even result in cohesive failure of the enamel when the bond is subjected to stress.

It was of particular interest that on these specimens acid dissolution of both prism cores and prism peripheries was observed for all the acids used. This is in contrast to the findings of Hoffman, et al (1969) and Poole and Johnson (1967), who claimed that acid etching causes a demineralisation of prism cores, whereas E.D.T.A. (a chelating agent) attacks their peripheral boundaries. It was observed, however, that core dissolution was the predominant pattern. These findings are in accordance

with those of Gwinnett (1971).

Plates 42, 43, 44 and 45 and 46 show the different types of prism dissolution caused by some of the acids tested. Such appearances were considered typical of the more heavily etched areas. These appearances were observed on samples etched with all the acids tested. The "classical" surfaces presented by Gwinnett (1971), see Plates 2 and 3, were not observed. Gwinnett's examples were etched much more strongly than most of the specimens examined in this study. It is doubted whether such appearances were truly representative of the surface areas of the teeth examined and consequently they are suspected as being absolute examples of two possible types of prism dissolution.

CONCLUSIONS

An analysis of the results has indicated that the following conclusions may be made:-

1. Pumicing of "normal" enamel surfaces results in a smooth, reflective surface when examined in a dry state, by the naked eye. Acid etching of the enamel surfaces can cause similarly observable changes to the enamel surface. Etched enamel surfaces appeared duller (more opaque) and whiter, when dry, than dry, polished enamel surfaces. Wet, etched enamel surfaces and wet, pumiced enamel surfaces had similar appearances.
2. The typical appearance (microscopically) of a "good bonding surface" was discussed. It was found to be a generalised roughening of the enamel surface, approximately 10-30 microns in depth and it resulted from the dissolution of enamel by the three methods observed and described by Gwinnett (1971).

The manufacturers' recommended etching times for the four etching solutions tested, were found to be inadequate. The etched surfaces produced by the tested solutions at these exposure times were not considered to be conducive to the attainment of maximal adhesion, on the particular teeth used in the tests.

The unexpectedly light etching produced by the tested etching solutions, at the recommended exposure times, was considered to be due to increased surface resistance to etching as a result of a post-developmental, pre-eruptive (and to a minor degree: post-eruptive) uptake of fluoride in the enamel surface.

Due to the failure of the etching solutions tested, to effect adequate surface changes, at the recommended exposure times, on the tooth samples tested, new exposure times, for each etching solution, were determined by histological assessment of surface changes, at different exposure times. The new exposure times recommended are:-

Etching Solutions - Products A, B and C = 2 minutes
(± ½ min.)

Etching Solution Product D = 3 minutes

As these new exposure times resulted from microscopic assessment, by only the author, the subjectiveness of the assessments is acknowledged.

The visual assessment (macroscopic) by the naked eye of acid etching effects (viz: the degree of reduction in reflectivity of the enamel surface), is an adequate means of such assessment. It remains in use because of the lack of an alternative for clinical use.

The predominant type of enamel prism dissolution was that of the prism-core-type. However, all the tested acids were also observed to preferentially dissolve the region of the enamel prism boundaries, in many instances. The pitted surface (etched crystallites) of etched prismless enamel was also observed.

The tremendous variations in surface appearances, in all the specimens examined, clearly demonstrated the heterogeneity of the enamel surface. The variations observed were similar to those reported in the literature.

3. When the repumiced enamel surface was visually assessed following completion of bonding, removal and repolishing procedures, it was considered to have recovered to its pre-bonding, pumiced condition.

This apparent recovery was found to be incomplete when they were examined microscopically. The incompleteness of the recovery, however, was only observed at high magnifications (in excess of 500 X original size).

The degree of surface recovery at such microscopic levels was observed to be greater when a finer prophylactic paste was used to further polish the surface.

Obviously some tooth structure is lost as a result of bonding procedures. Only in vivo studies will assess if

there is any clinical significance (e.g. increased incidences of abrasion, decalcification, caries, etc.) as a result of the microscopically, incomplete surface recovery and/or the minute loss of tooth structure.

Topical fluoride application is advocated as a prophylactic and/or conservative procedure following surface repolishing. Despite the lack of clinical research, it is felt that there would be no significance in the microscopic incomplete surface recovery and the minute loss of tooth structure.

4. All adhesives were observed to exhibit good wetting and spreading abilities when applied to the etched enamel, as directed by the respective manufacturers' instructions, in bonding procedures.

5. Plastic brackets were deemed to have more aesthetic appeal than the bonded stainless steel brackets. However, all the tested brackets were considered to be an aesthetic improvement over conventional stainless steel bands and brackets. The use of band-removing pliers for adhesive-bracket removal was found to cause permanent damage to the enamel surfaces, in some instances. Pin and ligature cutters (used with a pinching action across the adhesive) removed the adhesive and bracket with equal effectiveness and without any sign of iatrogenic trauma to the enamel surface. Consequently their use is recommended for adhesive-bracket

removal.

The opacity of the O.I.S. adhesive, although of less aesthetic appeal than the other adhesives, assisted in its removal from the enamel surface.

All the other adhesives were transparent and this physical property, made visual assessment of their removal difficult.

Areas (patches) of adhesive were observed on the enamel surface, after completion of removal and polishing procedures. The significance of the presence of such areas is not known.

7. The scanning electron microscope has been found to be an extremely valuable tool for such histological and topographical observations, made in this study. The depth of field of the instrument, at all magnifications, far exceeded those possible with any light microscope. Specimen preparation was extremely simple.

SUMMARY

The effects of four direct bonding systems, on the enamel surface, were examined visually and with the aid of a scanning electron microscope, with particular reference to the effects of their etching solutions.

It was observed that the manufacturers' recommended exposure times, of the etching solutions tested, were inadequate for the tooth samples used. New exposure times were advocated. Further research seems warranted, to test these new etching exposure times by mechanically testing bond strengths of the adhesives concerned.

It was also shown that the recovery of the enamel surface by a polishing process was generally good but a high magnification, microscopically incomplete.

In vivo, research is advocated to assess the clinical significance, if any, of such microscopically incomplete surface recovery and of the minute loss of tooth structure from the original enamel surface.

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Plate 1 - Acid Etched Enamel (from: Gwinnett, 1971)

A scanning electron microphotograph showing a single experimental area, within which, are a number of topographic variations. Prism cores may be etched preferentially (1), as are prism peripheries (2), while both may be etched to a similar degree resulting in a generally pitted appearance. 1,200X original size.

Plate 2 - Acid Etched Enamel (from: Gwinnett, 1971)

The prism cores are demineralised and the prism peripheries remain relatively intact. 2,000X original size. A scanning electron microphotograph.

Plate 3 - Acid Etched Enamel (from: Gwinnett, 1971)

In contrast to Plate 2, the cores remain relatively intact and the prism peripheries are selectively demineralised. 2,000X original size. A scanning electron microphotograph.

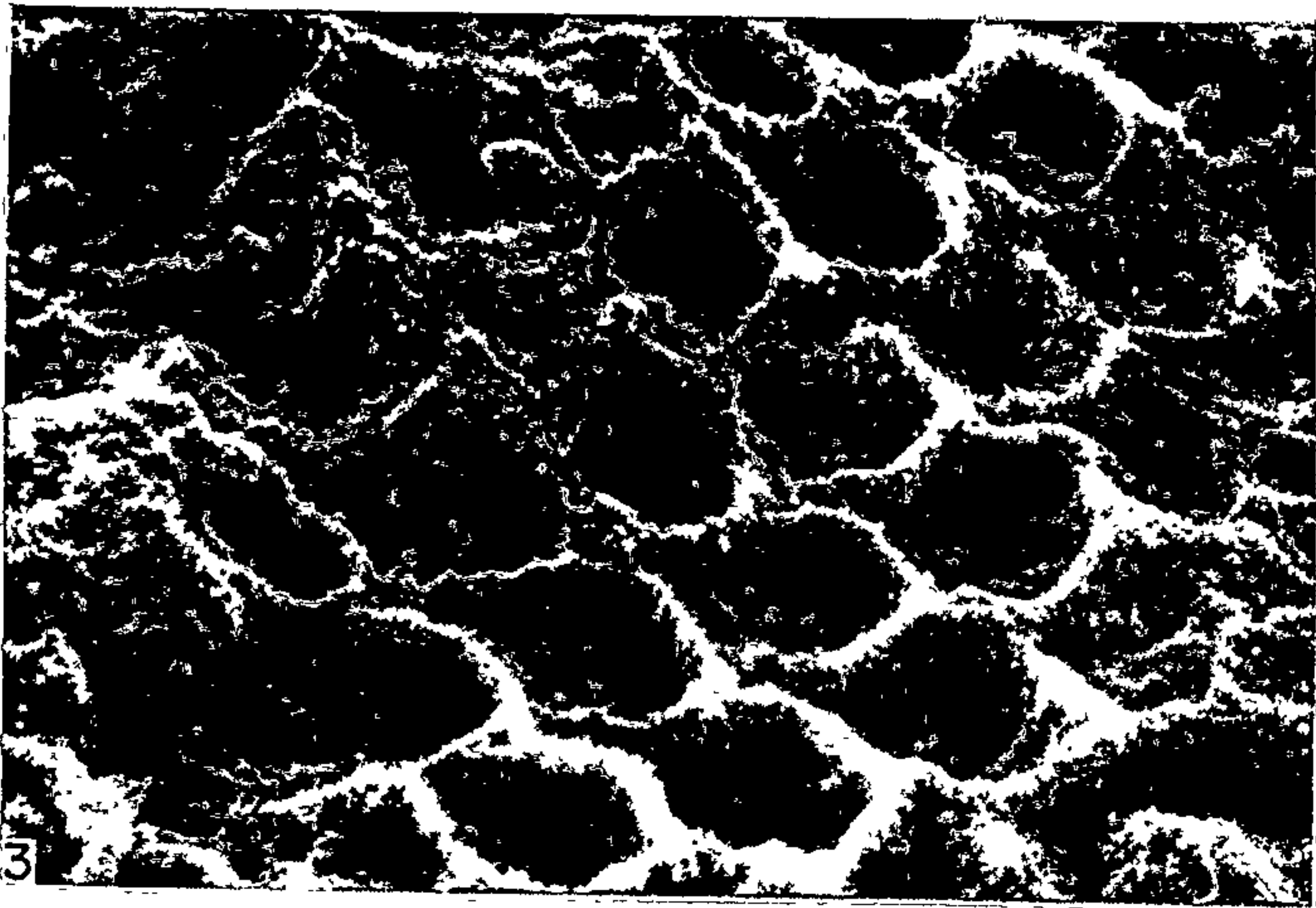
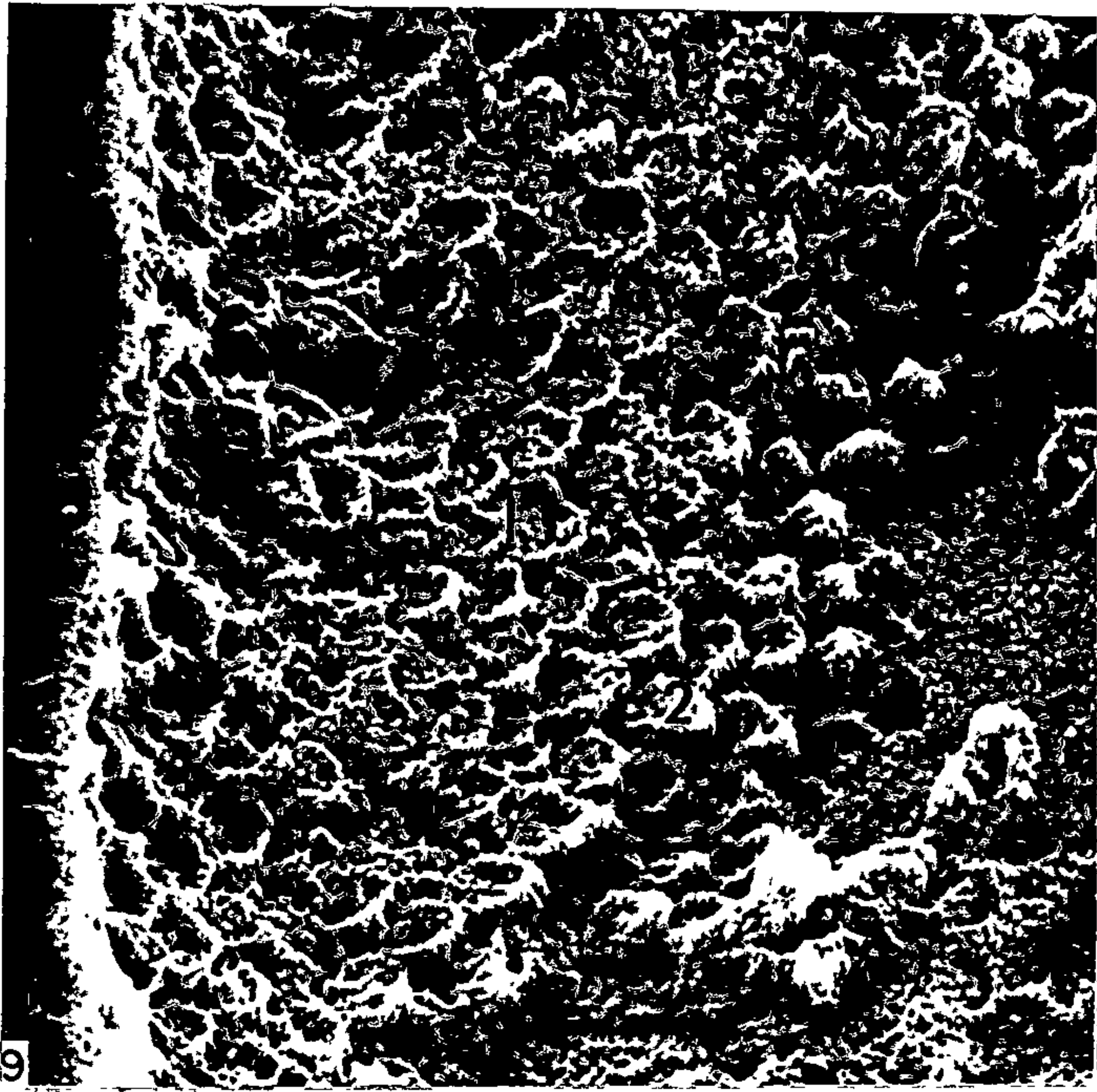


Plate 4 - Product A Materials

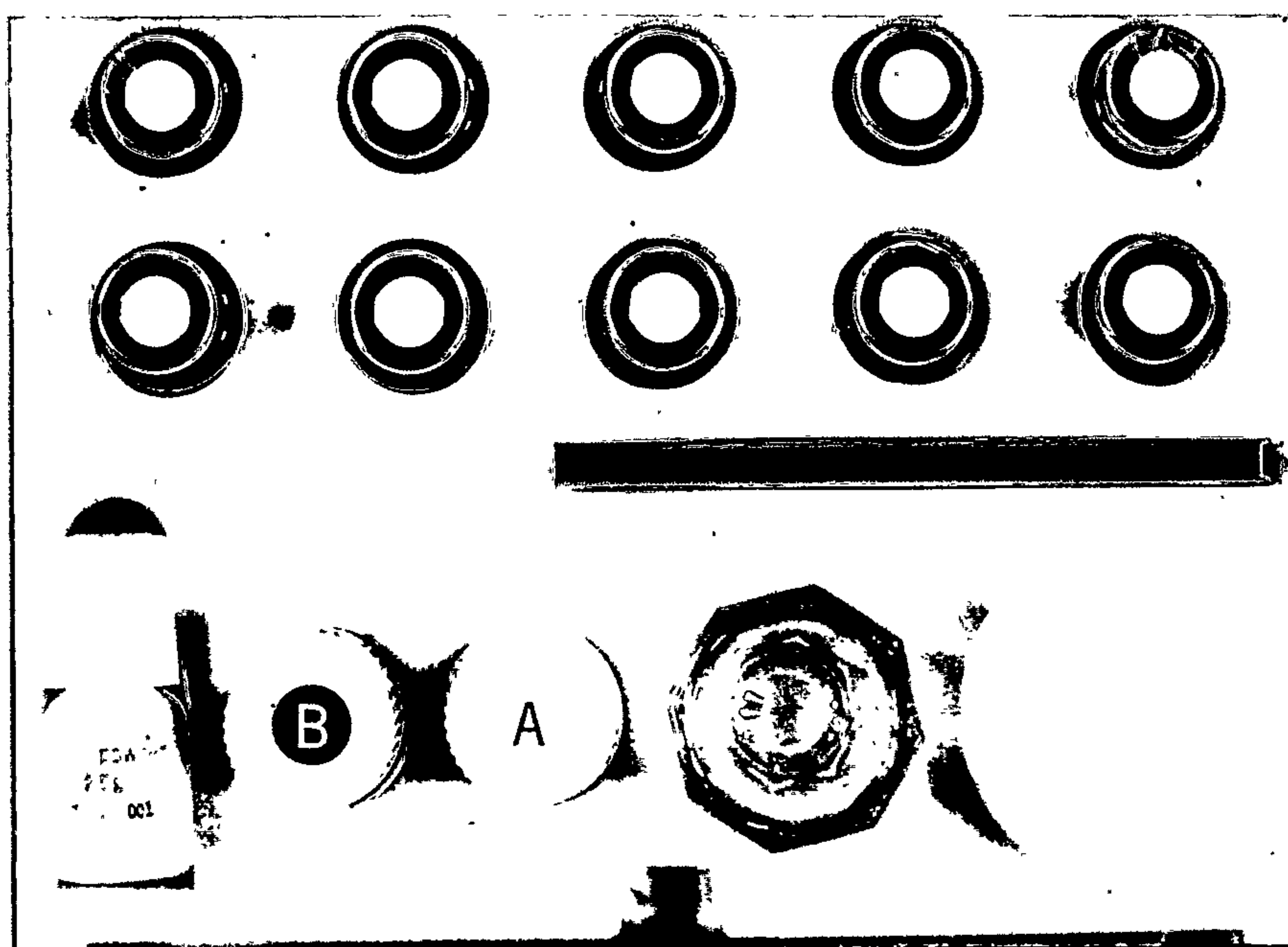


Plate 5 - Product B Materials

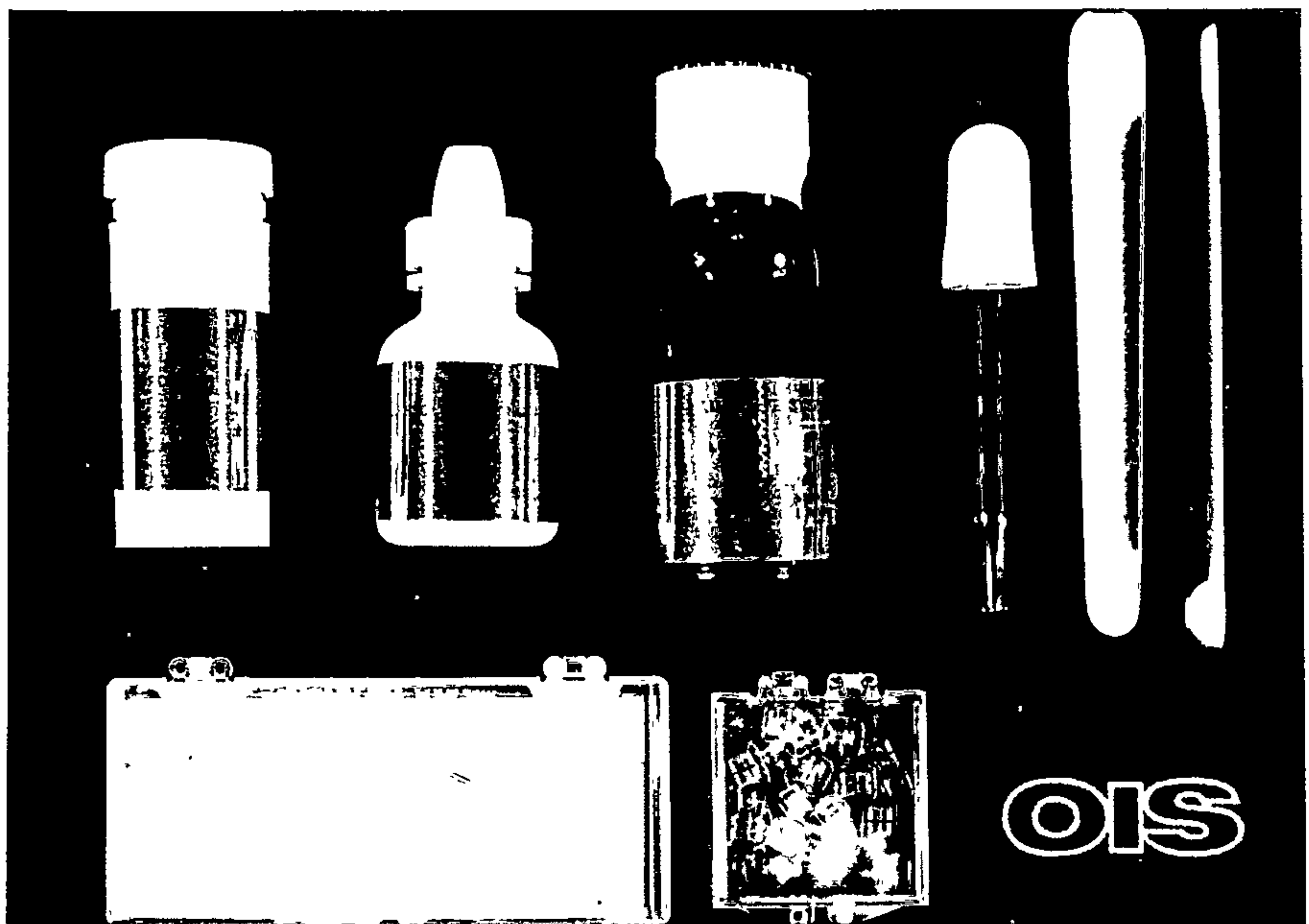


Plate 6 - Product C Materials

a) materials

b) ultra-violet light "gun" and housing

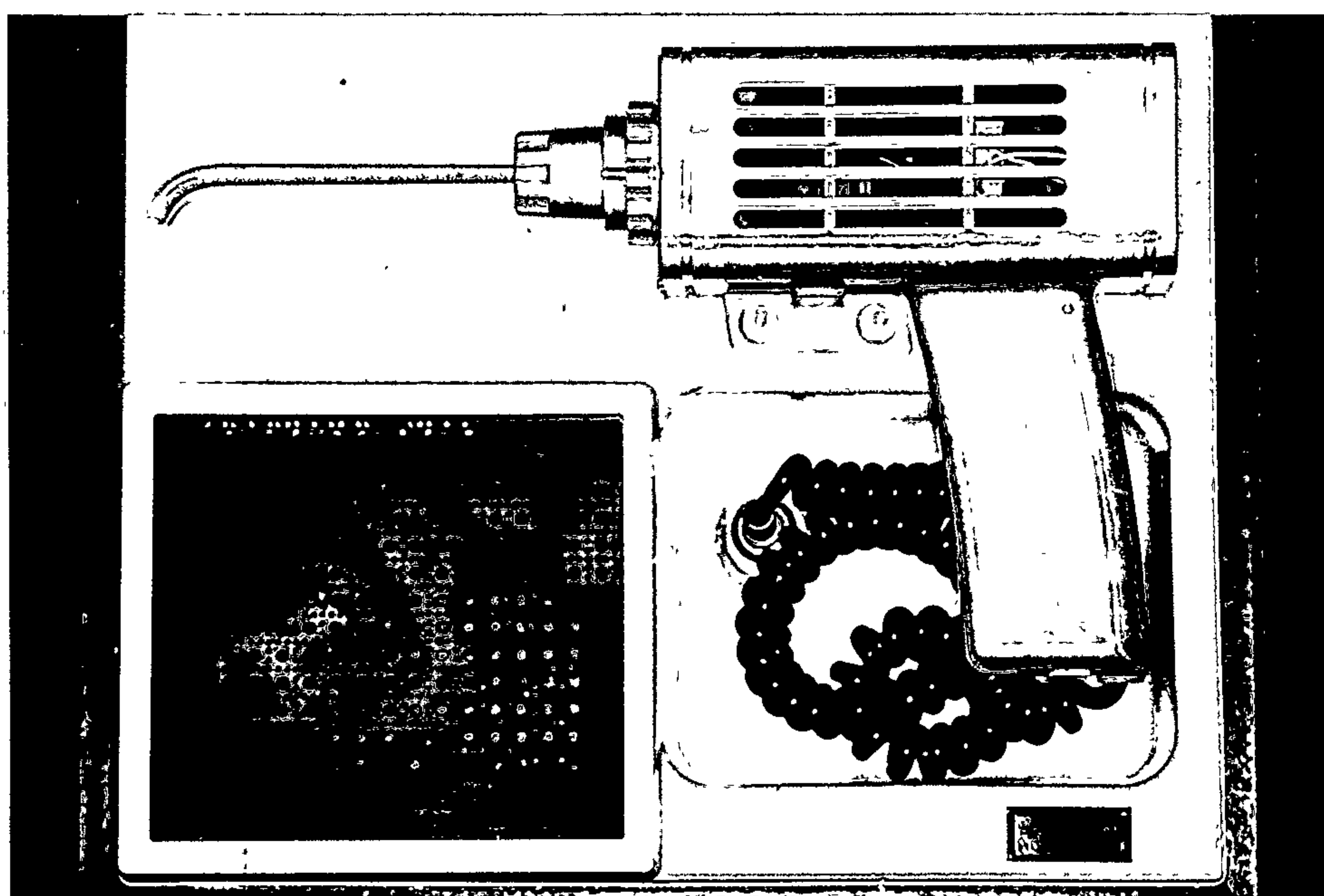
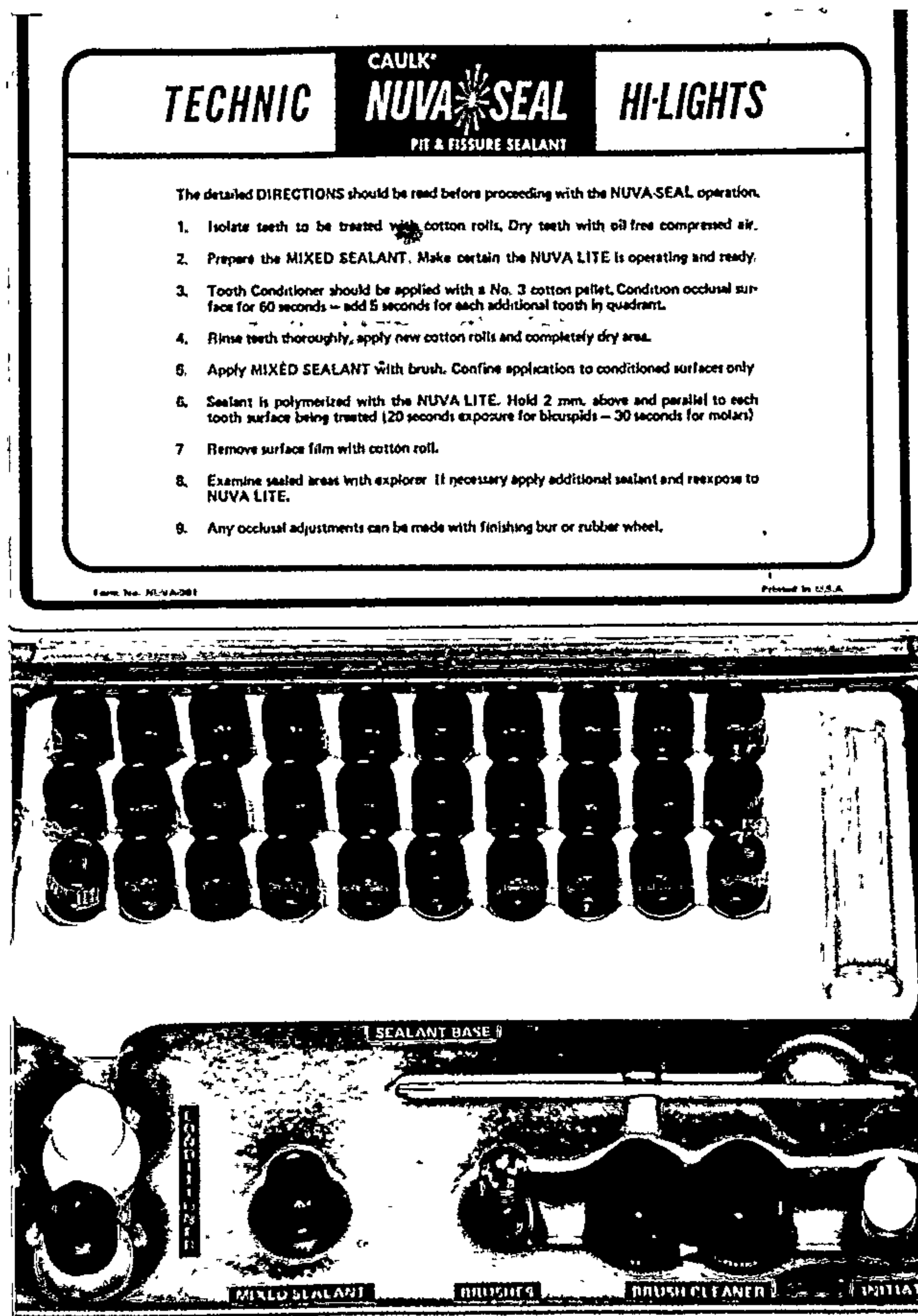


Plate 7 - Product D Materials



Plate 8 - The Brackets

From left to right, the brackets are from:-

- a) Product B
- b) Product A
- c) Product D

The brackets of Product A were also used for the direct bonding with Product C.

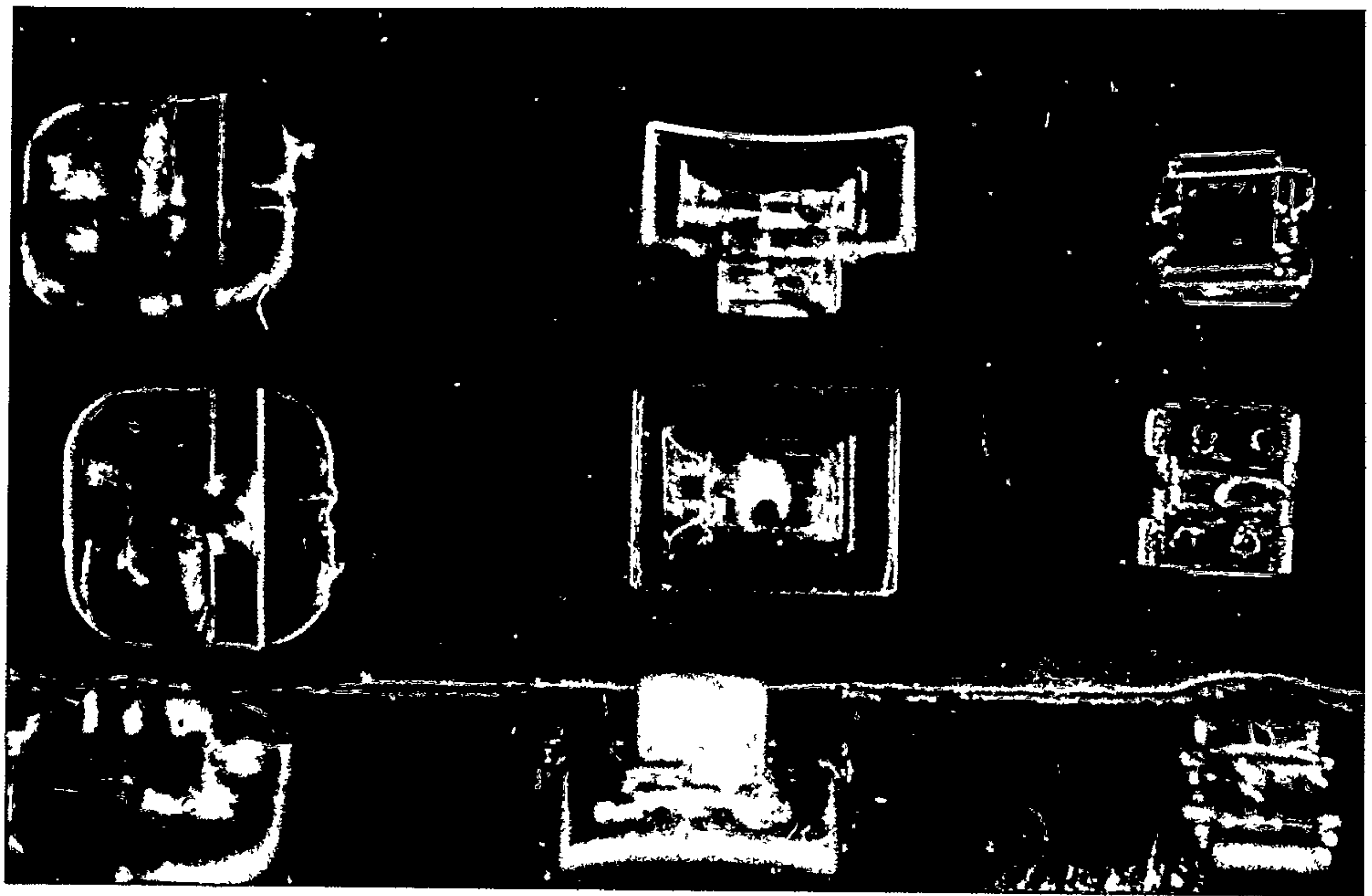


Plate 9 - Bonded Bracket

This photograph shows the bracket and adhesive of Product A, in position on the tooth surface.

Plate 10 - Bonded Bracket

This photograph shows the bracket and adhesive of Product B, in position on the tooth surface.

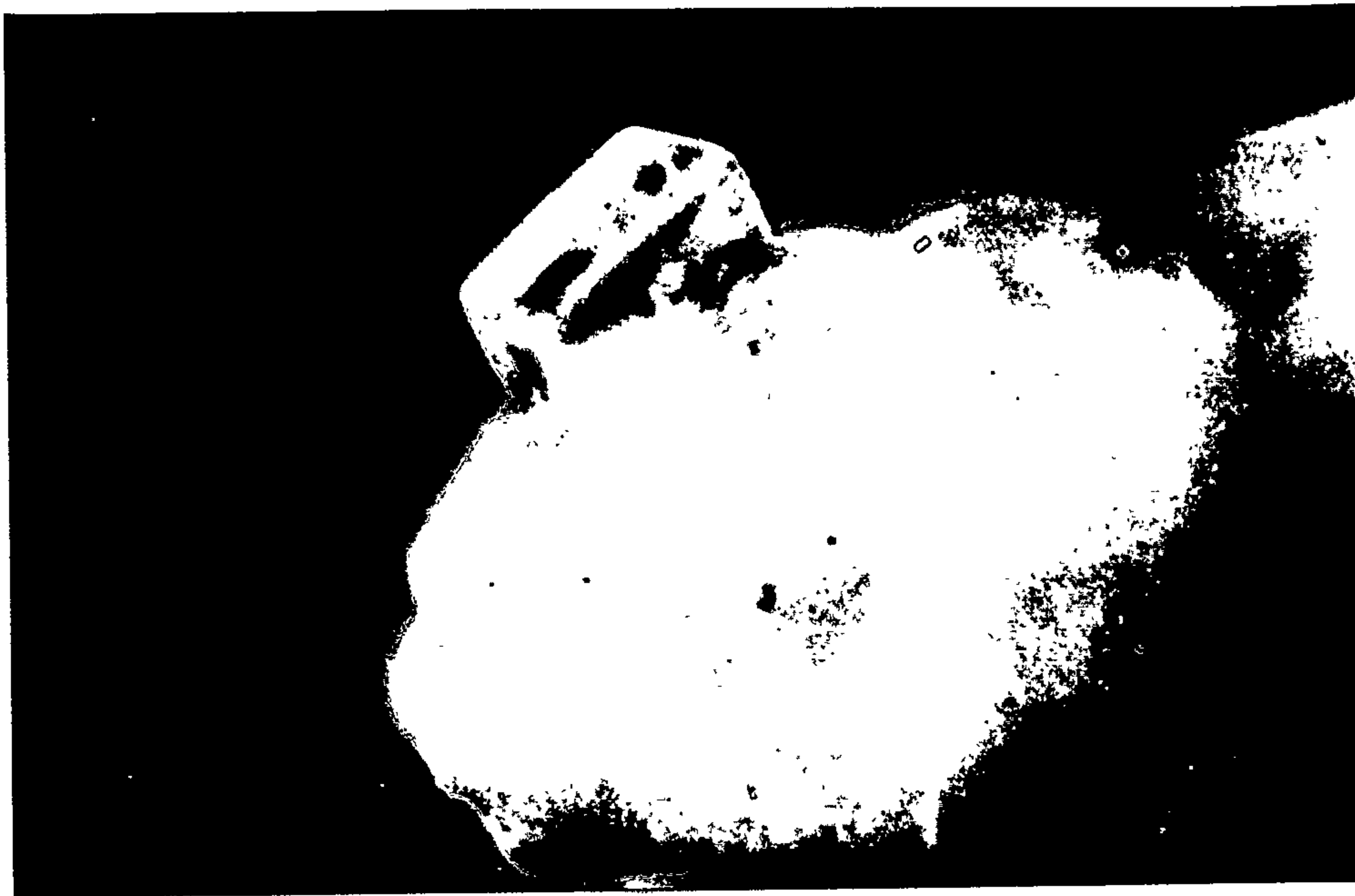


Plate 11 - Bonded Bracket

This photograph shows the bracket and adhesive of Product C, in position on the tooth surface.

Plate 12 - Bonded Bracket

This photograph shows the bracket and adhesive of Product D, in position on the tooth surface.

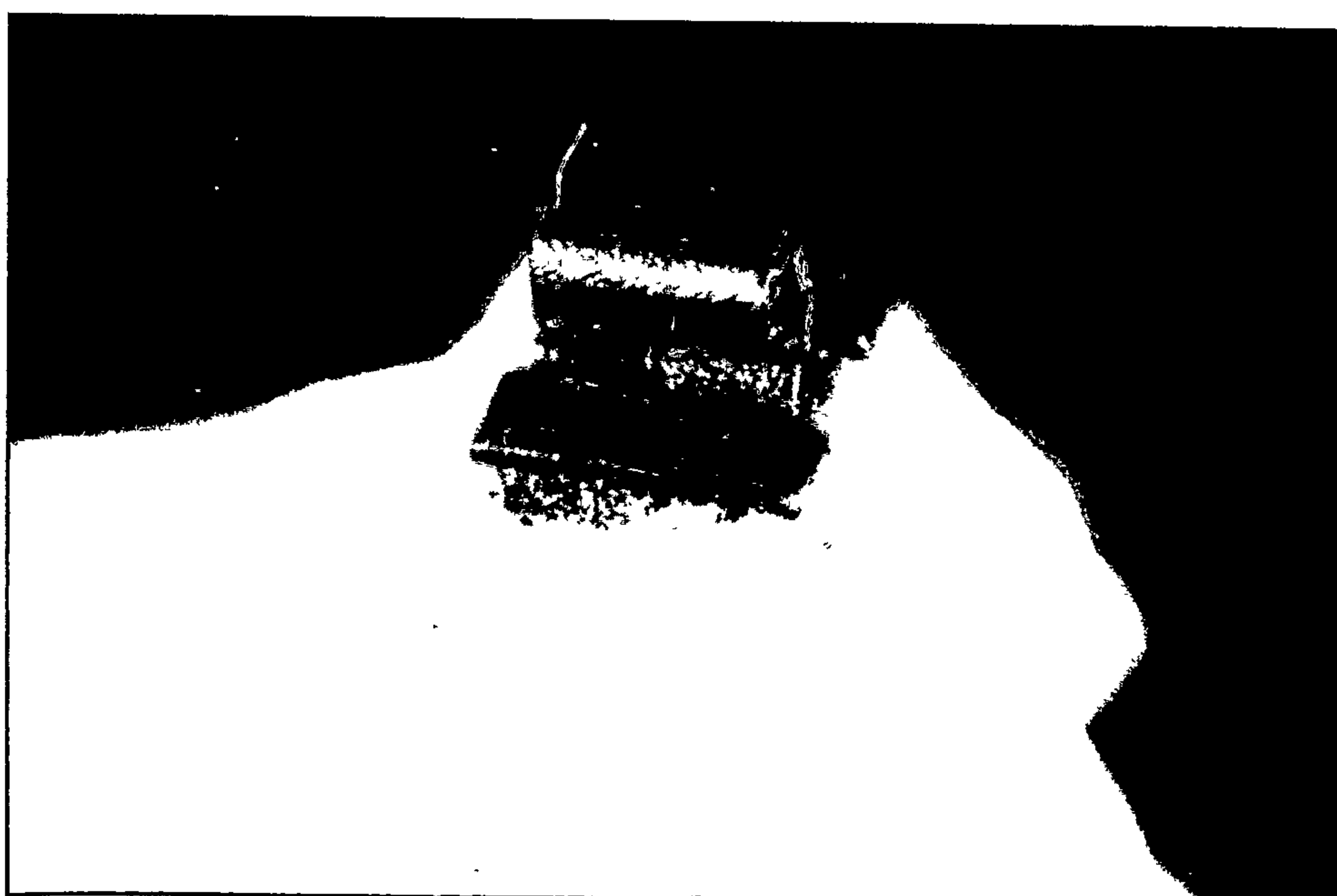
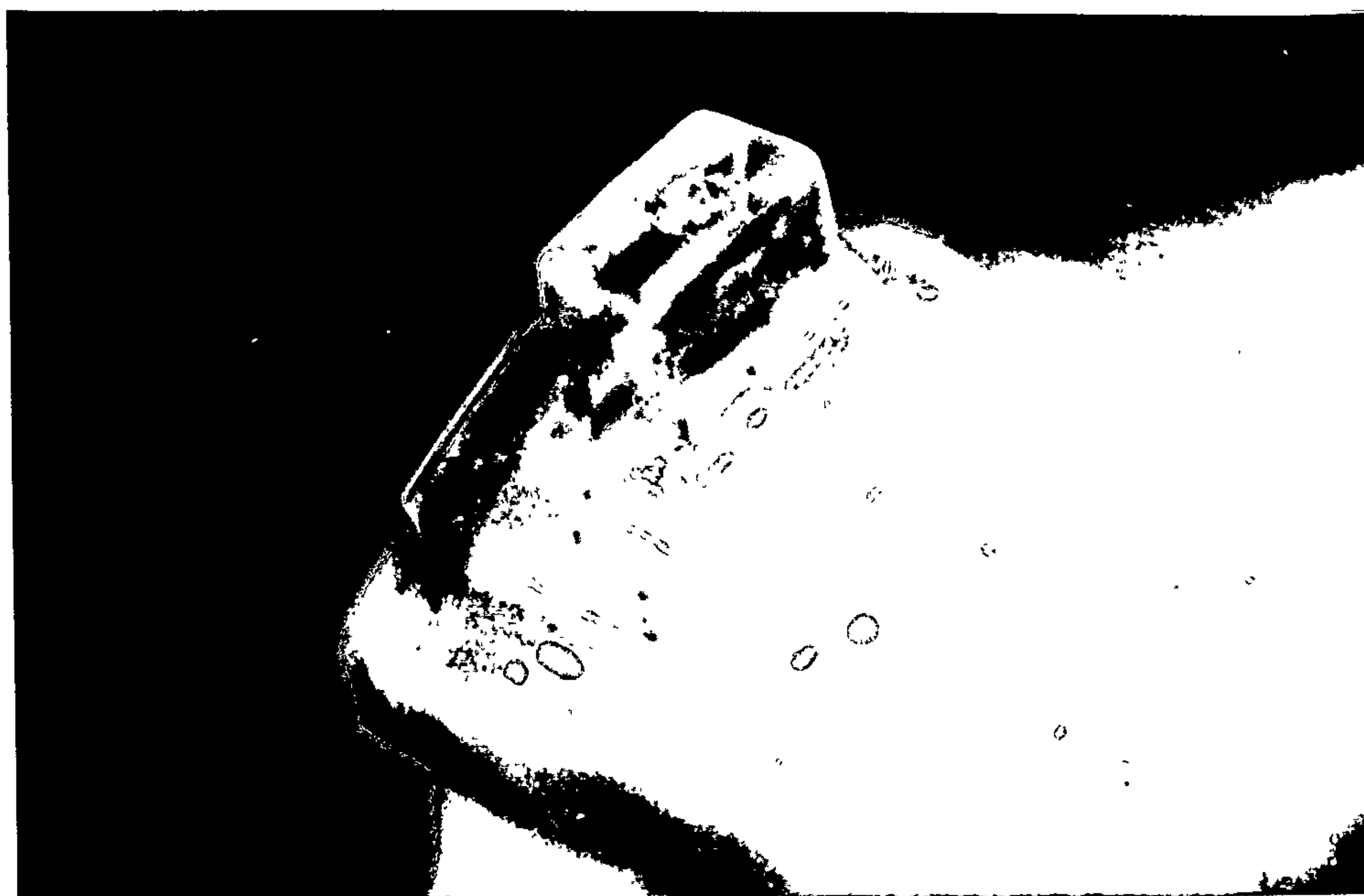
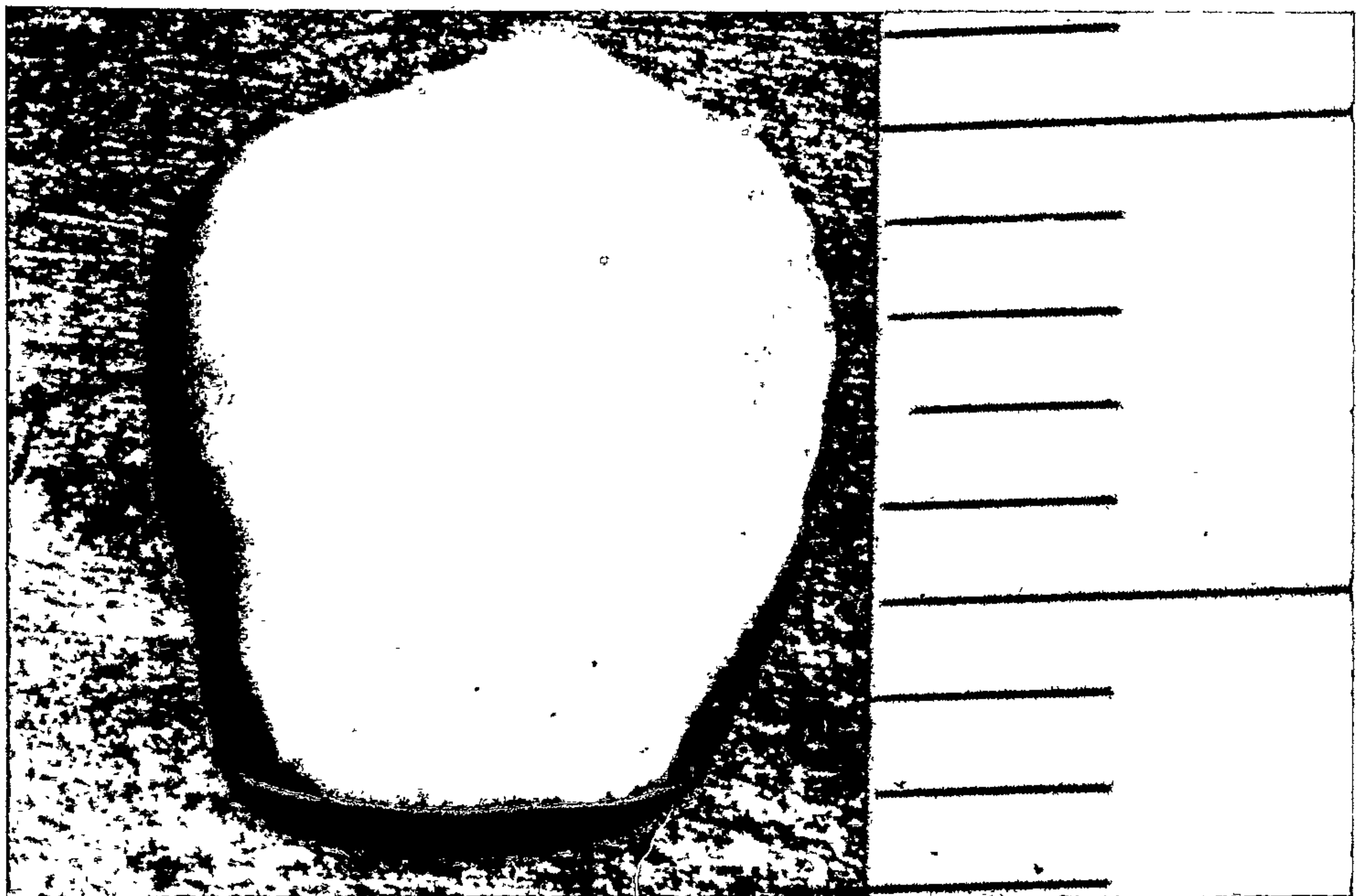


Plate 13 - Tooth Specimen

This photograph shows a typical specimen. The size of the specimen can be gauged from the graduations (mms) alongside it.

This specimen is one with a polished tooth surface and was not used in any of the tests.



Plates 14a-d - Adhesive Surface Preparation

Plate 14a

This photograph shows the plastic tubing placed on the tooth surface around the bracket and adhesive. It was held in position with sticky wax, which can be seen at the incisal and the cervical aspects on the outside of the ring.

Plate 14b

This photograph shows the plastic tube filled with resin.

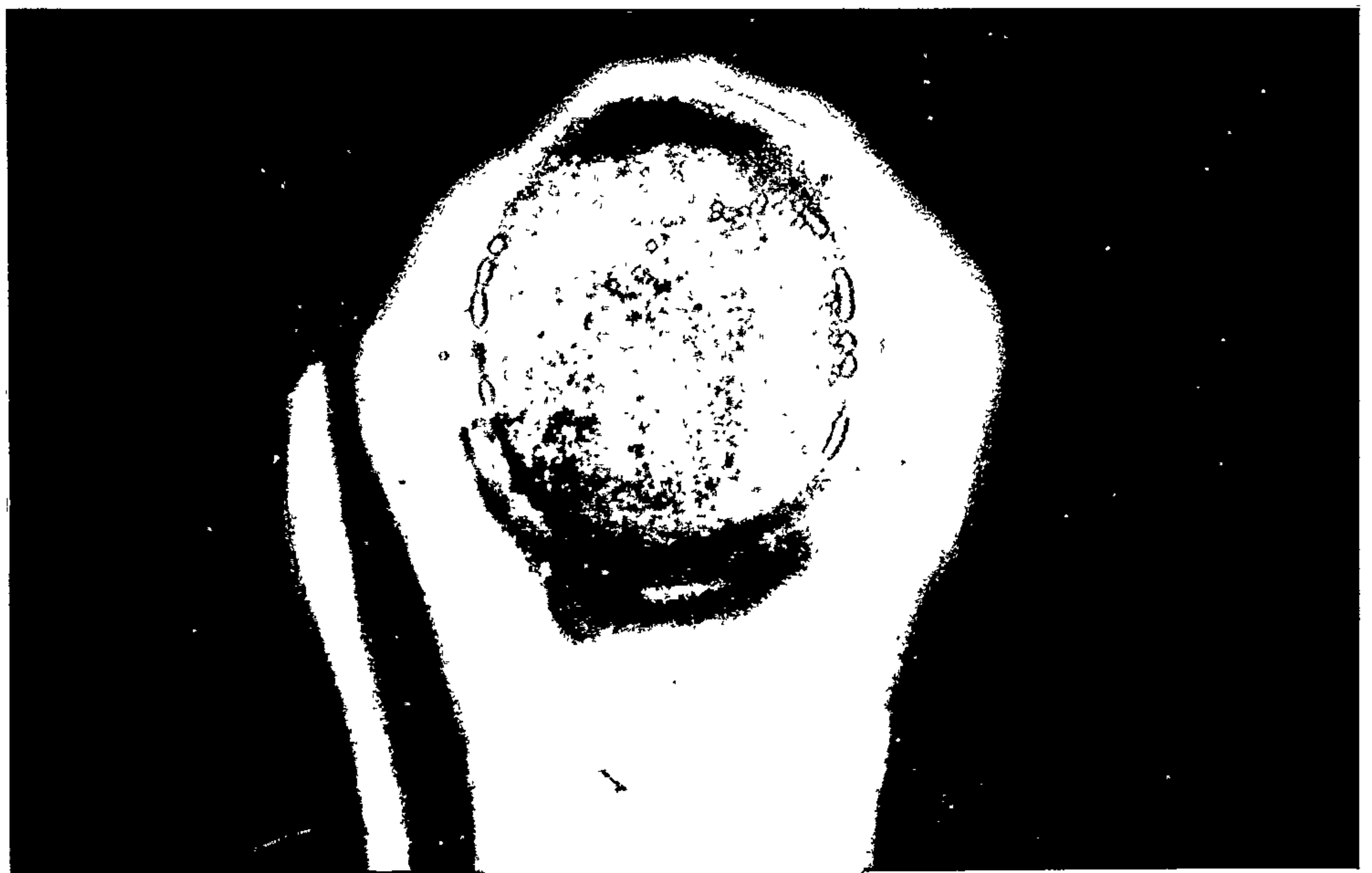
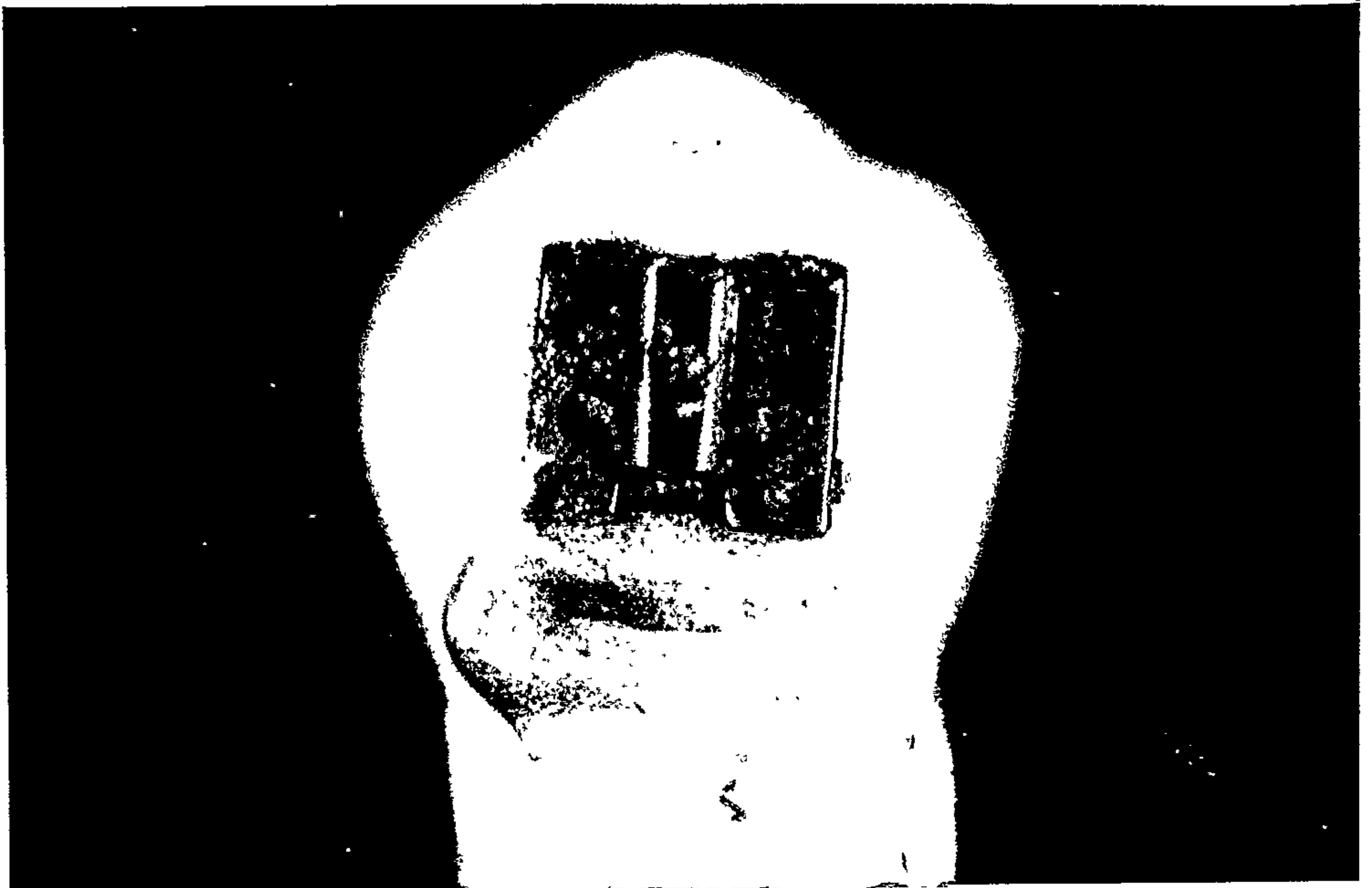


Plate 14c

This photograph shows the acrylic cylinder attached to the tooth enamel through bonding to the bracket and adhesive.

Plate 14d

This photograph shows the adhesive surface (the uppermost, concave surface) mounted on the acrylic cylinder with the enamel removed.



Plate 15 - The "Dynavac" high vacuum, coating machine

Plate 16 - Coated and Mounted Specimen

This photograph shows a specimen which has been mounted on an aluminium cylinder and then coated with a gold film in the high vacuum, coating machine.

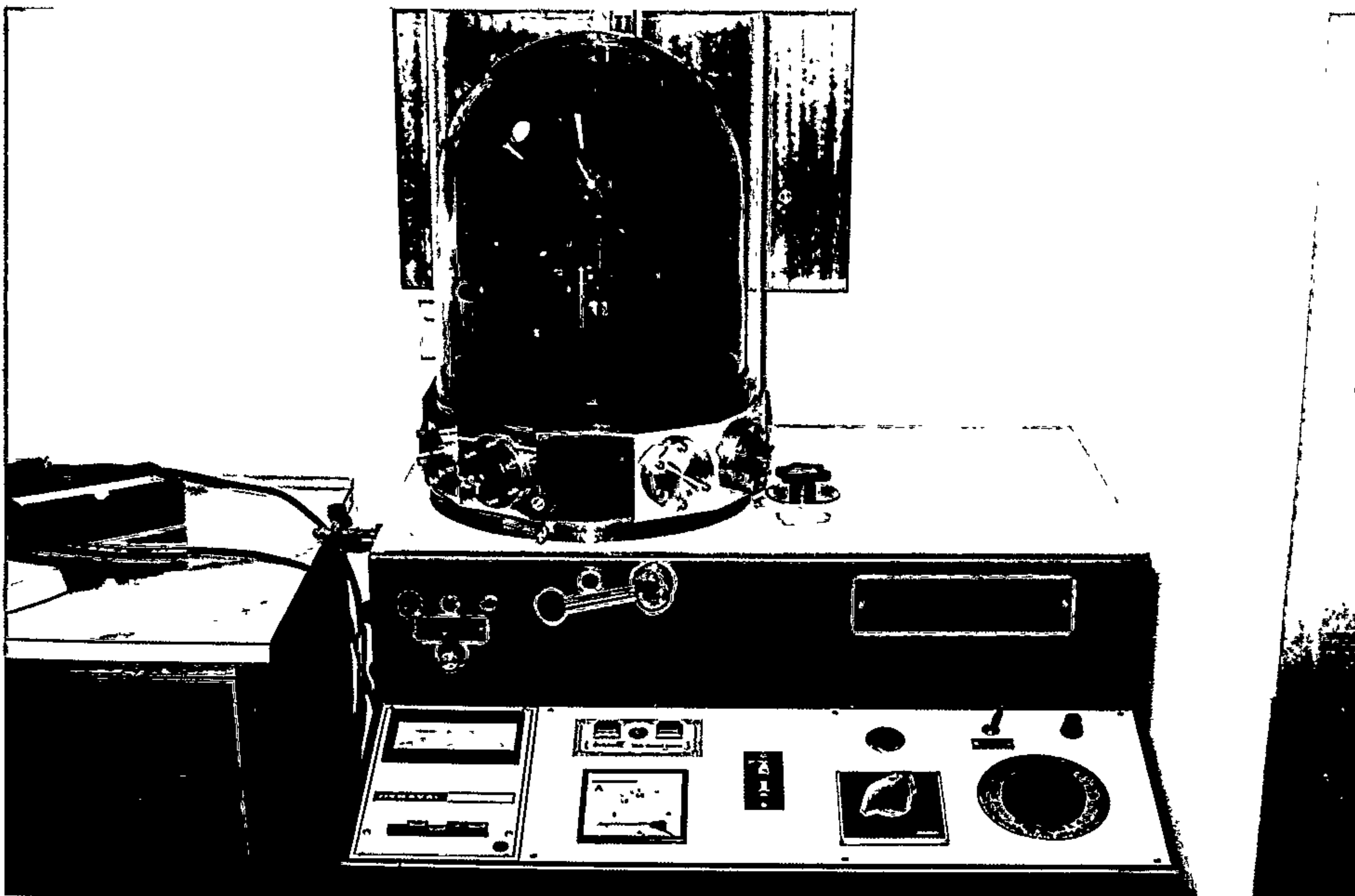


Plate 17 - The Scanning Electron Microscope

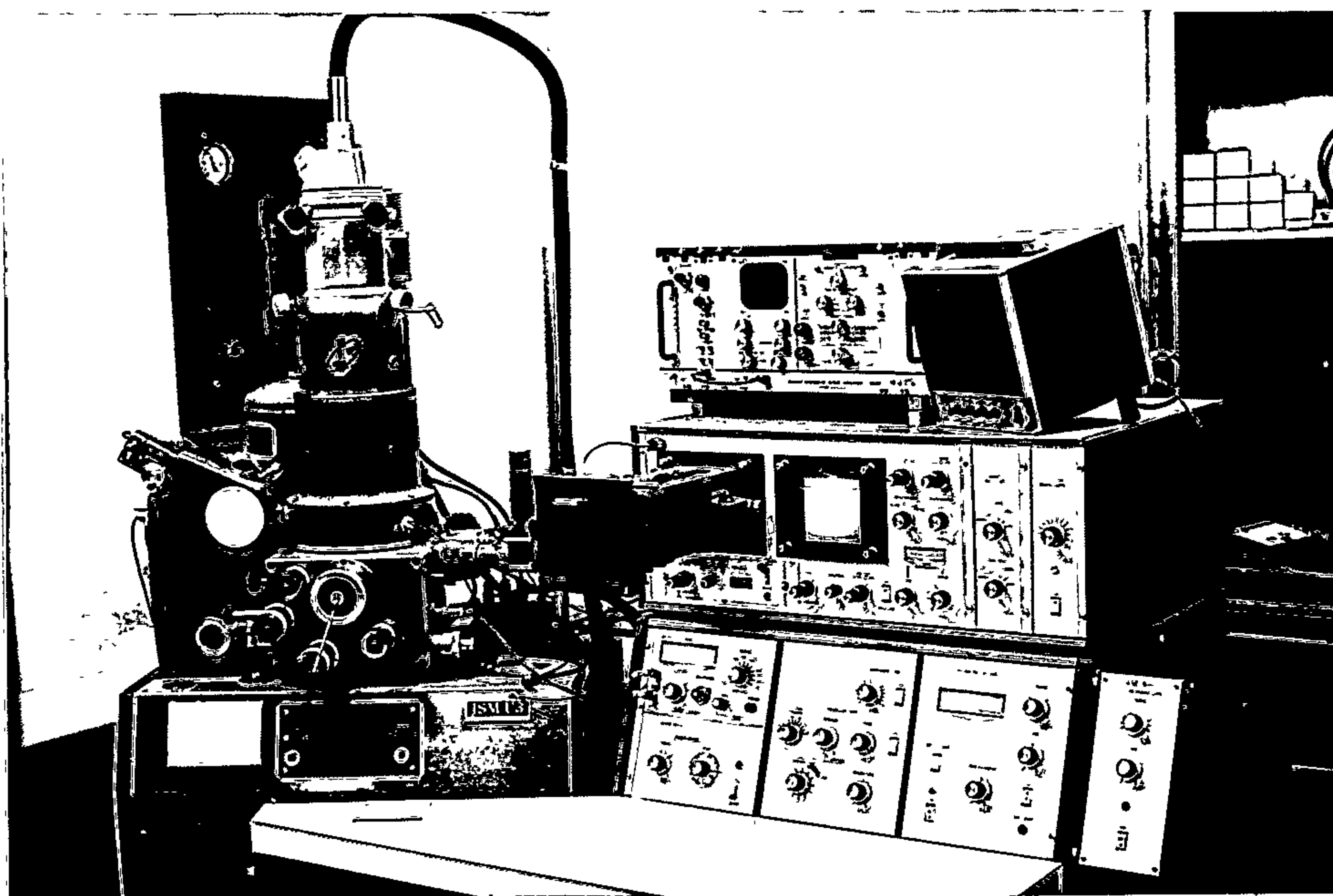


Plate 18 - Pumiced Enamel - Experiment V

These microphotographs show the typical appearance of a pumiced (polished) enamel surface.

- a) 65 X original size,
- b) 100 X original size,
- c) 300 X original size, and
- d) 1,000 X original size.

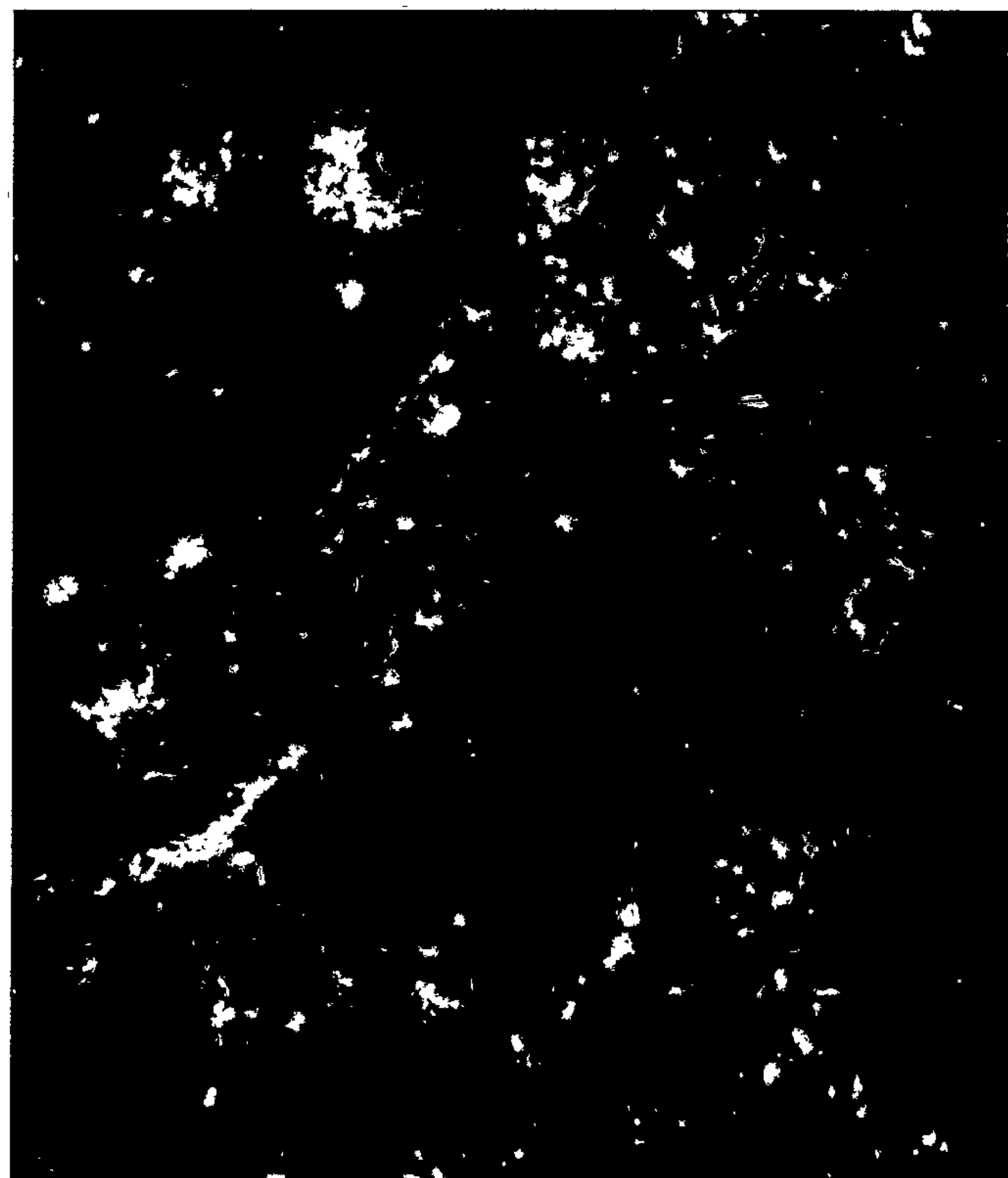
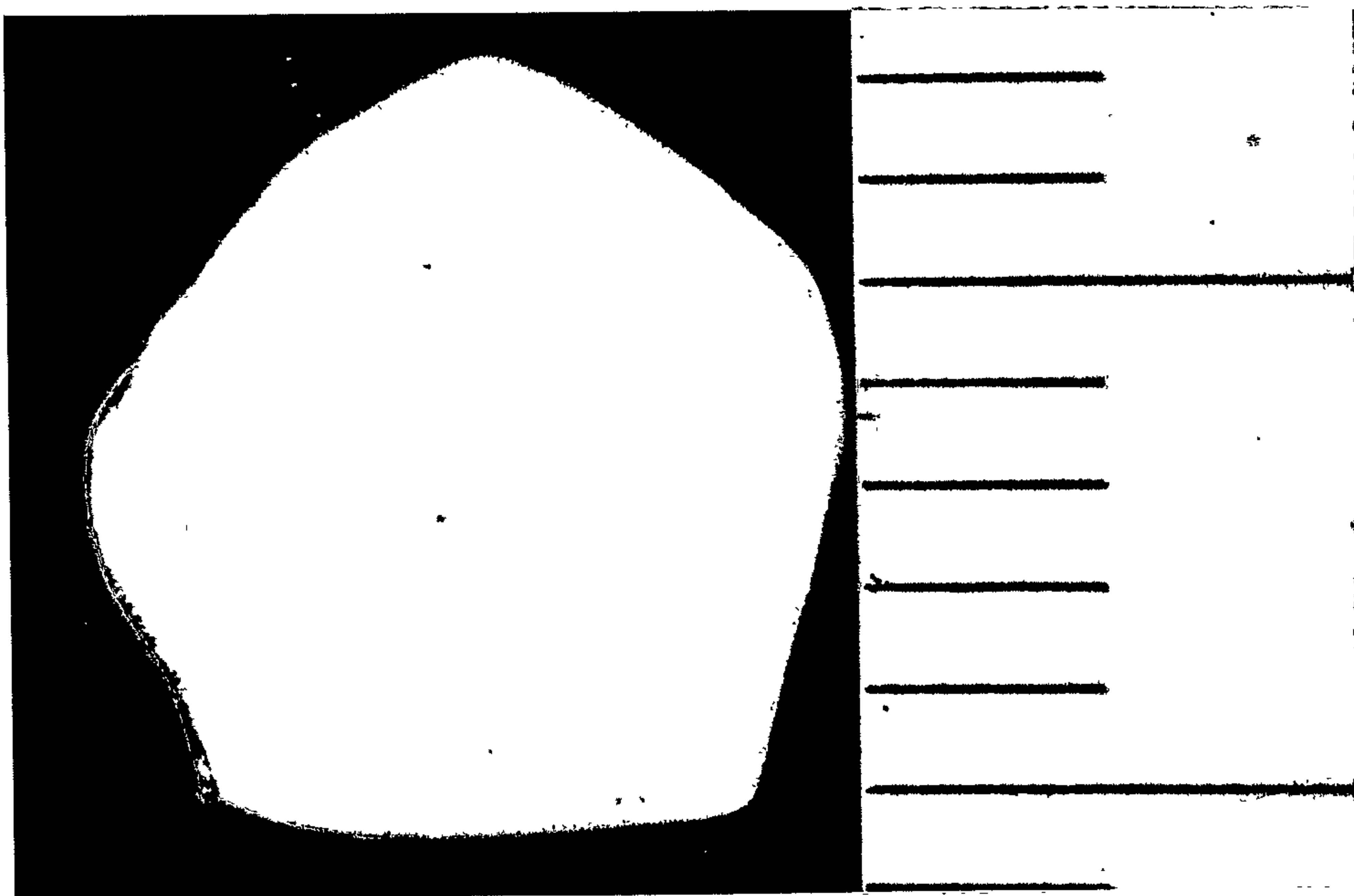


Plate 19 - Etched Enamel

This photograph shows a typical tooth specimen which has been etched.



Plates 20-32 inclusive (Experiments I to IV) are laid out in the following manner:

a	b
c	d

where: a) represents Product A treated enamel,
b) represents Product B treated enamel,
c) represents Product C treated enamel, and
d) represents Product D treated enamel. Unless otherwise indicated.

Plate 20 - Etched Enamel Microphotographs

- Experiment I
- 100 X original size
- Recommended exposure times.

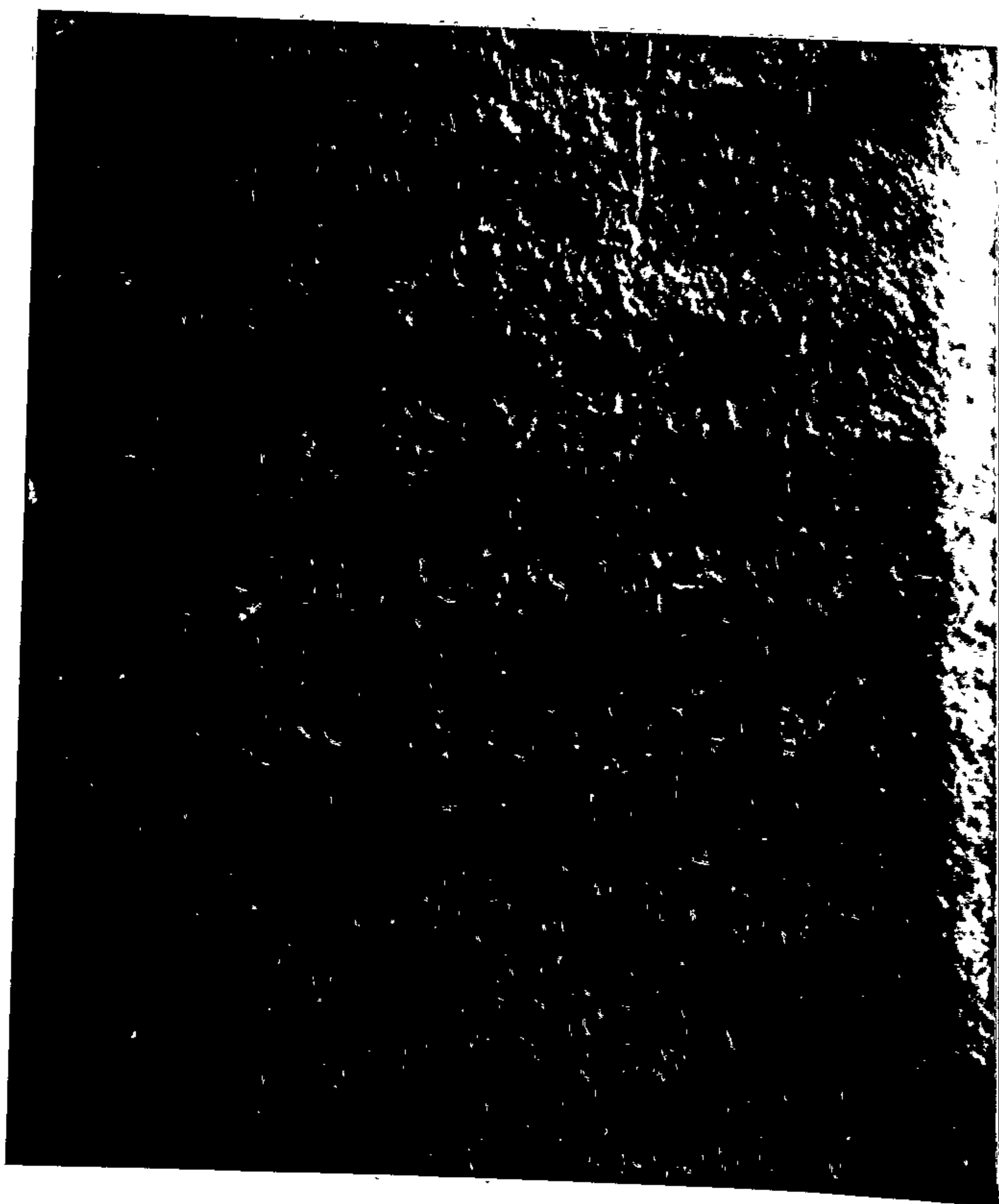
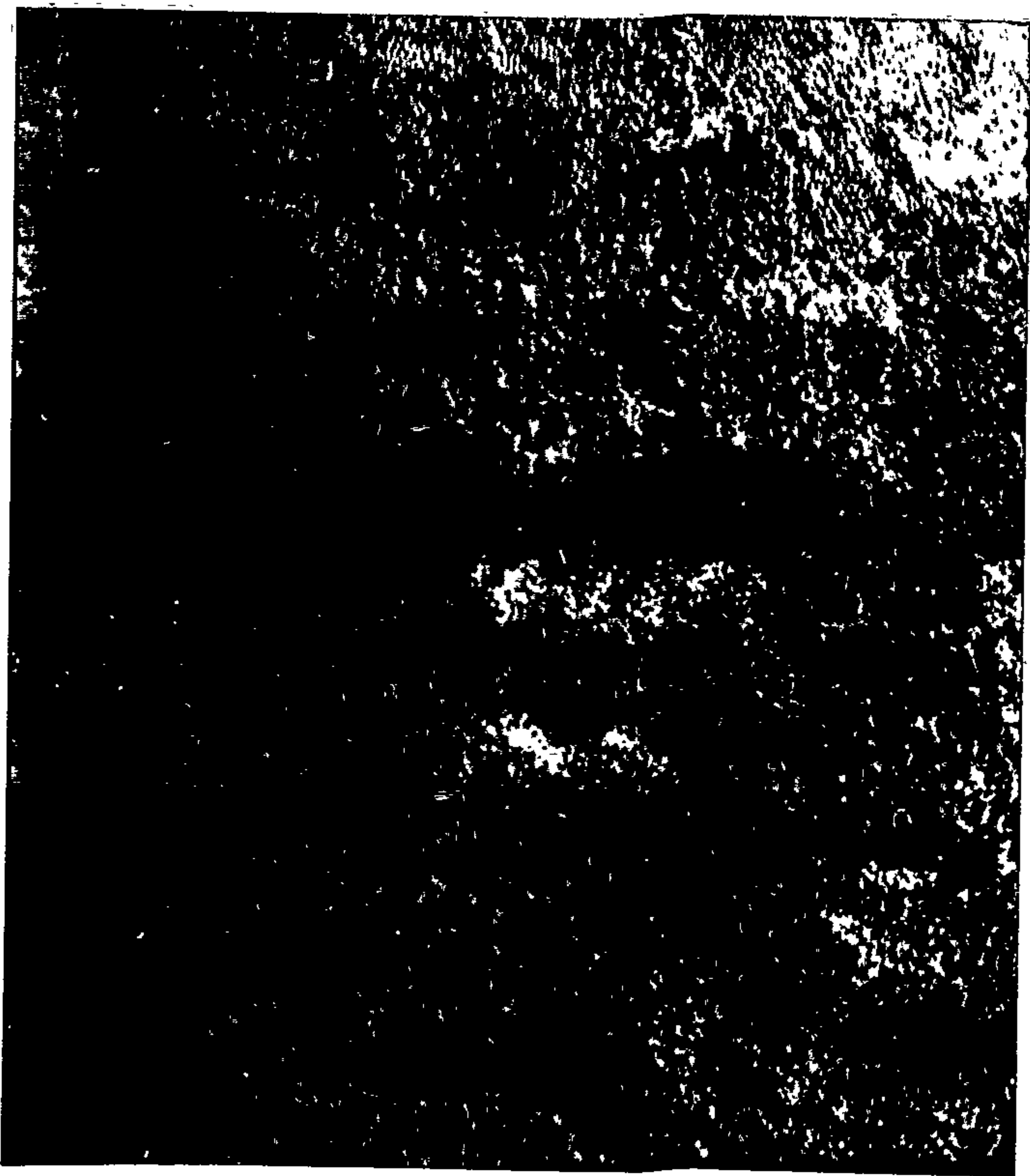
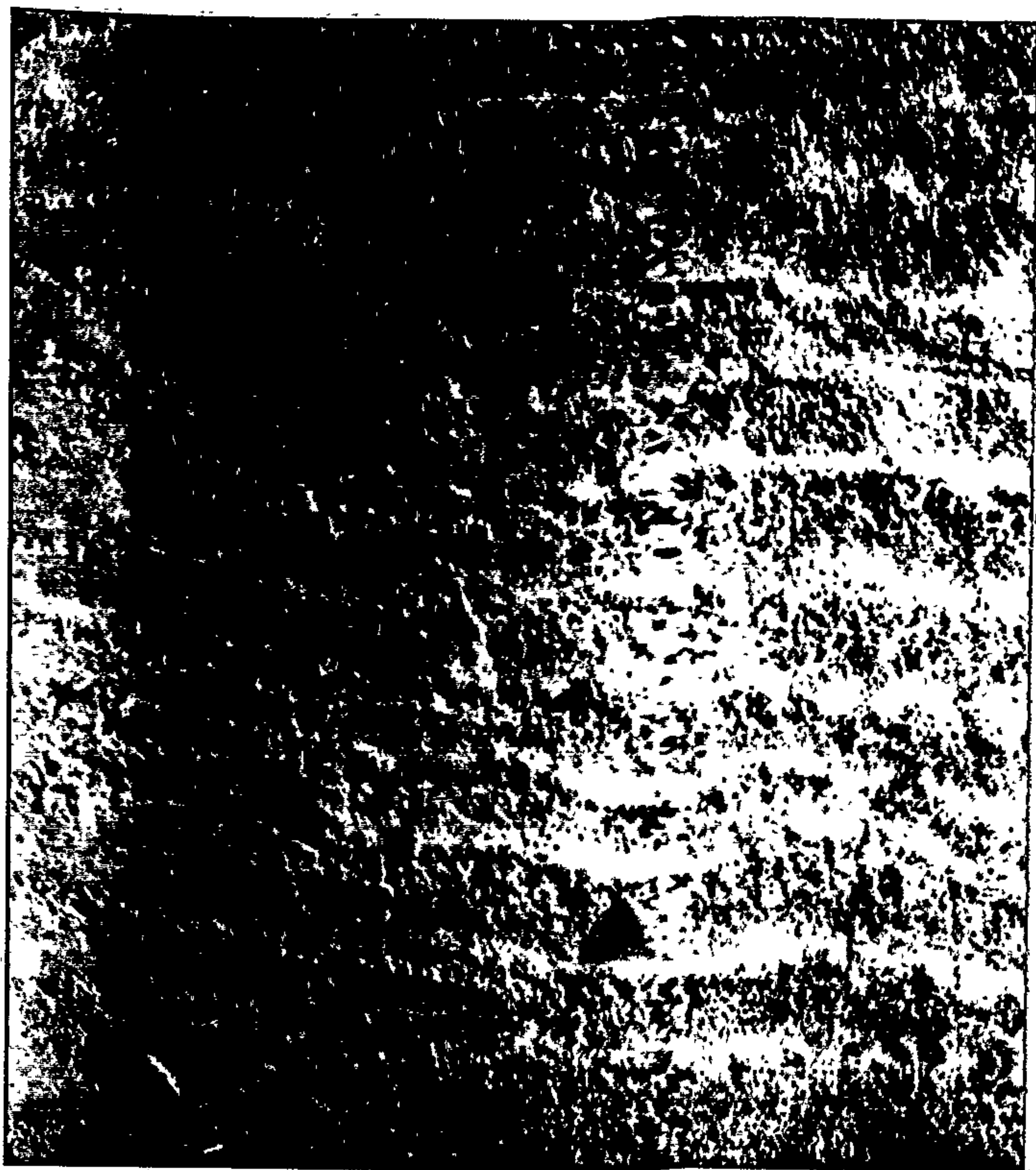


Plate 21 - Etched Enamel Microphotographs

- Experiment I
- 300 X original size
- Recommended exposure times.



Plate 22 - Etched Enamel Microphotographs

- Experiment I
- 1,000 X original size

Recommended exposure times.

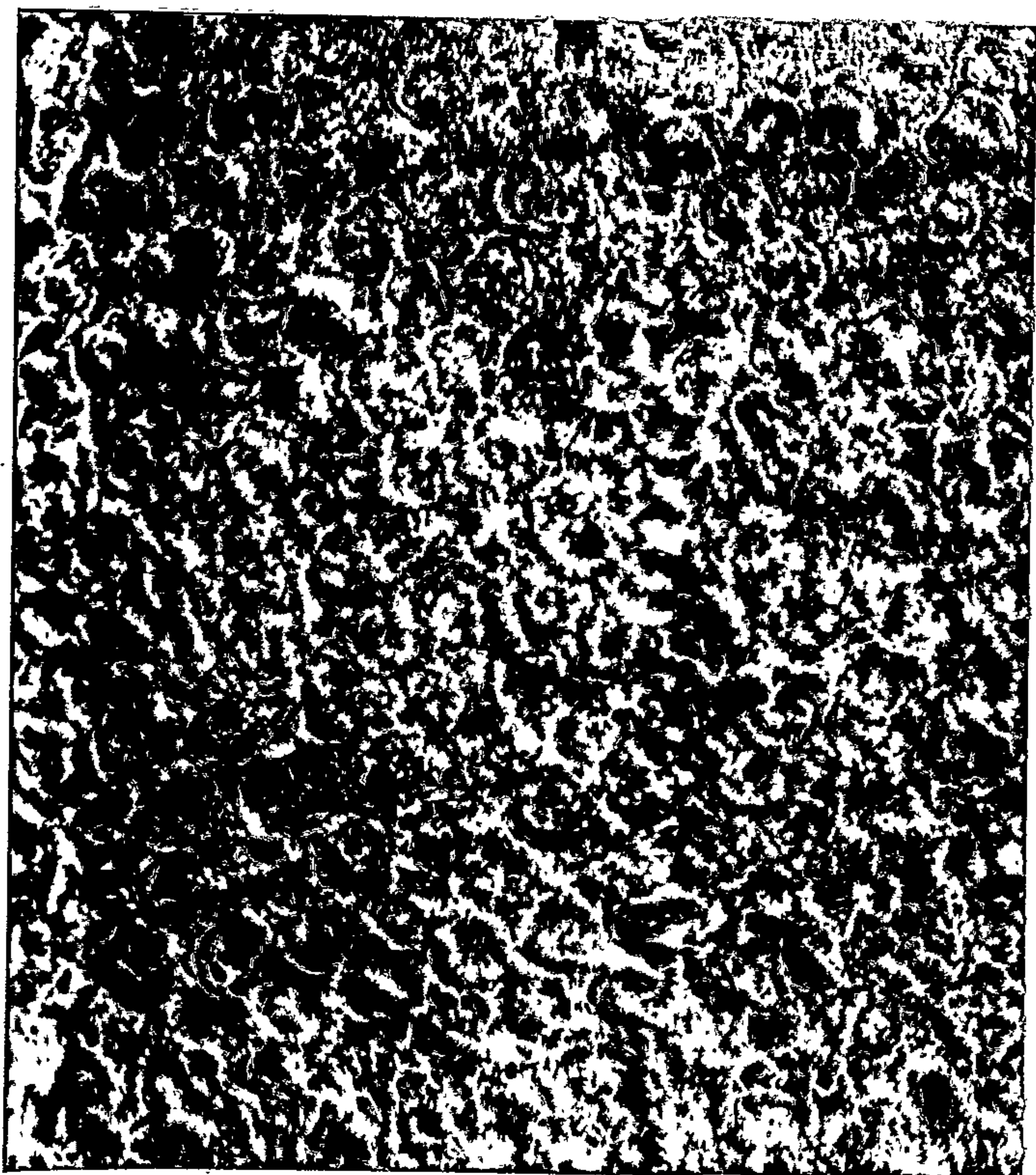
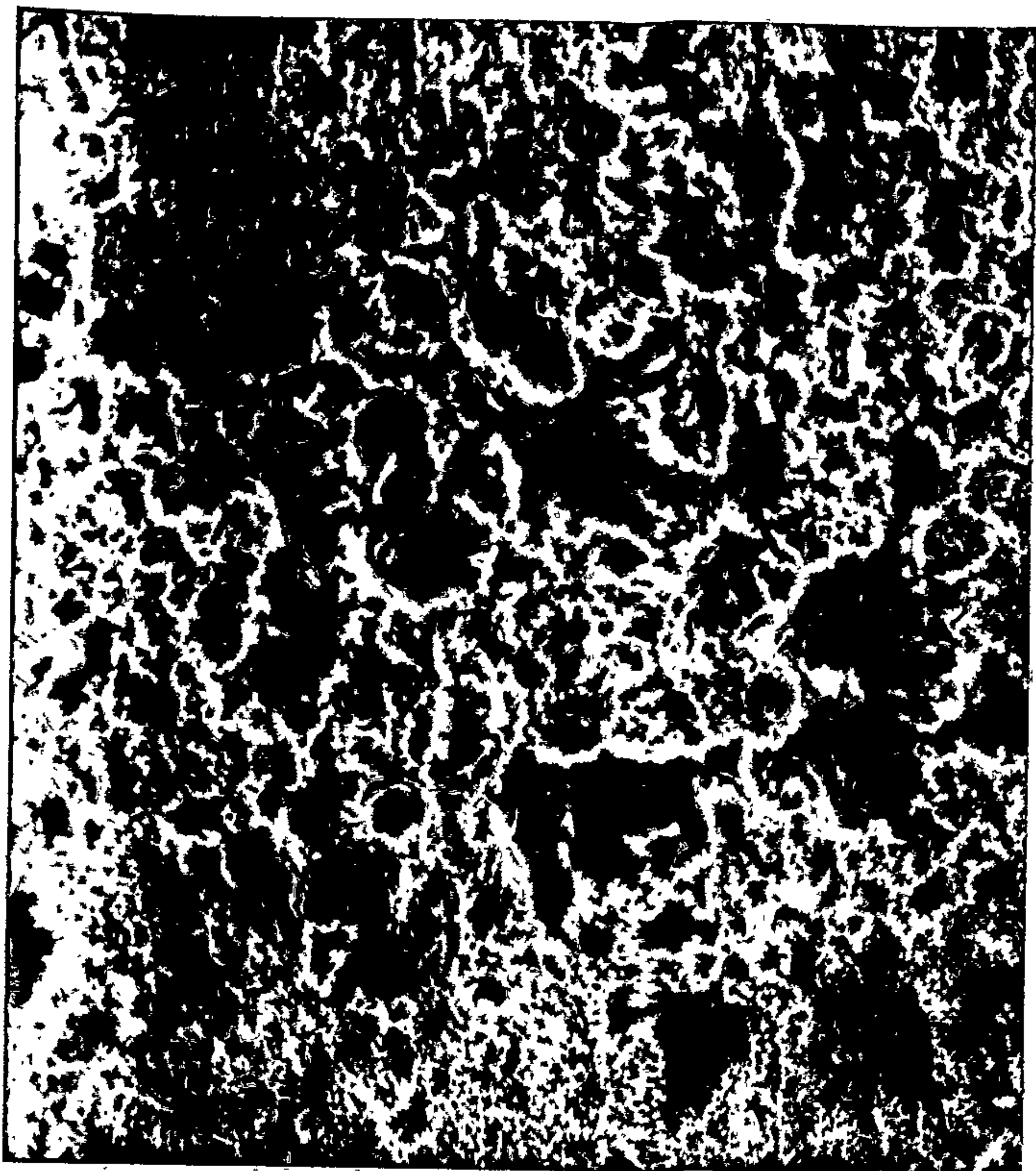


Plate 23 - Adhesive Surface Microphotographs

- Experiment II
- 100 X original size

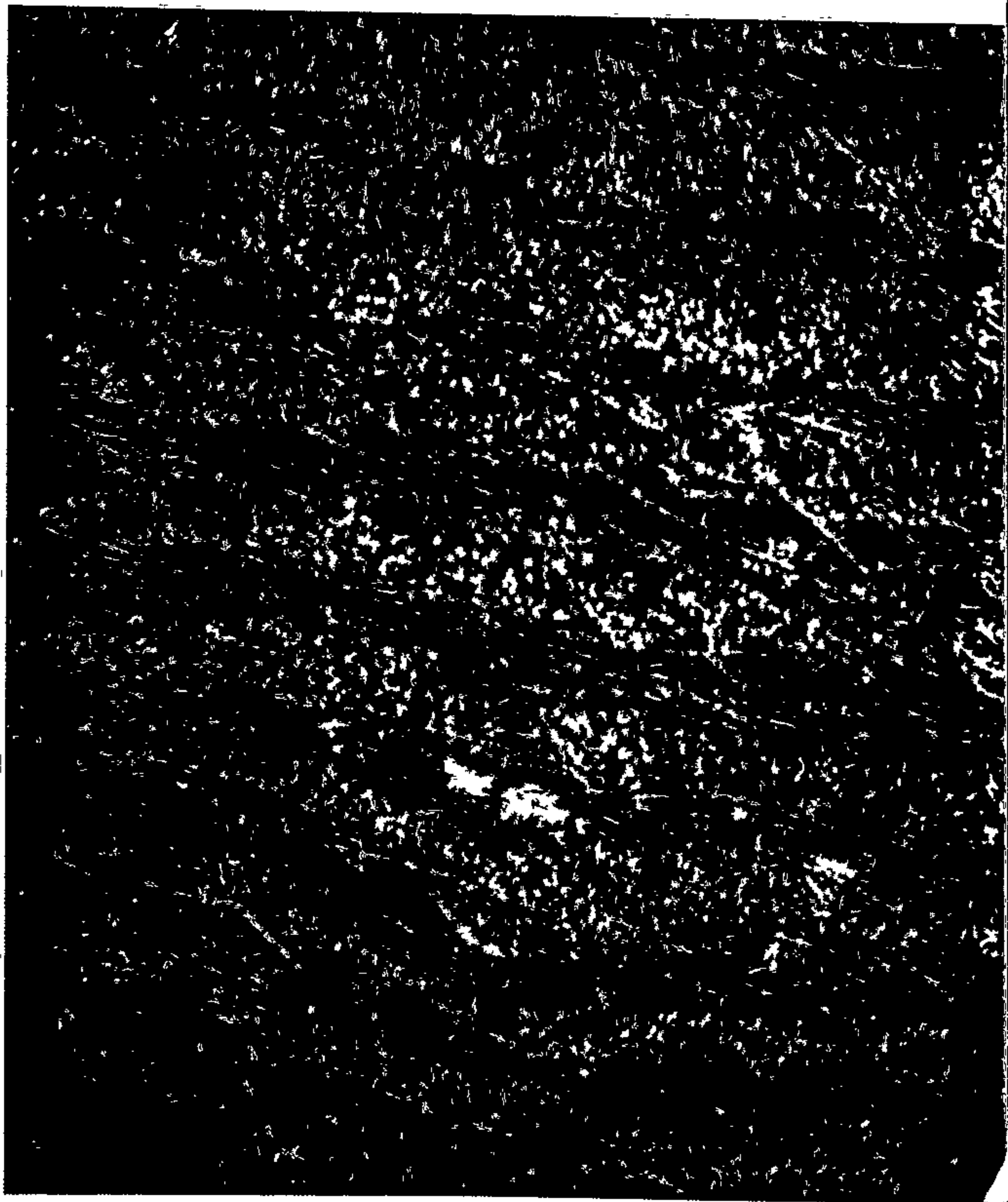
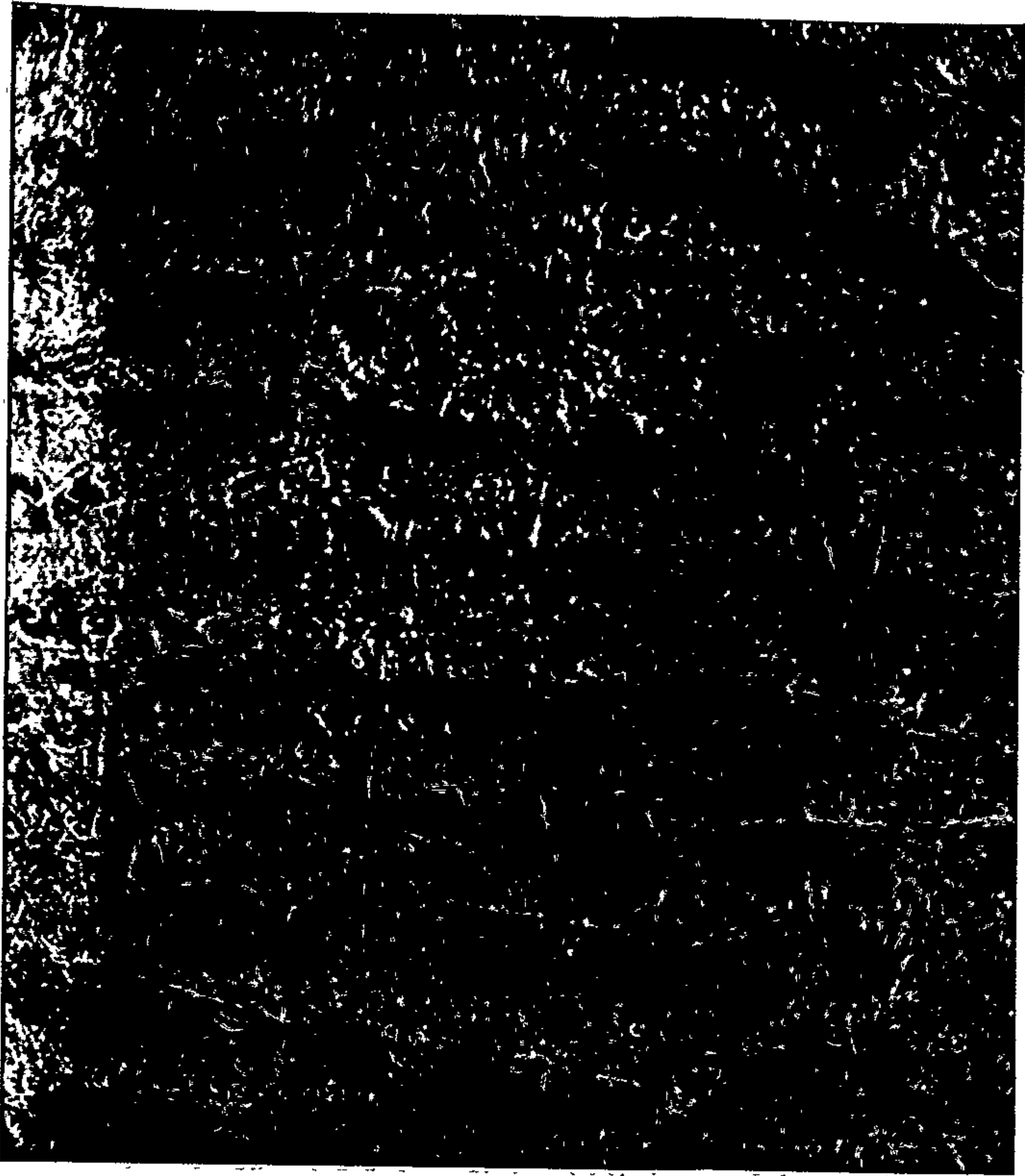


Plate 24 - Adhesive Surface Microphotographs

- Experiment II
- 300 X original size.

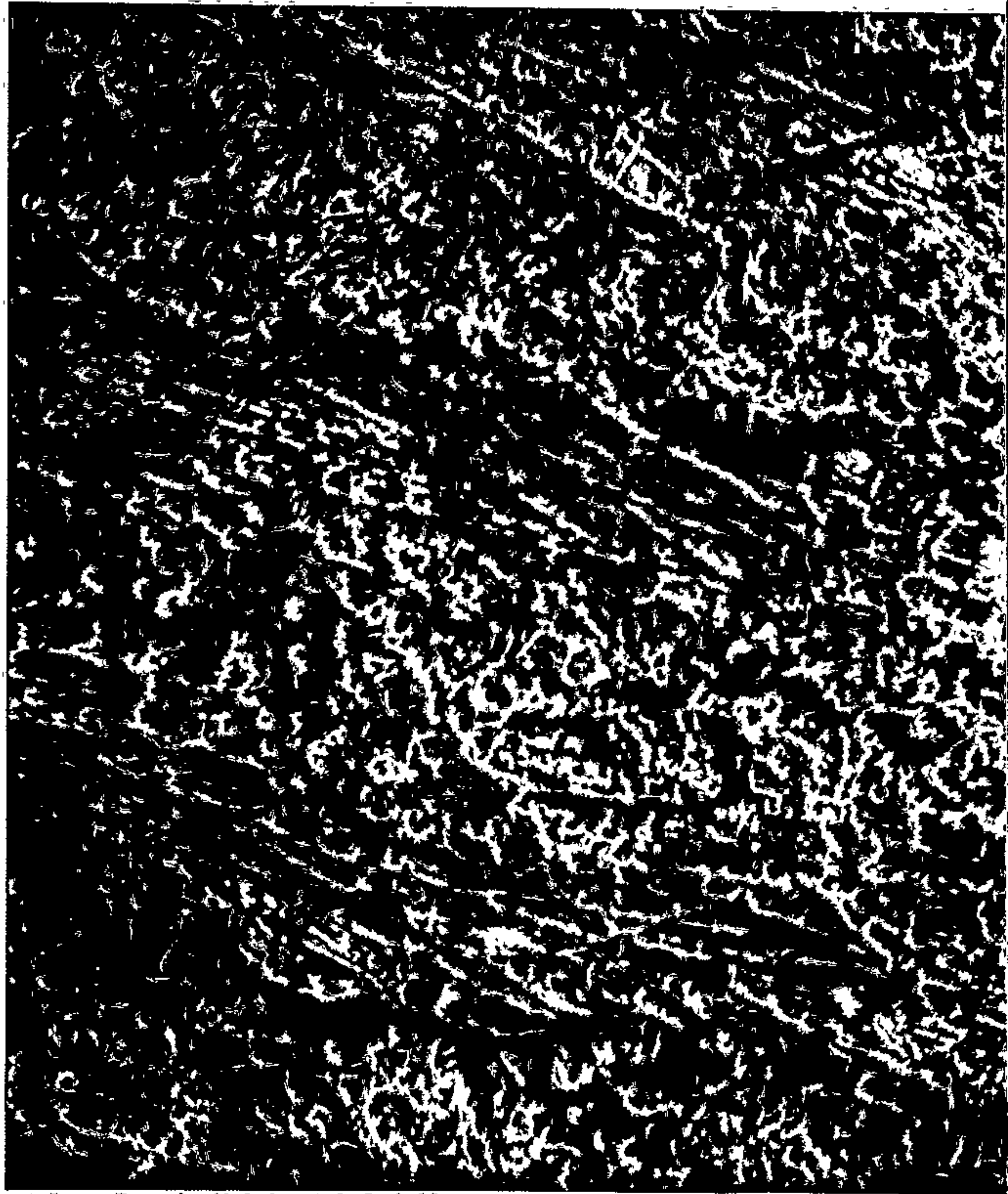
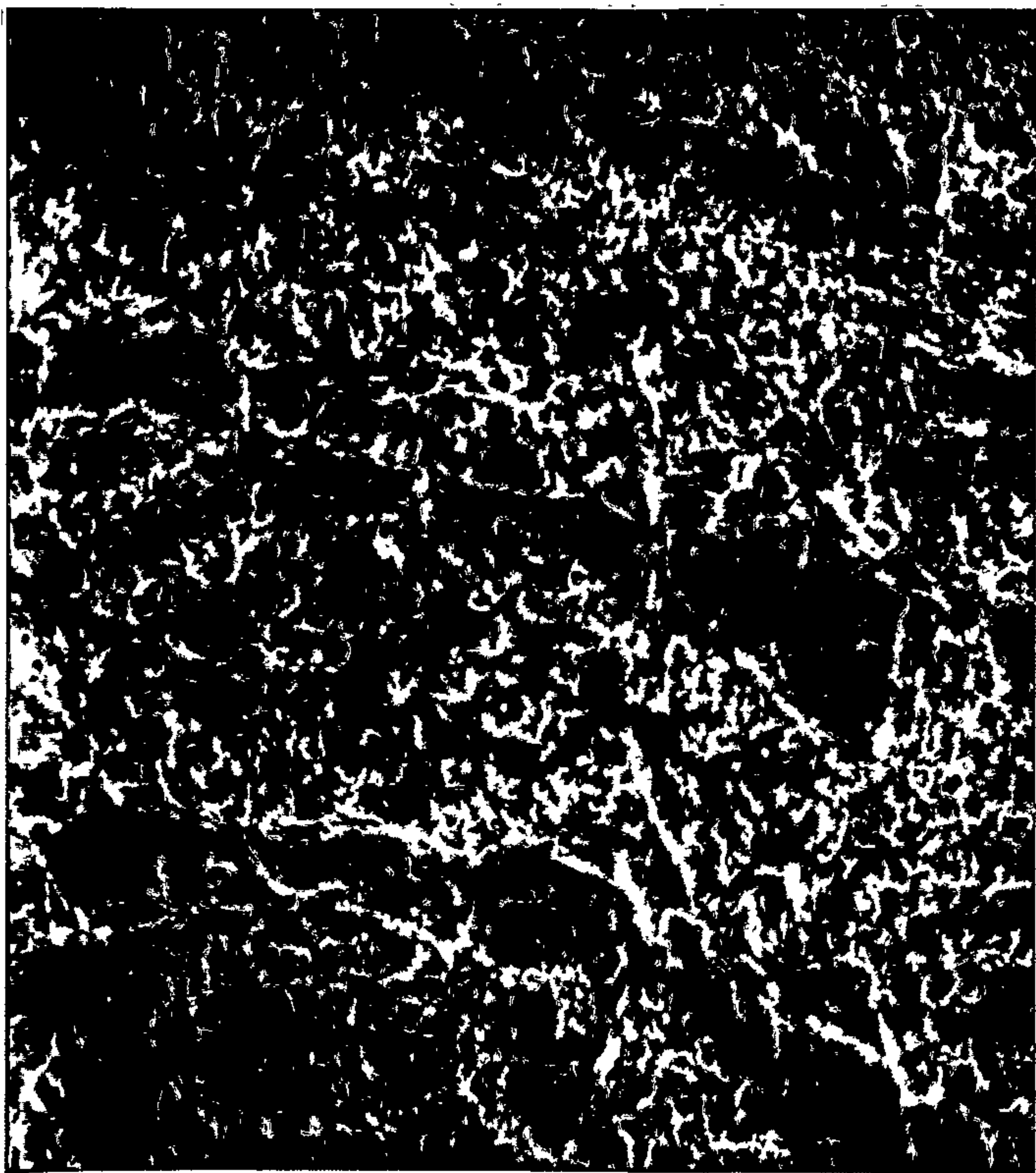
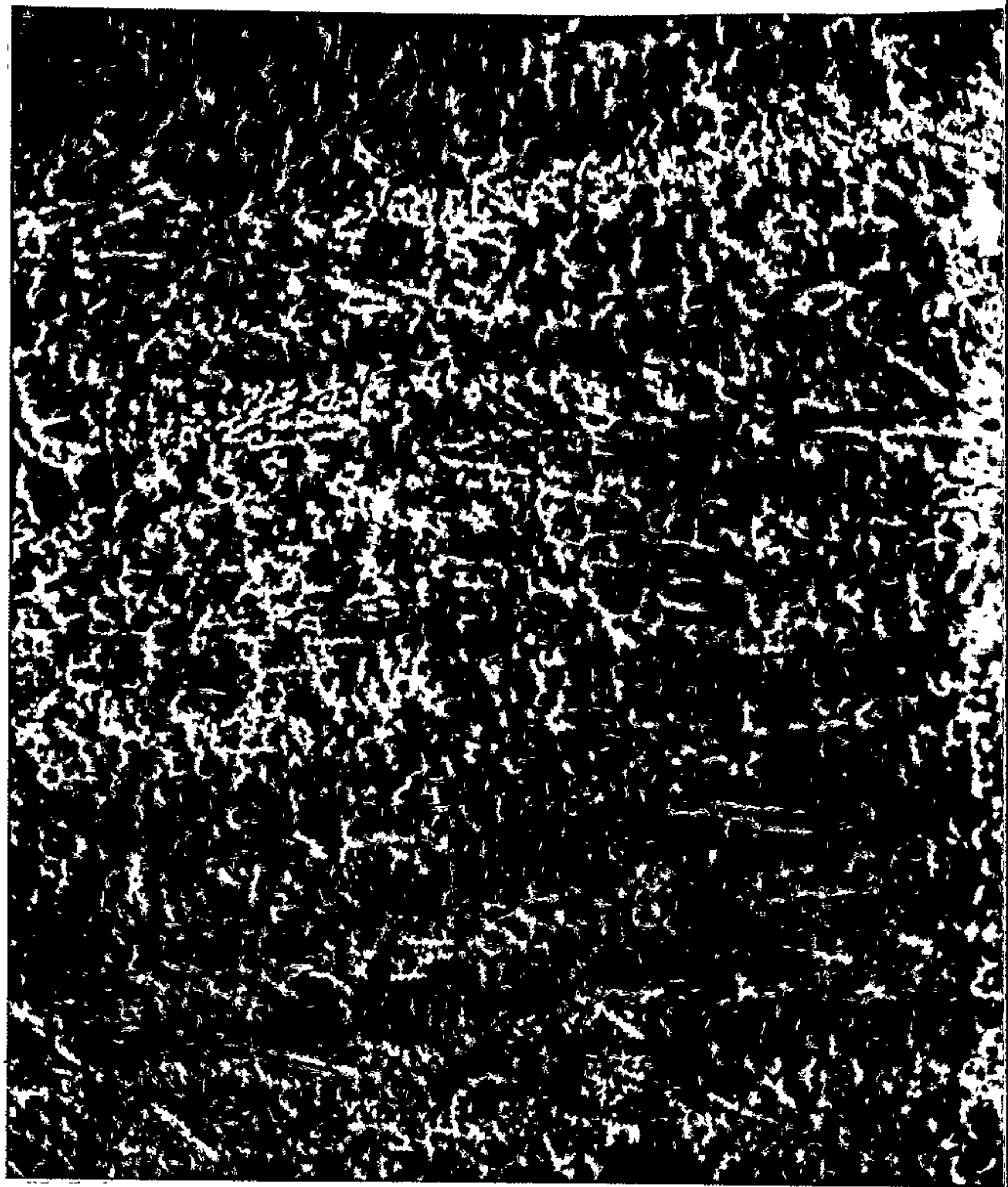
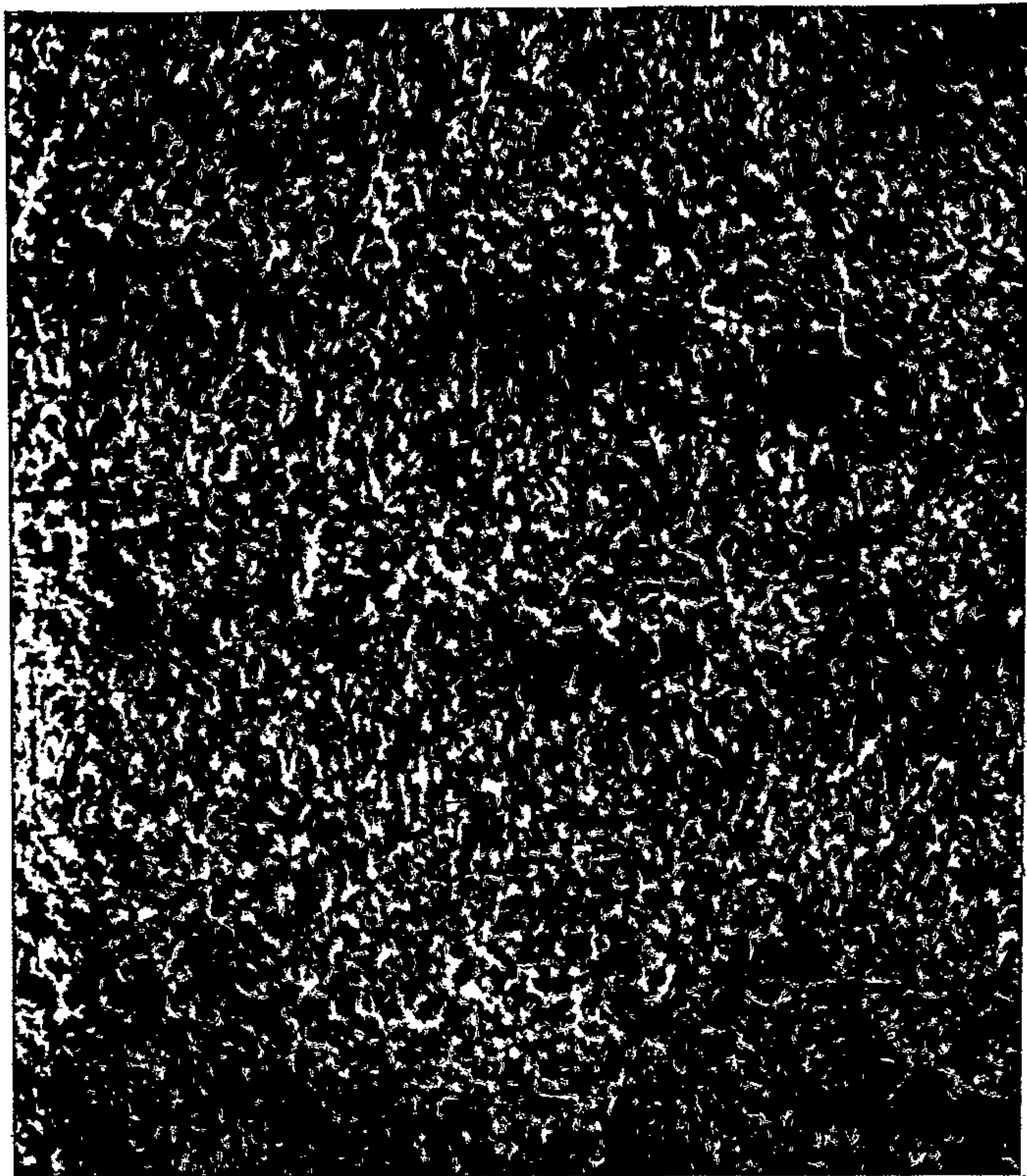


Plate 25 - Adhesive Surface Microphotographs

- Experiment II
- 1,000 X original size.

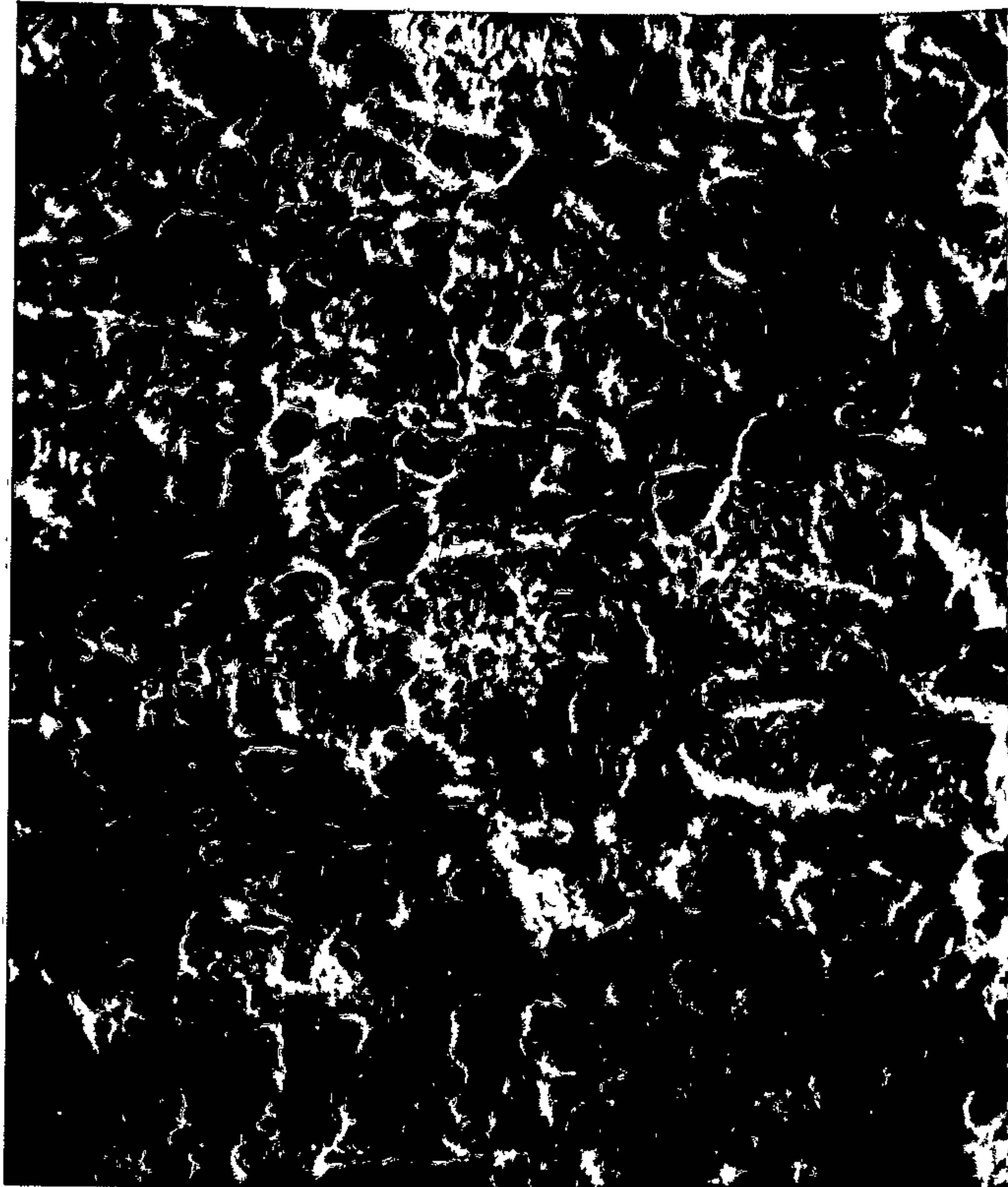


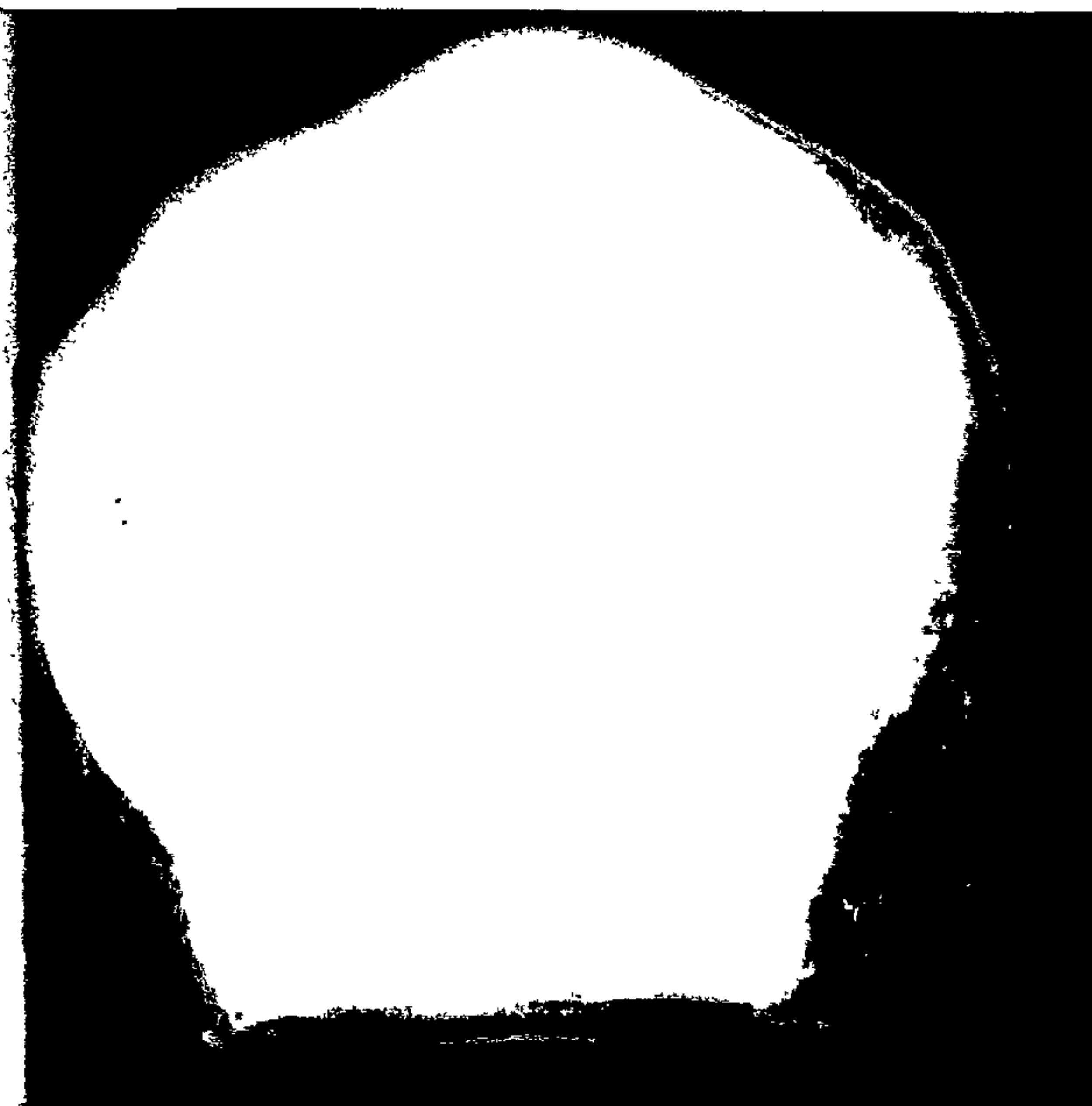
Plate 26 - Removal Surfaces

These photographs are presented to show how the surfaces appeared to the naked eye (with some magnification).

a) Product A

b) Product B

A



B



c) Product C

d) Product D

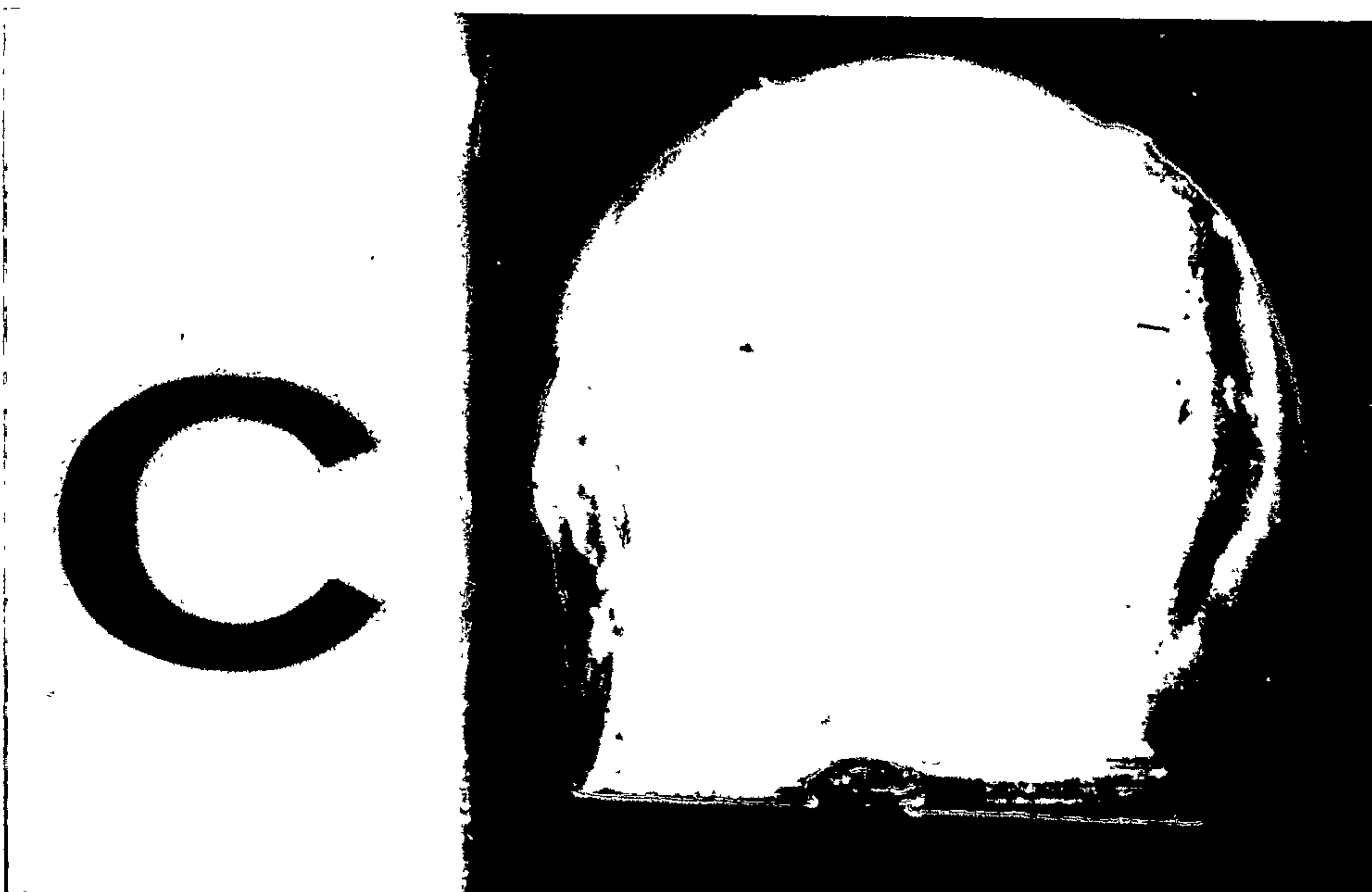


Plate 27 - "Removal" Surface Microphotographs

- Experiment III
- 100 X original size.



Plate 28 - "Removal" Surface Microphotograph

- Experiment III
- 300 X original size.

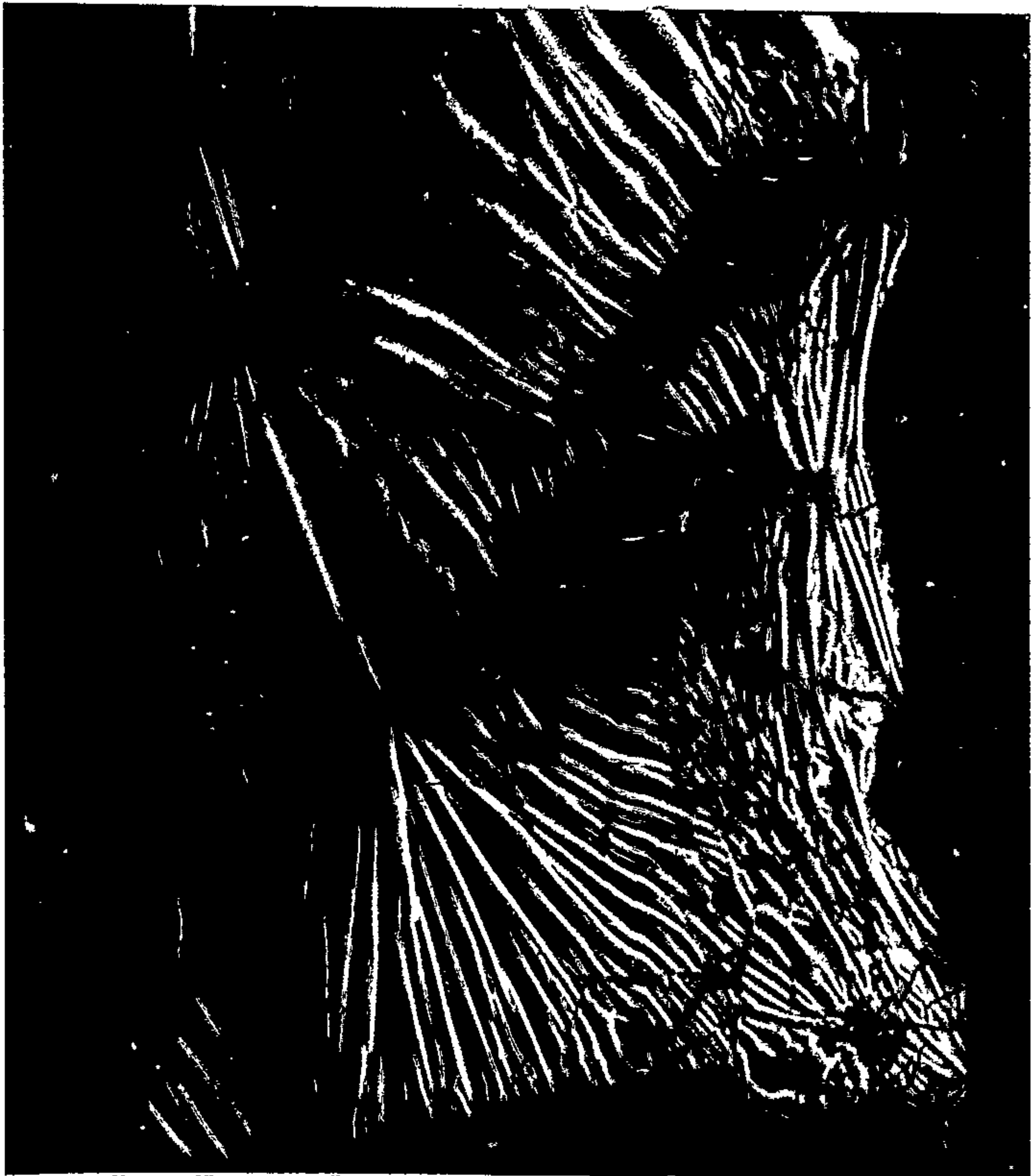
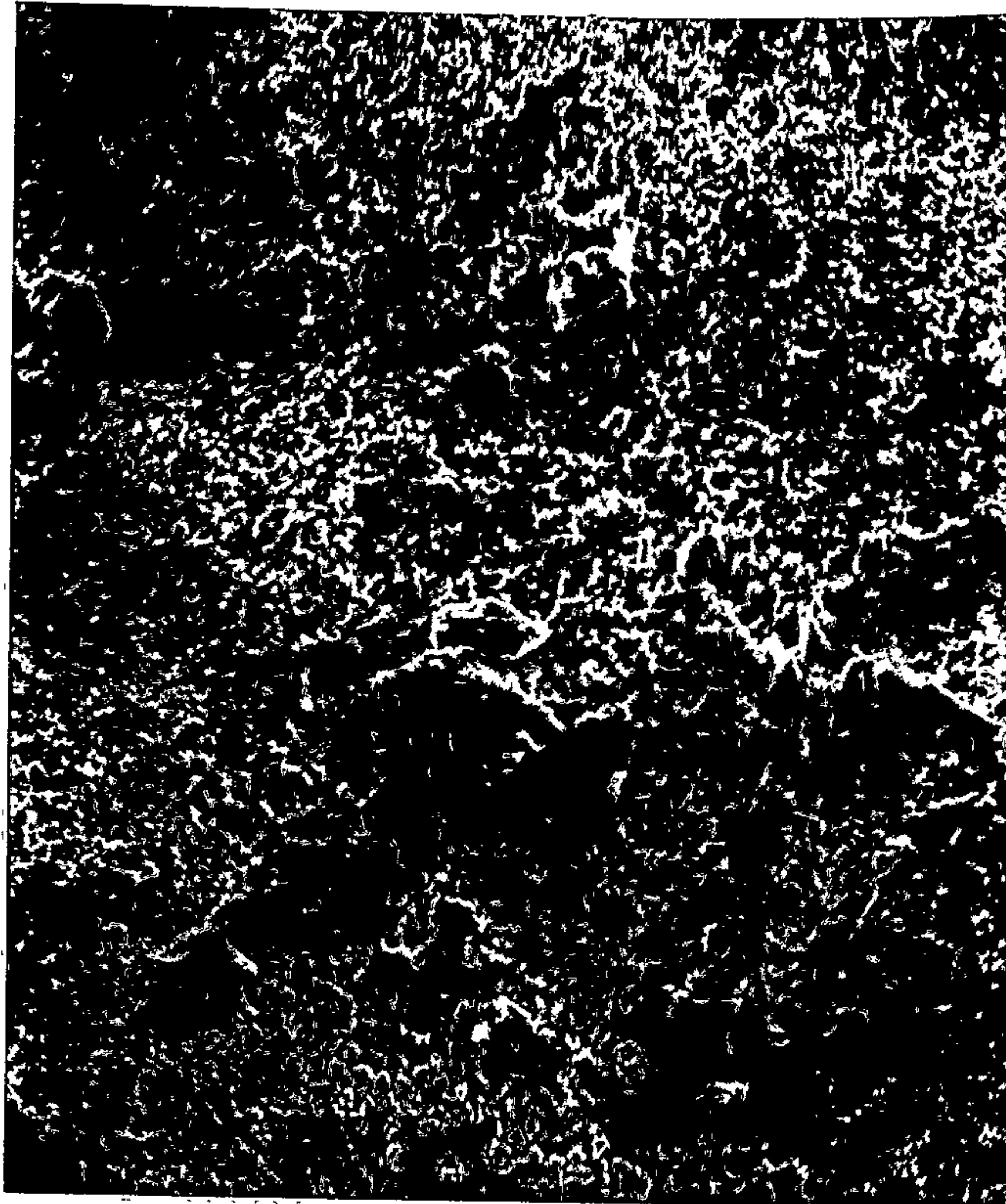
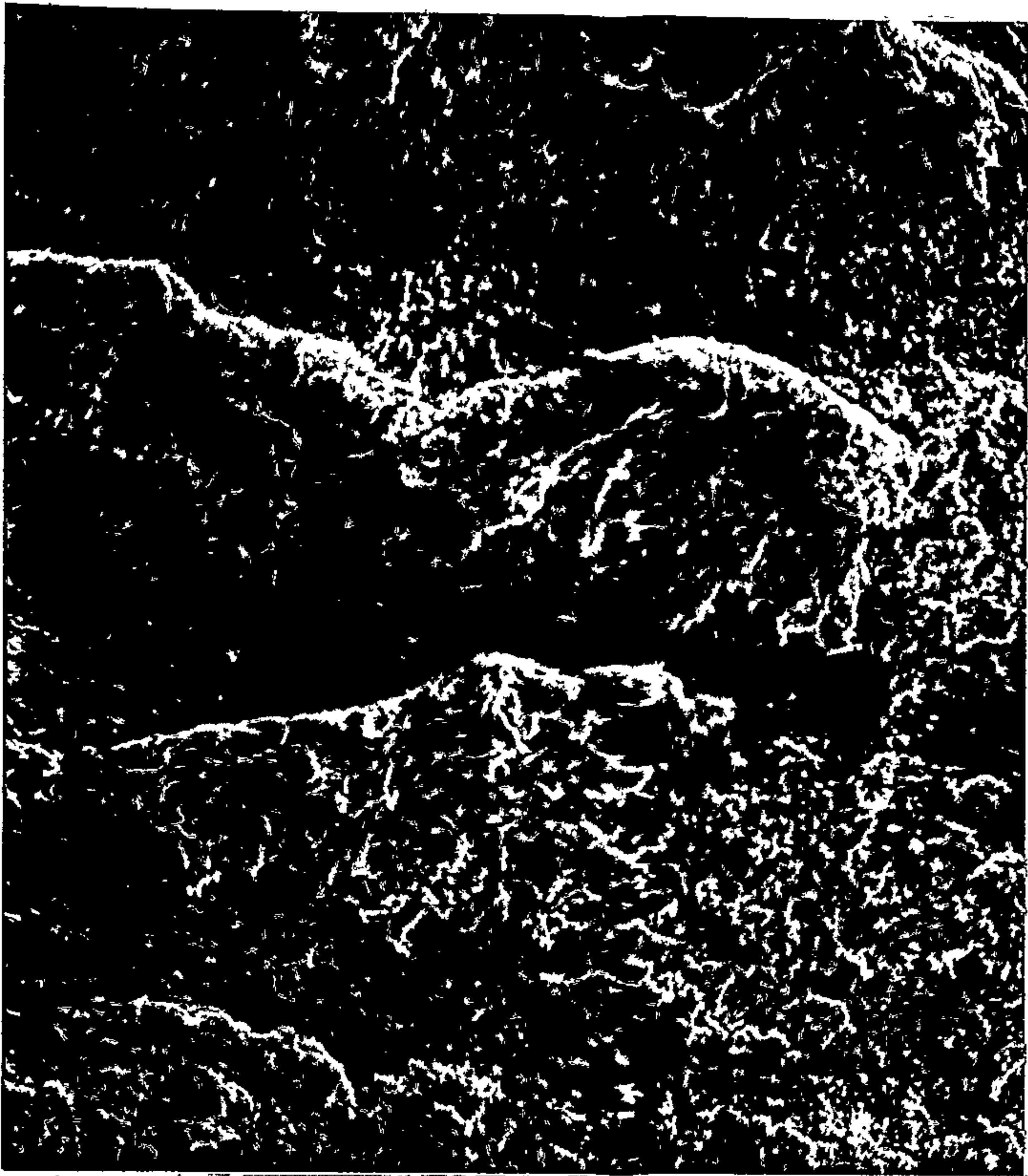


Plate 29 - "Removal" Surface Microphotographs

- Experiment III
- 1,000 X original size.



Plate 30 - Repolished Enamel Surface Microphotographs

- Experiment IV
- 100 X original size.

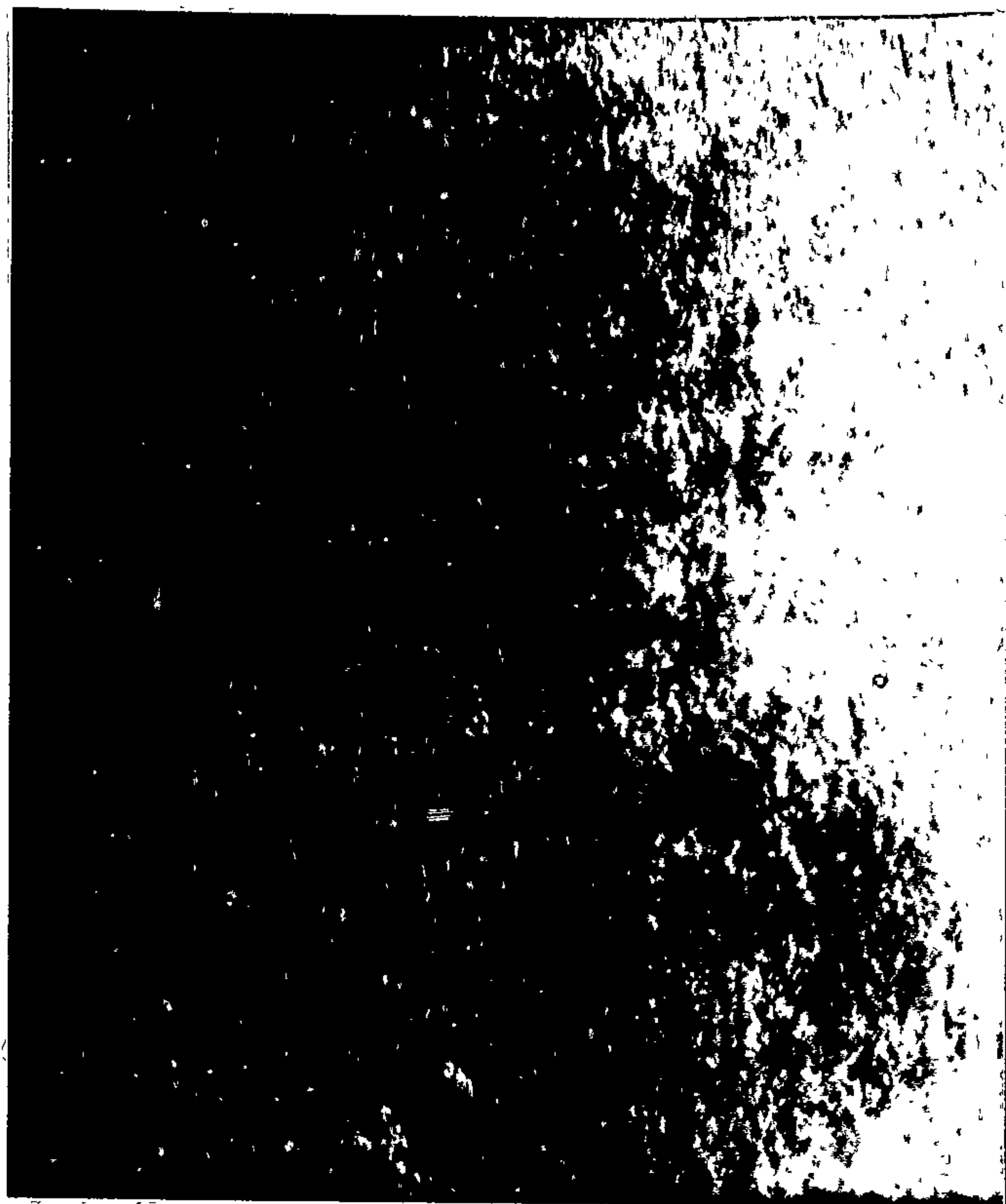


Plate 31 - Repolished Enamel Surface Microphotographs

- Experiment IV
- 300 X original size.

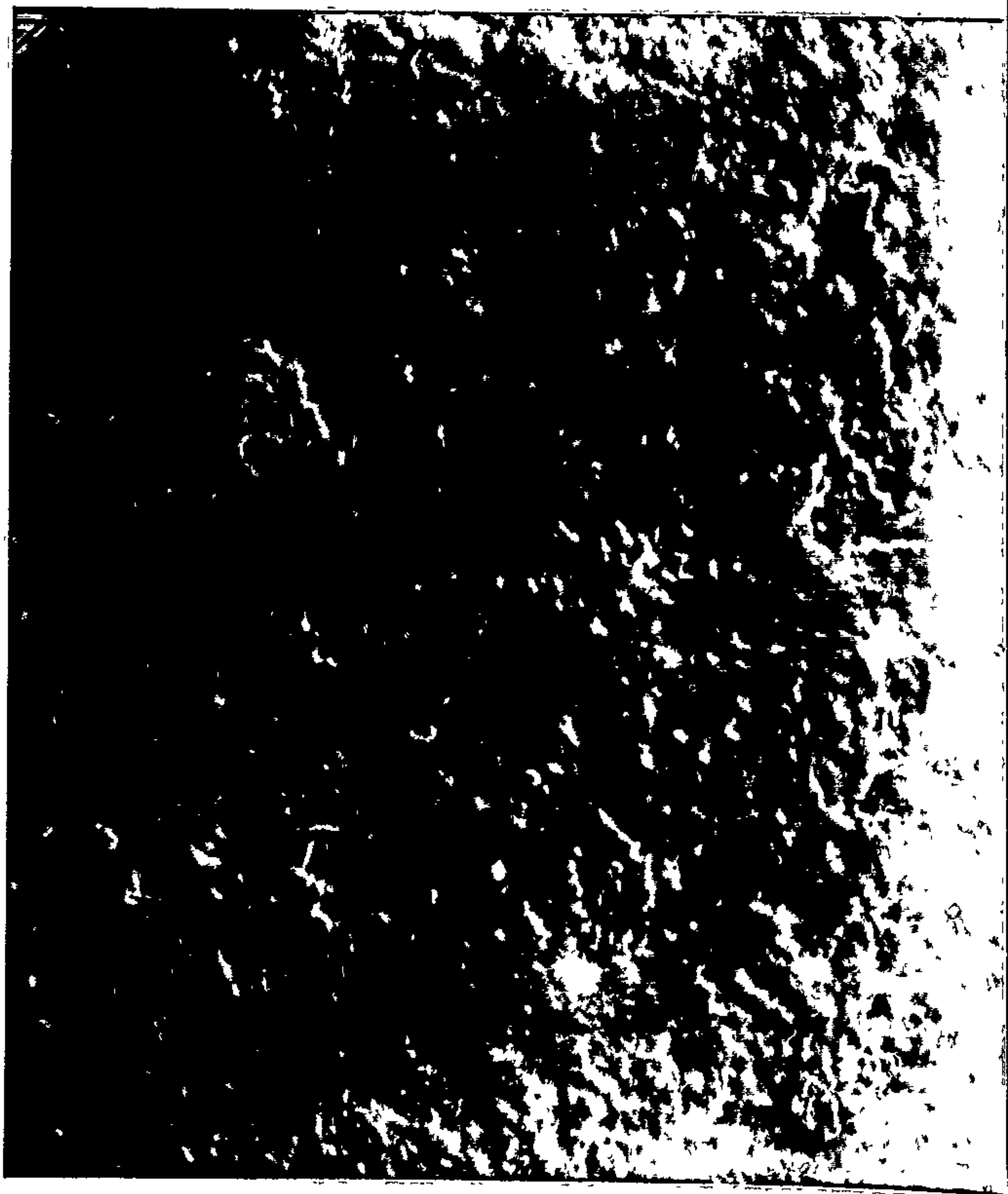
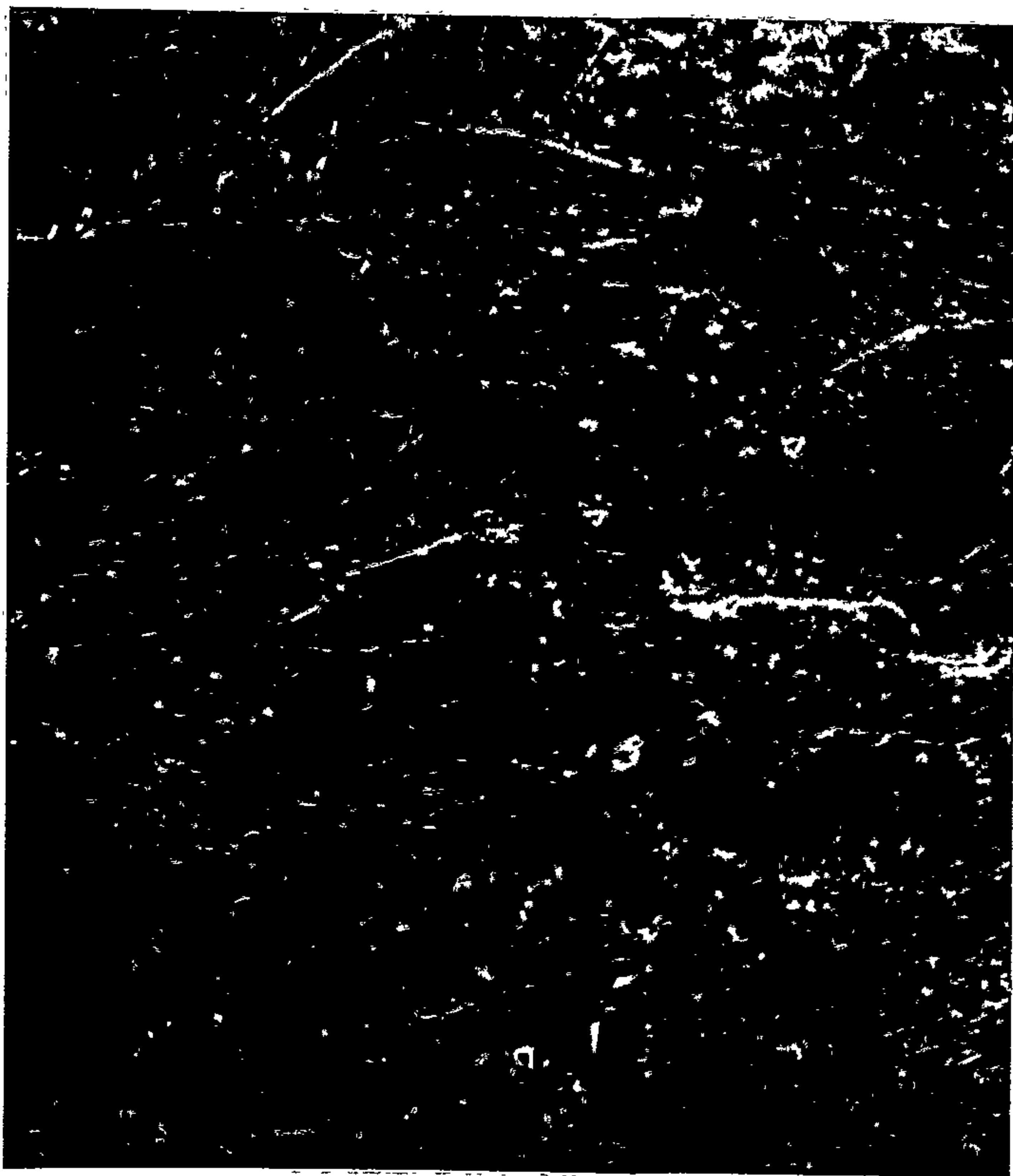
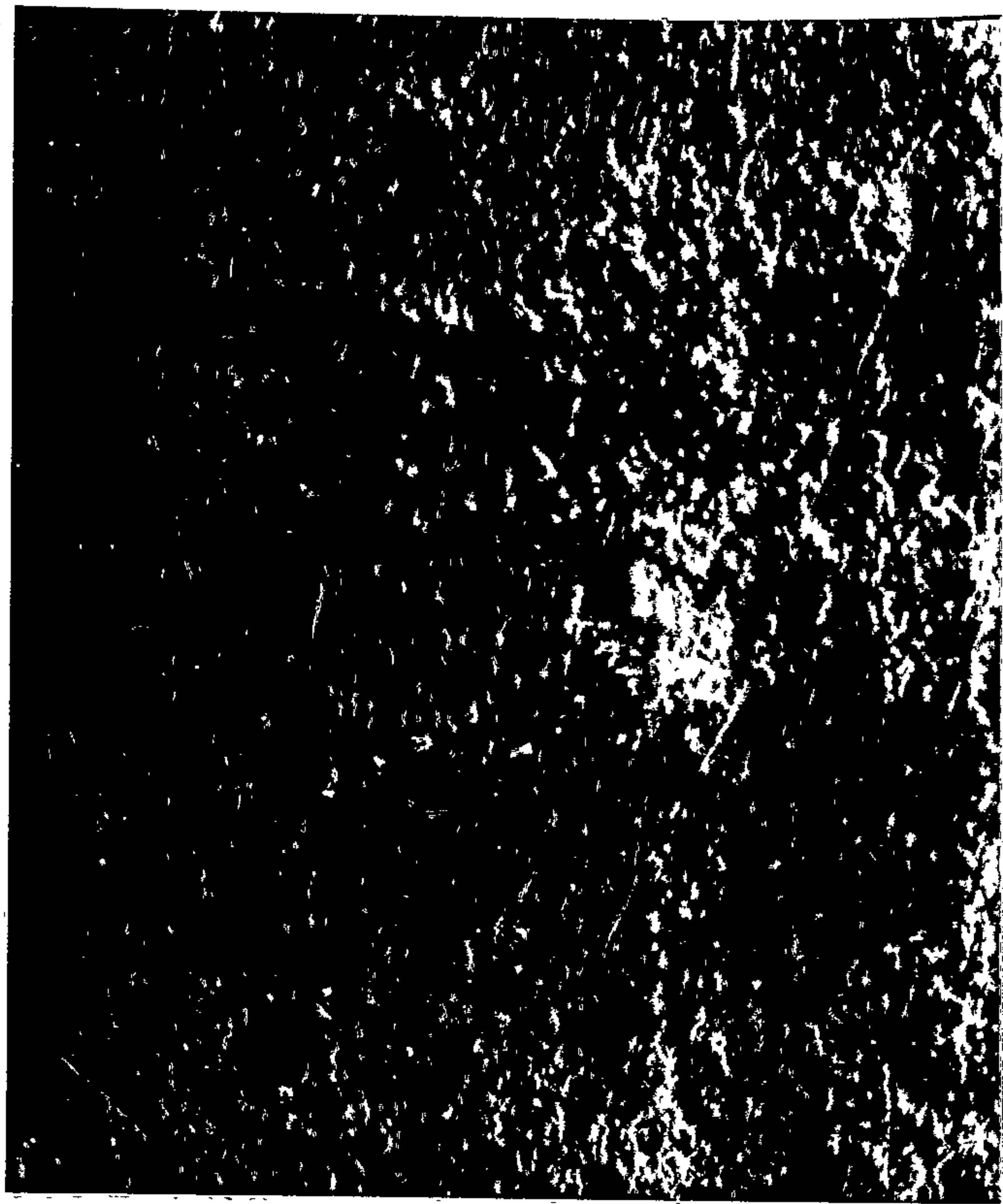
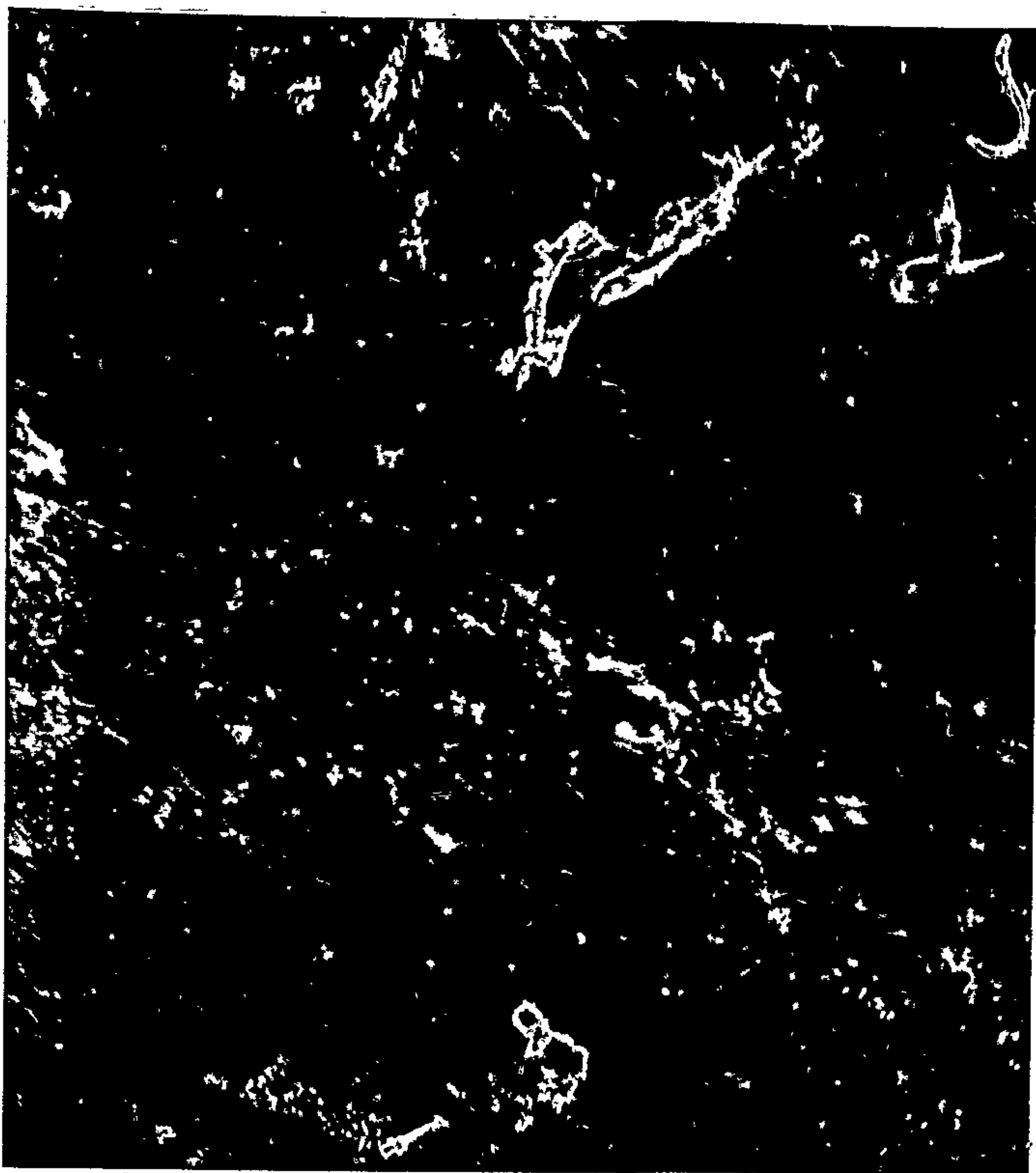
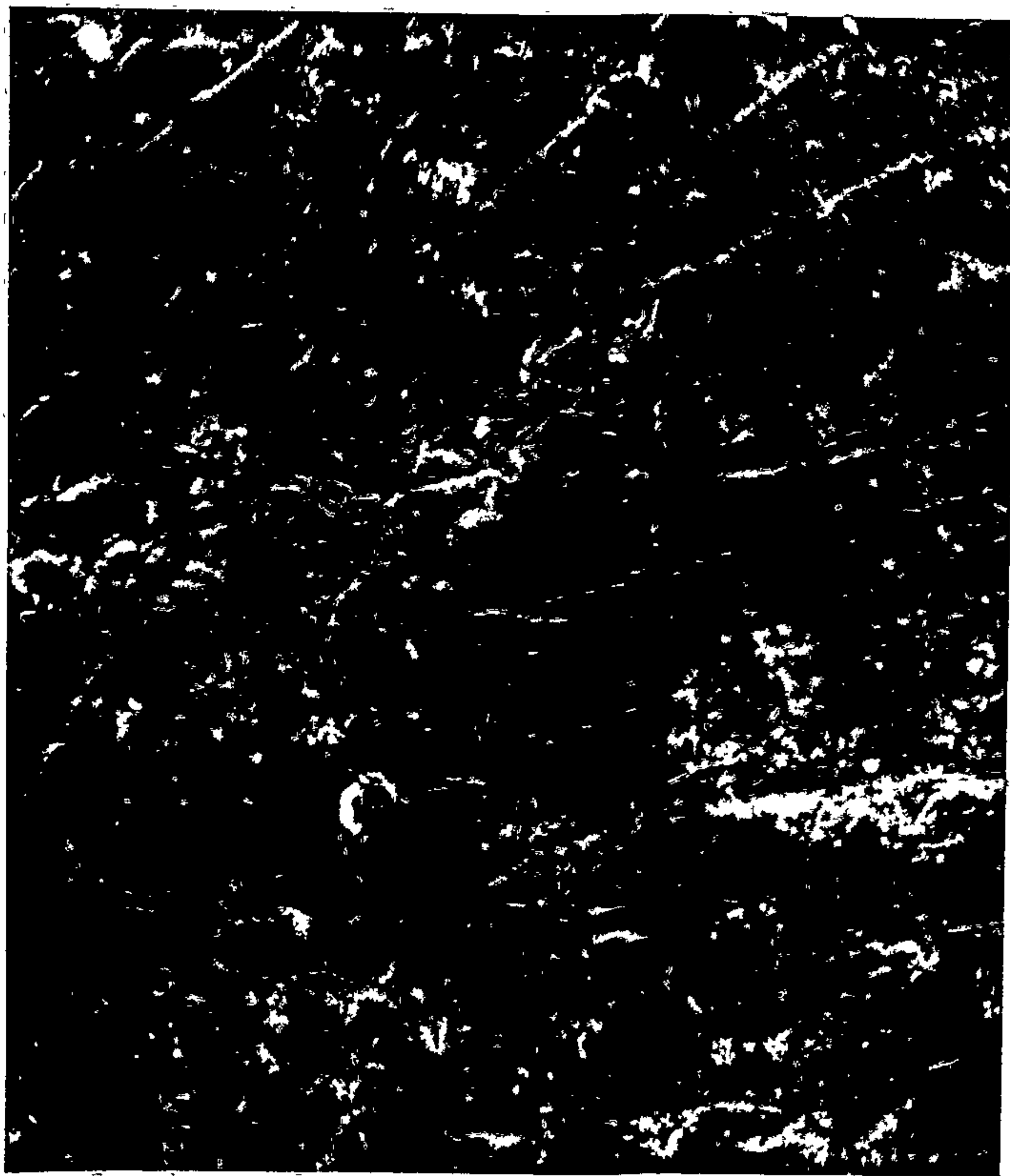
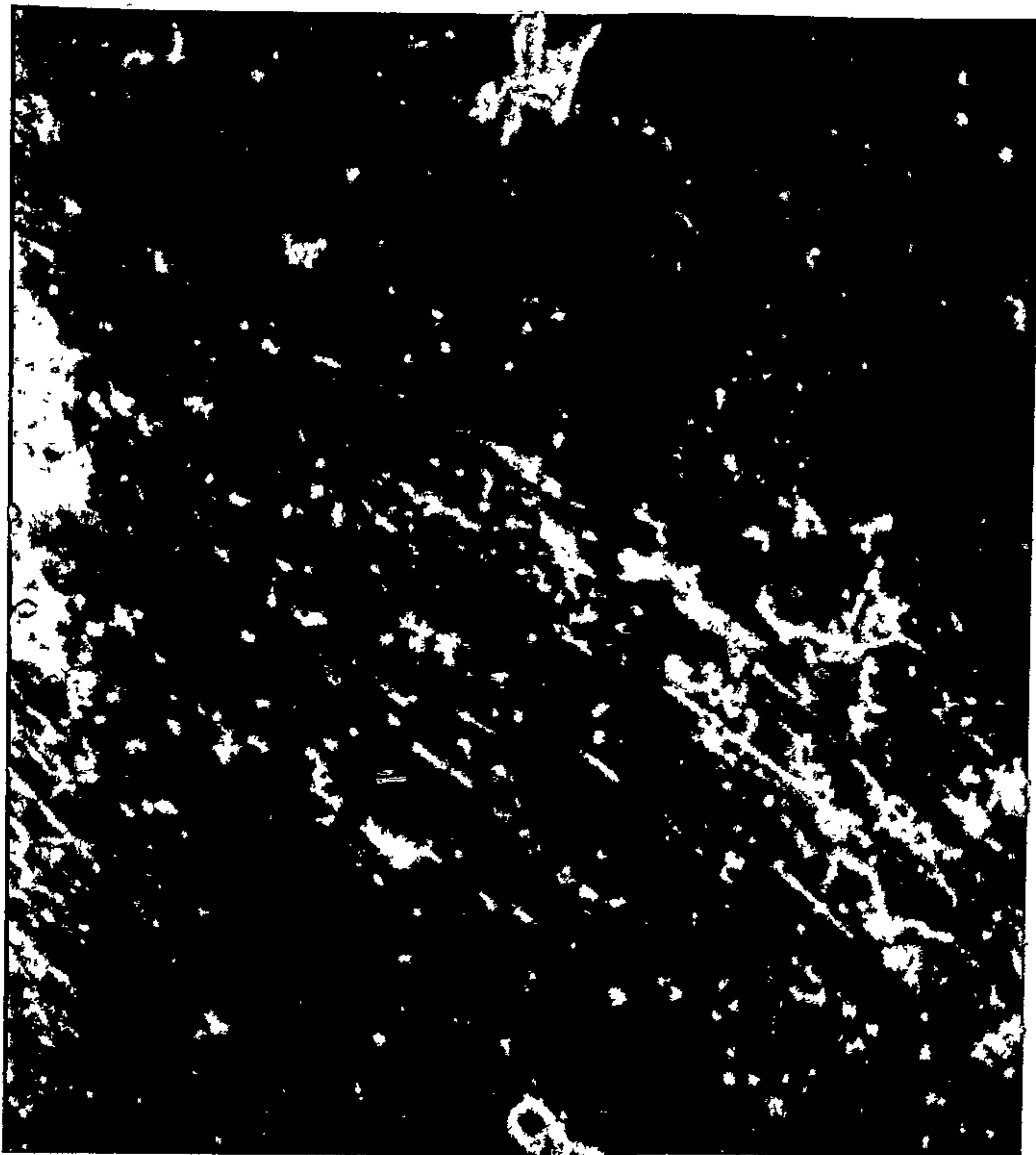
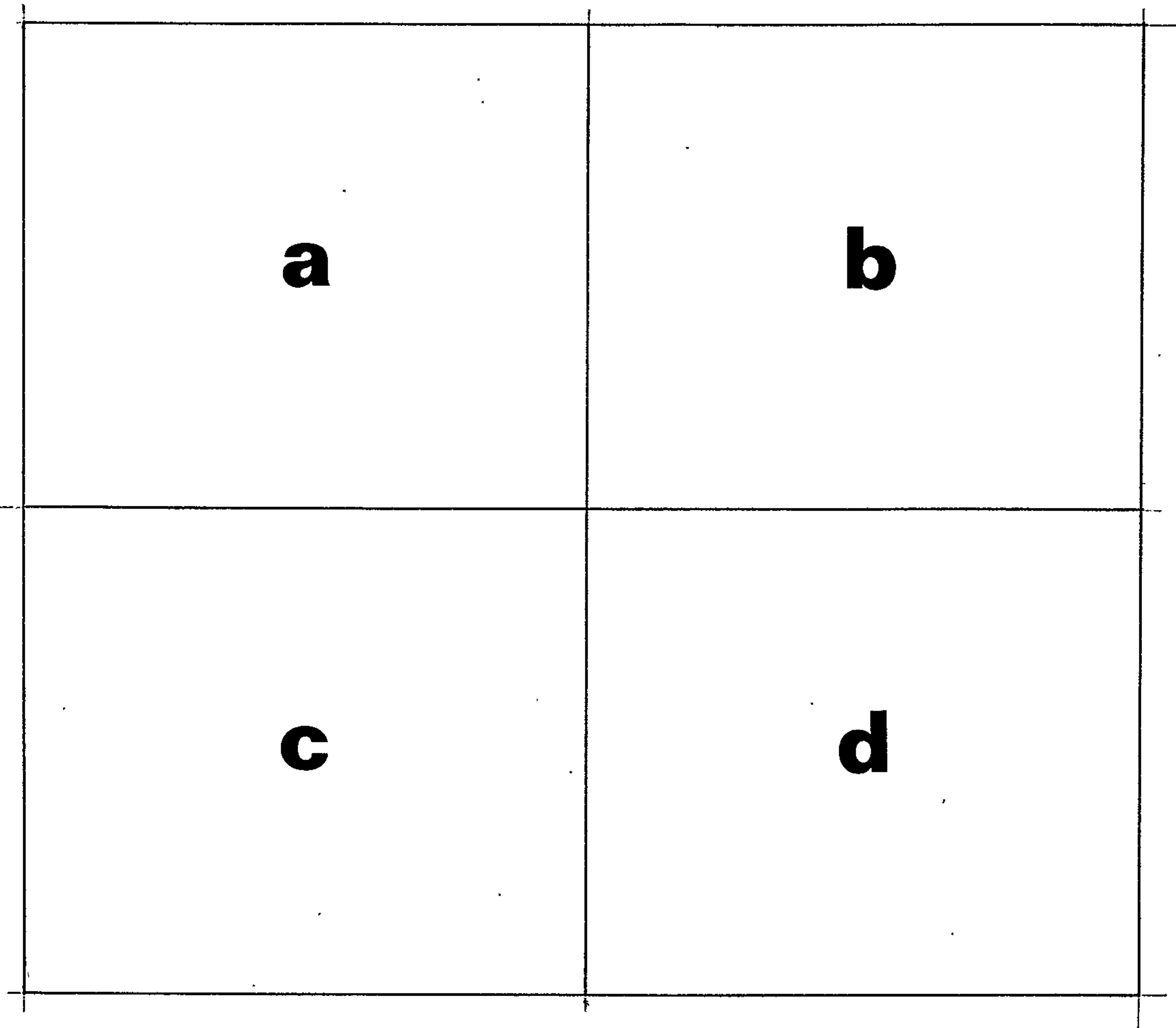


Plate 32 - Repolished Enamel Surface Microphotographs

- Experiment IV
- 1,000 X original size.



Plates 33-40 inclusive (Experiment VI) are laid out in the following manner:



where:

- a) represents 30 seconds of acid etching
- b) represents 1 minute of acid etching
- c) represents 2 minutes of acid etching
- d) represents 3 minutes of acid etching

The product used and the magnification used are detailed on the opposite page to the microphotographs.

Plate 33 - Etched Enamel Surface Microphotographs

- Effects of Product A's etching solution
- Experiment VI A
- 100 X original size.

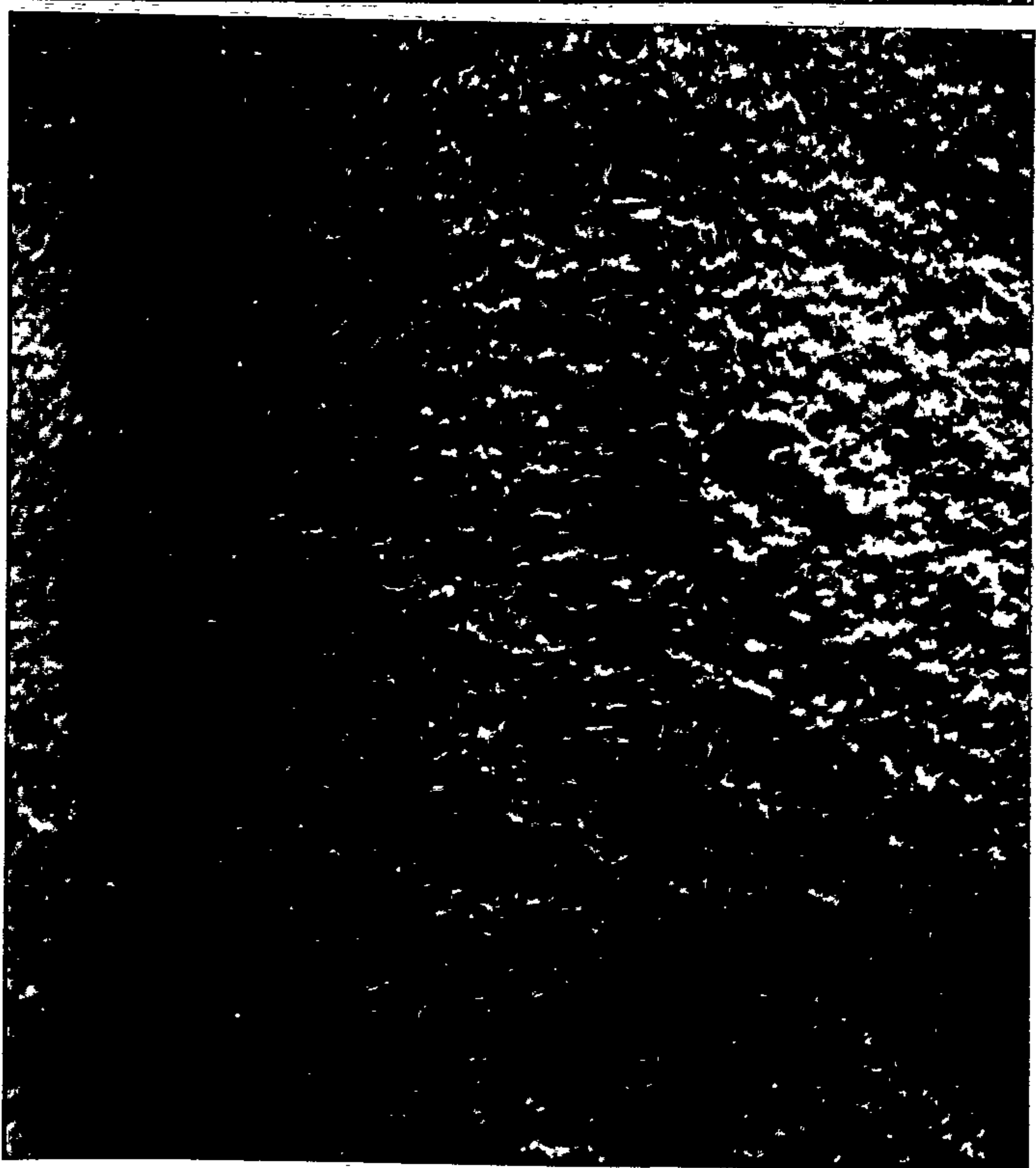
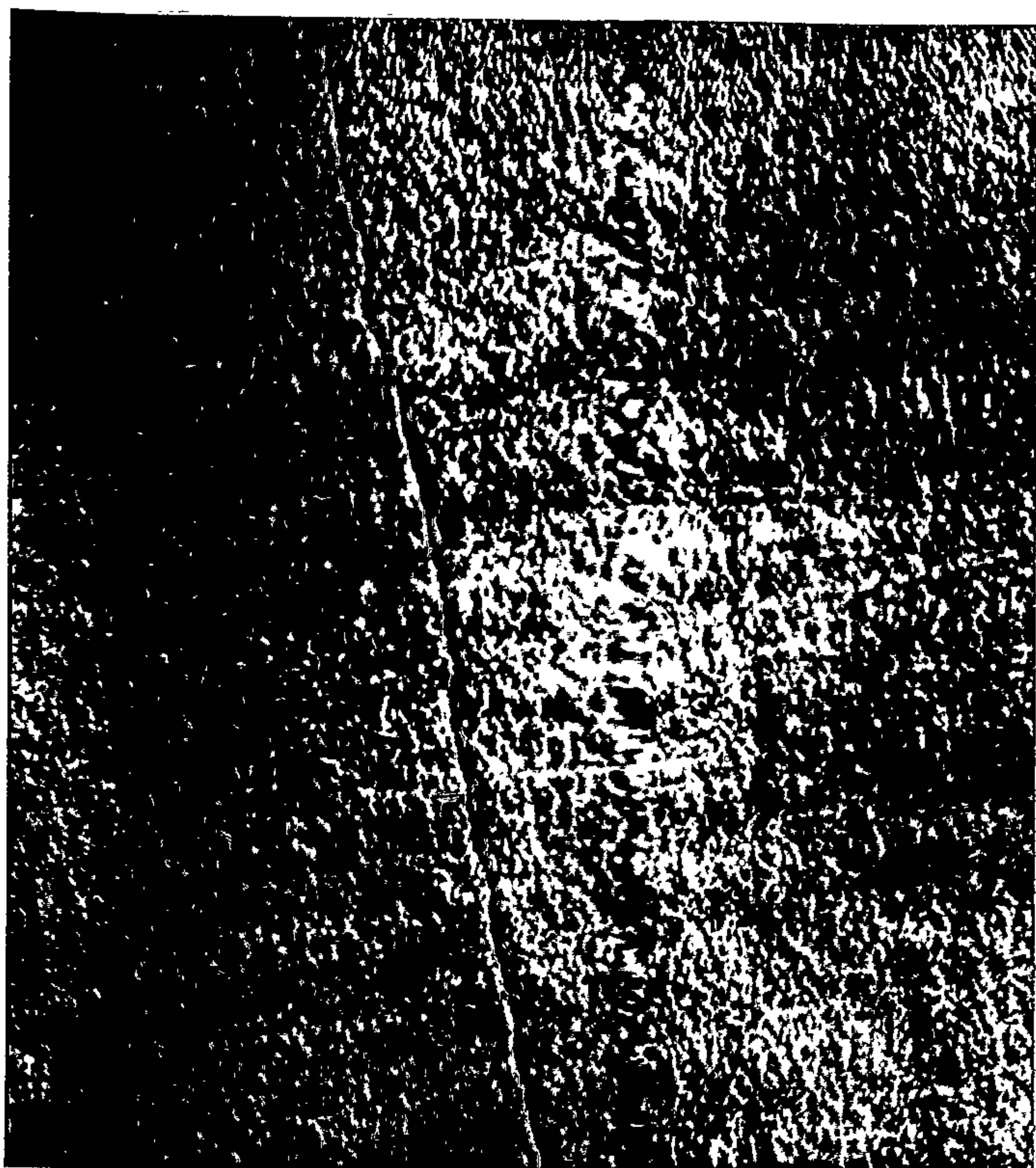


Plate 34 - Etched Enamel Surface Microphotographs

- Effects of Product B's etching solution
- Experiment VI A
- 1,000 X original size.

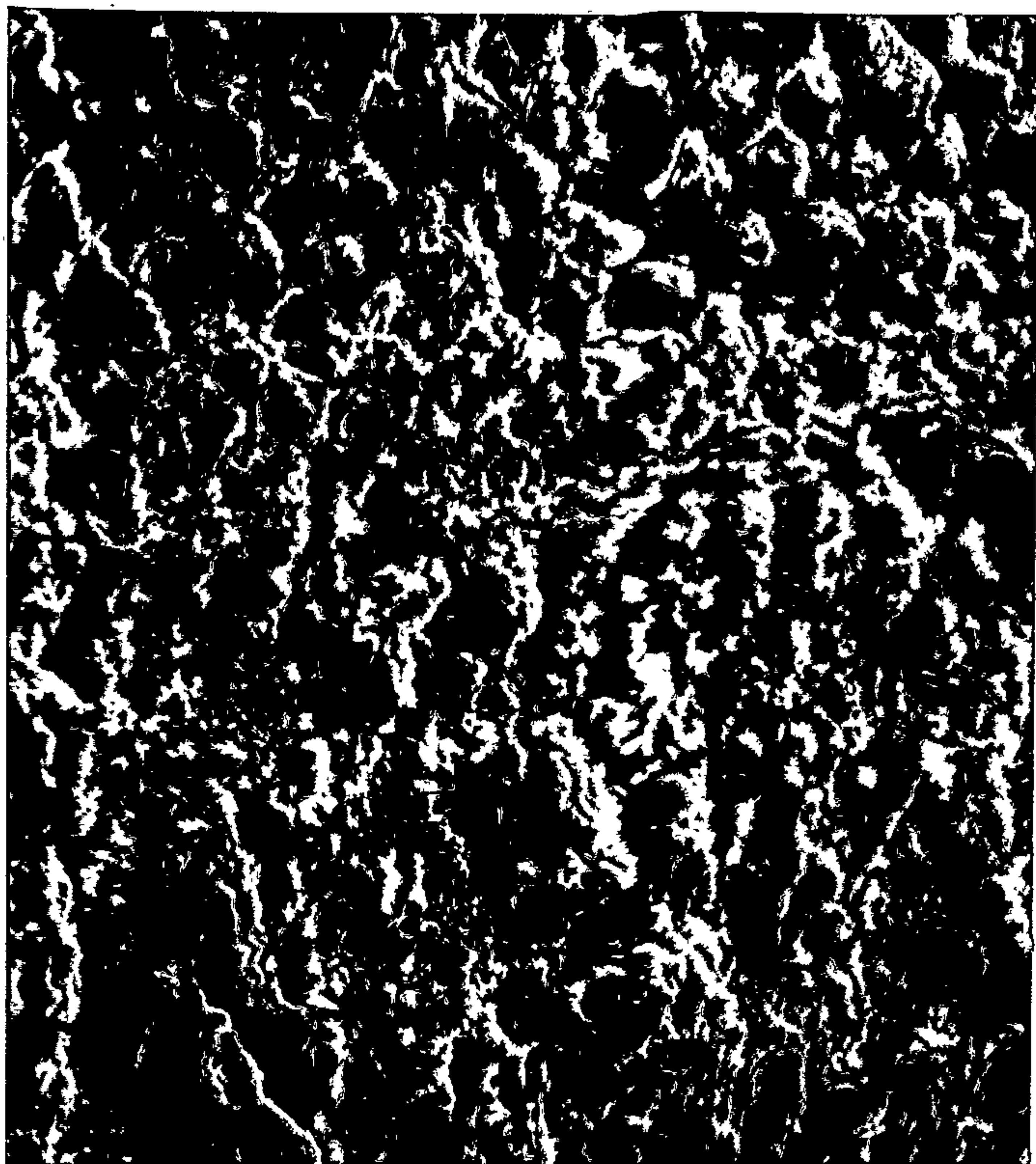


Plate 35 - Etched Enamel Surface Microphotographs

- Effects of Product B's etching solution
- Experiment VI B
- 100 X original size.

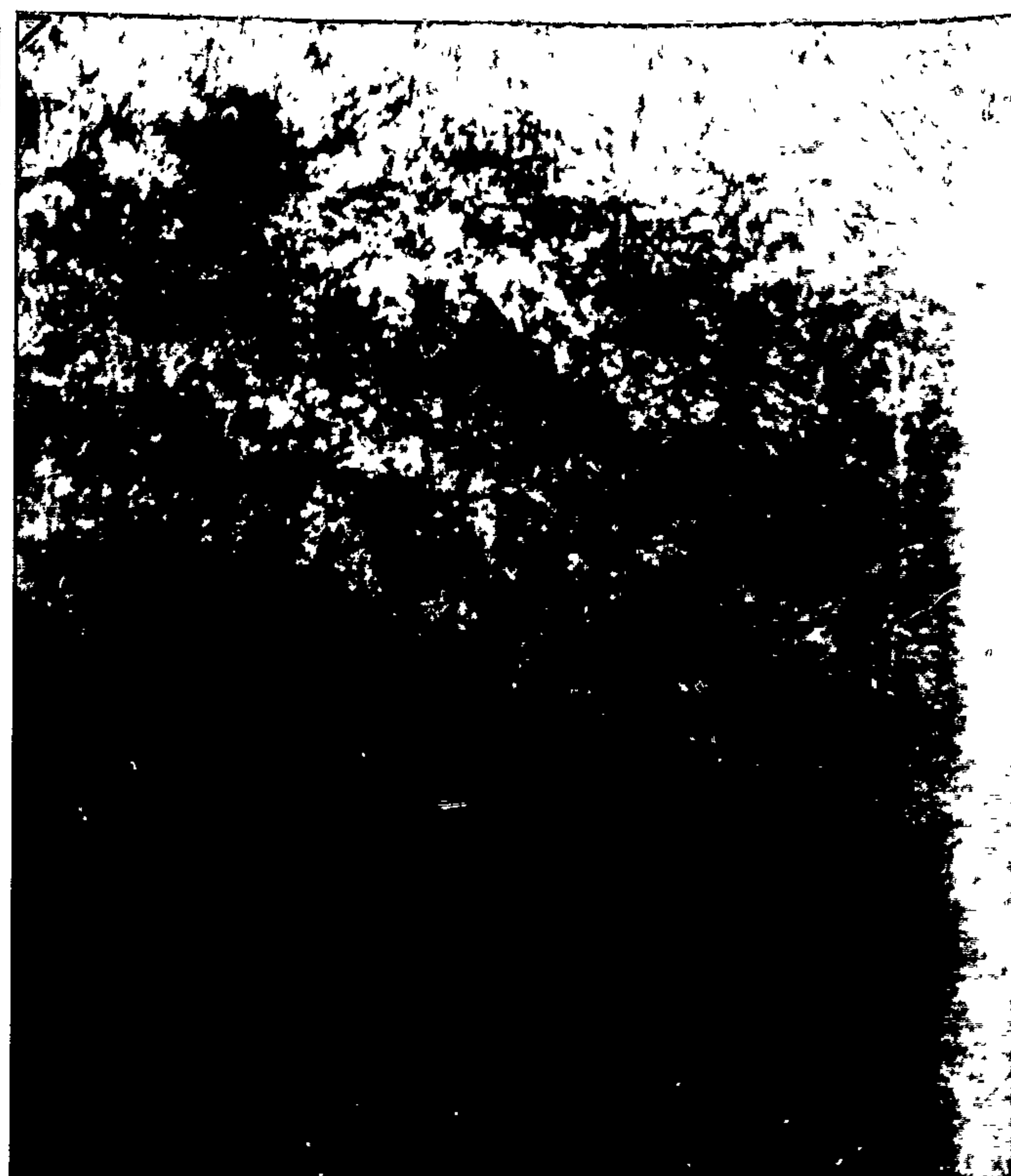
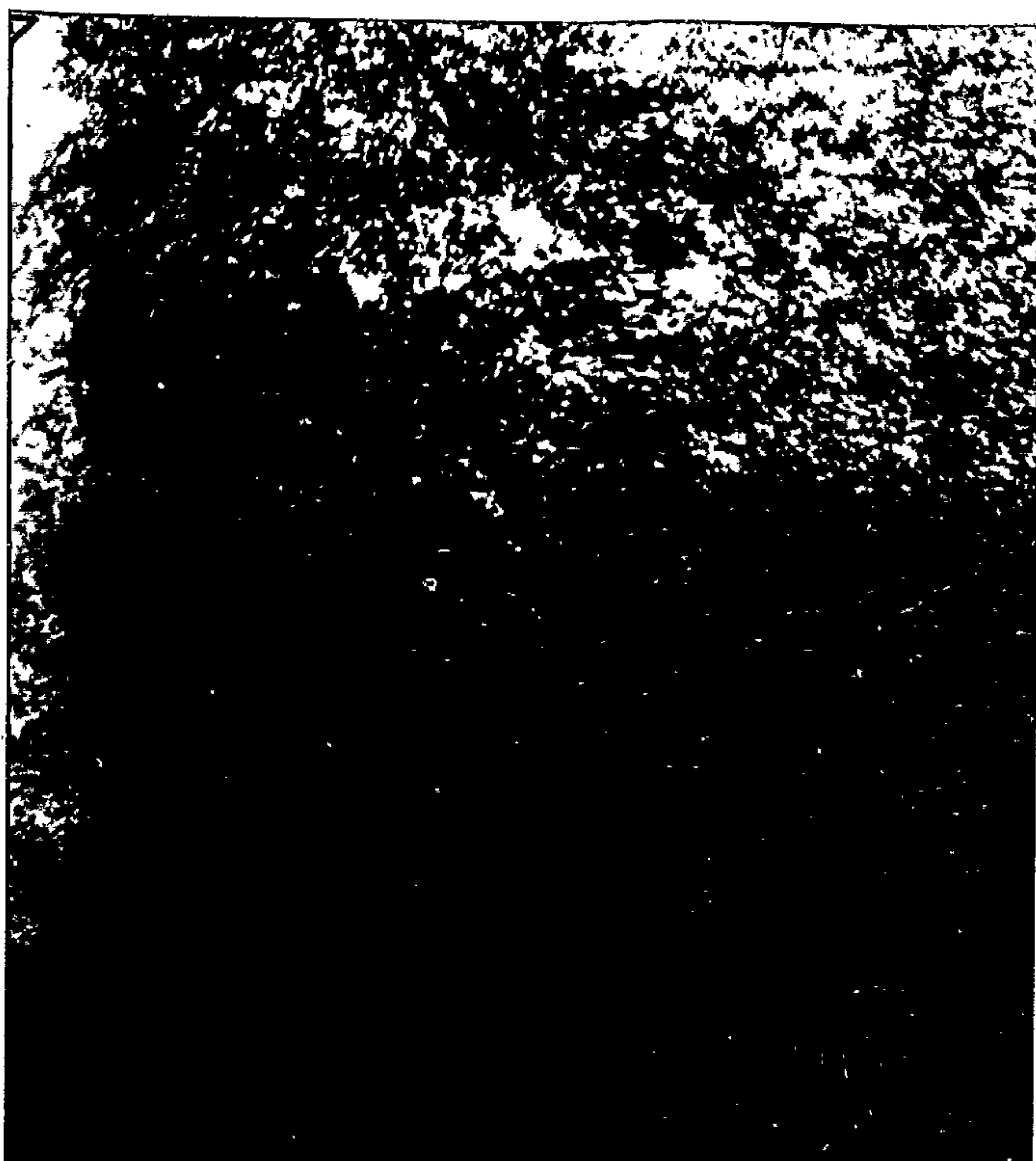


Plate 36 - Etched Enamel Surface Microphotographs

- Effects of Product B's etching solution
- Experiment VI B
- 1,000 X original size.

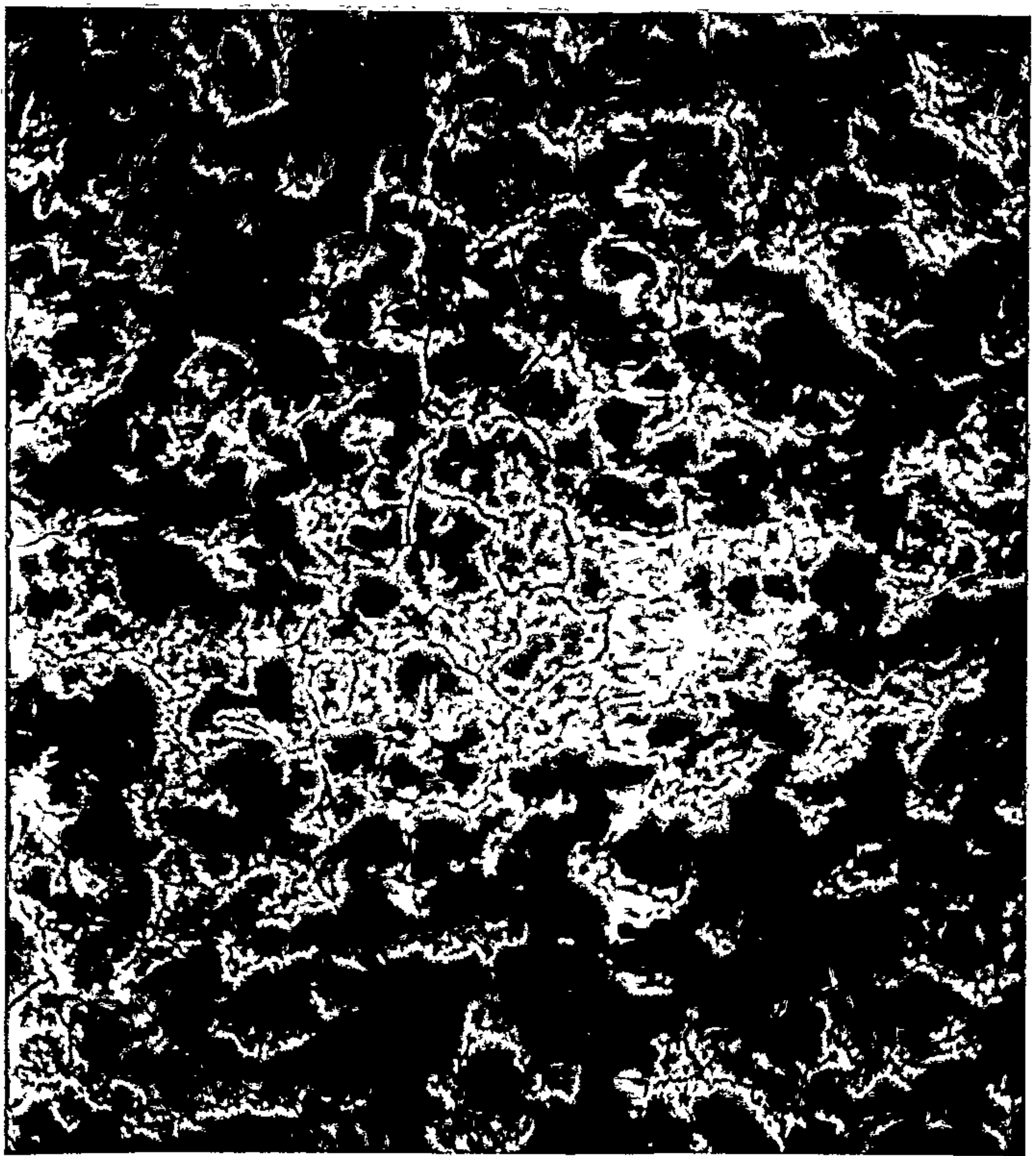
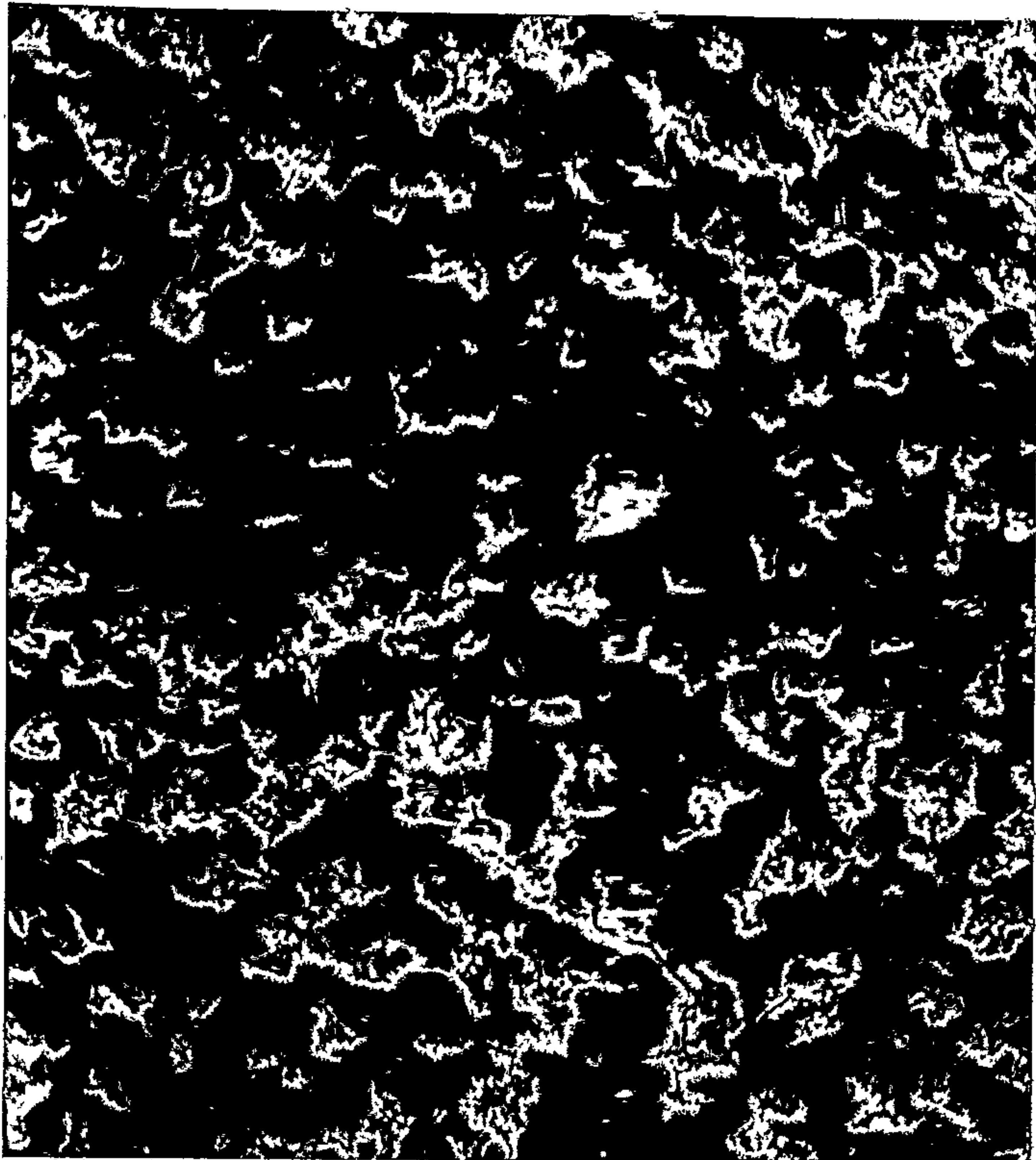


Plate 37 - Etched Enamel Surface Microphotographs

- Effects of Product C's etching solution
- Experiment VI C
- 100 X original size.

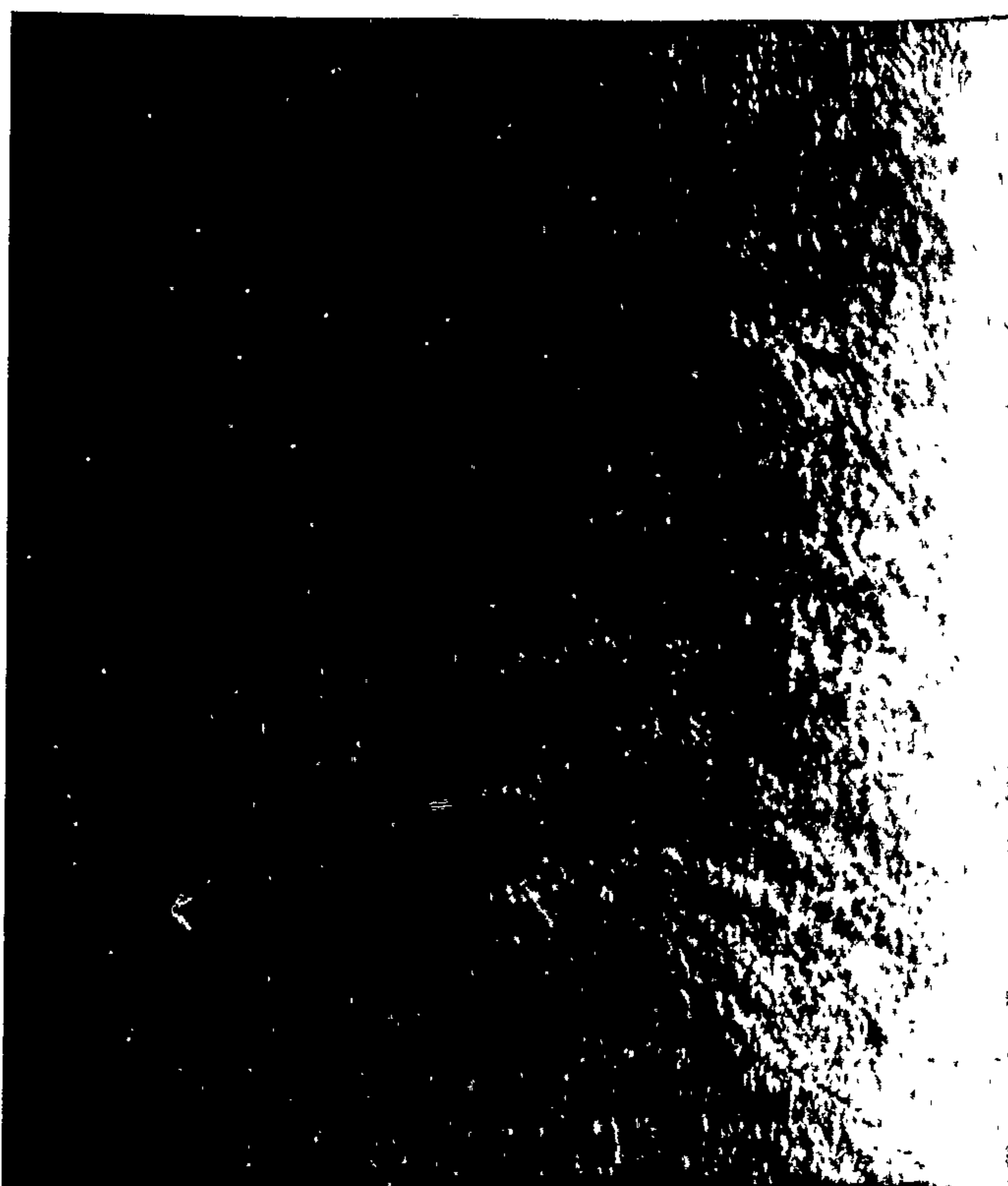
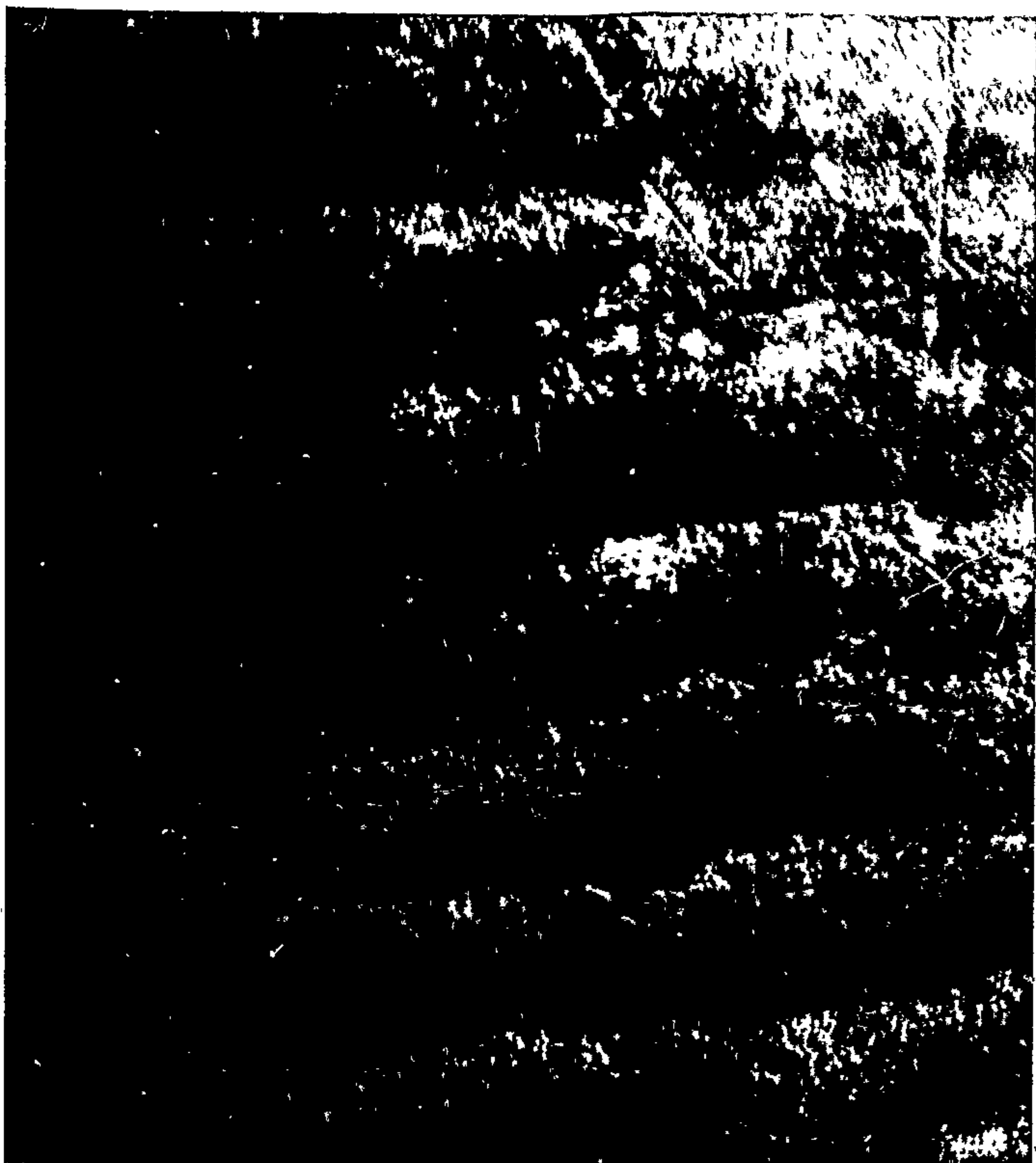


Plate 38 - Etched Enamel Surface Microphotographs

- Effects of Product C's etching solution
- Experiment VI C
- 1,000 X original size.

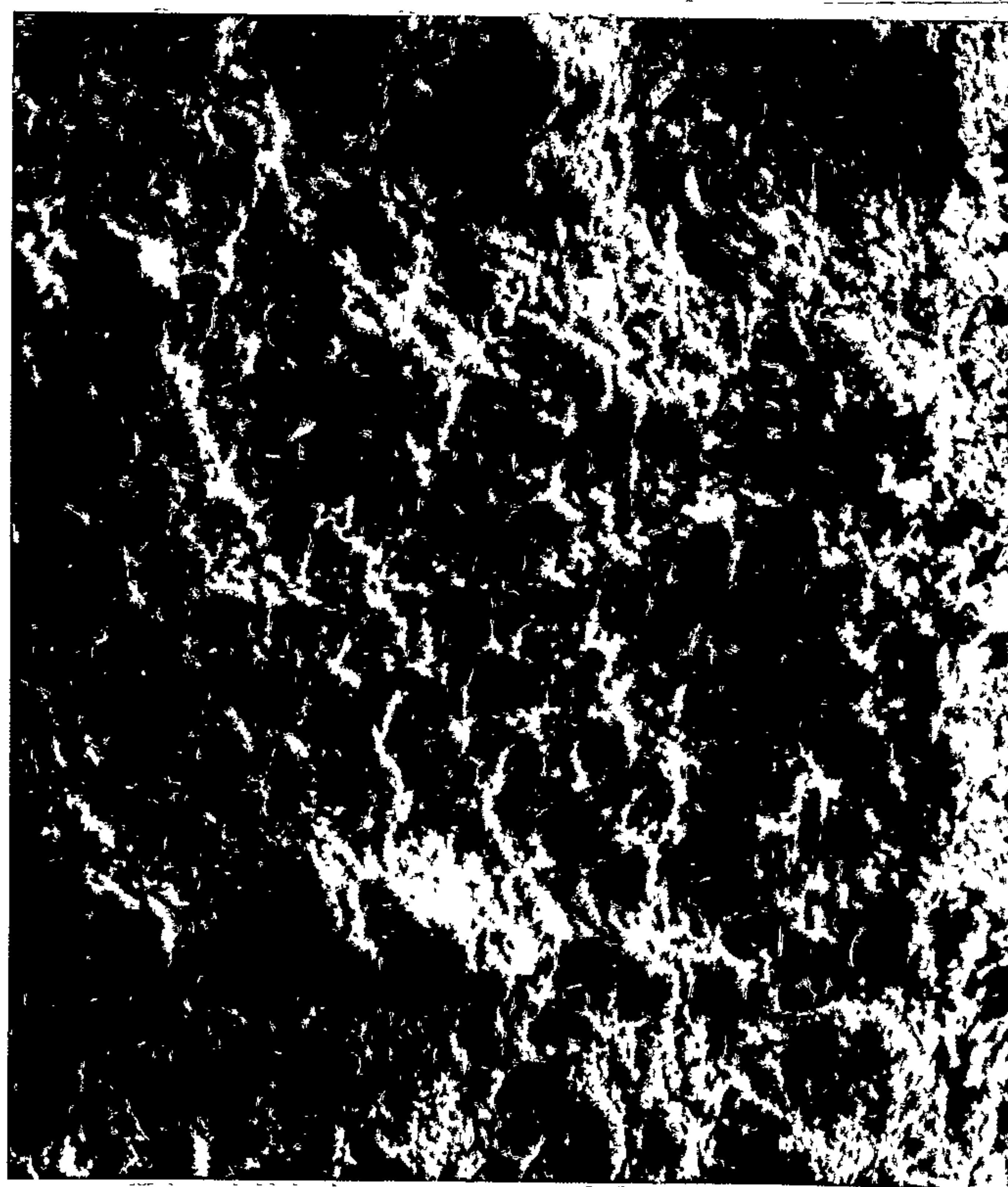
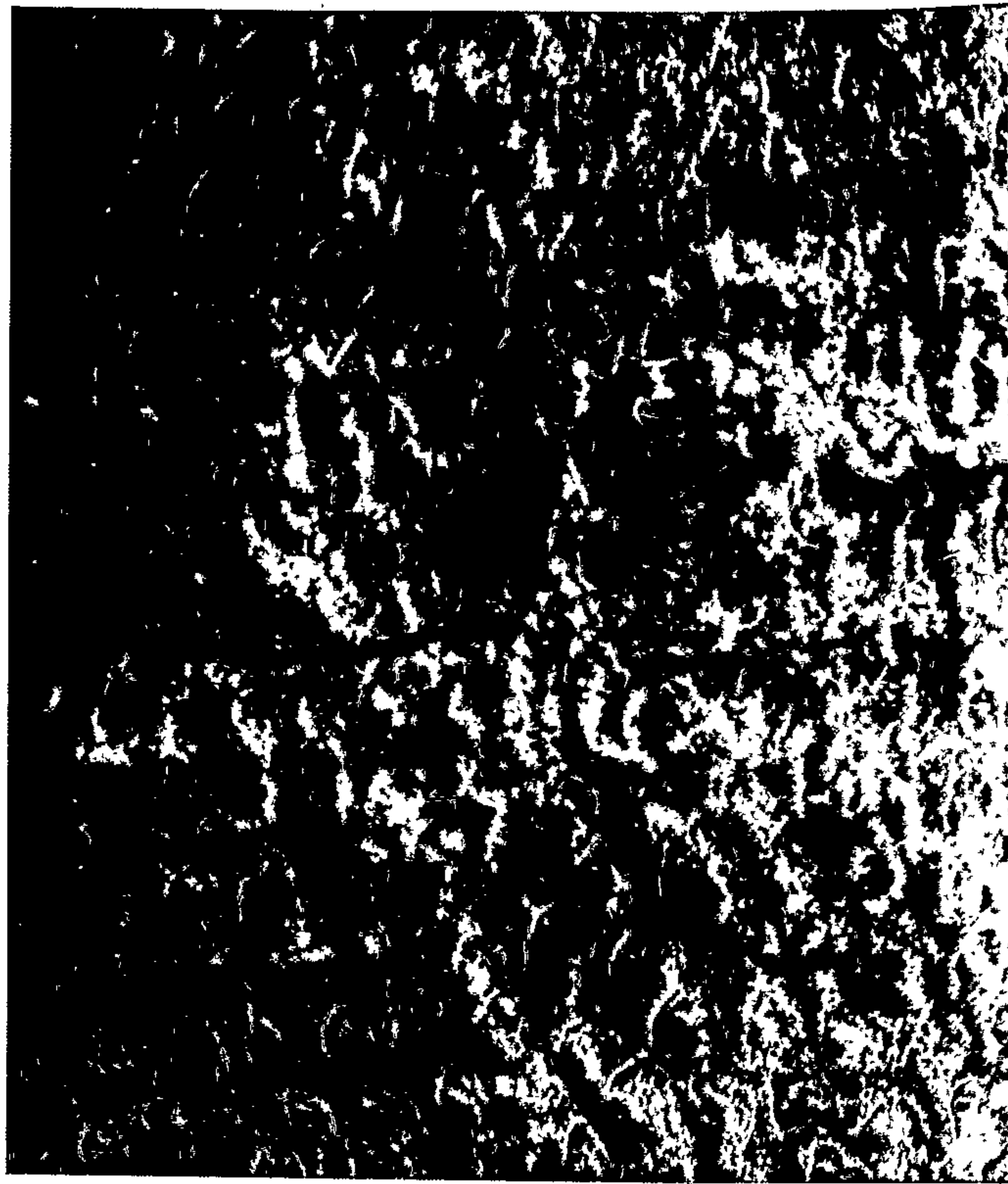


Plate 39 - Etched Enamel Surface Microphotographs

- Effects of Product D's etching solution
- Experiment VI D
- 100 X original size.

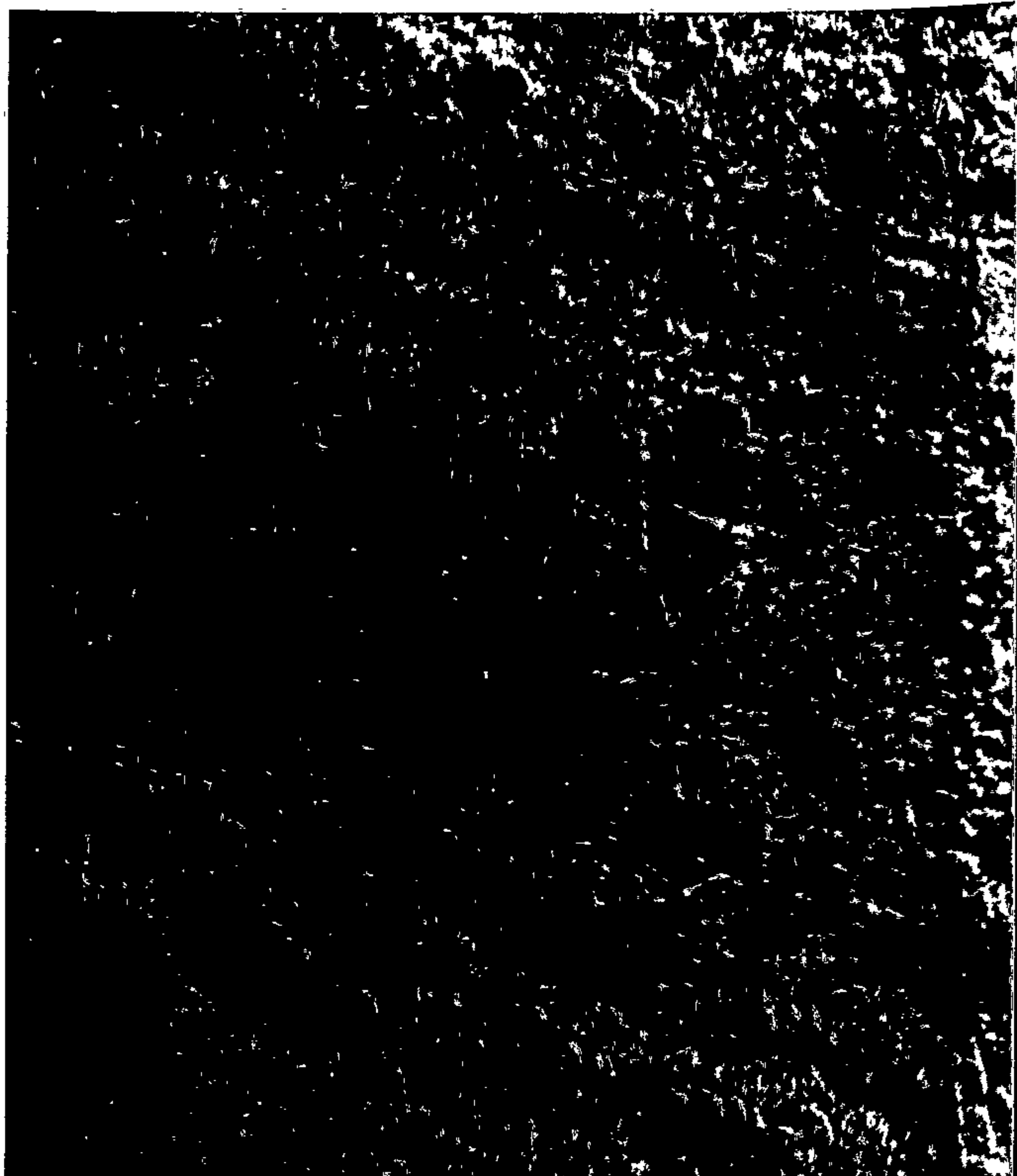
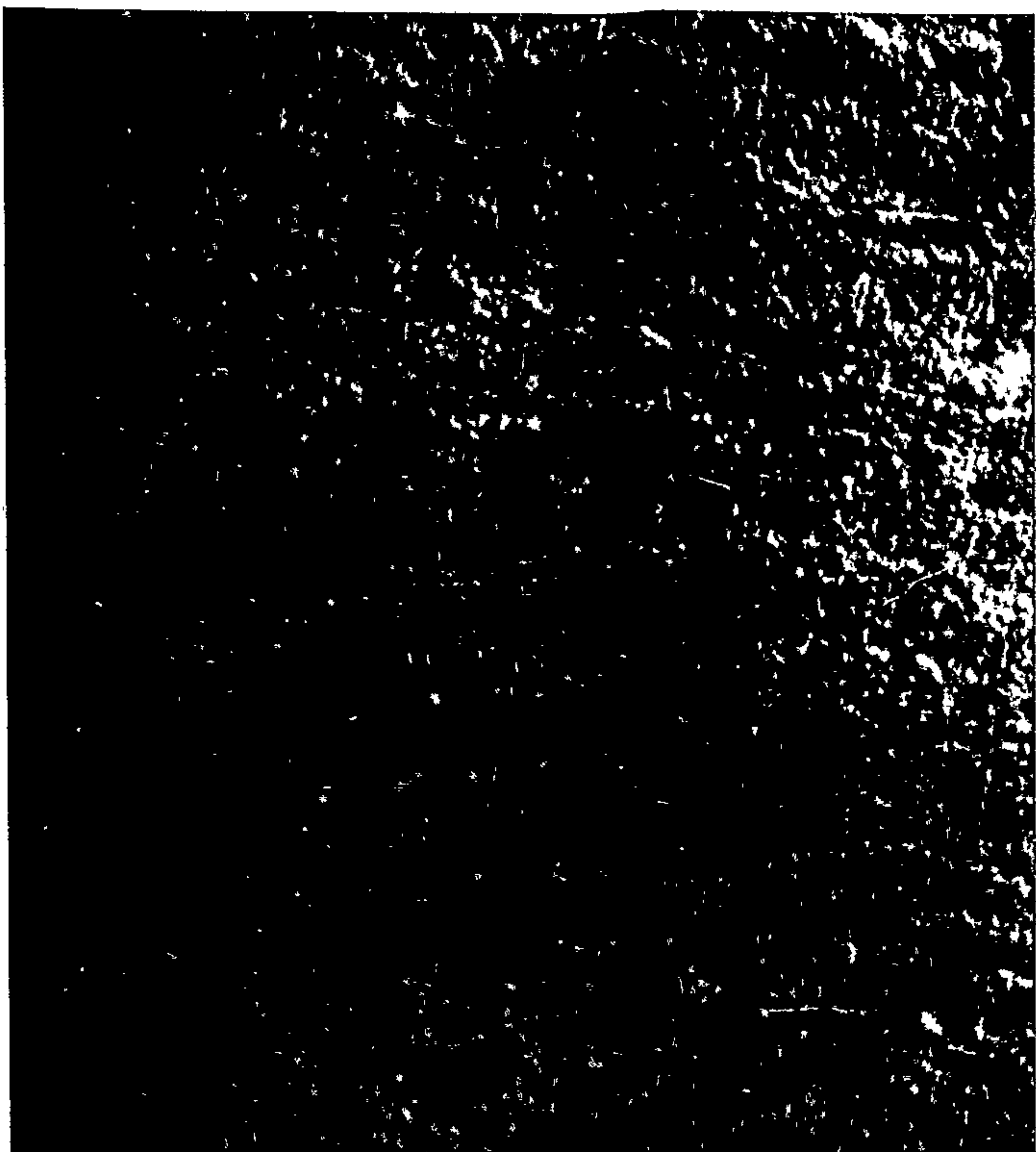


Plate 40 - Etched Enamel Surface Microphotographs

- Effects of Product D's etching solution
- Experiment VI D
- 1,000 X original size.

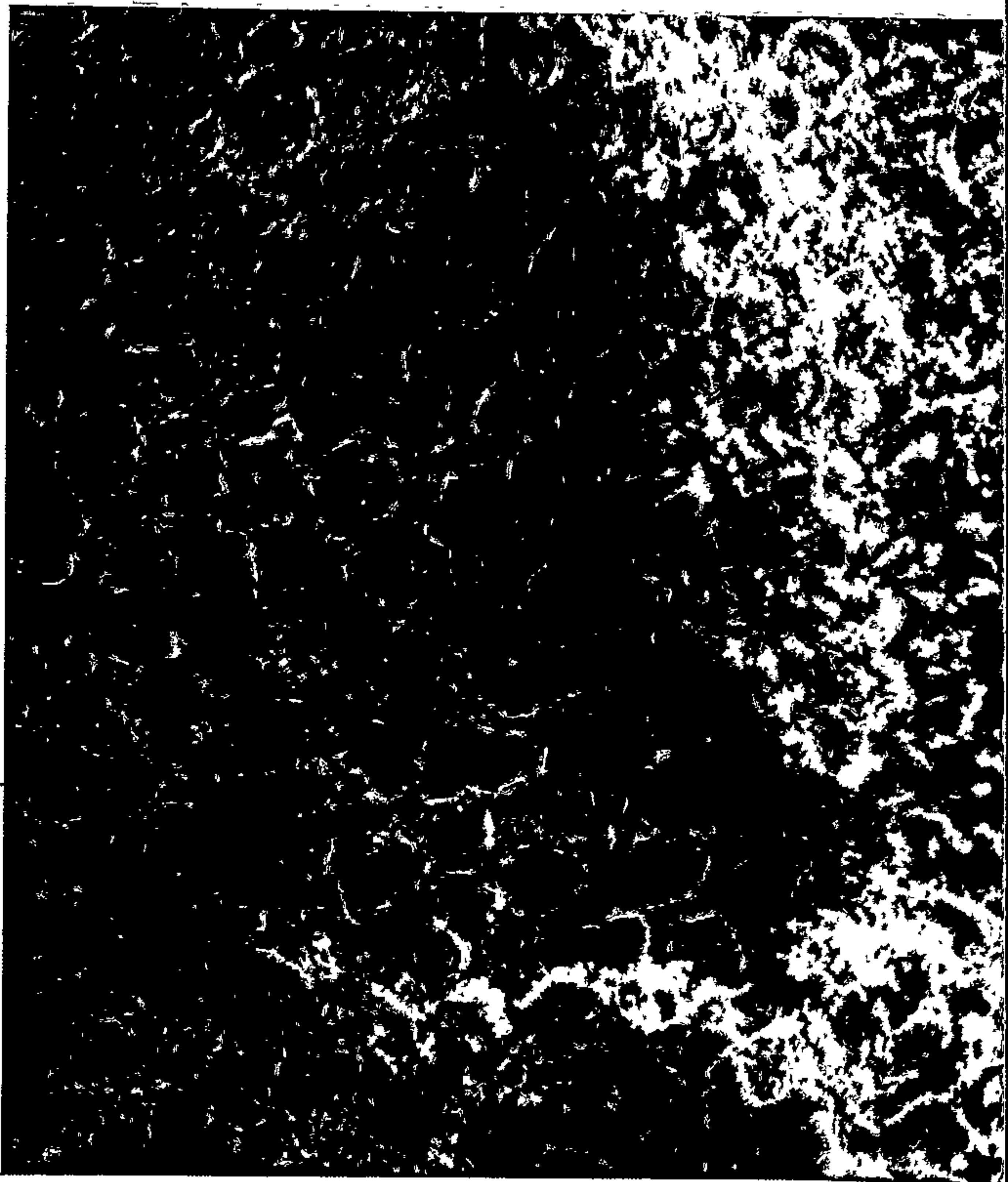
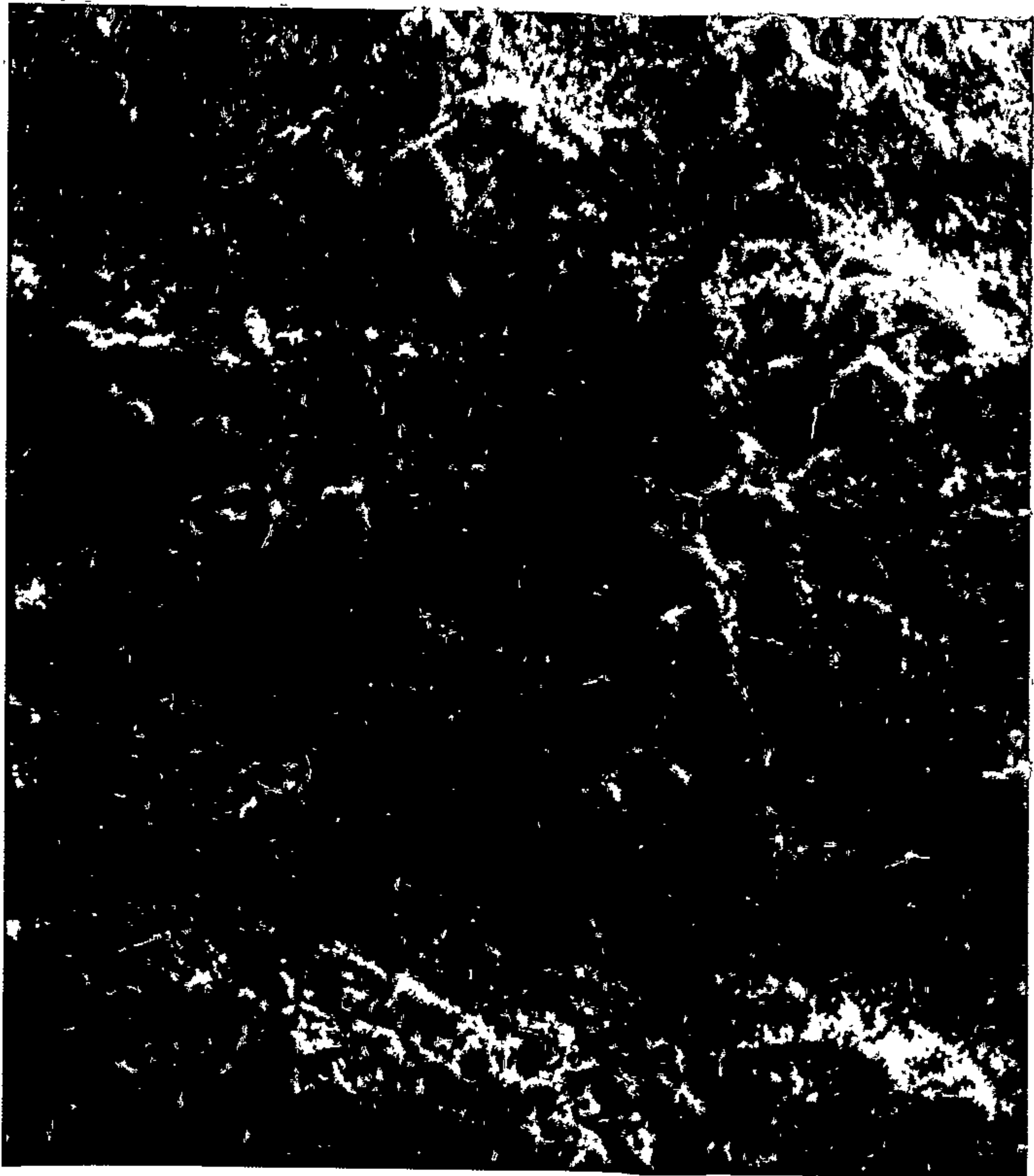
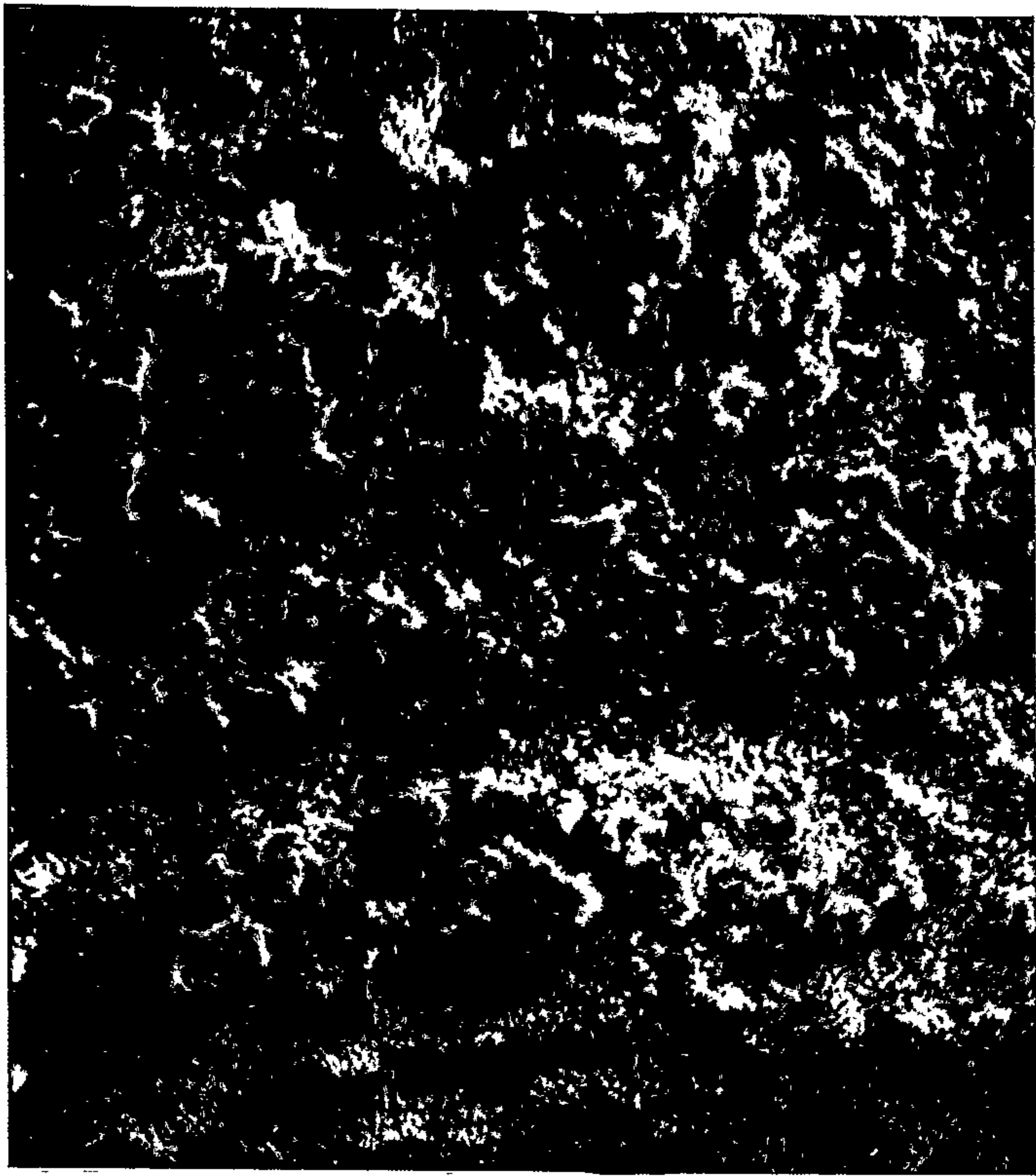


Plate 41 - Adhesive and Adjacent Enamel

This microphotograph shows some uncovered (unprotected) etched enamel adjacent to the adhesive remnant. Such areas were found on all bonded surfaces.

65 X original size.



Plate 42 - Prism Core - Type of Etching

Etching was effected by a 2 minute application of the etching solution of Product C (50% phosphoric acid and 7% zinc oxide, by weight).

a) 3,000 X original size.

b) 6,000 X original size.



Plate 43

Etching was effected by a 3 minute application of the etching of Product D (40.4% pyruvic acid).

a) 6,000 X original size.

b) 9,000 X original size.

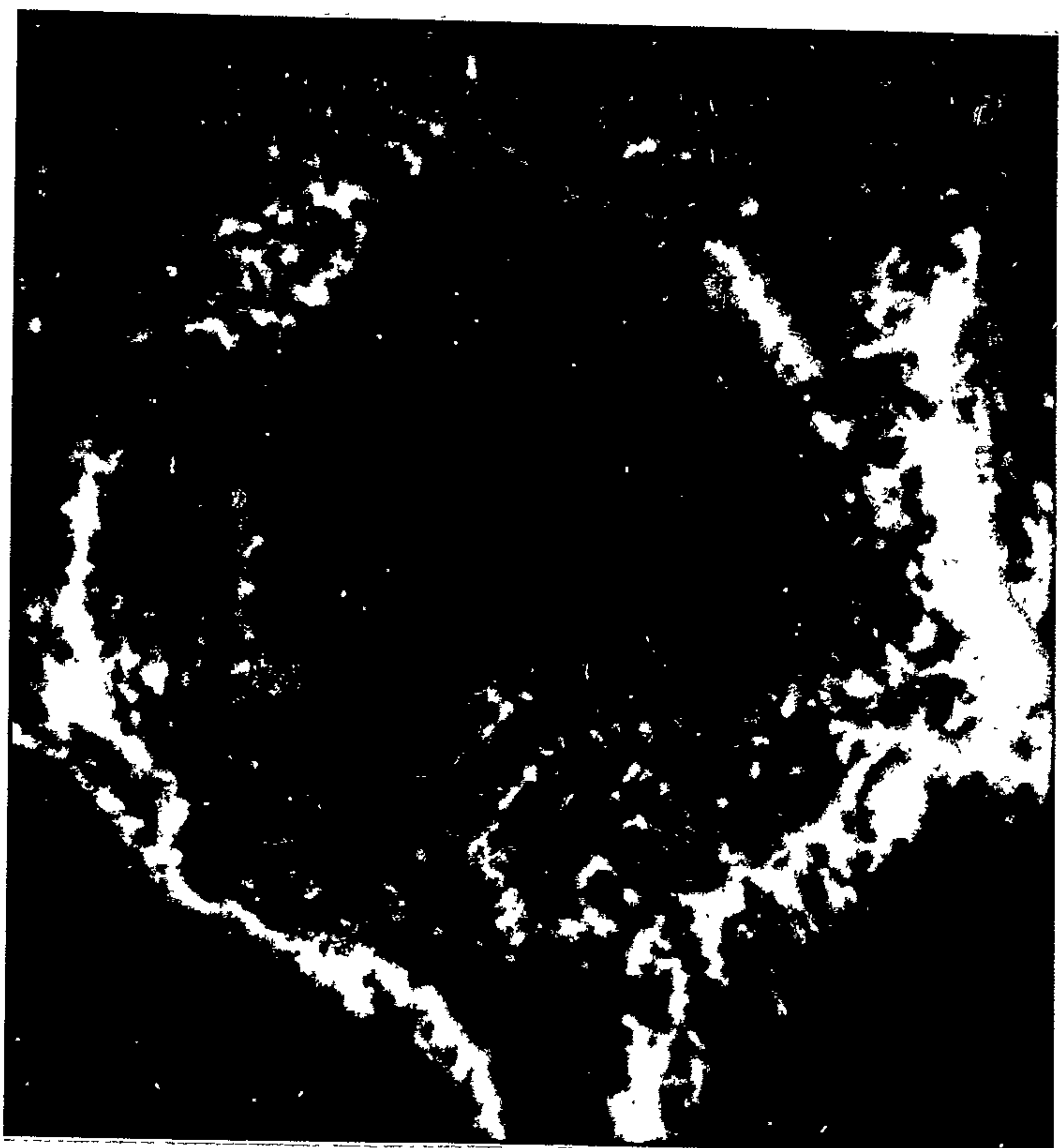
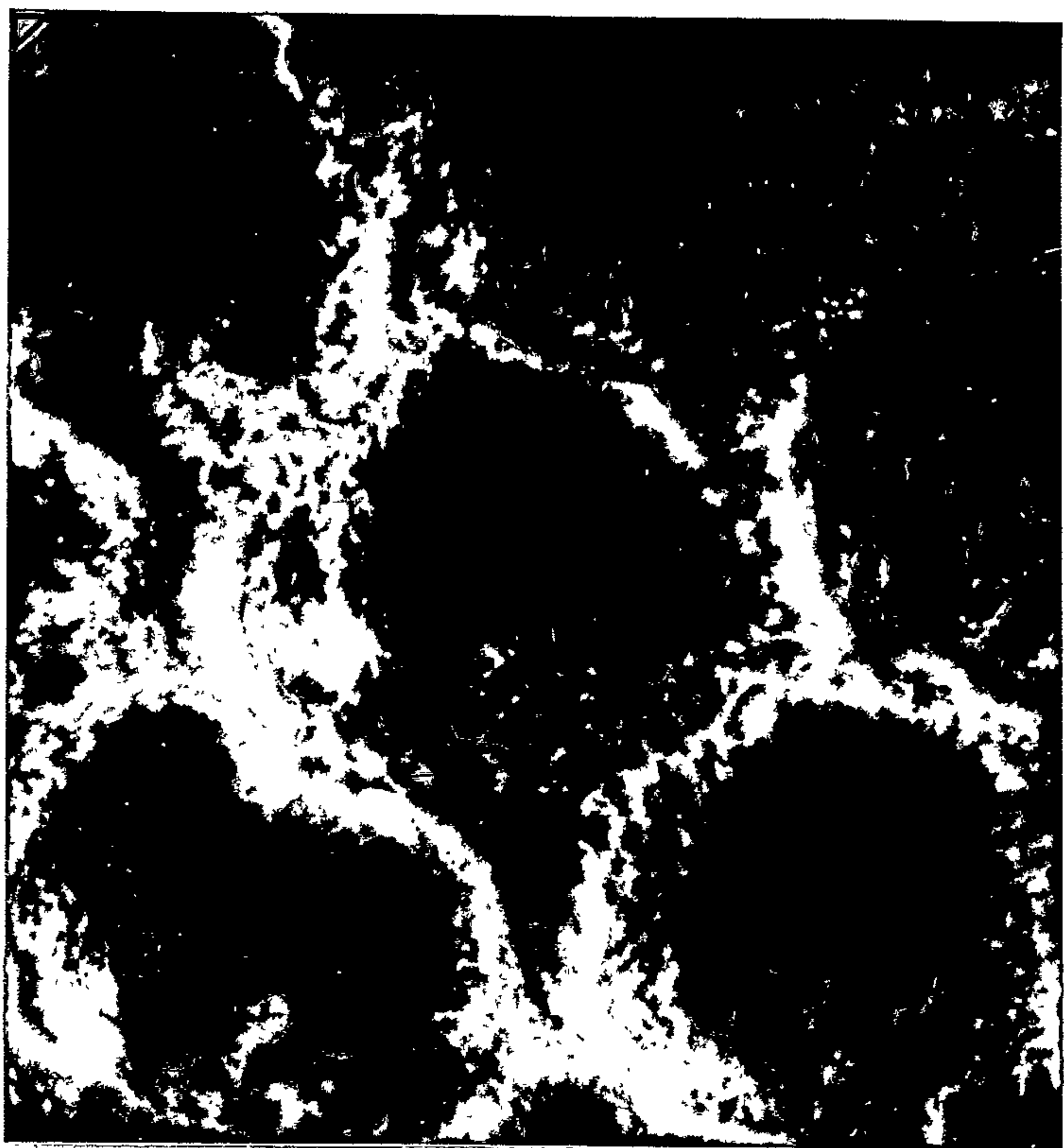


Plate 44 - Prism Periphery and Core-Types of Etching

Both these types of etching patterns can be seen in this microphotograph. These patterns were produced by a 3 minute application of Product D (40.4% pyruvic acid).

- a) The upper left half shows prism core-type while the prism periphery type can be seen in the lower right half.
1,000 X original size.

- b) As above.
4,000 X original size.

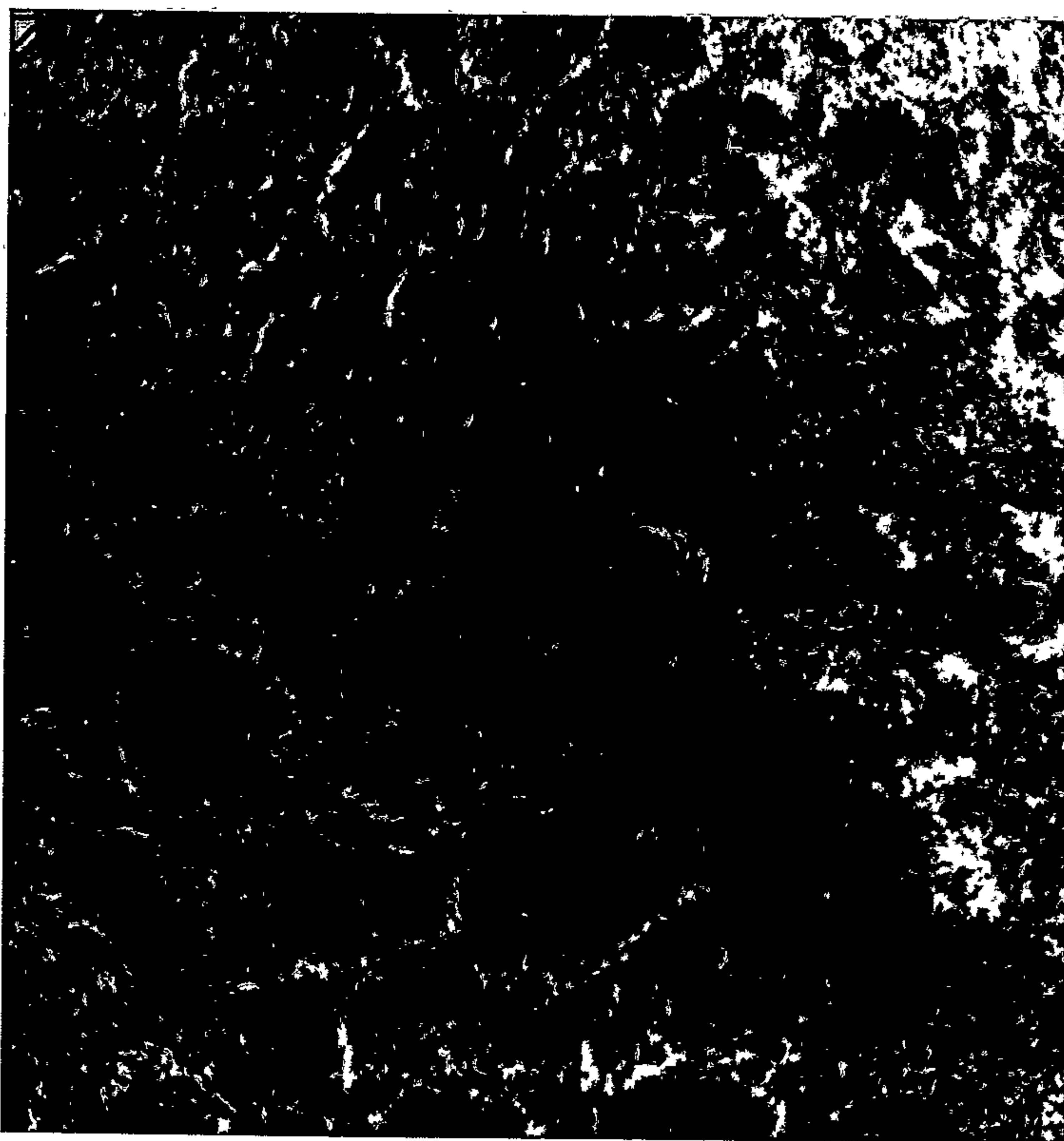
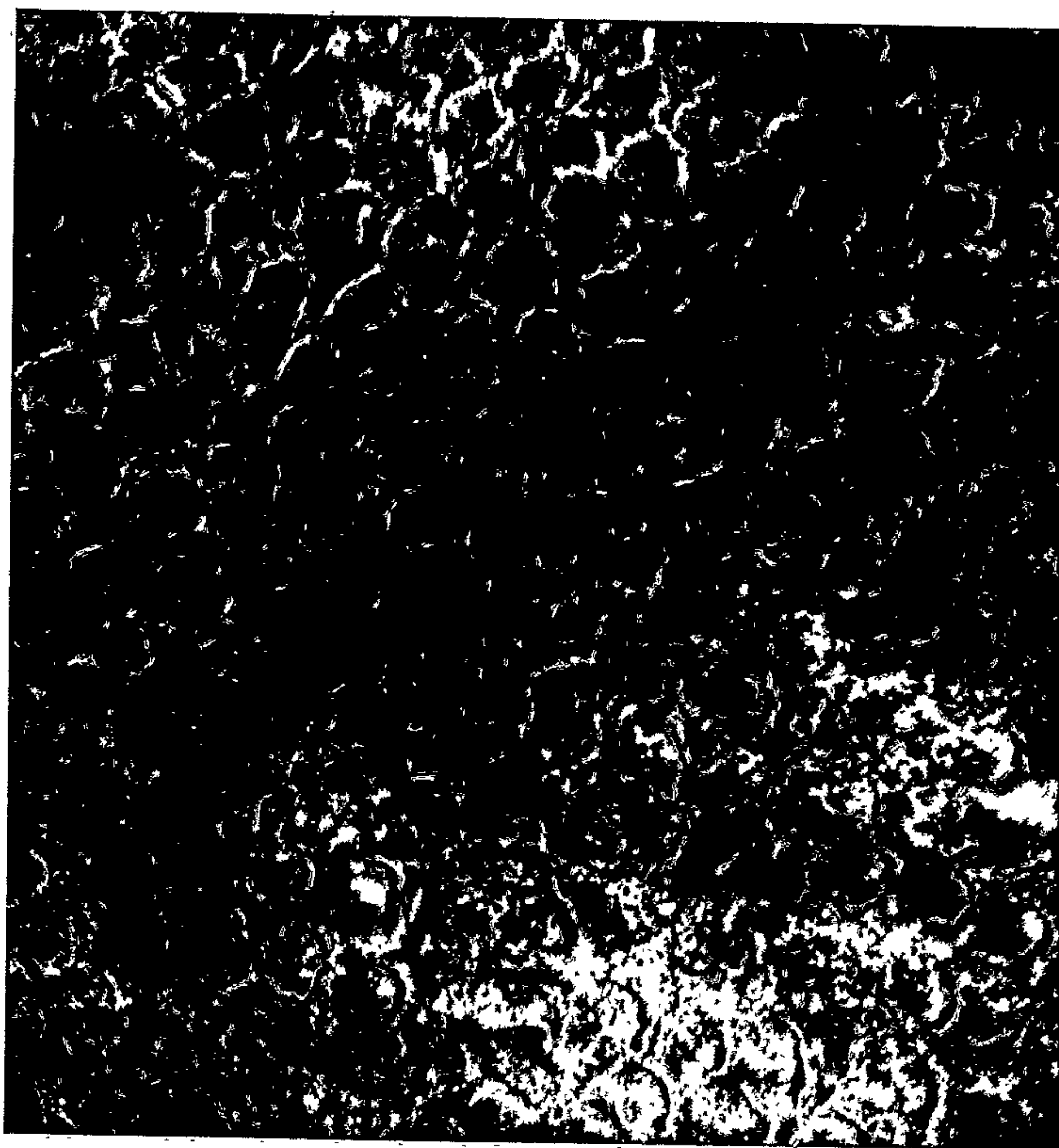


Plate 45 - Prism Periphery - Type of Etching

This etching pattern was produced by a 3 minute application of the etching solution of Product D (40.4% pyruvic acid).
4,500 X original size.

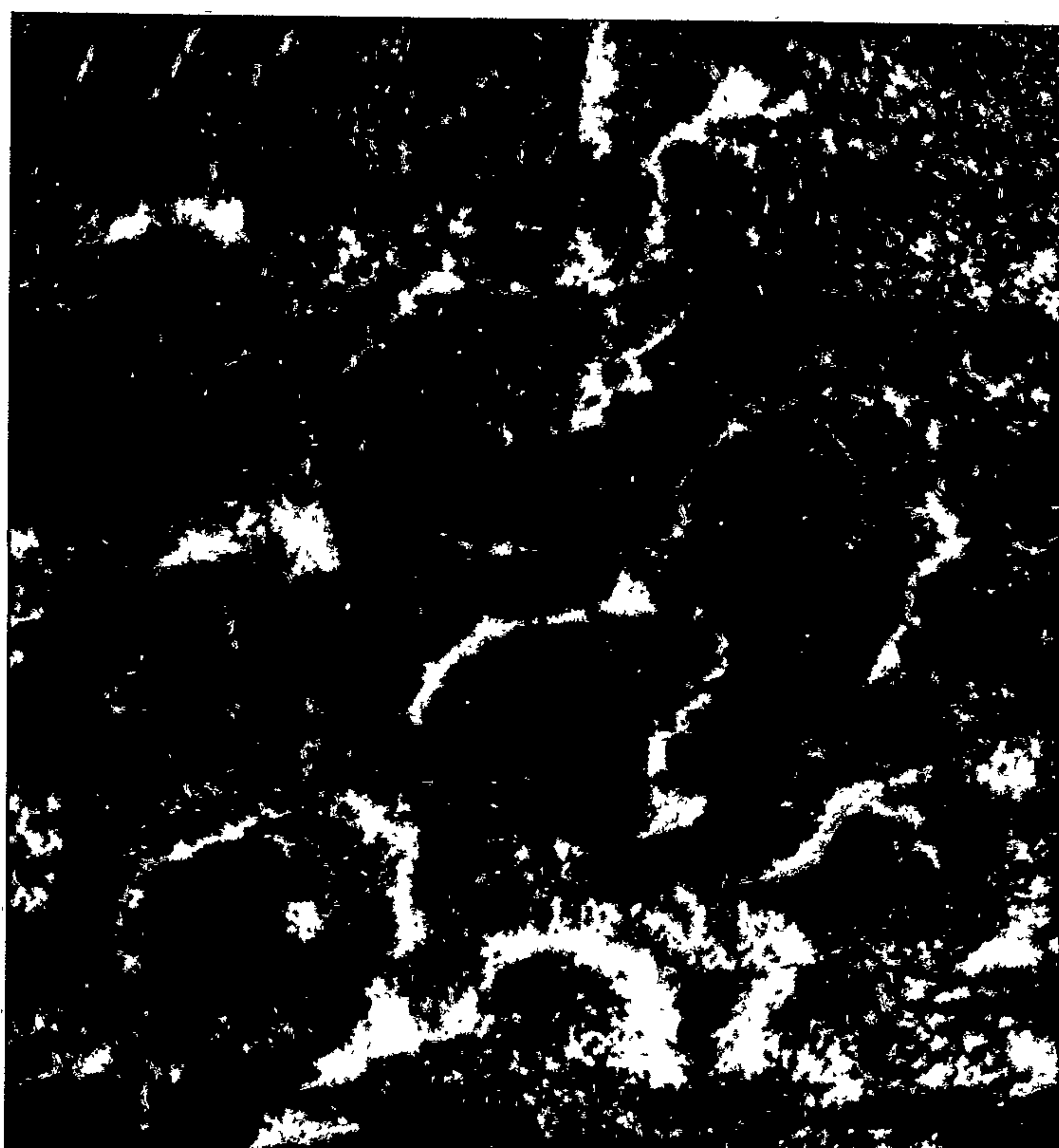


Plate 46 - A "Good Bonding Surface"

This surface was produced by a 3 minute application of the etching solution of Product D (40.4% pyruvic acid).
700 X original size.

